Mathematical Modelling of LiFePO$_4$ Cathodes

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under the supervision of

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LiFePO$_4$ is a commercially available battery material with good theoretical discharge capacity, excellent cycle life and increased safety compared with competing Li-ion chemistries. It has been the focus of considerable experimental and theoretical scrutiny in the past decade, resulting in LiFePO$_4$ cathodes that perform well at high discharge rates. This scrutiny has raised several questions about the behaviour of LiFePO$_4$ material during charge and discharge. In contrast to many other battery chemistries that intercalate homogeneously, LiFePO$_4$ can phase-separate into highly and lowly lithiated phases, with intercalation proceeding by advancing an interface between these two phases.

The main objective of this thesis is to construct mathematical models of LiFePO$_4$ cathodes that can be validated against experimental discharge curves. This is in an attempt to understand some of the multi-scale dynamics of LiFePO$_4$ cathodes that can be difficult to determine experimentally. The first section of this thesis constructs a three-scale mathematical model of LiFePO$_4$ cathodes that uses a simple Stefan problem (which has been used previously in the literature) to describe the assumed phase-change. LiFePO$_4$ crystals have been observed agglomerating in cathodes to form a porous collection of crystals and this morphology motivates the use of three size-scales in the model. The multi-scale model developed validates well against experimental data and this validated model is then used to examine the role of manufacturing parameters (including the agglomerate radius) on battery performance.

The remainder of the thesis is concerned with investigating phase-field models as a replacement for the aforementioned Stefan problem. Phase-field models have recently been used in LiFePO$_4$ and are a far more accurate representation of experimentally observed crystal-scale behaviour. They are based around the Cahn-Hilliard-reaction (CHR) IBVP, a fourth-order PDE with electrochemical (flux) boundary conditions that is very stiff and possesses multiple time and space scales. Numerical solutions to the CHR IBVP can be difficult to compute and hence a least-squares based Finite Volume Method (FVM) is developed for discretising both the full CHR IBVP and the more
traditional Cahn-Hilliard IBVP. Phase-field models are subject to two main physicality constraints and the numerical scheme presented performs well under these constraints.

This least-squares based FVM is then used to simulate the discharge of individual crystals of LiFePO$_4$ in two dimensions. This discharge is subject to isotropic Li$^+$ diffusion, based on experimental evidence that suggests the normally orthotropic transport of Li$^+$ in LiFePO$_4$ may become more isotropic in the presence of lattice defects. Numerical investigation shows that two-dimensional Li$^+$ transport results in crystals that phase-separate, even at very high discharge rates. This is very different from results shown in the literature, where phase-separation in LiFePO$_4$ crystals is suppressed during discharge with orthotropic Li$^+$ transport.

Finally, the three-scale cathodic model used at the beginning of the thesis is modified to simulate modern, high-rate LiFePO$_4$ cathodes. High-rate cathodes typically do not contain (large) agglomerates and therefore a two-scale model is developed. The Stefan problem used previously is also replaced with the phase-field models examined in earlier chapters. The results from this model are then compared with experimental data and fit poorly, though a significant parameter regime could not be investigated numerically. Many-particle effects however, are evident in the simulated discharges, which match the conclusions of recent literature. These effects result in crystals that are subject to local currents very different from the discharge rate applied to the cathode, which impacts the phase-separating behaviour of the crystals and raises questions about the validity of using cathodic-scale experimental measurements in order to determine crystal-scale behaviour.
I hereby declare that this submission is my own work and to the best of my knowledge it contains no material previously published or written by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at QUT or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by colleagues, with whom I have worked at QUT or elsewhere, during my candidature, is fully acknowledged.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project’s design and conception or in style, presentation and linguistic expression is acknowledged.

QUT Verified Signature

Steven Dargaville
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Abstract

Declaration

Acknowledgements

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1. Introduction

Li-ion battery technology was first pioneered by Whittingham [1] in 1976 and offers many advantages when compared to traditional battery chemistries. Li-ion batteries now account for the majority of portable secondary (rechargeable) batteries sold and are commonly used to power modern electronic devices. Fig. 1.1 shows a schematic of a common cell, with the two electrodes (cathode and anode) separated by a liquid electrolyte.

During the discharge of a Li-ion battery, electrochemical reactions occur in both the cathode and the anode, with the reaction at the anode (graphite is typically used as an anode material) supplying Li$^+$ and e$^-$ to the cathode. The Li$^+$ ions are transported through the liquid electrolyte with e$^-$ transported through an external circuit (allowing the battery to perform work). Fig. 1.1 shows this current path during discharge, which is common to all Li-ion batteries. The cathode itself is made up of a porous collection of binder, carbon and active material in the form of (often nano-sized) individual crystals. This porous structure is fully saturated with a liquid (or polymer) electrolyte. This allows Li$^+$ to be transported directly to the reaction site on the surface of a crystal, while e$^-$ move from the cathodic current collector through the (highly-conductive) carbon to reach the reaction site.

Various chemistries have been used in the cathode of Li-ion batteries, including LiCoO$_2$ (lithium cobalt-oxide), LiMn$_2$O$_4$ (lithium manganese oxide) and LiFePO$_4$ (lithium iron-phosphate) [2]. For excellent reviews of recent advances and challenges in Li-ion battery technology, please see [3–6]. LiFePO$_4$ in particular has been the subject of substantial research in the past decade or so, beginning with the work of Padhi et al. [7]. LiFePO$_4$ batteries are now commercially available and are used in many applications, including hybrid/electric vehicles. The overall reaction that occurs during charge/discharge in LiFePO$_4$ is given by

$$\text{FePO}_4 + \text{Li}^+ + e^- \xrightleftharpoons{\text{charge}} \xleftleftharpoons{\text{discharge}} \text{LiFePO}_4.$$  

(1.0.1)
LiFePO$_4$ offers several advantages when compared with other Li-ion chemistries. The non-toxic base materials and strength of the Fe-P-O bond make the material very safe while the structural similarity between FePO$_4$ and LiFePO$_4$ give the material excellent cycle life [7].

In many early studies, LiFePO$_4$ showed a discharge capacity much lower than the theoretical capacity of the material (170 mAh/g), even at fairly low currents. This is due to two main factors. Firstly, the transport of Li$^+$ in solid LiFePO$_4$ material is slow. The diffusion coefficient of Li$^+$ in LiFePO$_4$ has been reported [8, 9] as between $10^{-11}$ to $10^{-21}$ m$^2$/s. Secondly, LiFePO$_4$ is considered an insulator, with an electrical conductivity of $10^{-7}$ S/m [10], which is much lower [11] than that of LiCoO$_2$ for example, at 1 S/m. Careful morphology control is therefore required to ensure adequate performance from LiFePO$_4$ cathodes. Typically, this involves constructing nano-sized crystals of active material (hence reducing diffusion limitations in the solid) and mixing (or synthesising) these crystals with some form of highly conductive carbon (that enhances the conductivity of the entire cathode and ensures adequate e$^-$ transport to a reaction site). With these modifications, LiFePO$_4$ has become a competitive Li-ion battery chemistry.
There has, however, been great debate in the literature surrounding LiFePO$_4$. Some topics of note include whether LiFePO$_4$ can be doped to enhance the electrical conductivity of the material [10, 12–16] and on the inclusion of an ion-conducting surface phase to support high-rate charge/discharge [17–19]. In recent years, there has been considerable investigation into the nature of phase-separation in LiFePO$_4$. By Gibbs phase rule (see Chapter 10 in Huggins [20]), the phase-separating behaviour of electrochemical systems can be determined by examining the voltage profiles; a flat profile suggests a phase-separating material while a monotonically decreasing voltage suggests the material is filling homogeneously. Padhi et al. [7] noted that the voltage profile of LiFePO$_4$ cathodes at low currents is characterised by a voltage plateau (at approximately 3.42 V) and determined that the reaction given in (1.0.1) actually proceeds by advancing an interface between highly and lowly lithiated forms of LiFePO$_4$ (namely Li$_{1−\xi}$FePO$_4$ and Li$_y$FePO$_4$, respectively, with $\gamma, \xi \ll 1$, see [21–24]).

A number of groups however, have begun to question if LiFePO$_4$ phase-separates during charge/discharge. Temperature, crystal size, applied current and strain [25–30] have all been implicated in the suppression of phase-separation, resulting in material that may fill homogeneously through the entire Li$^+$ mass fraction, not just in those concentration regions bordered by the “end-members” Li$_{1−\xi}$FePO$_4$ and Li$_y$FePO$_4$ (these end-members are discussed further in Section 1.1.3). Experimental measurements of phase-separation in LiFePO$_4$ are complicated by several factors. When measuring data from an entire cathode, the voltage profile, for example, can be considered an averaged voltage across $10^{10} - 10^{17}$ individual crystals [27]. Recently, this fact has been playing an increasing role in interpreting experimental measurements, as the response of a complete, multiscale battery cathode to experimental techniques is very nonlinear and can mask the behaviour of individual crystals.

Measurements performed on individual crystals can sometimes yield direct information about crystal-scale behaviour (see for example [31] who investigated the spatial variation in Li-ion diffusion times in LiCoO$_2$ crystals), though this is often hampered by the size scales considered (the diameter of individual crystals can be as small as 10-20 nm). Also, many experimental techniques can only measure the \textit{ex situ} behaviour, as opposed to the \textit{in situ} behaviour. While the equilibrium state (and hence the state measured by \textit{ex situ} methods) of an individual LiFePO$_4$ crystal may be one where phase-separation occurs, the behaviour far from equilibrium (i.e., during discharge) may be very different.
These difficulties allow mathematical modelling to play a key role in determining the behaviour of LiFePO$_4$ cathodes. Quantitatively simulating the multi-scale porous structure of a battery cathode, coupled to a model of an individual crystal allows the importance of macroscopic variables like cathode thickness to be determined while observing crystal-scale behaviour under discharge conditions. These simulations can then be compared against experimental data, namely the measured cell voltage during discharge, which is impacted by all of the (physical and electrochemical) processes that occur in a battery electrode and can therefore be an excellent test for multi-scale modelling approaches. The main objective of this thesis is to develop and investigate mathematical models of LiFePO$_4$ cathodes that can be validated against relevant experimental data. This research objective is outlined in Section 1.2. In the next section, a brief overview of the existing literature on mathematical modelling of LiFePO$_4$ is given, along with background material on the modelling approaches used in this thesis.

1.1 Literature review & background material

This section provides a brief overview of mathematical modelling approaches for electrochemically active porous thin-films and in particular LiFePO$_4$ cathodes. A brief discussion of experimental results and methodologies was used at the beginning of the chapter to motivate this thesis; a comprehensive review of experimental results is not given in this section. Relevant experimental findings are introduced throughout each of the thesis chapters, however for more details, please see any of the substantial reviews in the literature. These include [32, 33] who focus on synthesis techniques used to manufacture LiFePO$_4$ and Tang et al. [34] who provide excellent analyses of experimental results in LiFePO$_4$. For other experimentally-focused reviews, see [35–38].

Mathematical modelling of battery cathodes relies on an understanding of the various current pathways taken by ionic species in the cathode under the influence of an electric field and this section gives a more detailed description of this transport across the different scales present in a Li-ion cathode. Fig. 1.2 shows a schematic of a porous cathode fully saturated with liquid electrolyte, with several solid phases shown. The solid phases include (inert) binder, individual crystals of active material and highly-conductive carbon distributed throughout the cathode. Fig. 1.2 can be considered a magnified schematic of the cathode shown in Fig. 1.1, with the separator given by the dotted line in Fig. 1.1. This separator ensures no electrical contact can be made between the two electrodes, while allowing Li$^+$ transport in the electrolyte.
A single reaction site is shown on the surface of a crystal in Fig. 1.2 and in LiFePO$_4$, given (1.0.1), both Li$^+$ and e$^-$ are transported through the cathode to this reaction site. As pictured, Li$^+$ ions are transported through the porous cathode via the electrolyte. Electrons move from the current collector (that is connected to the external circuit shown in Fig. 1.1) through the solid material in the cathode to the reaction site. In Fig. 1.2, carbon surrounds most of the crystals, forming a highly conductive network that allows easy transport of e$^-$. Depending on the synthesis (and mixing) methods used to build the cathode, a fully connected carbon network may not exist and electrons may have to move through the active material. Given the difference in the electrical conductivity between carbon and active material (particularly in LiFePO$_4$, with 16 orders of magnitude difference), this comes with a significant energy cost. A careful balance of carbon and active material is required; excessive amounts of carbon decrease the energy density of a cathode, while too little carbon (or carbon that is distributed poorly) inhibits e$^-$ transport.
Once the reaction has occurred on the surface of an individual crystal, a single Li$^+$ ion and e$^-$ are inserted into the lattice of the crystal. Any equations concerned with the transport of ionic species in individual crystals of active material are known as “crystal-scale” equations in this thesis and are outlined in Section 1.1.3. The transport of Li$^+$ ions and e$^-$ through the porous cathode (known as the “cathode-scale”) are governed by macro-homogeneous porous electrode theory (MHPET) as detailed in the next section. It should be noted that these two size scales (the cathode and crystal scales) differ in size more than Fig. 1.2 would imply; individual crystals typically have a radius of 50 nm, with the cathode thickness and area around 20-60 µm and 1 cm$^2$, respectively. As mentioned in Section 1, this means the cathode is comprised of $10^{10}$ to $10^{17}$ crystals, making the simulation of ion transport through each individual pore and crystal in the cathode impossible without some form of homogenisation or volume averaging.

### 1.1.1 Macro-homogeneous porous electrode theory

Macro-homogeneous porous electrode theory (MHPET) is a modelling framework based on volume averaging that is used to represent the transport of ionic species in the (multi-scale) structure of porous electrochemically-active systems. It was developed by John Newman [39] in 1962 and has been used extensively since that time to model a range of battery chemistries. In particular, Doyle et al. [40] first used MHPET to model a complete Li-ion cell (i.e., cathode and anode). For a more detailed review of MHPET than the one given here, please see [41, 42].

#### Ion transport in the electrolyte

In the electrolyte, there can be several ionic species (the solute ions) dissolved in a neutral solvent. Volume averaging of a mass balance equation in the pores results in [42] the concentration of the $i$th ionic species given by

$$\frac{\partial \epsilon C_i}{\partial t} = R_i - \nabla \cdot N_i,$$

where $C_i$ (mol m$^{-3}$) is the intrinsic concentration of species $i$ (i.e., averaged over the electrolyte within the pores), $\epsilon$ is the mass fraction of electrolyte in the cathode (i.e., the porosity if the electrode is fully saturated), $R_i$ (mol m$^{-3}$ s$^{-1}$) is a superficial (i.e., averaged over both the solid and electrolyte) reaction term that represents any intercalation of species $i$ from the electrolyte into the solid material and $N_i$ (mol m$^{-2}$) is the superficial flux of species $i$ in the electrolyte, averaged through a plane (containing
both solid and electrolyte) in the cathode. The reaction term $R_i$ represents a coupling point between the cathode-scale and crystal scale equations, as variables on both scales influence the reaction rate. This coupling is described in more detail in Section 1.1.2.

The superficial current in the electrolyte, $i_e (A \, m^{-2})$, is due to the motion of all the ionic species and can therefore [42] be written as

$$i_e = F \sum_i z_i N_i,$$  \hspace{1cm} (1.1.2)

where $z_i$ is the charge number of species $i$ (i.e., the number of proton charges carried by the ion) and $F$ (C) is Faraday’s constant. The form of $N_i$ is given by a model of forces that influence the transport of the ionic species through the pores. Most cathodic models of battery materials use dilute solution theory [42] (based on the Nernst-Planck equation), which assumes that the solute ions (of which $Li^+$ is one species in Li-ion batteries) are subject to diffusion, convection and migration. Forces due to migration are caused by the influence of the electric field on charged species. A dilute solution approximation in a porous cathode [42] gives $N_i$ as

$$N_i = -\epsilon z_i u_i F C_i \nabla \Phi_e - \epsilon D_i \nabla C_i + C_i \mathbf{v},$$  \hspace{1cm} (1.1.3)

where $\Phi_e$ (V) is the electric potential in the electrolyte, $u_i$ is the mobility (m$^2$ mol J$^{-1}$ s$^{-1}$) of species $i$ that determines how much the ions move in response to an electric field, $D_i$ (m$^2$ s$^{-1}$) is the diffusion coefficient of species $i$ in the solvent and $\mathbf{v}$ (m s$^{-1}$) is the velocity of the solvent.

This framework assumes the solute ions are infinitely dilute and only interact with solvent molecules. The activity coefficients of each species are also assumed to be unity (i.e., an ideal solution assumption). An alternative to this that still assumes solute ions are infinitely dilute but relaxes the assumption of ideality (and frames fluxes as due to a gradient in chemical potential) is known as moderately dilute solution theory [42] and results in the form of $N_i$ given by

$$N_i = -\epsilon u_i C_i \nabla \mu_i + c_i \mathbf{v},$$  \hspace{1cm} (1.1.4)

where $\mu_i$ (J mol$^{-1}$) is the electrochemical potential of species $i$. The electrochemical potential is often denoted as $\bar{\mu}$, to differentiate it from the chemical potential, though in this thesis (except for in (1.1.10)) $\mu$ always refers to the electrochemical potential. The diffusion coefficient of species $i$ is not explicitly shown in (1.1.4), though it can
be related to the mobility, $u_i$, through the Einstein relation [43]. The potential in the electrolyte, $\Phi_e$ is also not explicitly shown in (1.1.4) as a consequence of using the electrochemical potential (see Newman and Thomas-Alyea [42] for a discussion on $\Phi_e$ in a moderately dilute solution).

Concentrated solution theory can also be used [42] to determine $N_i$, which accounts for all solute-solute (and solute-solvent) interactions and is based on the Maxwell-Stefan equation (see [42, 44, 45] for the exact form of $N_i$ and more detail on transport theory in general). The use of the Maxwell-Stefan equation also requires a more careful definition of $\mathbf{v}$ than the one used above, as the assumption of infinite dilution allows the advective velocity of the ionic species to be simplified to the velocity of the solvent. Concentrated solution theory removes this assumption and the advective velocity of each ionic species must therefore be defined in terms of a reference velocity.

Using dilute (or moderately dilute) solution theory is often a good approximation in Li-ion batteries. Psaltis and Farrell [45] for example, showed that in a ternary electrolyte similar to that used in dye-sensitised solar-cells, the main differences between the Nernst-Planck and Maxwell-Stefan approaches was localised to the double layer within 1 nm of the solid/electrolyte interface. The double layer is neglected in this thesis, though given the size scales that modern electrochemical devices (including LiFePO$_4$ cathodes) are based, a full Maxwell-Stefan approach may sometimes be warranted, particularly when considering reaction kinetics close to an interface. Using a Maxwell-Stefan approach comes with considerable computational expense and the various transport parameters required can be very difficult to measure or simulate. As such, in this thesis, moderately dilute solution theory is used to describe Li$^+$ transport in the electrolyte of the porous cathode.

In LiFePO$_4$ (and other Li-ion batteries), the electrolyte used is often a solution of LiPF$_6$ in an organic solvent. The LiPF$_6$ molecules disassociate into Li$^+$ and PF$_6^-$ ions, making the solution a binary electrolyte (in that there are only two ionic species) and 1:1 (in that for each molecule of LiPF$_6$ that disassociates, there is an equal number of positive and negative charge released). The electroneutrality of the solution, given by

$$\sum_i z_i C_i = 0,$$

(1.1.5)
allows the concentration of only one species in a binary electrolyte to be tracked. Conservation of volume can be expressed as

\[ \bar{v}_{\text{Li}} C_{\text{Li}} + \bar{v}_{\text{PF}_6} C_{\text{PF}_6} + \bar{v}_{\text{solv}} C_{\text{solv}} = 1, \quad (1.1.6) \]

where the \( \bar{v} \) (m\(^3\) mol\(^{-1}\)) terms are the partial molar volumes of each species in the electrolyte. The combination of (1.1.6) and (1.1.5) therefore allows the concentration of the solvent \( C_{\text{solv}} \) (mol m\(^{-3}\)) to be easily determined if required.

Equations (1.1.1) and (1.1.3) (or (1.1.4)) can be then be simplified to obtain

\[ \frac{\partial \epsilon C_e}{\partial t} = \nabla \cdot (D_e \nabla \epsilon C_e - \mathbf{v} C_e) + (1 - t_{\text{Li}}) R, \quad (1.1.7) \]

where \( t_{\text{Li}} \) is the (constant) transference number of \( \text{Li}^{+} \) ions, which determines what fraction of current is carried by \( \text{Li}^{+} \) and \( D_e \) (m\(^2\) s\(^{-1}\)) is a diffusion coefficient that contains contributions from both ionic species in the electrolyte [42]. The exact definition of \( D_e \) depends on whether dilute or moderately dilute solution theory is used (see [42]) to govern the transport of ions in the electrolyte. In this thesis, experimental measurements of \( D_e \) are used, with \( D_e \) subsequently replaced with an effective diffusion coefficient, \( D_{\text{eff}} \) (m\(^2\) s\(^{-1}\)), corrected for the measured tortuosity of the cathode.

Equation (1.1.7) is the well-known advection-diffusion-reaction equation, which determines the intrinsic concentration, \( C_e \) (mol m\(^{-3}\)), of either of the ionic species in a dilute, 1:1, binary electrolyte. It should be noted that the potential has been explicitly eliminated from (1.1.7) due to the electroneutrality of the electrolyte. In this thesis, \( C_e \) refers to the concentration of \( \text{Li}^{+} \) in the electrolyte, as the \( \text{PF}_6^- \) ions do not contribute to the reaction at the cathode (the subscript for \( R \) in (1.1.7) has therefore been removed). Furthermore, in this thesis (and in most battery systems), \( \mathbf{v} = \mathbf{0} \), hence the transport of \( \text{Li}^{+} \) in electrolyte through the porous cathode driven by both diffusion and the electric field is represented by a diffusion equation with a source/sink term, namely

\[ \frac{\partial \epsilon C_e}{\partial t} = \nabla \cdot (D_{\text{eff}} \nabla \epsilon C_e) + (1 - t_{\text{Li}}) R. \quad (1.1.8) \]

**Electron transport in the solid and potential**

On the cathode-scale of a Li-ion battery, as shown in Fig. 1.2, the transport of \( e^- \) through the solid material must also be considered. A volume averaged form of Ohm’s
law can be used to determine the superficial current moving through the solid, or

\[ i_s = -\sigma_s \nabla \Phi_s \]  

(1.1.9)

where \( \sigma_s \) (S m\(^{-1}\)) is the effective conductivity of the solid in the cathode and \( \Phi_s \) (V) is the electric potential in the solid phase. If \( e^- \) only move through the conductive carbon phase in the cathode, \( \sigma_s \) would simply be the conductivity of carbon, which is very large, at approximately \( 10^8 \) S m\(^{-1}\). If instead, like shown in Fig. 1.2, \( e^- \) are forced to travel through both carbon and the active material, the conductivity is a function of both the mass fractions and conductivity of carbon and active material, along with the degree of carbon connectivity in the cathode.

Typically, the concentration of \( e^- \) is not modelled, as it is assumed electrons are always available at a reaction site. The impact of \( e^- \) transport on the potential in the solid phase, however, is accounted for by (1.1.9). The potential in the electrolyte was briefly mentioned in connection with (1.1.3) and (1.1.4), though \( \Phi_e \) does not explicitly appear in (1.1.8). Using (1.1.2) and (1.1.4), the current in the electrolyte can be written as

\[ i_e = -\kappa_{\text{eff}} \nabla \Phi_e - \frac{2\kappa_{\text{eff}}(t_{\text{Li}} - 1)}{F} \nabla \mu_e^*, \]  

(1.1.10)

where \( \kappa_{\text{eff}} \) (S m\(^{-1}\)) is the effective conductivity of the electrolyte (corrected in a manner similar to \( D_{\text{eff}} \)) and \( \mu_e^* \) (J mol\(^{-1}\)) is the chemical potential (not the electrochemical potential) of the electrolyte (i.e., the Li\(^+\) ions given a binary electrolyte). Equation (1.1.10) can be used to determine the potential in the electrolyte, \( \Phi_e \). It should be noted that (1.1.10) is valid under concentrated solution theory [42] (and also moderately dilute and dilute solution theory). The exact definition of many of the variables in (1.1.10) change between the transport theories (e.g., the transference number must be referenced to the solvent velocity). See Newman and Thomas-Alyea [42] for a discussion of the differences between the analogous forms of (1.1.10) under the three different transport frameworks.

In this thesis, the chemical potential in (1.1.10) is explicitly removed by substituting for the (intrinsic) activity in the electrolyte in order to allow the use of an experimentally measured form of the (concentration-dependent) activity. The activity is related to the chemical potential [46] by

\[ a_e = \gamma_e C_e = \exp \left( \frac{\mu_e - \mu_e^T}{R_e T} \right), \]  

(1.1.11)
where $R_g \ (J \ mol^{-1} \ K^{-1})$ is the universal gas constant, $T \ (K)$ is the temperature, $\mu_{\Theta}^e \ (J)$ is a reference chemical potential (typically defined at $a_e=1$) and $\gamma_e$ is the dimensionless activity coefficient of $\text{Li}^+$ in the electrolyte. The term $\gamma_e$ is normally replaced with the mean ionic activity coefficient, $\gamma_{\pm}$, as the activity coefficient of an individual ion in a solution cannot be measured. Activities are dimensionless quantities and the use of a (dimensionless) activity coefficient means there is an implicit unit concentration with dimensions m$^3$ mol$^{-1}$ that is set to unity in any expression of activity \cite{47}.

The transport of $\text{Li}^+$ ions in the electrolyte through the porous cathode, along with the impact that both $\text{Li}^+$ and $e^-$ transport on the cathode scale have on the potentials in the electrolyte and solid is characterised above. Before advancing to discuss the form of the reaction rate $R$, the various cathodic-scale potentials used in the model should be defined further. One of the most important potentials to consider is the cell potential, $E_{\text{cell}} \ (V)$, which is given by the difference between the potential difference across the cathode, $\Delta \Phi_{\text{cath}} \ (V)$, and anode, $\Delta \Phi_{a} \ (V)$, or

$$E_{\text{cell}} = \Delta \Phi_{\text{cath}} - \Delta \Phi_{a}.$$  

Here the potential differences across each of the electrodes is given by the potential difference between the solid material and the electrolyte (for example, $\Delta \Phi_{\text{cath}} = \Phi_{s} - \Phi_{e} \ (V)$). The cell potential, $E_{\text{cell}}$ is the voltage that is measured experimentally when a battery is discharged and hence any validation performed on a mathematical model of a battery cathode must be performed on this voltage. In this thesis, $\text{LiFePO}_4$ cathodes are modelled, rather than a complete cell, as the limiting factor in discharges is normally the cathode.

Finally, the rate of the intercalation reaction in each of the electrodes is dependent on the overpotential of each electrode, which is often defined as the potential difference of the electrode measured with respect to the equilibrium potential of the electrode, $\Delta \Phi_{\text{cath}}^{\text{eq}}$. The cathodic overpotential, $\eta \ (V)$, can therefore be written as

$$\eta = \Delta \Phi_{\text{cath}} - \Delta \Phi_{\text{cath}}^{\text{eq}}, \quad (1.1.12)$$

where the equilibrium potential is the potential difference at the current mass fraction if the current were set to zero and the cathode allowed to relax. This equilibrium potential is given by the Nernst equation \cite{42} and given a non-homogeneous concentration of ionic species in the active material (as there is in phase-separating systems) this equilibrium
potential is spatially dependent on the crystal-scale variables. In this thesis, following Farrell et al. [48], the overpotential is instead defined as

$$\eta = \Delta \Phi_{\text{cath}} - E_{\text{ref}},$$  \hspace{1cm} (1.1.13)

where $E_{\text{ref}}$ (V) is a constant reference potential, which is set to be the open-circuit potential of a complete LiFePO$_4$ cell at $t = 0$ (i.e., the equilibrium potential of the complete cell at $t = 0$). This necessitates the use of a different form of $R$ than would be typically used, but the advantage of this modification is that the overpotential is no longer dependent on the crystal-scale spatial variables, as this dependence is moved into $R$, which is already defined in terms of both crystal and cathode-scale variables. Assuming two size scales are present, this makes $\eta$ a cathodic-scale variable. This simplifies both the form of the equation for $\eta$ and the numerical techniques used to solve a multi-scale model. It should be noted that with the modified form of $R$ (outlined below) the definition of $\eta$ given in (1.1.13) is algebraically equivalent to that implied by (1.1.12) (this is outlined in greater detail in Chapter 4). Equation (1.1.13) also avoids defining $\eta$ in terms of the experimentally measured open-circuit potential across all mass fractions.

The modelling of battery cathodes in this thesis is performed under galvanostatic conditions, where a fixed discharge current is applied to the cathode. This condition is included by considering that conservation of charge in the cathode dictates that

$$\nabla \cdot (i_e + i_s) = 0.$$  \hspace{1cm} (1.1.14)

Integrating (1.1.14) then gives

$$i_e + i_s = \frac{I}{A} \hat{x},$$  \hspace{1cm} (1.1.15)

where $I$ (A) is the discharge current applied to the cathode, $A$ (m$^2$) is the cross-sectional area of the cathode and $\hat{x}$ is a unit vector normal to the solid/electrolyte interface. Equation (1.1.15) simply states that the sum of the current in the solid and electrolyte must be equal to the applied discharge current. The combination of (1.1.9), (1.1.10) and (1.1.15) imply that both $i_e$ and $i_s$ must be solved for. In this thesis, rather than solve the first-order, partial differential equations (PDEs) for the current in the solid and electrolyte (which can be difficult numerically), the definition of $\eta$ used in (1.1.13) allows a single, second order PDE in conservative form to be solved for $\eta$ directly, without the need to solve for $i_e$ and $i_s$ explicitly (and $R$ only explicitly depends on $\eta$).
This can be accomplished by considering that the reaction term $R$ characterises the amount of charge removed from the electrolyte, or

$$\nabla \cdot i_e = FR,$$  \hspace{1cm} (1.1.16)

where $F$ (C mol$^{-1}$) is Faraday’s constant. Substituting (1.1.10) into (1.1.16) and using (1.1.9), (1.1.15) along with the definition of $\eta$ in (1.1.13) gives

$$\nabla \cdot \left( \frac{\sigma_s \kappa_{\text{eff}}}{\sigma_s + \kappa_{\text{eff}}} \left( \nabla \eta + \frac{2(1-t_{\text{Li}})}{F} \nabla \mu^*_e + \frac{I}{\sigma_s A} \mathbf{x} \right) \right) = FR.$$  \hspace{1cm} (1.1.17)

The conservative form of (1.1.17) allows the equation to be discretised easily with the Finite Volume Method [49], which is the discretisation method used in this thesis. It should be noted that the terms inside the divergence in (1.1.17) represent $i_e$ (see (1.1.16)), which makes boundary conditions on the current easy to apply. Equations (1.1.8) and (1.1.17) define the cathode-scale equations required to describe the volume-averaged transport of ionic species through the porous cathode and the potential under MHPET. These two equations (and associated boundary and initial conditions) form the basis of the (multi-scale) cathodic models found in Chapters 2 and 5.

MHPET has been used extensively in the past several decades to model various systems and effects, including material or cell degradation, porosity changes and thermal effects, amongst others. Of particular relevance to this thesis, is the work of Farrell et al. [48]. Farrell et al. [48] introduced a third size scale to model the experimentally observed morphology of alkaline battery cathodes. This size scale, referred to as the “particle-scale” in this thesis, is composed of carbon-coated agglomerates of individual crystals. When constructing battery cathodes, the goal is often to have individual crystals entirely coated in carbon (as carbon is normally more conductive than the active material and hence the potential loss on the cathode-scale is reduced), but this can be difficult, particularly for material produced on a commercial scale. This multi-scale morphology has been observed in LiFePO$_4$ [50] and forms the basis for the model presented in Chapter 2. In terms of Fig. 1.2, the individual crystals shown would instead be considered porous agglomerates of individual crystals. The equations outlined above for Li$^+$ transport in the electrolyte and overpotential using MHPET are essentially replicated on the particle-scale, though care must be taken to volume average over the correct phases on each scale, particularly when considering the boundary conditions that connect each scale.
1.1.2 Reaction kinetics

The form of $R$, which is the reaction term that determines the rate at which ions intercalate from the electrolyte into individual crystals of active material, in (1.1.8) and (1.1.17) (and hence the coupling between the cathode and crystal scales) has been neglected in the previous sections. The term $R$ represents the amount of charge removed from the electrolyte per (superficial) unit volume and is dependent on the reaction rate on the crystal surface, which is defined on the crystal scale per unit area of active material. If a shrinking-core model is used on the crystal-scale, which is outlined below (and in Chapter 2), it is assumed that the reaction proceeds uniformly across the crystal surface and $R$ can therefore be written [42] as

$$R = \frac{(1 - e) ai_n}{F}, \quad (1.1.18)$$

where $a$ ($\text{m}^{-1}$) is a ratio of surface area to volume of an individual crystal and $i_n$ (A m$^{-2}$) is known as the transfer-current density, which is the amount of charge transferred on the crystal surface per second. The form of (1.1.18) can be modified if the surface reaction is non-uniform across the crystal surface (see Chapters 4 and 5).

In order to derive an expression for $i_n$, the Arrhenius equation must be considered, which is an empirically derived relation that is used in reaction kinetics [51] and is given by

$$k = A \exp \left( \frac{-E_A}{k_b T} \right). \quad (1.1.19)$$

Here $k$ (s$^{-1}$) is a rate constant determining the speed of the reaction, $k_b$ (J K$^{-1}$) is Boltzmann’s constant, $A$ (s$^{-1}$) is generally known as the frequency factor and $E_A$ (J) is the activation energy, which is the size of the energy barrier that must be surmounted for the reaction to occur. It is the role of a kinetic theory to predict the form of $A$ and $E_A$, as the rate constants $k_f$ and $k_b$ for the forward and backward reaction in (1.0.1), described by (1.1.19), can be related to $i_n$. It should be noted that the theory described below, when applied along with MHPET, requires all activities (and concentrations) to be the averaged intrinsically and that (1.1.19) and the electrochemical potentials used below are written down per molecule, as opposed to per mole like in (1.1.11) (the universal gas constant can be used instead of $k_b$ in the derivation, making the other quantities defined per mole). Also, concentrations of species are defined throughout this section (and the remainder of the thesis), where lowercase $c$ ($\text{m}^{-3}$) represents a number density (that is often nondimensionalised by a site density, e.g., see Chapter 4), with uppercase $C$ (mol m$^{-3}$) defined per mole.
The kinetic theory used to determine $A$ and $E_A$ in many battery systems (and this thesis) is based on transition state theory [51], often known as activated complex theory. This theory posits that there is an intermediate substance known as the activated complex, through which the reaction occurs. This requires some reaction occurring between two substances, $A$ and $B$, to produce a product $P$; transition state theory predicts the reaction occurs like $A + B \leftrightarrow AB^\ddagger \rightarrow P$, where $AB^\ddagger$ is the activated complex (the $\ddagger$ symbol is commonly used [51] to refer to properties of the activated complex).

Outlined below is a brief description of the application of transition state theory in deriving a Butler-Volmer expression that is used to determine $i_n$. For more details, please see [28, 52–54] for a derivation of kinetic terms using concentrated solution theory (as used in Chapters 4 and 5) and [51] for an alternate derivation that uses dilute solution theory (as used in Chapter 2)).

For some general reaction involving one electron, oxidant $O$ and reductant $R$ (that are both charged species), proceeding with rate $k_f$ and $k_b$ in the backward and forward direction, respectively, given by

$$
O + e \xrightleftharpoons[k_b]{k_f} R,
$$

the forward (or equivalently the backward) rate can be described [54] using (1.1.19) as

$$
k_f = \tilde{A}_f \exp \left( -\frac{\mu^\text{ex}_O - \mu^\text{ex}_{\ddagger}}{k_b T} \right),
$$

where $\tilde{A}_f$ ($s^{-1}$) is the frequency factor of the forward reaction, $\mu^\text{ex}_O$ (J) is the excess electrochemical potential of the oxidant and $\mu^\text{ex}_{\ddagger}$ is the excess electrochemical potential of the activated complex. The excess chemical potential can be considered the portion of the potential neglected by assuming ideality, or $\mu = k_b T \ln a + \mu^\Theta = k_b T \ln c + \mu^\text{ex}$. The electrochemical potentials of the species (neglecting the electron, see [54] for a derivation that includes this) are then assumed to be broken up into chemical and electrostatic components, namely

$$
\mu_O - \mu^\Theta_O = k_B T \ln a_O + z_O e \Phi_e - e \Phi_s,
$$

$$
\mu_R - \mu^\Theta_R = k_B T \ln a_R + z_R e \Phi_e,
$$

where $e$ (C) is the elementary charge on a proton and $\mu^\Theta_O$ and $\mu^\Theta_R$ are the reference chemical potentials for the oxidant and reductant, respectively. The excess electrochemical
potential of the activated state is then written as including a linear combination of the potentials of the oxidant and the reductant (a similar step is performed in [51]), or

\[ \mu^\text{ex}_+ = k_b T \ln \gamma_+ + e(1 - \alpha)(z_O \Phi_e - \Phi_s + \mu^\Theta_O) + \alpha(z_R e \Phi_e + \mu^\Theta_R), \]

where \( \alpha \) is the standard symmetry coefficient [51]. The net rate of the reaction, \( v_{\text{net}} \) (m\(^{-3}\) s\(^{-1}\)), can be written [51] as

\[ v_{\text{net}} = k_f c_O - k_b c_R. \]  

(1.1.21)

Assuming that the overpotential can be written down as (1.1.12) and substituting the expressions for \( \mu^\text{ex}_+ \), \( \mu_O \) and \( \mu_R \) into (1.1.20) (and the equivalent expression for \( k_b \)), (1.1.21) can be used to derive \( i_n \) as

\[ i_n = i_0 \left[ \exp\left( -\frac{\alpha \eta}{k_b T} \right) - \exp\left( \frac{(1 - \alpha) \eta}{k_b T} \right) \right] \]  

(1.1.22)

where \( i_0 \) (A m\(^{-2}\)) is the exchange current density (i.e., the current that flows at equilibrium, when \( \mu_O = \mu_R \) and \( \eta = 0 \)) given by [53]

\[ i_0 = \frac{\rho_s e k_0 (1 - \alpha) a_R^\alpha}{\gamma_+}, \]

where \( k_0 \) (s\(^{-1}\)) is the standard rate constant (see [53, 54] for the form of \( k_0 \) in this derivation) and \( \rho_s \) (m\(^{-2}\)) is the density of Li\(^+\) sites on the surface of the crystal. Equation (1.1.22) is known as a Butler-Volmer expression and determines the rate of reaction in terms of concentrations of the reactive species at whatever interface is present between the oxidant and reductant, which in this thesis is the interface between the surface of a crystal of active material and the electrolyte.

Section 1.1.1 mentioned that in this thesis, \( \eta \) in the cathode is defined in terms of a reference state, which in Chapter 2 and Chapter 5 is the equilibrium potential of a LiFePO\(_4\) cell at \( t = 0 \) (see (1.1.13)). Equation (1.1.22) can be modified to use this definition of \( \eta \) by moving \( \Delta \Phi^\text{eq}_\text{cath} \) from the exponent in (1.1.22) using the Nernst equation, written down with respect to the reference state, or

\[ \Delta \Phi^\text{eq}_\text{cath} = E_{\text{ref}} + \frac{k_b T}{e} \ln \left( \frac{a_O a^0_R}{a_R a^0_O} \right), \]  

(1.1.23)

where the superscript “0” refers to values at the reference state and we should note the reference chemical potentials for the oxidant and reductant have been absorbed into
Combining (1.1.13), (1.1.22) and (1.1.23) gives a modified form of the Butler-Volmer expression (that is often known as the current-overpotential equation [51]), expressed as

\[ i_n = i_0^0 \left[ \frac{a_O^0}{a_R^0} \exp \left( \frac{-\alpha \eta}{k_b T} \right) - \frac{a_R^0}{a_R^0} \exp \left( \frac{(1 - \alpha) \eta}{k_b T} \right) \right], \tag{1.1.24} \]

where the exchange current density, \( i_0^0 \) (A m\(^{-2}\)), is now defined at the reference state and is given by

\[ i_0^0 = \rho_s c k_0 (a_O^0)^{(1-\alpha)} (a_R^0)^{\alpha}. \]

As aforementioned, the use of (1.1.13) and (1.1.24) is algebraically equivalent to (1.1.12) and (1.1.22).

In this thesis, only the reaction at the cathode is considered, and it is described by (1.0.1). The active species are therefore the surface concentration of Li\(^+\) in the solid (or the presence of free space for Li\(^+\) in the solid) that is determined from a crystal-scale model (outlined below), and the Li\(^+\) concentration at the surface of a crystal in the electrolyte. As (1.1.24) shows, the reaction rate is also dependent on the overpotential at the surface of the crystal. Both the overpotential (given (1.1.13)) and the Li\(^+\) concentration in the electrolyte are considered to be cathode-scale variables and as such, to apply (1.1.24), these variables are considered constant over the surface of a crystal (which is small compared to the size of the cathode).

### 1.1.3 Crystal-scale models

Modelling the transport of ionic species in individual crystals of active material during charge and discharge is where the majority of chemistry-specific information resides in a battery model (along with the form of \( R \) described in Section 1.1.2). In Li-ion batteries for example, the MHPET described above was written down assuming a cathodic morphology and electrolyte system common to many Li-ion cells. By using different models on the crystal-scale that reflect the behaviour of the active material used, different battery chemistries can be simulated while keeping the same cathodic framework. The behaviour of ions as they are transported through solid battery material can be very complicated. Many battery materials (including MnO\(_2\), which is used in the cathode of alkaline cells [48]) transport ions homogeneously, in that the lattice structure favours a continuously varying concentration of ions. As mentioned in Section 1, this is different to LiFePO\(_4\), where distinct phases have been observed at certain Li\(^+\) concentrations and intercalation/deintercalation is often assumed to proceed by moving an interface...
between these two phases. Outlined below is a description of the main crystal-scale models that have been used to describe the charge/discharge of LiFePO$_4$ material.

**Shrinking-core**

The first mathematical model of LiFePO$_4$ cathodes used a shrinking-core model on the crystal-scale, which was based on a diagram from Padhi et al. [7], which showed a highly-lithiated shell of Li$_{1-\xi}$FePO$_4$ consuming a core of lowly-lithiated Li$_{\gamma}$FePO$_4$. In their model, Srinivasan and Newman [21] assumed that the transport of Li$^+$ in (undischarged) FePO$_4$ crystals was homogeneous and governed by a diffusion equation in one-dimensional spherical coordinates, $r$ (m), with intercalation proceeding evenly across the surface until the crystal is composed entirely of Li$_{\gamma}$FePO$_4$, or

$$ \frac{\partial C_s}{\partial t} = \nabla \cdot (D_{Li} \nabla C_s); \quad 0 \leq r \leq r_o, \quad (1.1.25) $$

where $C_s$ (mol m$^{-3}$) is the concentration of Li$^+$ in the crystal lattice, $D_{Li}$ (m$^2$ s$^{-1}$) is the (isotropic) diffusion coefficient of Li$^+$ in the lattice and $r_o$ (m) is the radius of the crystal. A phase-boundary was then assumed to form close to the surface of the crystal (at radius $r_1$), separating the lowly lithiated material in the core from the highly
lithiated shell. The crystal-scale behaviour during this movement was then governed by a one-dimensional, one-phase Stefan problem in spherical coordinates [55]. Lithium diffuses throughout the (growing) shell to reach the interface, governed by

$$\frac{\partial C_s}{\partial t} = \nabla \cdot (D_{Li} \nabla C_s), \quad r_1 \leq r \leq r_0,$$

(1.1.26)

with the $Li^+$ concentration in the inner shell ($0 \leq r \leq r_1$) held constant. The interface position, $r_i$, is determined by a standard Stefan boundary condition (based on a mass-balance) at the interface, given by

$$\frac{dr_i}{dt} \propto D_{Li} \nabla C_s \cdot \hat{r}, \quad \text{on } r = r_i,$$

(1.1.27)

where $\hat{r}$ is a unit vector normal to the interface. When the interface reaches the centre of the crystal ($r_i = 0$), (1.1.27) was replaced with a no-flux condition at the centre of the crystal

$$D_{Li} \nabla C_s = 0, \quad \text{on } r = r_i = 0,$$

and homogeneous diffusion was assumed to complete the discharge from $Li_{1-\xi}FePO_4$ to $LiFePO_4$. A schematic of this process is shown in Fig. 1.3.

This model accounts for the homogeneous transport of $Li^+$ at small and large mass fractions (though the initial transformation to $Li\gamma FePO_4$ is neglected when solving the system numerically) and the observed phase-change, which is consistent with experimental measurements confirming the existence of the “solid-solutions” $Li_{1-\xi}FePO_4$ and $Li\gamma FePO_4$ [22–24]. Srinivasan and Newman [21] also measured the values of $\gamma$ and $\xi$ (the difference in concentration between the phase-separated states is known as the miscibility gap) by examining the open-circuit potential of a $LiFePO_4$ cathode.

In recent years, it has become clear that a shrinking-core is not a good model of the behaviour of $LiFePO_4$ during charge and discharge [56]. In particular, a one-dimensional shrinking-core model neglects the anisotropic diffusion of $Li^+$ in $LiFePO_4$ (in defect-free material). In the lattice, $Li^+$ moves rapidly down “tunnels” in the $b [010]$ crystallographic direction and slowly in other directions [8, 57, 58]. This is in contrast to a shrinking-core model that assumes radial symmetry. Phase-boundaries [22, 30, 59] in $LiFePO_4$ are also restricted to various crystallographic directions, as opposed to appearing radially. An analogous Stefan problem could be solved in two (or more) dimensions with rectangular coordinates, allowing the use of anisotropic diffusivities and phase-boundaries aligned in a planar fashion. Ignoring the various mathematical difficulties associated with this (including tracking the interface in higher dimensions),
perhaps the most significant issue with Stefan problems is that they assume that phase-boundaries form. Phase-boundaries should form when it is energetically favourable and this is dependent on many conditions that change during charge/discharge. A shrinking-core model also assumes that the size of the miscibility gap is constant, which contradicts experimental observations [24] (the size of the miscibility/spinodal gaps and the presence of phase-boundaries are thermodynamic properties that are intimately related and discussed in the next section). The assumption of radially symmetric intercalation across the crystal surface has also been contradicted by recent work [22, 60, 61], which suggests that the intercalation of Li$^+$ is preferred close to existing phase-boundaries.

Finally, the use of a shrinking-core type mechanism presents several mathematical difficulties. Firstly, Stefan problems like the shrinking-core presented by Srinivasan and Newman [21] are ill-posed and exhibit finite time blow-up [62] (without some form of regularisation like kinetic undercooling), where the interface velocity becomes infinite. From a modelling perspective, this can challenge numerical schemes and requires a strategy designed to avoid the singularity when the phase-boundary reaches the centre of the crystal. The use of a shrinking-core also makes it difficult to simulate cycling, particularly if this cycling is done at different states of charge, as multiple phase-boundaries may appear (and hence need to be tracked explicitly, see Figure 3 in Srinivasan and Newman [63] for example).

Despite all the problems outlined above, shrinking-core models have found success in simulating LiFePO$_4$ when used in a cathodic model (the crystal-scale model used in Chapter 2 of this thesis is shrinking-core). Srinivasan and Newman [21] in particular obtained excellent fits to discharge data from LiFePO$_4$ cathodes, as did Kasavajjula et al. [64] (based on a modified shrinking-core model). This is due to the fact that in many battery systems, the behaviour of the battery is governed by electrical and electrolytic resistances on the cathode scale, rather than by crystal-scale phenomena (this point is examined further in Chapter 5).

**Diffusion equation**

Several modelling studies have used a diffusion equation (on a fixed domain), typically in one-dimensional spherical coordinates (i.e., (1.1.25)), to represent the transport of Li$^+$ in LiFePO$_4$ material throughout the entire Li$^+$ mass fraction [65–68]. These models assume that the material does not phase separate under any circumstances and are often used due to their simplicity. Thorat et al. [67] and Farkhondeh and Delacourt [68]
both modify the diffusivity in an attempt to capture some of observed phase-change
dynamics, but even with heavy modification, simple diffusion-based models cannot
simulate many of the features of Li$^+$ transport in LiFePO$_4$ crystals. As with shrinking-core
based models, when embedded in a complete cathodic model, it is possible to
match discharge curves.

**Phase-field models**

In order to motivate a discussion of the use of phase-field models as applied to LiFePO$_4$
crystals, outlined below is a (very brief) introduction to the theory of spinodal decom-
position. Modern spinodal theory gained attention in the seminal work of Cahn and
Hilliard [69] (see [70] for an excellent pedagogical description of this theory). This
theory has been heavily used to describe many phase-separating systems over the past
several decades. As an illustrative example, the Cahn-Hilliard equation is derived below
for one thermodynamic variable (namely concentration), though for a careful derivation
of the $n$-component case, please see [71].

In a volume $\Omega$ (m$^3$) with surface $\Gamma$ (m$^2$), assuming a functional $g$ (J) exists that describes
the local free energy in the system per molecule and is dependent on the dimensionless
concentration of a single species, $c$, and it's derivatives, a Taylor series can be used to
expand $g$ about the homogeneous free energy $g_{\text{hom}}$ (i.e, the free energy of the system
with no concentration gradients). This results [69] in

\[
\begin{align*}
g[c, \nabla c, \nabla^2 c, \ldots] &= g_{\text{hom}}[c] + K_1 \nabla^2 c + K_2 (\nabla c)^2 + \ldots, \\
\end{align*}
\]  

(1.1.28)

where $K_1$ and $K_2$ (J m$^2$) are terms that involve derivatives of $g$ at the homogeneous
state, (e.g., $K_1 = \partial g / \partial \nabla^2 c$), where it should be noted that any terms of the form
$\partial g / \partial c$ do not appear as the Taylor series has been expanded about $g[c, 0, 0, \ldots] = g_{\text{hom}}$.
Integrating (1.1.28) over $\Omega$ and neglecting any change in the free energy from surface
effects results in an expression for the free energy, $G(t)$ (J), across the entire volume, namely

\[
G(t) = \rho \int_{\Omega} g_{\text{hom}} + K(\nabla c)^2 + \ldots 
\]  

(1.1.29)

where $\rho$ (m$^{-3}$) is the (number) density of Li$^+$ sites in the lattice and $K$ (J m$^2$) is a
function of both $K_1$ and $K_2$ and is known as the gradient penalty.

The chemical potential of the molecules in the lattice, $\mu$ (J), is defined as [46] the
change in free energy as the number of molecules changes. Typically this would be
computed by $\partial G / \partial c$, but as $G$ is a functional, variational calculus [72] must be used
to compute $\delta G/\delta c$, the variational derivative. Truncating (1.1.29) up to the first order terms, results in an expression for the chemical potential per molecule in the lattice given by

$$\mu = \frac{\partial g_{\text{hom}}}{\partial c} - \nabla \cdot (K \nabla c).$$

(1.1.30)

By assuming that fluxes are driven by gradients in the chemical potential (as in Section 1.1.1) and using the Einstein relation [43] to convert mobilities to diffusivities, the Cahn-Hilliard equation can be derived by using the standard continuity equation for conservation of mass, resulting in

$$\frac{\partial c}{\partial t} + \nabla \cdot \left( \frac{cD}{k_b T} \nabla \left( \frac{\partial g_{\text{hom}}}{\partial c} - \nabla \cdot (K \nabla c) \right) \right) = 0.$$

(1.1.31)

The Cahn-Hilliard equation, given by (1.1.31), is a fourth-order PDE that has been studied extensively in a number of contexts. Models based on the ideas outlined above are known as phase-field models and if no-flux boundary conditions are applied on $\Gamma$, it can be proved (see [71] for example) that the solution of the Cahn-Hilliard equation is the concentration distribution that minimises the free energy of (1.1.29) through time.

Importantly, under certain parameter regimes where it is energetically favourable, solutions to the Cahn-Hilliard equation will phase-separate, with a diffuse interface separating two regions of different concentration (and if the width of this diffuse interface goes to zero, a Stefan problem can be recovered [73]). These parameter regimes are based around the choice of $g_{\text{hom}}[c]$, the homogeneous free energy. In this thesis, $g_{\text{hom}}$ is chosen based on a regular solution model [46], which describes how the mixing of chemical species influences the free energy of the mixture. The “regular solution” parameter (or enthalpy of mixing), $\Omega_m$ (J), influences the number of critical points in the homogeneous free energy curve, which as described in the next section, determines whether the material phase-separates. It can be shown (see [74] for example) that for a regular solution model with 1 component (i.e., describes the mixing of a single species), $\Omega_m > 2k_b T$ forces the mixture to phase separate. This parameter can be related to experimental measurements (see [30] in particular) and in LiFePO$_4$, $4k_b T \lesssim \Omega_m \lesssim 7k_b T$ has been used, which is well within the parameter regime where phase-separation occurs at equilibrium. Please see [74] for an excellent pedagogical description of the role of ideal and regular solution models in phase-separating systems. A qualitative description of phase-separation and free energy is now given below, with specific attention paid to how several quantities defined loosely in the previous sections (e.g., miscibility gap) can be formalised.
The tendency of a material to phase-separate can be characterised by considering the free energy in the system at equilibrium. The second law of thermodynamics enforces that the free energy of a closed system must approach a minimum at equilibrium. If the free energy of a system can be minimised by phase-separating, then the system will phase-separate. Fig. 1.4 shows a plot of the free energy of two different materials (or indeed the free energy of a single system under different conditions, this will be discussed later in this section) that differ in their behaviour at equilibrium. At a total mass fraction of 0.5 (i.e., the average dimensionless ionic concentration), the purple curve is at an energy minimum. Any infinitesimal perturbation of the mass fraction results in an increase in free energy.

The blue curve in Fig. 1.4 however, exhibits a double-well structure and the energy curve therefore has two minimums. The presence of more than one minimum in the energy is common to all phase-separating systems. At a total mass fraction of 0.5 (the solid red point), any perturbation will decrease the free energy, resulting in a system comprised of two phases at mass fractions of approximately 0.17 and 0.78, which both represent energy minimums. This phase-separated state still has a total mass fraction of 0.5. If the phase-separating material were at a mass fraction of 0.6, it would still separate
into the two phases at mass fractions of 0.17 and 0.78, but the relative amount of each phase would change. The blue curve therefore represents material that phase-separates, whereas the material represented by the purple curve would fill homogeneously. The free energy curves shown in Fig. 1.4 can also represent the difference in free energy between a regular solution model with \( \Omega_m < 2k_bT \) (the purple curve) and \( \Omega_m > 2k_bT \) (the blue curve). The difference between the two mass fractions that represent different phases (i.e., the minimums in the blue curve) is known as the miscibility gap and in LiFePO\(_4\) this can be considered as the concentration difference between the highly (Li\(_{1-\xi}\)FePO\(_4\)) and lowly-lithiated (Li\(_\gamma\)FePO\(_4\)) form of LiFePO\(_4\), as mentioned in Section 1.

Given the total mass fraction remains fixed at each point along the \( x \) axis in Fig. 1.4, it should be noted that an argument cannot be made that the homogeneous material for example, if at a total mass fraction of 0.6, would deintercalate to reach the energy minimum at 0.5, as this would change the total mass fraction. Fig. 1.4 should also not be confused with a diagram that represents the free energy as the mass fraction is modified during intercalation/deintercalation.

The dashed line in Fig. 1.4 is known as a “common-tangent”, which can be constructed by joining any energy minimising states by a straight line. If the free energy on this line, at a fixed total mass fraction, is lower than the free energy on the blue-curve, then the material phase-separates at that mass fraction. This can be seen in Fig. 1.4, where the open red circle on the tangent line is at a lower free energy than the solid red line at a mass fraction of 0.5. This can be rationalised as at equilibrium, different phases in a material must have the same chemical potential [46] (i.e., the gradient of the free energy must be the same). At total mass fractions below 0.17 or greater than 0.78, the material fills homogeneously (as a common tangent cannot be constructed that has an energy state lower than the blue curve). Two inflection points are also shown in Fig. 1.4 (the open black circles). Between a mass fraction of 0.3 and 0.65, the system is unstable to infinitesimal perturbations and phase-separation will therefore always be observed at equilibrium. This region is known as the spinodal region, with the difference in mass fractions commonly known as the spinodal gap. Importantly, both the miscibility and spinodal gaps can shrink under various conditions, including increased temperature, resulting in material that may have an energy curve like the blue curve close to equilibrium, but like the purple curve far from equilibrium.

The spinodal gap is smaller than the miscibility gap, and the region between the inflection points and the energy minimums (i.e., from 0.17 to 0.3 and 0.65 to 0.78) is considered “metastable”. It therefore requires a small perturbation (much larger than
the infinitesimal perturbation mentioned previously) in order to form a nucleation point from which a phase-separated region forms. In this thesis, phase-separation by nucleation is not considered, as most of the phase-field simulations are performed under discharge conditions (i.e., as the mass fraction changes). The spinodal region (at equilibrium), in the simulations in this thesis, is very close to the miscibility region in LiFePO$_4$ and even at low discharge rates, the mass fraction moves quickly through the (small) miscibility region to enter the spinodal. In general, mechanisms for nucleation have a long history in phase-field models (see [75] for example).

The Bazant group have been using phase-field models in recent years to model the behaviour of individual LiFePO$_4$ crystals, starting with the work of Singh et al. [76] (see also [71] for slight corrections to the work of Singh et al. [76]). Typically, no-flux conditions are applied to phase-field models (resulting in the traditional Cahn-Hilliard IBVP) in order to study the appearance of phase-boundaries at equilibrium in different materials. Singh et al. [76] took a phase-field model that represents the concentration distribution of Li$^+$ in a LiFePO$_4$ crystal and applied flux conditions to the boundary in order to simulate the intercalation of Li$^+$ ions (resulting in the Cahn-Hilliard-reaction IBVP). In LiFePO$_4$, the rapid diffusion of Li$^+$ in the $b$ crystallographic direction allows the three-dimensional, fourth-order Cahn-Hilliard-reaction (CHR) IBVP to be depth-averaged, resulting in a much simpler one or two-dimensional, second-order PDE (which [54] refers to as the “Allen-Cahn-reaction” (ACR) model). Under certain circumstances, the highly anisotropic diffusivity that allows depth-averaging may be modified, resulting in the need to solve the full (two or three dimensional) CHR IBVP numerically, which is difficult. Chapter 3 presents a numerical method designed to solve the full CHR system, with Chapter 4 using this technique to examine solutions of the CHR IBVP when depth-averaging is not valid.

In general, the use of phase-field models (and specifically the depth-averaged system upon which most of results in LiFePO$_4$ have been based) in LiFePO$_4$ has been very successful at modelling crystal-scale dynamics. The anisotropic diffusivity of Li$^+$ in LiFePO$_4$ is accounted for in the model and the addition of anistropic elastic strain can replicate experimentally observed phase-boundary alignment [30]. Phase-field models are also thermodynamically consistent, in that phase-boundaries will only form when it is energetically favourable. This is very important, as the work of Bai et al. [28] first showed that under high currents, phase-field models predict the suppression of phase-separation in LiFePO$_4$ (with coherency strain suppressing this further [30]). This results in simulations that phase-separate at low current, but fill homogeneously at high current. Bai et al. [28] argued that this phase-suppression could be responsible for the
observed high performance of LiFePO₄ cathodes and the excellent cycle life.

The suppression of phase-separation is driven by a reduction in the size of the miscibility/spinodal gaps. It has long been established that the size of these gaps can shrink under certain conditions at equilibrium (like high temperature [69]), and in LiFePO₄, this was used to show that the miscibility gap shrinks with decreasing crystal size [77] as has been observed experimentally [24]. The work of the Bazant group also shows the importance of considering the behaviour of phase-separating systems far from equilibrium. Other theoretical [27] and experimental work [78] has also concluded that the transformation of FePO₄ to LiFePO₄ via phase-separation is suppressed far from equilibrium (i.e., under discharge conditions).

The dependence of the chemical potential on concentration gradients of Li⁺ in a phase-field model (see (1.1.30)) influences the reaction rate through the activities in the Butler-Volmer expression outlined in Section 1.1.2. This results in much higher rates of intercalation near existing phase-boundaries [28, 71], which matches the conclusions offered by several experimental groups [22, 60, 61]. This is in contrast to a purely diffusion-based model (like a shrinking-core), where the chemical potential in the solid (when using an ideal or regular solution model) is strictly a function of concentration [53]. The Butler-Volmer expression in Chapter 2 uses concentrations (instead of activities) and the chemical potential in the solid, while not explicitly modelled, is independent of concentration gradients. If a phase-field model is used on the crystal scale, care must be taken to use a Butler-Volmer derived from concentrated solution theory that includes this dependence.

In short, phase-field models incorporate a range of experimentally observed phenomena in LiFePO₄ and are thermodynamically consistent. Perhaps the only disadvantage of using phase-field models is that they can be difficult to analyse analytically and solve numerically. Until very recently, the use of phase-field models in LiFePO₄ had been restricted to simulating the discharge of individual crystals, but Ferguson and Bazant [53] coupled a one-dimensional depth-averaged model (ACR) on the crystal-scale to a cathode scale model based on MHPET (see Section 1.1.1) and simulated the discharge of a LiFePO₄ cathode. The results from this model were not validated against cathode-scale experimental data however, though one would hope that given the strengths of phase-field models and the range of experimental verified behaviour they exhibit on the crystal scale, validation of a cathodic-scale model that uses phase-field models on the crystal scale could be performed with less fitting than is necessary with a shrinking-core or diffusion based model (examining this idea forms the basis of Chapter 5).
1.1.4 Many-particle effects

Intimately connected to the thermodynamically consistent battery models detailed in the previous section is the work of Dreyer et al. [79] (also see [80]). Dreyer et al. [79] showed that in a system where a global flux is applied (i.e., a fixed cathodic discharge rate, see (1.1.15)) across many crystals that phase-separate, the behaviour of crystals as part of a “many-particle” system can be very different to that implied by the behaviour of an individual crystal. Dreyer et al. [79] used this to explain the observed difference in voltage (hysteresis) between charge and discharge in LiFePO$_4$ and noted that these many-particle effects apply in many systems, not just electrochemical systems.

In particular, the work of Dreyer et al. [79] predicts that the presence of many phase-separating crystals (phase-separating as implied by the chemical potential at equilibrium, not necessarily during discharge) in an electrode is unstable (see [80] for a proof of this) and hence crystals are far more likely to discharge sequentially, as they will exchange lithium with neighbouring crystals through the electrolyte (i.e., neighbouring crystals will both intercalate and deintercalate during discharge). Mathematical models of cathodes, comprised of phase-separating material, which are not thermodynamically consistent (i.e., most existing models) have helped inform the common view that all (or most) of the crystals in the cathode would fill at the same time, or that crystals would fill sequentially with nearby crystals staying at a fixed mass fraction. It appears that this is not an accurate picture of the charge/discharge process in cathodes made up of many phase-separating crystals.

In one-dimension, depending on the discharge rate (amongst other parameters) many-particle effects would produce an intercalation wave that moves through an electrode. The sequential discharges of crystals can be observed in traditional battery models, but this is driven by electronic or electrolytic limitations. Namely, if the electronic conductivity of a cathode is small, crystals closest to the current collector will discharge first, with the overpotential decreasing as electrons are forced to move through the poor conductor. Similarly, if the ionic species in the electrolyte are depleted within the cathode, the overpotential will grow and diffusion will replenish the ions, though they will be consumed immediately by crystals closest to the electrolyte reservoir. Many-particle effects are caused purely by the non-monotonic chemical potential of phase-separating systems and operate in a parameter regime where “communication” between crystals is unrestricted (i.e., electronic and electrolytic limitations do not apply).
In certain parameter regimes, any thermodynamically consistent model of a battery cathode should exhibit these many-particle effects. Burch [71] first showed that a collection of three crystals, governed by a phase-field model and constrained by a constant global flux, exhibit “mosaic-instabilities” where a crystal undergoing phase-separation during intercalation will influence its neighbours to deintercalate. These crystals were not part of a cathodic simulation and so the electric potential or electrolyte concentrations were not modelled. In their cathodic model, Ferguson and Bazant [53] also showed the presence of “discrete-filling”, where crystals discharge sequentially throughout the cathode. The impact of these “many-particle” effects (under the different names outlined above) is rapidly becoming acknowledged in electrochemical systems, and in particular LiFePO$_4$.

The sequential discharge of individual crystals is very relevant to LiFePO$_4$, as a cathode where an intercalation front is moving through can be considered “phase-separating”, as the cathode will be separated into regions that are fully lithiated and regions that are not. This impacts the application of Gibbs phase rule, used to determine the phase-separating behaviour of the material from cathode-scale observations of voltage curves. The flat voltage profiles seen in LiFePO$_4$ discharge curves may simply be the result of a cathode that is “phase-separating”, as opposed to being indicative of individual crystals undergoing a phase-change. This is examined further in Chapter 5, where the inclusion of a phase-field model on the crystal scale of a cathodic model, as detailed in the previous sections, results in a thermodynamic consistency on all scales (like the recent work of [53]).

Given the existing literature outlined above, the next sections detail the research objectives of this thesis and the original contributions of the research presented.
1.2 Research objectives

Objective 1: Develop a multi-scale mathematical model of LiFePO₄ cathodes

Like many battery materials, the porous structure of LiFePO₄ cathodes can be considered multi-scale. Agglomerates of individual crystals have been observed experimentally and given the low conductivity of LiFePO₄, the electrical resistance from these agglomerates may significantly affect the discharge capacity of the material, even when discharged at relatively low current. The first objective of this thesis was to construct a mathematical model of LiFePO₄ that includes this multi-scale structure, while capturing some of the observed phase-change dynamics of LiFePO₄ on the crystal scale. The impact of this multi-scale structure on battery performance will be examined and after validating against experimental data, possible modifications of manufacturing parameters will be recommended that would maximise performance.

Objective 2: Develop an appropriate numerical method to solve phase-field models

The phase-field model used to simulate crystals of LiFePO₄ can be difficult to solve numerically, particularly if depth-averaging cannot be performed. In order to examine the behaviour of crystals governed by these models, accurate numerical techniques must be developed. Phase-field models must satisfy a physicality constraint on the free energy (gradient-stability) and time-stepping schemes have been developed that satisfy this constraint. Spatial discretisations that simultaneously satisfy discrete mass conservation and gradient-stability however, are less prolific. The specific focus of Objective 2 is to develop a spatial discretisation that could satisfy both constraints.

Objective 3: Apply two-dimensional phase-field models to the crystal-scale discharge of LiFePO₄ material and compare the results to existing reduced order models and to recently observed experimental phenomena

It has become clear in recent years that a shrinking-core model is not an accurate representation of the phase-change in LiFePO₄ crystals. Experimental observations of LiFePO₄ material have driven this understanding and phase-field models have been developed that account for many observed phenomena. These phase-field models are typically depth-averaged that results in a simpler equation system. The third objective of this thesis is to investigate the use of phase-field models in representing the behaviour
of LiFePO$_4$ material in parameter regimes where depth-averaging is not valid. The numerical method outlined in Objective 2 will therefore be required to solve the model system. These parameter regimes are centred around crystals where Li$^+$ diffusion plays an important role, like in the presence of defects, where experimental and theoretical calculations suggest Li$^+$ transport may not be a one-dimensional process as assumed when depth-averaging.

**Objective 4: Develop a mathematical model of modern LiFePO$_4$ cathodes that includes the crystal-scale model developed in Objective 3 and compare the results from such a model against both experimental data and existing models, including that developed in Objective 1**

Modern cathodes typically do not contain agglomerates and can be discharged at very high rates. As such, the final objective of the thesis is to modify the multi-scale cathodic model developed to satisfy Objective 1, embed the crystal-scale model outlined in Objective 3 within such a cathodic model (and therefore use the numerical technique from Objective 2) and finally attempt to validate the results against experimental data from modern, high-rate cathodes. The model resulting from this objective will couple recent experimental findings on the crystal-scale with the observed morphology of modern cathodes in a thermodynamically consistent fashion. As such, many-particle effects should be evident in simulations and their role in determining discharge behaviour will be examined. The final part of Objective 4 is to compare the results from this model against existing models, including those with crystals governed by depth-averaged and shrinking-core equations.
1.3 Thesis outline

This thesis is presented by publication. The original contributions of this thesis are given in the form of four journal articles. These four papers comprise the individual chapters of the thesis and the abstracts of these works are given below. Individual author contributions are also outlined. For a summary of the novelty of these papers, see Section 1.4.

Chapter 2: A multi-scale model for LiFePO$_4$ cathodes

For this chapter, the associated reference is:


**Abstract:** A mathematical model is developed to simulate the discharge of a LiFePO$_4$ cathode. This model contains 3 size scales, which match with experimental observations present in the literature on the multi-scale nature of LiFePO$_4$ material. A shrinking-core is used on the smallest scale to represent the phase-transition of LiFePO$_4$ during discharge. The model is then validated against existing experimental data and this validated model is then used to investigate parameters that influence active material utilisation. Specifically the size and composition of agglomerates of LiFePO$_4$ crystals is discussed, and we investigate and quantify the relative effects that the ionic and electronic conductivities within the oxide have on oxide utilisation. We find that agglomerates of crystals can be tolerated under low discharge rates. The role of the electrolyte in limiting (cathodic) discharge is also discussed, and we show that electrolyte transport does limit performance at high discharge rates, confirming the conclusions of recent literature.

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<td>Supervision of research, review of manuscript</td>
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Chapter 3: A FVM for the Cahn-Hilliard-reaction IBVP

For this chapter, the associated reference is:

S. Dargaville and T.W. Farrell. A least squares based finite volume method for the
Cahn-Hilliard and Cahn-Hilliard-reaction equations. Under Review.

**Abstract:** A vertex-centred finite volume method (FVM) for the Cahn-Hilliard (CH)
and recently proposed [71, 76] Cahn-Hilliard-reaction (CHR) equations is presented.
Information at control volume faces is computed using a high-order least-squares ap-
proach based on Taylor series approximations. This least-squares problem explicitly
includes the variational boundary condition (VBC) that ensures that the discrete equa-
tions satisfy all of the boundary conditions. We use this approach to solve the CH and
CHR equations in one and two dimensions and show that our scheme satisfies the VBC
to at least second order. For the CH equation we show evidence of conservative, gra-
dient stable solutions, however for the CHR equation, strict gradient-stability is more
challenging to achieve.

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Chapter 4: The effect of two-dimensional Li$^+$ transport

For this chapter, the associated reference is:


**Abstract:** We examine the solution of the two-dimensional Cahn-Hilliard-reaction (CHR) equation in the $xy$ plane as a model of Li$^+$ intercalation into LiFePO$_4$ material. We validate our numerical solution against the solution of the depth-averaged equation, which has been used to model intercalation in the limit of highly orthotropic diffusivity and gradient penalty tensors. We then examine the phase-change behaviour in the full CHR system as these parameters become more isotropic, and find that as the Li$^+$ diffusivity is increased in the $x$ direction, phase separation persists at high currents, even in small crystals with averaged coherency strain included. The resulting voltage curves decrease monotonically, which has previously been considered a hallmark of crystals that fill homogeneously.

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Chapter 5: Model comparisons for high-rate LiFePO$_4$ cathodes

For this chapter, the associated reference is:


**Abstract:** We construct a two-scale mathematical model for modern, high-rate LiFePO$_4$ cathodes. We attempt to validate against experimental data using two forms of the phase-field model developed recently [28, 30, 76, 81] to represent the concentration of Li$^+$ in nano-sized LiFePO$_4$ crystals. We also compare this with the shrinking-core based model we developed previously [82]. Validating against high-rate experimental data, where electronic and electrolytic resistances have been reduced is an excellent test of the validity of the crystal-scale model used to represent the phase-change that may occur in LiFePO$_4$ material. We obtain poor fits with the shrinking-core based model, even with fitting based on “effective” parameter values. Surprisingly, using the more sophisticated phase-field models on the crystal-scale results in poorer fits, though a significant parameter regime could not be investigated due to numerical difficulties. Separate to the fits obtained, using phase-field based models embedded in a two-scale cathodic model results in “many-particle” effects consistent with those reported recently [79].

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1.4 Original contributions

The original contributions of this thesis, represented in the papers outlined in Section 1.3 are summarised below.

Contribution 1

The first mathematical model of LiFePO$_4$ cathodes [21] used a shrinking-core to represent phase-change on the crystal-scale along with MHPET to describe the cathode-scale. In this thesis, the shrinking-core model of Srinivasan and Newman [21] is embedded in a multi-scale framework based on that of Farrell et al. [48]. The use of a multi-scale framework in order to simulate LiFePO$_4$ cathodes is novel. The results from this model suggest that both the presence of agglomerates and thick cathodes can limit the discharge capacity of LiFePO$_4$ cathodes.

Contribution 2

The least-squares based Finite-Volume scheme developed to solve the Cahn-Hilliard and Cahn-Hilliard-reaction equations is novel. Existing least-squares based Finite Volume Methods (FVM) are typically used to solve second-order diffusion-advection problems where the boundary conditions are easily satisfied. This is not the case for the fourth-order Cahn-Hilliard (CH) and Cahn-Hilliard-reaction (CHR) initial boundary value problems (IBVPs) and the modification used in this work to enforce boundary conditions is original. Existing numerical literature also focuses on the CH IBVP (that uses a no-flux boundary condition). To date, there is no literature on the solution of the (much stiffer) CHR IBVP. The least-squares based FVM presented in this work performs well, satisfying appropriate physicality constraints in most simulations.

Contribution 3

The use of phase-field models to simulate the discharge of individual LiFePO$_4$ crystals was pioneered by the Bazant group [76], however most of the analysis of these models has been restricted to a depth-averaged version of the CHR IBVP. Other works have examined solutions of phase-field models [83–85] that do not involve depth-averaging, but not under electrochemically-relevant discharge conditions. Defect formation has also been considered previously [81], but this work was focused on the effect of defects blocking ion-channels. Recent theoretical work [58] suggests Li$^+$ ions move around
defects, which helps to explain experimental measurements of isotropic diffusion of Li$^+$ in LiFePO$_4$ [86], as Li$^+$ diffusion is normally considered to be a (strongly) orthotropic/anisotropic process. As such, examining the solution of the full CHR IBVP in two-dimensions, with isotropic diffusivities driven by defect-formation and electrochemical BCs is novel. The results from these simulations differ from those that use a depth-averaged equation. In particular, at high currents with isotropic Li$^+$ transport, phase-separation persists in individual crystals of LiFePO$_4$.

**Contribution 4**

Recently, Ferguson and Bazant [53] used a depth-averaged equation on the crystal-scale of a cathodic model to simulate LiFePO$_4$ cathodes, though they did not validate against experimental data. Previous cathode-scale modelling work where validation is performed is limited to low-rate material (< 5C) with shrinking-core (or diffusion) models on the crystal scale. The final contribution of this thesis is to compare and contrast the ability of several crystal-scale models (a shrinking-core, depth-averaged and two-dimensional CHR IBVP), embedded on the smallest scale of a two-scale cathodic model, to validate against experimental data from modern, high-rate cathodes. Notably, the use of the two-dimensional CHR IBVP on the crystal-scale of a cathodic model is novel and solving this system efficiently requires the development of code implemented in parallel, with significant optimisations made across both scales. The results from this cathodic model confirm the many-particle effects examined in recent literature and emphasise the difficulties in using cathode-scale measurements to infer crystal-scale behaviour.
2. A multi-scale model for LiFePO₄ cathodes

For this chapter, the associated reference is:


2.1 Introduction

LiFePO₄ has recently been gathering considerable attention as a cathodic material for use in Li-ion cells. Padhi et al. [7] first showed LiFePO₄ as a viable candidate for reversible lithiation/delithiation and the material has since become the focus of considerable research, to the point where secondary LiFePO₄ cells are now regarded as commercially viable. The high theoretical capacity (170 mAh/g), thermal stability and low environmental impact of LiFePO₄ cells [7, 87] offer many potential advantages when compared with existing technologies.

However, in practice it has proven difficult to extract (close to) the theoretical capacity from the material, especially at high discharge rates. Padhi et al. [7] for example, achieved only 70% of theoretical capacity with a very low discharge rate of 2.0 mA/g. The performance of the material is hampered by poor electronic conductivity [10] (∼10⁻⁷ S/m) coupled with poor ionic conductivity [88] (∼10⁻⁹ S/m). Improving the performance of a LiFePO₄ cell requires addressing both these transport limitations. Traditionally, work has focused on two methods designed to mitigate the effect of the material’s poor electronic conductivity, with excellent results.

The first of these is based on the controversial work of Chung et al. [10], which involves doping the material with supervalent cations. Chung et al. [10] claim that this improves the electronic conductivity of the material by approximately 8 orders of magnitude.
Some authors have questioned the results of this work, proposing that a conductive network forms as a result of the milling process [12, 89]. Theoretical calculations also seem to indicate that the supervalent doping of LiFePO$_4$ appears energetically unlikely [90], although recent work by Wagemaker et al. [91] seems to show that supervalent doping can occur in the LiFePO$_4$ lattice.

The second approach involves introducing carbon at some stage of the manufacturing process in order to increase the overall electronic conductivity of the cell. Many different synthesis methods use this process to produce a well-connected, electronically conductive network throughout the cathode, which enhances electronic transport. Low-cost, efficient synthesis methods are a current research topic, and almost all synthesis methods modify the morphology of LiFePO$_4$ to produce material with varying crystal size and carbon content/coating [32]. As such it can be difficult to directly ascertain which parameters are affecting utilisation.

Gaberscek et al. [88] compared the experimental results from 9 different research groups (with varying synthesis methods) and concluded that the reduction of crystal size (caused by the synthesis method and/or the addition of carbon) and subsequent reduction in diffusion length for Li$^+$ within the oxide, is the main cause of the performance improvement, rather than the enhanced electronic transport caused by a well-connected conductive network, as was previously thought. This is due to the electronic conductivity being two orders of magnitude greater than the ionic conductivity (contrary to many other lithium-based materials).

Mathematical modelling of a LiFePO$_4$ cathode requires a model of the phase-transition that occurs between FePO$_4$ and LiFePO$_4$ during charge/discharge. The majority of the literature uses a version of the shrinking-core model presented by Padhi et al. [7] and first modelled mathematically by Srinivasan and Newman [21]. Srinivasan and Newman [21] use this shrinking-core in a cathodic model, coupled with two crystal sizes and extensive fitting based on experimental data to generate excellent results. Other modelling work includes that by authors such as Zhang and White [92], Chunsheng et al. [93] and Kasavajjula et al. [64], who all use a modified shrinking core in a cathodic model. Work by authors such as Laffont et al. [22], Chen et al. [60] and Allen et al. [59], however, have shown that a shrinking-core model is not an accurate representation of the phase-change process.

Recent work by Singh et al. [76] uses a more general model to describe the LiFePO$_4$ phase transition, which can be applied to any intercalation compound. They are able
to generate a range of behaviours that a simple shrinking core model cannot display, although the authors do not use this model in a full cathode simulation. Singh et al. [76] qualitatively show that performance can be considered to be surface-reaction-limited (SRL). This matches well with the work of Kang and Ceder [17], who show that LiFePO$_4$ can be used in a supercapacitor-like device at rates as high as 400C, given improved surface absorption and transfer (although this work has recently been criticised by Zaghib et al. [18]).

In this work we are interested in quantitatively investigating the effect that cathode structure has on active material utilisation during discharge. Our aim is to identify the key parameters across all observed size scales within a LiFePO$_4$ cathode that determine active material utilisation, with a view to understanding the complex interplay between crystal sizing, agglomeration, carbon coating, and solid phase ionic and electronic conductivity. In an initial attempt to achieve this, we propose a mathematical model where the shrinking core model of Srinivasan and Newman [21] is embedded in a multi-scale framework based on that developed by Farrell et al. [48] for alkaline cells. We adopt an isotropic shrinking-core at the smallest size scale of this model because we believe that such a model is sophisticated enough to capture the essential phase-change behaviour of LiFePO$_4$, yet simple enough to allow for computational tractability in a multi-scale framework. In the future, a more accurate phase change model, like that of Singh et al. [76] will be incorporated into the model framework developed here.

As noted earlier, our intention here is to concentrate on investigating the effect of multi-scale structures on material utilisation. This approach is particularly suited to LiFePO$_4$ as the material seems to posses up to three distinct size scales, each of which affects the discharge of a LiFePO$_4$ cell. It has been shown experimentally that LiFePO$_4$ can be made porous by using appropriate synthesis methods [94], or more often that secondary particles form from agglomerates of smaller crystals. One of the effects of introducing carbon during the synthesis process is to reduce the formation of agglomerates [95]. In early work without careful morphology control, considerable crystal agglomeration occurs [50], and even in more recent material agglomerated particles are often still present [61, 96–101], although the sizes of agglomerates in these later materials are reduced from that of early materials. In this work, we assume that agglomerates of crystals form to yield porous particles that are coated in carbon. This morphology is observed in the experimental literature, for example, Fig. 8 in Myung et al. [96] and Fig. 5 Maccario et al. [100] show carbon appearing on the outside of small agglomerations of crystals.
The non-porous crystals of active material represent the first size scale observed in LiFePO₄ cathodes, whilst the porous agglomerates represent the second size scale. The third size scale is the cathode itself, which consists of graphite, binder and a porous agglomeration of the porous LiFePO₄ particles described above. In this paper we develop a multi-scale mathematical model that accounts for these observed size scales within a LiFePO₄ cathode. We then discuss the numerical solution of this model and validate the solution against existing experimental curves given by Srinivasan and Newman [21]. This validated multi-scale model then allows us to investigate key parameters on both the particle and cathodic scales that significantly affect material utilisation. On the particle scale, we recommend appropriate crystal and particle sizes, given different carbon coating and doping schemes, while on the cathodic scale we investigate electrolytic limitations and discuss optimum values for cathode thickness.

2.2 Model development

We follow the conventions of Farrell et al. [48] and designate the three size scales described above as crystal, particle and cathodic. A schematic diagram of each scale is given in Fig. 2.1. The crystal scale is formed from a single indivisible crystal of material, assumed to be spherical and radially symmetric. The electrochemical reaction occurs at the surface of this crystal and the phase-transition on this scale from FePO₄ to LiFePO₄ follows the shrinking-core model of Srinivasan and Newman [21]. We set the diffusion coefficient of Li⁺ in LiFePO₄ to be constant. In fact, $D_{Li}$ is anisotropic and dependant on concentration [57, 102], however the assumption that $D_{Li}$ is constant is reasonable given that there is not a large concentration variation in the outer layer of the shrinking core. We also assume that the phase transition that occurs in LiFePO₄ is discrete (i.e., there is no intermediate, or “mushy” [55] phase between the regions of high and low concentration) and that there is no volume or density change during this process (in reality there is a 6.81% increase and 2.59% decrease in volume and density, respectively, during discharge [7]).

The particle scale consists of a spherically symmetric, porous agglomeration of equally-sized crystals, surrounded by a well-connected, electronically conductive network (carbon). The pores of this particle are assumed to be fully saturated with a well-stirred, binary electrolyte composed of LiPF₆ salt (which we assume disassociate into Li⁺ and PF₆⁻) in an organic solvent. Due to a lack of complete transport parameters for any one solvent, we use parameters for several different organic solvents, namely EC:EMC, PC
and DEC. Furthermore, we assume that the solution is electrically-neutral, and we neglect any double-layer effects. In addition, we assume that the electronic conductivity of the LiFePO$_4$ material is constant.

Similarly we assume the cathodic scale is made up of porous agglomerates of particles, connected by carbon and with some volume of inert binder present. The pores are flooded with electrolyte and we assume that the inner boundary of the cathode ($x = x_i$) is in contact with a reservoir of excess electrolyte solution and the outer boundary ($x = x_o$) is in electronic contact with a current collector.
2.2.1 Crystal scale

On this scale, the transition from FePO$_4$ (charged) to LiFePO$_4$ (discharged) occurs. The overall charge transfer reaction is given by [21]

$$\text{FePO}_4 + \text{Li}^+ + e^- \xrightleftharpoons{\text{discharge}} \xleftleftharpoons{\text{charge}} \text{LiFePO}_4$$ (2.2.1)

(2.2.1) however, does not describe the transient behaviour of the material. Following Srinivasan and Newman [21], the discharge mechanism begins with a crystal fully composed of FePO$_4$. The initial intercalation of lithium converts the entire crystal to a homogeneous lithium deficient state (Li$_{\gamma}$FePO$_4$ where $\gamma \ll 1$). Given the continued insertion of lithium, a highly lithiated shell (Li$_{1-\xi}$FePO$_4$ where $\xi \ll 1$) then forms around a lithium-deficient core. The continued intercalation of lithium then causes the shell to consume the core, converting the entire crystal to Li$_{1-\xi}$FePO$_4$. Finally, the highly lithiated material continues to accept lithium, until the transition to fully lithiated material (LiFePO$_4$) occurs. Only the highly lithiated shell (Li$_{1-\xi}$FePO$_4$) is assumed to act like an intercalation electrode, in that it can freely accept lithium.

As such, we consider a spherical crystal of material with radial coordinates $r$ (m) ($0 \leq r \leq r_o$) as shown in Fig. 2.1. Like Srinivasan and Newman [21], we neglect the initial (and rapid) transition of single-phase FePO$_4$ to single phase Li$_{\gamma}$FePO$_4$ ($\gamma \ll 1$). Thus the model begins discharge with the Li$_{\gamma}$FePO$_4$/Li$_{1-\xi}$FePO$_4$ phase interface close to the outer radius of the crystal. This gives the initial condition on the interface as [21]

$$r_i(t) = r_i^0; \quad \text{at } t = 0,$$ (2.2.2)

where $r_i(t)$ (m) is the position of the phase interface between Li$_{1-\xi}$FePO$_4$ and Li$_{\gamma}$FePO$_4$, and $r_i^0$ (m) is the initial position of the interface. This implies that initially we have a thin shell of highly lithiated material in the crystal. The concentration of lithium present in the lithium-deficient core (Li$_{\gamma}$FePO$_4$) is denoted as $C_0$ (mol/m$^3$), the concentration at which the transition to highly lithiated material (Li$_{1-\xi}$FePO$_4$) occurs is $C_{eq}$ (mol/m$^3$) and $C_{max}$ (mol/m$^3$) is the concentration of lithium in fully lithiated LiFePO$_4$. These concentrations are assumed to be constant. We wish to solve for the concentration of lithium in the shell $C_s(r,t)$ (mol/m$^3$) where the transport of lithium through the shell is described by the diffusion equation in spherical coordinates. Hence $C_s$ is given by [21]

$$\frac{\partial C_s}{\partial t} = D_Li \nabla^2 C_s; \quad (r_i \leq r \leq r_o),$$ (2.2.3)
where $D_{Li} \ (m^2/s)$ is the diffusion coefficient of lithium in Li$_{1-\xi}$FePO$_4$ and $t \ (s)$ is time. The input of lithium occurs at the surface of the crystal, which gives the boundary condition [21]

$$D_{Li} \nabla C_s = \frac{i_n}{F} \hat{r}; \quad \text{at} \ r = r_o, \tag{2.2.4}$$

where $F \ (C/mol)$ is Faraday’s constant ($C/mol$), $\hat{r}$ is a unit vector normal to the crystal surface and $i_n \ (A/m^2)$ is the transfer current density due to the electrochemical reaction at the surface. This reaction current couples the crystal and particle size scales and is given in Section 2.2.2. Initially we set the concentration in the highly lithiated shell as $C_{eq}$, namely [21]

$$C_s = C_{eq}; \quad \text{at} \ t = 0, \ r_i \leq r \leq r_o. \tag{2.2.5}$$

The concentration at the interface is fixed, giving the Dirichlet condition [21]

$$C_s = C_{eq}; \quad \text{at} \ r = r_i(t), \tag{2.2.6}$$

and a standard Stefan condition [55] is derived from a mass balance at the interface to give [21]

$$\frac{dr_i}{dt} = \frac{D_{Li}}{(C_0 - C_{eq})} \nabla C_s \cdot \hat{r}; \quad \text{at} \ r = r_i(t). \tag{2.2.7}$$

If the phase-interface reaches the centre of the crystal ($r_i = 0$), then the entire crystal is composed of Li$_{1-\xi}$FePO$_4$. At this stage the boundary condition changes to a no-flux condition given by [21]

$$D_{Li} \nabla C_s = 0; \quad \text{at} \ r = r_i = 0, \tag{2.2.8}$$

and lithium diffuses homogeneously through the crystal. When solving these equations (either by themselves or embedded in the full multi-scale model), care must be taken, as the system is quite ill-conditioned. In order to facilitate the numerical solution on this scale, we follow Srinivasan and Newman [21] and nondimensionalise the system using

$$C^*_s = \frac{C_s}{C_{max}}; \quad r^*_i = \frac{r}{r_o},$$

and then apply a Landau transformation to fix the boundaries of the problem, namely

$$s = \frac{r^* - r^*_i}{1 - r^*_i}, \quad 0 \leq s \leq 1,$$

where $r^*_i$ is the value of $r^*$ at $r = r_i$. Applying this transform modifies the model equation so that it is no longer in conservative form. This is undesirable when solving the
model equations with the Finite Volume Method [49] (FVM), as we do in Section 2.2.4. To remedy this, we depart from Srinivasan and Newman [21] and use the identities given in Illingworth et al. [103] to transform the equation into conservative form. In terms of our notation, these identities are

\[
\frac{\partial}{\partial t} \left( C_s^* (1 - r_i^*) [s(1 - r_i^*) + r_i^*]^2 \right) = \frac{\partial C_s^*}{\partial t} \left( 1 - r_i^* \right) \left[ s(1 - r_i^*) + r_i^* \right]^2
\]

\[+ \frac{dr_i^*}{dt} C_s^* [s(1 - r_i^*) + r_i^*] \left( 2(1 - r_i^*)(1 - s) - [s(1 - r_i^*) + r_i^*] \right), \quad (2.2.9)\]

and

\[
\frac{\partial}{\partial s} \left( C_s^* s [s(1 - r_i^*) + r_i^*]^2 \right) = \frac{\partial C_s^*}{\partial s} s \left[ s(1 - r_i^*) + r_i^* \right]^2
\]

\[+ C_s^* [s(1 - r_i^*) + r_i^*] \left( [s(1 - r_i^*) + r_i^*] + 2s(1 - r_i^*) \right). \quad (2.2.10)\]

Applying (2.2.9) and (2.2.10) to the non-conserved, nondimensional form of (2.2.3), we obtain the nondimensional lithium distribution \(C_s^*(s, t)\), in conservative form, across a fixed domain \((0 \leq s \leq 1)\), namely,

\[
\frac{\partial}{\partial t} \left( C_s^* (1 - r_i^*) [s(1 - r_i^*) + r_i^*]^2 \right) = \frac{\partial}{\partial s} \left( [s(1 - r_i^*) + r_i^*]^2 \left( \frac{dr_i^*}{dt} C_s^* (1 - s) + \frac{p_1}{(1 - r_i^*)} \frac{\partial C_s^*}{\partial s} \right) \right). \quad (2.2.11)\]

The boundary conditions defined over the fixed domain \(s \in (0, 1)\) in nondimensional form are then

\[
C_s^* = p_3; \quad \text{at } t = 0, \quad (2.2.12)
\]

\[
C_s^* = p_3; \quad \text{at } s = 0, \quad (2.2.13)
\]

\[
\frac{\partial C_s^*}{\partial s} = -(1 - r_i^*) p_4; \quad \text{at } s = 1. \quad (2.2.14)
\]

The condition on the interface, in nondimensional form, becomes

\[
\frac{dr_i^*}{dt} = \frac{p_5}{(1 - r_i^*)} \frac{\partial C_s^*}{\partial s}; \quad \text{at } s = 0, \quad (2.2.15)
\]

with the initial condition as

\[
r_i^* = p_2; \quad \text{at } t = 0. \quad (2.2.16)
\]
Again, when the crystal is fully used (i.e., \( r_\iota(t) = 0 \)) then (2.2.13) is replaced by

\[
\frac{\partial C_\iota}{\partial s} = 0; \quad \text{at } s = 0. \tag{2.2.17}
\]

The nondimensional parameters listed above are given by

\[
p_1 = \frac{D_{Li}}{r_o^2}; \quad p_2 = \frac{r_0^i}{r_o}; \quad p_3 = \frac{C_{eq}}{C_{max}}; \quad p_4 = \frac{i_n r_o}{D_{Li} F C_{max}}; \quad p_5 = \frac{D_{Li} C_{max}}{r_o^2 (C_0 - C_{eq})}. \tag{2.2.18}
\]

It is important to note that the nondimensionalisation is only applied to the crystal scale problem. The equations that follow for the particle and cathode scales are dimensioned.

### 2.2.2 Particle scale

We now consider a porous, spherical agglomeration of crystals with radial coordinate \( R (m) \) \((0 \leq R \leq R_o)\) as shown in Fig. 2.1. We begin by expressing conservation of charge on the particle scale as

\[
\nabla \cdot (i_{e(p)} + i_{s(p)}) = 0, \tag{2.2.19}
\]

where \( i_{s(p)} \) (A/m\(^2\)) is the current density (per total unit area) in the solid phase and \( i_{s(p)} \) (A/m\(^2\)) is the current density (per total unit area) in the solution, both on the particle scale. Equation (2.2.19) can be integrated to give \( i_{e(p)} + i_{s(p)} = 0 \), which tells us that charge that leaves the solution enters the solid. We know this occurs via the electrochemical reaction given in (2.2.1), at a rate given by the transfer current density (per total unit area on the particle scale), \( i_{n(p)} \) (A/m\(^2\)). Using Gauss’s divergence theorem, this allows us to write

\[
\int_{V_{e(p)}} \nabla \cdot i_{e(p)} \, dV = \int_{A_c} i_{e(p)} \cdot \hat{r} \, dA_c,
\]

where \( V_{e(p)} \) (m\(^3\)) is the volume of electrolyte surrounding a single crystal, \( A_c \) (m\(^2\)) is the surface area of a crystal and \( \hat{r} \) is a unit vector normal to the crystal surface. Noting that

\[
V_{e(p)} = (\epsilon(p) 4\pi r_o^3)/(1 - \epsilon(p)), \tag{2.2.20}
\]

and setting

\[
\epsilon(p) i_{n(p)} = i_{e(p)} \cdot \hat{r}, \tag{2.2.21}
\]
where $\epsilon(p)$ is the volume fraction of pore space on the particle scale, we have that

$$\nabla \cdot i_{e(p)} = (1 - \epsilon(p)) a i_{n(p)}. \quad (2.2.22)$$

Here $a$ (m$^{-1}$) is the electrochemically active surface area of a single crystal of LiFePO$_4$. We must be careful if we derive $a$ from a Brunauer, Emmett and Teller (BET) surface area measurement [104], as we want the source term in (2.2.22) to be given per total unit volume, as is the divergence of $i_{e(p)}$. If we choose to set a crystal radius in Section 2.2.1, then $a = 3/r_o$; however if we wish to derive a crystal radius from BET measurements then $r_o = 3/a$ and $(1 - \epsilon(p))a = a_b \rho_b$, where $a_b$ (m$^2$/kg) is the BET measurement and $\rho_b$ (kg/m$^3$) is the bulk density. Typical measurements [10, 95, 105] of $a_b$ in modern oxides are generally around 28300 - 36700 m$^2$/kg.

We can use concentrated solution theory [42] to describe the solution phase potential on the particle scale, $\Phi_{e(p)} (V)$, as

$$\nabla \Phi_{e(p)} = -\frac{i_{e(p)}}{\kappa_{e(p)}} + \frac{2 R g T}{F} (1 - t_{Li})(1 - t_{Li}) \nabla \ln a_{e(p)}, \quad (2.2.23)$$

where $\kappa_{e(p)}$ (S/m) is the effective conductivity of the electrolyte on the particle scale (corrected for tortuosity and porosity [106]), $t_{Li+}$ is the transport number for lithium in the electrolyte (assumed to be constant [107]), $R_g$ (J/(mol K)) is the universal gas constant, $T$ (K) is the temperature, $F$ is Faraday’s constant and $a_{e(p)}$ (mol/m$^3$) is the activity of the electrolyte on the particle scale.

The solid phase potential on the particle scale, $\Phi_{s(p)} (V)$, is given by Ohm’s law,

$$i_{s(p)} = -\sigma_{s(p)} \nabla \Phi_{s(p)}, \quad (2.2.24)$$

where $\sigma_{s(p)}$ (S/m) is the effective solid-phase conductivity (LiFePO$_4$) on the particle scale. Noting that the surface overpotential on the particle scale, $\eta_{(p)} (V)$ is given by,

$$\eta(p) = \Phi_{s(p)} - \Phi_{e(p)} - E_{\text{ref}}, \quad (2.2.25)$$

where $E_{\text{ref}}$ is the equilibrium potential of the cathode at a well-defined reference state, we may combine (2.2.22), (2.2.23) and (2.2.24) to obtain

$$\nabla \cdot \left( \frac{\sigma_{s(p)} \kappa_{e(p)}}{\sigma_{s(p)} + \kappa_{e(p)}} \left( \nabla \eta(p) + \frac{2 R g T}{F} (1 - t_{Li}) \nabla \ln a_{e(p)} \right) \right) = (1 - \epsilon(p)) a_i n(p). \quad (2.2.26)$$
The form of (2.2.26) is convenient given the discretisation scheme (FVM) used in Section 2.2.4.

Assuming that the advective velocity contribution to the flux of ionic species within the pores of the particle may be ignored, then species conservation within the electrolyte phase of the particle is given by,

\[ \frac{\partial \epsilon(p) C_e(p)}{\partial t} = \nabla \cdot (D_{\text{eff}}(p) \nabla C_e(p)) + \frac{1}{F} (1 - t_{\text{Li}}) (1 - \epsilon(p)) a_{i_n(p)}, \tag{2.2.27} \]

where \( C_e \) (mol/m\(^3\)) is the intrinsic electrolyte concentration on the cathodic scale and \( D_{\text{eff}}(p) \) (m\(^2\)/s) is the effective diffusion coefficient of lithium (again corrected for tortuosity and porosity [106]) in the electrolyte.

A Butler-Volmer expression is used to determine the transfer current density, \( i_{n(p)}(R, t) \) (A/m\(^2\)), entering each crystal on the particle scale, namely,

\[
    i_{n(p)}(R, t) = i_0 \left[ \frac{C_s^*(1, R, x, t)}{p_3} \exp \left( \frac{\alpha_a F}{R_g T \eta(p)} \right) - \left( \frac{1 - C_s^*(1, R, x, t)}{1 - p_3} \right) \left( \frac{C_e(p)(R, t)}{C_e^0} \right) \exp \left( -\frac{\alpha_c F}{R_g T \eta(p)} \right) \right], \tag{2.2.28}
\]

where \( i_0 \) (A/m\(^2\)) is the exchange current density, \( C_e^0 \) (mol/m\(^3\)) is the initial intrinsic concentration of lithium in the electrolyte and \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients, respectively. In (2.2.28), \( C_s^*(1, R, x, t) \) represents the nondimensional concentration of Li\(^+\) at the surface of each crystal \( (C_s^*(1, t)) \) as determined by the crystal scale model in Section 2.2.1. The function notation is designed to reiterate the multi-scale nature of the model, as \( C_s^*(1, t) \) must be determined at each radial position \( R \) within the porous particle at each position \( x \) in the cathode.

Boundary conditions for the particle are given by symmetry conditions at \( R = 0 \) and continuity conditions at \( R = R_o \), namely,

\[
\nabla C_e(p) = 0; \quad \text{at } R = 0, \tag{2.2.29}
\]

\[
i_{e(p)} = 0; \quad \text{at } R = 0 \tag{2.2.30}
\]

\[
C_e(p) = C_e^0; \quad \text{at } R = R_o, \tag{2.2.31}
\]

\[
\eta(p) = \eta; \quad \text{at } R = R_o, \tag{2.2.32}
\]
where \( C_e (\text{mol/m}^3) \) and \( \eta (\text{V}) \) are the electrolyte concentration and local overpotential on the cathodic scale, respectively, and are defined in Section 2.2.3. We note that (2.2.30) infers a condition on \( \eta(p) \) via (2.2.22) and (2.2.26). Furthermore, initially, all particles are assumed to be at a state of equilibrium, thus,

\[
C_e(p) = C_e^0; \quad \text{at } t = 0. \tag{2.2.33}
\]

where \( C_e^0 (\text{mol/m}^3) \) is the initial concentration of lithium in the electrolyte.

### 2.2.3 Cathode scale

On the cathode scale we consider a porous agglomeration of particles, graphite and binder flooded with electrolyte, with spatial coordinate \( x \) \((x_i \leq x \leq x_o)\) as shown in Fig. 2.1. Conservation of volume on the cathodic scale dictates that,

\[
\epsilon_{\text{LiFePO}_4} + \epsilon_g + \epsilon_b + \epsilon = 1, \tag{2.2.34}
\]

where \( \epsilon_{\text{LiFePO}_4}, \epsilon_g, \epsilon_b \) and \( \epsilon \) are the volume fractions of porous oxide, graphite, binder and electrolyte, respectively, on the cathode scales.

We assume that charge that enters the porous oxide particles, via the mass transport of species within the electrolyte phase of the cathode, must exit the particles by the graphite phase. We may integrate the divergence of the total current density on the cathode scale to obtain,

\[
i_e + i_g = \frac{I}{A} \hat{x}, \tag{2.2.35}\]

where \( i_e \) and \( i_g \) \((\text{A/m}^2)\) are the current densities per total unit area in the solution and graphite on the cathode scale, respectively; \( I \) \((\text{A})\) is the applied discharge current (which we obtain from multiplying the discharge rate, \( DR \) \((\text{mA/g})\), by the weight of active material, \( w_{\text{LiFePO}_4} \) \((\text{kg})\)), \( A \) \((\text{m}^2)\) is the cross-sectional surface area of the cathode and \( \hat{x} \) is a unit vector normal to the graphite/electrolyte interface at all points.

The rate of reaction of a species on the cathode scale is characterised by the “appearance” or “disappearance” of the species across the boundaries of a given porous particle. For an electrolytic species, we can integrate the flux density of this species over the surface of each oxide particle within the cathode to obtain

\[
\nabla \cdot i_e = \frac{3\epsilon_{\text{LiFePO}_4}}{R_o} (i_e(p) \cdot \hat{R})|_{R=R_o}, \tag{2.2.36}
\]

48
where $\hat{R}$ is a unit vector normal to the surface of a porous particle. We can describe the solid phase potential on the cathode scale as

$$i_g = -\sigma_g \nabla \Phi_g,$$  \hspace{1cm} (2.2.37)

where $\sigma_g$ (S/m) is the effective conductivity of the carbon network and $\Phi_g$ (V) is the potential in the graphite phase. In a manner similar to that used in Section 2.2.2, the solution phase potential on the cathode scale, $\Phi_e$ (V), is given by,

$$\nabla \Phi_e = \frac{i_e}{\kappa_{\text{eff}}} + \frac{2R_g T}{F}(1 - t_{\text{Li}})\nabla \ln a_e,$$  \hspace{1cm} (2.2.38)

where $\kappa_{\text{eff}}$ (S/m) is the effective conductivity of the electrolyte on the cathode scale (corrected for tortuosity and porosity [106]) and $a_e$ (mol/m$^3$) is the activity of the electrolyte on the cathode scale. We note that the local overpotential on the cathode scale is given by,

$$\eta = \Phi_g - \Phi_e - E_{\text{ref}},$$  \hspace{1cm} (2.2.39)

and so we can combine (2.2.35), (2.2.37) and (2.2.38) to obtain

$$\nabla \cdot \left( \frac{\sigma_g \kappa_{\text{eff}}}{\sigma_g + \kappa_{\text{eff}}} \left( \nabla \eta + \frac{2R_g T}{F}(1 - t_{\text{Li}})\nabla \ln a_e + \frac{I}{\sigma_g A} \hat{x} \right) \right) = \frac{3\epsilon_{\text{LiFePO}_4}}{R_o} (i_{e(p)} \cdot \hat{R})|_{R=R_o}. $$  \hspace{1cm} (2.2.40)

Again (2.2.40) provides a convenient form for discretisation.

We can write the intrinsic concentration of lithium in the electrolyte on the cathode scale as

$$\frac{\partial \epsilon C_e}{\partial t} = \nabla \cdot (D_{\text{eff}} \nabla C_e) - \frac{3\epsilon_{\text{LiFePO}_4}}{R_o} (D_{\text{eff}(p)} \nabla C_{e(p)} \cdot \hat{R})|_{R=R_o}. $$  \hspace{1cm} (2.2.41)

Given the assumptions outlined in Section 2.2, the boundary conditions for the cathodic scale are

$$C_e = C_e^0; \hspace{1cm} \text{at } x = x_1,$$  \hspace{1cm} (2.2.42)

$$i_e = \frac{I}{A} \hat{x}; \hspace{1cm} \text{at } x = x_1,$$  \hspace{1cm} (2.2.43)

$$\nabla C_e = 0; \hspace{1cm} \text{at } x = x_o,$$  \hspace{1cm} (2.2.44)

$$i_e = 0; \hspace{1cm} \text{at } x = x_o,$$  \hspace{1cm} (2.2.45)

where again we note that the boundary conditions in $i_e$ can easily be transformed into boundary conditions for $\eta$ using (2.2.36) and (2.2.40). Initially we assume that the
Table 2.1: Listing of the model equations for each size scale. Please see Table 2.2 for a listing of the parameters.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Variable</th>
<th>Eq. No.</th>
<th>ICs &amp; BCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>$C_s$</td>
<td>(2.2.11)</td>
<td>(2.2.12), (2.2.13), (2.2.14), (2.2.17)</td>
</tr>
<tr>
<td></td>
<td>$r_i$</td>
<td>(2.2.15)</td>
<td>(2.2.16)</td>
</tr>
<tr>
<td>Particle</td>
<td>$\eta(p)$</td>
<td>(2.2.26)</td>
<td>(2.2.30), (2.2.32)</td>
</tr>
<tr>
<td></td>
<td>$C_{e(p)}$</td>
<td>(2.2.27)</td>
<td>(2.2.29), (2.2.31), (2.2.33)</td>
</tr>
<tr>
<td></td>
<td>$i_{\text{n}(p)}$</td>
<td>(2.2.47)</td>
<td>-</td>
</tr>
<tr>
<td>Cathode</td>
<td>$\eta$</td>
<td>(2.2.40)</td>
<td>(2.2.43), (2.2.45)</td>
</tr>
<tr>
<td></td>
<td>$C_e$</td>
<td>(2.2.41)</td>
<td>(2.2.42), (2.2.44), (2.2.46)</td>
</tr>
</tbody>
</table>

cathode is in a state of equilibrium, thus

$$C_e = C_{e}^0, \quad \text{at } t = 0.$$  \hspace{1cm} (2.2.46)

We note that the closed-circuit potential of the cell, $E_{\text{cell}}$ (V), can be approximated by

$$E_{\text{cell}} = \Phi_{e}|_{x=x_0} - \Phi_{e}|_{x=x_1} - \frac{R_c I}{A}$$

$$= \eta|_{x=x_1} + E_{\text{ref}} - \frac{R_c I}{A},$$

where $R_c$ ($\Omega \text{ m}^2$) represents any contact resistance that may exist at the cathode/current collector boundary. In addition, we note that the conductivity of the graphite phase will be extremely high in comparison to either the electrolyte or LiFePO$_4$, and so the potential loss through this phase will be negligible.

### 2.2.4 Numerics

The equations, boundary and initial conditions that govern discharge of our three-scale LiFePO$_4$ cathode are listed in Table 2.1. The system was discretised using the Finite Volume Method [49] and the solution algorithm was implemented in MATLAB. We note that (2.2.26) and (2.2.40) are (once discretised) purely algebraic, meaning we must solve a nonlinear system of differential-algebraic equations (DAE), generically of the form $F(t, y, \dot{y}) = 0$. Each of the routines to calculate $F$ on each size scale were written in a modular form. This enables us to run the code in three different configurations, namely we can simulate the discharge of a single isolated crystal, or a single isolated particle composed of a number of crystals, or an entire cathode composed of many...
particles that are themselves composed of many crystals.

The multi-scale nature of the model means that the routine that calculates \( F \) on the crystal scale is called over 10 million times in a typical cathodic simulation. This provided a natural point of optimisation. The crystal scale was written in C++ and used in MATLAB through the MEX interface, resulting in a 60% reduction in total run time, when compared to the purely (vectorised) MATLAB version.

One of the main concerns when solving this system numerically comes from the form of (2.2.28). This equation determines the reaction current and is a source term in (2.2.26). Hence \( \eta(p) \) (and therefore \( \eta \)) are very sensitive to change, as the exponential terms in (2.2.28) behave like \( \sim \exp(36\eta(p)) \). Whenever the concentration on the outside of a crystal approaches \( C_{\text{max}} \) and the overpotential, \( \eta \), increases sharply, this forces a severe reduction in the time step; a plot of \( E_{\text{cell}} \) at low discharge rates (see Fig. 2.2 for example) shows an almost vertical gradient at the end of discharge.

This point, coupled with the need to solve a DAE system, required us to use a robust solver. We used the IDA module (for DAE systems) from Sundials [108] (SundialsTB in MATLAB) to advance our stiff, nonlinear DAE system \( \mathbf{F}(t, \mathbf{y}, \dot{\mathbf{y}}) = 0 \) in time, coupled with the globally convergent, banded, Newton solver [109] in Sundials to solve the nonlinear system. IDA provides time-stepping with a backwards-differentiation function (BDF) (of up to order 5) with constraints on the size of the time-step to control error. Appropriate error control is essential when solving this system, and indeed probably any system that involves equations of Arrhenius form. Even small errors early in the simulation rapidly compound, to give inaccurate solutions. We would consider this scheme to be the minimum required, in terms of numerical sophistication, in order to solve the nonlinear system efficiently. Any form of fixed-point iteration would converge far too slowly and likely force an intolerable reduction in the size of the time-step.

In terms of the equation system, several steps are necessary to make it amenable to solving, even with an efficient solver, such as the one outlined above. Foremost, nondimensionalisation of the crystal scale, given that many of the parameters vary by orders of magnitude. Nondimensionalisation of the other scales was not performed, as the main problem on the higher scales was the exponential term in (2.2.28), which would not change if nondimensionalised. Given this, we were careful to ensure that terms that varied by large degrees (e.g., \( \kappa_e \) and \( \sigma_g \)) were balanced in the code, to avoid inadvertent scalings.
The form of (2.2.28) was also modified by absorbing the concentration terms into the exponential, that is,

\[
i_{n(p)}(r,t) = i_0 \left[ \exp \left( \ln \left\{ \frac{C_{s(p)}^*(1, R, x, t)}{p_3} \right\} + \frac{\alpha_F R s T}{F} \eta(p) \right) \right. \\
- \exp \left( \ln \left\{ \frac{1 - C_{s(p)}^*(1, R, x, t)}{1 - p_3} \right\} + \ln \left\{ \frac{C_{e(p)}(R, t)}{C_0^e} \right\} - \frac{\alpha_F R s T}{F} \eta(p) \right) \right].
\] (2.2.47)

This reduces the size of the exponent, especially when the concentration at the surface approaches \(C_{\text{max}}\). Without this modification, Sundials often required a time step (even with moderately high tolerances) of size below machine precision.

We also must deal with the “advective” term in (2.2.11) introduced by using the Landau transform. We used flux-limiting [110] with a Van-Leer limiter to calculate this term.

On the crystal scale, the boundary condition at \(s = 0\) changes to a no-flux condition when \(r_i \approx 0\). This introduces a discontinuity in the problem. IDA can implicitly handle small discontinuities in a system, however, unfortunately in our case the discontinuity is not small and causes convergence issues when running particle scale simulations. Helpfully IDA provides a root-finding feature that we use to stop the solver when \(r_i = 0\) in any crystal. When this occurs the solver is reset, as the time-stepping method (BDF) depends on previous time steps, which are invalid once the boundary condition changes. This also means we do not need to define when the moving boundary comes “close enough” to the crystal centre, as the solver detects (to near machine precision) when this occurs.

On the particle scale, a significant source of non-conservation comes from evaluating the \(i_{e(p)} |_{R=R_0}\) and \(\left(D_{\text{eff}(p)} \nabla C_{e(p)} \right) |_{R=R_0}\) terms in (2.2.40) and (2.2.41), respectively. In order to calculate \(i_{e(p)}\) at \(R = R_0\), we require the gradient in \(\eta(p)\) at \(R = R_0\) (similarly for \(\nabla C_{e}\)). If care is not taken with this term, the cathode scale does not conserve charge by up to 10-20%, which is considerable. We use a backward difference to approximate this gradient, while increasing the number of nodes and using a nonlinear grid (with refinement at \(R = R_0\)) to help keep this approximation accurate. The results from this investigation showed that the utilisation and overpotential were not affected by increasing the number of nodes on the particle scale, even when the distance between nodes was smaller than the crystal diameter.

We found that using 19 nodes on the crystal scale, 15 on the particle and 10 on the cathode balanced the run time (several hours) with the increased accuracy and conser-
Figure 2.2: Discharge curves of the model (solid) compared to experimental data from Srinivasan and Newman [21] (symbols) for a range of constant discharge rates.

vation obtained. Even with this level of refinement, at the end of a simulation there is still a conservation difference of 1-2%. This is still non-trivial, but any increase in grid resolution increased the run time considerably. Again a move to a more sophisticated solution technique (either through a more advanced time stepping method or spatial discretisation) would decrease the severity of this problem. We also note that this problem would be exacerbated if a non-conservative discretisation scheme like finite differences were used, instead of the FVM.

2.3 Results and discussion

2.3.1 Model validation

Before exploring some of the results from the model, we first validate the output against the experimental results given by Srinivasan and Newman [21]. Fig. 2.2 shows that our model compares well with their experimental data, across a range of discharge rates. The majority of the parameters used to generate Fig. 2.2 were taken from Srinivasan and Newman [21] (see Table 2.2 and 2.3). Only 3 parameters were adjusted to generate
The fit shown in Fig. 2.2. The value of the exchange current density ($i_0$) that Srinivasan and Newman [21] used to fit their model is $3.14 \times 10^{-6}$ A/m$^2$. We found using a value of $5.4 \times 10^{-5}$ A/m$^2$ gave the best fit for our model. Like Srinivasan and Newman [21] we found it necessary to introduce a contact resistance, $R_c$ (Ω m$^2$), to account for the large decrease in cell potential at higher discharge rates (this is not often seen in experiments, see the discharge curves of Myung et al. [96], Choi and Kumta [95] and Chung et al. [10], for example). Our value of $3.6 \times 10^{-3}$ Ω m$^2$ does not differ greatly from that of Srinivasan and Newman [21] ($6.5 \times 10^{-3}$ Ω m$^2$).

The final parameter adjusted was the particle radius $R_o$. An agglomerate radius of 500 nm provided the best fit to the data. The size (and existence) of agglomerates is determined by synthesis methods, and we have no way of knowing if the Srinivasan and Newman [21] material contains agglomerates. There is a large size range where

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>$1 \times 10^{-4}$</td>
<td>m$^2$</td>
<td>[21]</td>
</tr>
<tr>
<td>$C_e^0$</td>
<td>$1 \times 10^3$</td>
<td>mol/m$^3$</td>
<td>[21]</td>
</tr>
<tr>
<td>$C_{\text{max}}$</td>
<td>20950</td>
<td>mol/m$^3$</td>
<td>[21]</td>
</tr>
<tr>
<td>$D_{\text{Li}}$</td>
<td>$8 \times 10^{-18}$</td>
<td>m$^2$/s</td>
<td>[21]</td>
</tr>
<tr>
<td>$F$</td>
<td>96487</td>
<td>C/mol</td>
<td>[21]</td>
</tr>
<tr>
<td>$i_0$</td>
<td>$5.4 \times 10^{-5}$</td>
<td>A/m$^2$</td>
<td>(a)</td>
</tr>
<tr>
<td>$M_{\text{solv}}$</td>
<td>0.11813 (in DEC)</td>
<td>kg/mol</td>
<td>[111]</td>
</tr>
<tr>
<td>$R_o$</td>
<td>$5 \times 10^{-7}$</td>
<td>m</td>
<td>(a)</td>
</tr>
<tr>
<td>$R_c$</td>
<td>$3.58 \times 10^{-3}$</td>
<td>Ω m$^2$</td>
<td>(a)</td>
</tr>
<tr>
<td>$R_g$</td>
<td>8.314472</td>
<td>J/(mol K)</td>
<td>[48]</td>
</tr>
<tr>
<td>$r_o$</td>
<td>$52 \times 10^{-9}$</td>
<td>m</td>
<td>[21]</td>
</tr>
<tr>
<td>$x_i$</td>
<td>0</td>
<td>m</td>
<td>-</td>
</tr>
<tr>
<td>$x_o$</td>
<td>$6.25 \times 10^{-5}$</td>
<td>m</td>
<td>[21]</td>
</tr>
<tr>
<td>$t_{Li^+}$</td>
<td>0.38</td>
<td>-</td>
<td>[107]</td>
</tr>
<tr>
<td>$T$</td>
<td>298.15</td>
<td>K</td>
<td>[48]</td>
</tr>
<tr>
<td>$\bar{V}_{Li^+}$</td>
<td>$-9 \times 10^{-6}$ (in PC)</td>
<td>m$^3$/mol</td>
<td>[112]</td>
</tr>
<tr>
<td>$\bar{V}_{PF_6}$</td>
<td>$72 \times 10^{-6}$ (in PC)</td>
<td>m$^3$/mol</td>
<td>[112]</td>
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<tr>
<td>$\bar{V}_{\text{solv}}$</td>
<td>$87 \times 10^{-6}$ (in EC:EMC)</td>
<td>m$^3$/mol</td>
<td>[113]</td>
</tr>
<tr>
<td>$w_{\text{LiFePO}_4}$</td>
<td>$7.6 \times 10^{-6}$</td>
<td>kg</td>
<td>[21]</td>
</tr>
<tr>
<td>$\alpha_{a, c}$</td>
<td>0.5</td>
<td>-</td>
<td>[48]</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.13643</td>
<td>-</td>
<td>Derived from [21]</td>
</tr>
<tr>
<td>$\epsilon_g + \epsilon_b$</td>
<td>0.4093</td>
<td>-</td>
<td>Derived from [21]</td>
</tr>
<tr>
<td>$\epsilon_{\text{LiFePO}_4}$</td>
<td>0.45426</td>
<td>-</td>
<td>Derived from [21]</td>
</tr>
<tr>
<td>$\epsilon_{(p)}$</td>
<td>0.25</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>3600</td>
<td>kg/m$^3$</td>
<td>[21]</td>
</tr>
<tr>
<td>$\sigma_g$</td>
<td>$7 \times 10^8$</td>
<td>S/m</td>
<td>[48]</td>
</tr>
<tr>
<td>$\sigma_{s(p)}$</td>
<td>$1 \times 10^{-7}$</td>
<td>S/m</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Table 2.2: Parameter values used in the model. (a) - Fit to experimental curves in Fig. 2.2.
Table 2.3: Equations for parameter values used in the model. If not explicitly listed, particle scale parameters use the same values given above, with appropriate particle scale variables (e.g., \(a_{e(p)}\)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (= a_e m \gamma_{\pm})</td>
<td>(3/r_o)</td>
<td>(m^{-1})</td>
<td>[48]</td>
</tr>
<tr>
<td>(a_e) (= \rho_e m \gamma_{\pm})</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(C_{eq}) (= C_{max})</td>
<td>0.9525</td>
<td>(\text{mol/m}^3)</td>
<td>[21]</td>
</tr>
<tr>
<td>(C_0) (= C_{max})</td>
<td>0.02</td>
<td>(\text{mol/m}^3)</td>
<td>[21]</td>
</tr>
<tr>
<td>(C_{solv}) (= (1 - C_e(\bar{V}<em>{Li^+} + \bar{V}</em>{PF_6^-})) / \bar{V}_{solv})</td>
<td>-</td>
<td>(\text{mol/m}^3)</td>
<td>-</td>
</tr>
<tr>
<td>(D_e) (= 5.34 \times 10^{-10} \exp(-0.65(1 \times 10^{-3} C_e)))</td>
<td>(\text{m}^2/\text{s})</td>
<td>[21]</td>
<td></td>
</tr>
<tr>
<td>(D_{eff}) (= \epsilon D_e/\tau)</td>
<td>(\text{m}^2/\text{s})</td>
<td>[106]</td>
<td></td>
</tr>
<tr>
<td>(I) (= DR \times w\text{LiFePO}_4)</td>
<td>(A)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(m) (= C_e / C_{solv} M_{solv})</td>
<td>(\text{mol/kg})</td>
<td>[107]</td>
<td></td>
</tr>
<tr>
<td>(r_{p}^0)</td>
<td>(0.99 r_o)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

agglomerates can form, from as small as several crystals [96] to large clusters, of radius between 500 nm [50] and several microns [97, 100]. For the crystal radius, we used that determined by Srinivasan and Newman [21] (\(r_o = 52\) nm).

In order to generate a better fit in Fig. 2.2, we could have taken the approach of Kasavajjula et al. [64], who modified some of the phase parameters (like the size of the miscibility gap) in the Srinivasan and Newman [21] shrinking-core model. These authors show that the addition (and tuning) of several extra parameters can change the shape of the simulated discharge curves considerably. This approach was not taken here, as the fit given in Fig. 2.2 is sufficient, especially given that we believe that an alternative to the shrinking-core approach is required in future crystal scale modelling of LiFePO\(_4\), rather than further modification of the shrinking-core mechanism.

The multi-scale nature of our model requires some idea of the porosity on both the particle and cathode scale. Srinivasan and Newman [21] estimate a porosity of 0.25 and the total volume fraction of LiFePO\(_4\) to be 0.3407. Accordingly, we set \(\epsilon_{(p)} = 0.25\) and then use this coupled with the volume fraction of LiFePO\(_4\) to obtain \(\epsilon_{\text{LiFePO}_4} \approx 0.45\) and \(\epsilon \approx 0.14\) (where \(\epsilon_{\text{LiFePO}_4}\) and \(\epsilon\) are cathodic scale volume fractions, which do not include the particle scale porosities). With these values, (2.2.34) allows us to calculate that \(\epsilon_b + \epsilon_g \approx 0.4\). There is no need to determine the individual volume fractions, as
\( \epsilon_b \) and \( \epsilon_g \) never appear explicitly in the model (Srinivasan and Newman [21] state their electrode contains 8% carbon and 10% binder by weight).

Thus far we have not specified the value of \( C_{\text{max}} \) (and therefore \( C_{\text{eq}} \) and \( C_0 \)) on the crystal scale. Srinivasan and Newman [21] calculate \( C_{\text{max}} \) based on their experimentally observed (at very low discharge rates) maximum oxide capacity \( Q_{\text{max}} = 156 \text{ mAh/g} \) and the density of LiFePO\(_4\) \( (\rho = 3.6 \text{ g/cm}^3) \). We note that this value of \( Q_{\text{max}} \) is lower than the theoretical capacity of LiFePO\(_4\), which is 170 mAh/g. In the more recent literature there has been great success in extracting very close to this theoretical capacity from the cells. In order to validate our model against the Srinivasan and Newman [21] experimental data, we have taken \( Q_{\text{max}} = 156 \text{ mAh/g} \), as this is consistent with that reported by Srinivasan and Newman [21] for their oxide. This leads to concentration values of \( C_{\text{max}} = 20950 \), \( C_{\text{eq}} = 19954.875 \) and \( C_0 = 419 \text{ mol/m}^3 \). Furthermore, for the sake of simplicity in the presentation of the model parameters we have chosen to maintain this value of \( Q_{\text{max}} \) (and hence \( C_{\text{max}}, C_{\text{eq}} \) and \( C_0 \)) for the results presented in Section 2.3. The choice of \( Q_{\text{max}} \) has no effect on the utilisation trends observed in this section, however we note that in order to replicate the experimental discharge of the more recent literature using our model we always take \( Q_{\text{max}} = 170 \text{ mAh/g} \) (i.e., \( C_{\text{max}} = 22834 \text{ mol/m}^3 \)).

### 2.3.2 Particle scale

Given the validation of our model in the previous section we now consider the discharge of a single porous LiFePO\(_4\) particle in a container of excess, well stirred electrolyte. We use the model in this manner in an effort to identify and investigate the key parameter(s) that determine active material utilisation on the porous particle scale. In order to discharge a single particle, we must modify the boundary conditions on the particle scale (in a manner similar to Farrell and Please [114]). For the electrolyte, we set \( C_{\text{e}(p)}|_{R=R_o} = C_{\text{e}}^0 \), and for the overpotential, we set a galvanostatic condition at the outer boundary of the particle, namely, \( i_{\text{e}(p)}|_{R=R_o} = I/4\pi R_o^2 \). We note that the weight of active material is much smaller when discharging a single particle, so in the following section, \( w_{\text{LiFePO}_4} \), and hence the applied current, \( I \), take different values from that used to generate Fig. 2.2.

Fig. 2.3 shows the utilisation of a single particle as the particle radius is increased, for different discharge rates. Fig. 2.3a and Fig. 2.3b show the effect of modifying the diffusion coefficient \( (D_{\text{Li}}) \) and the electronic conductivity \( (\sigma_{s(p)}) \) of LiFePO\(_4\) respectively.
(a) Effect of changing $D_{l\alpha}$. Dotted line: $8 \times 10^{-19}$ m$^2$/s, solid line: $8 \times 10^{-18}$ m$^2$/s, dashed line: $8 \times 10^{-17}$ m$^2$/s.

(b) Effect of changing $\sigma_{s(p)}$. Dotted line: $1 \times 10^{-8}$ S/m, solid line: $1 \times 10^{-7}$ S/m, dashed line: $1 \times 10^{-6}$ S/m.

Figure 2.3: Particle-scale utilisation vs agglomerate size, for different discharge rates. 
- •: DR = 20 mA/g, ■: DR = 200 mA/g.
This is in an attempt to quantitatively determine the degree to that porous agglomerates of LiFePO$_4$ crystals are electronically and ionically limited. We chose to vary the diffusivity to investigate ionic conductivity limitations, whilst keeping the crystal size ($r_o = 52$ nm) fixed. Similar trends would have been observed if we had kept $D_{Li}$ fixed and varied $r_o$. We can see that both Fig. 2.3a and Fig. 2.3b show that as the size of the particle increase, the utilisation decreases.

Furthermore, at low discharge rates (20 mA/g) Fig. 2.3a shows that the transport of lithium on the crystal scale is not limiting the particle discharge, as the utilisation increases only slightly as $D_{Li}$ increases by an order of magnitude, from $8 \times 10^{-18}$ m$^2$/s to $8 \times 10^{-17}$ m$^2$/s. The drop in utilisation as $D_{Li}$ decreases to $8 \times 10^{-19}$ m$^2$/s, is more significant with smaller particles ($R_o \leq 2.5 \mu m$), but is less so as $R_o$ increases. At a higher discharge rate of 200 mA/g, for small particles, the effect of decreasing the diffusivity is much more evident, with utilisation peaking at around 30% for small particles compared to 80% for the same particle when $D_{Li}$ is increased by one order of magnitude. Smaller crystals would be required in order to tolerate higher discharge rates, especially if the porous agglomerate of crystals is large ($R_o > 2.5 \mu m$). We note that for high DR, increasing $D_{Li}$ above $1 \times 10^{-18}$ m$^2$/s however, does not increase the utilisation beyond around 80% for small particles. This shows that the particle discharge is not ionically limited. Increasing the discharge rate would of course create a more obvious difference between the solid and dashed lines.

Fig. 2.3b shows the result of modifying the electrical conductivity of LiFePO$_4$ ($\sigma_{s(p)}$), where the solid lines are the same as in Fig. 2.3a. We observe that for a discharge rate of 20 mA/g, if we increase $\sigma_{s(p)}$ by only one order of magnitude, we increase the particle utilisation to almost 100%, even as the agglomerate becomes large. This shows that particles, especially as they grow in size, are electronically limited. Even at a higher discharge rate (200 mA/g), the utilisation shows a marked increase across the range of particle sizes with the conductivity at $\sigma_{s(p)} = 1 \times 10^{-6}$ S/m. Decreasing the conductivity decreases the utilisation considerably, a trend that is exacerbated at higher discharge rates. It also increases the rate at which the utilisation drops off as the agglomerate (particle size) grows; for example, for the 20 mA/g discharge rate, when $\sigma_{s(p)} = 1 \times 10^{-6}$ S/m, the utilisation for a small particle (0.78 $\mu m$) is still around 88%, however (approximately) doubling the particle size (1.82 $\mu m$) halves the utilisation, to only 43%.

These results clearly show why reducing the size of the crystals and preventing agglomeration have been successful in increasing the performance of LiFePO$_4$ cells; the small
diffusion coefficient of Li$^+$ limits ionic transport, forcing the use of nanometer-sized crystals, while the small electronic conductivity limits electronic transport and requires the reduction (or elimination) of agglomerated particles. In this sense, the diffusion coefficient controls the acceptable size of individual LiFePO$_4$ crystals and the electronic conductivity determines the size of agglomerates.

In their work, Gaberscek [115] explore electronic limitations of particles by providing an equation that gives a rough criterion on the maximum size of an agglomerate such that there are no “significant problems due to electronic conduction” [115]. Assuming the ratio of electronic to ionic conductivities is 50 and neglecting the density differences between a single crystal and agglomerates, the authors give an estimate of $D \leq 7d$, where $D$ is the diameter of an acceptable particle and $d$ is the diameter of the crystals that agglomerate to make this particle. For low discharge rates, this matches quite well with the results shown in Fig. 2.3b.

We note that in some cases [116] the ratio of electronic to ionic conductivity has been reported closer to $1 \times 10^4$. In this case, given that the ratio of crystal to particle densities is approximately 1.17 (calculated using the porosity and density given in Table 2.2 and 2.3; the ratio is certainly $> 1$), then we obtain that $D \leq 143d$. Such a particle (judging by the results shown in Fig. 2.3b) would almost certainly be electronically limited. The equation given by Gaberscek [115] is qualitatively sensible, as there is a definite limit to the size of an agglomerate given the difference between ionic and electronic conductivities. However, this formula does not consider that the crystals in a particle could become ionically limited, when given the results above, they can, even when the electronic conductivity is much greater than the ionic.

For example, Fig. 2.3a shows that for small agglomerates (0.78 $\mu$m) discharged at 200 mA/g, a diffusivity of $D_{Li} = 8 \times 10^{-19}$ m$^2$/s adversely affects utilisation. A similar result could have been obtained by fixing $D_{Li}$ at $8 \times 10^{-18}$ m$^2$/s and increasing $r_o$ from 52 nm to approximately 165 nm. This implies that if small agglomerates (0.78 $\mu$m) were formed from crystals with $r_o = 165$ nm, this particle would be ionically limited. It is in this sense that we note the formula given by Gaberscek [115] is only applicable when the crystals in an agglomerate are small enough to never be ionically limited at any discharge rate.

Ideally, the crystal size should be made as small as possible, so that the only possible limitations are electronic in nature. This recommendation however, neglects the effect of size-dependant crystal effects like the size of the miscibility gap [24], or grain-
boundary diffusion, which are not considered in this work.

Once the crystal size has been made small enough to prevent ionic limitations, the agglomerate size then depends on two factors; firstly the electronic conductivity and secondly the discharge rate. As the discharge rate is increased, the agglomerate must either be made smaller, or the electronic conductivity of the LiFePO$_4$ material must be increased. We note that the highest discharge rate in Fig. 2.3b is 200 mA/g. This corresponds to approximately 1.17 C, which in reality is quite low. Given realistic rates and the controversy over the ability to increase $\sigma_{s(p)}$, it is easy to see why the literature has moved to surrounding (small) crystals entirely in carbon.

The results presented above however do suggest that agglomerates can be tolerated under certain regimes. Given the size of the crystals used (52 nm), small particles are typically not ionically limited. At low discharge rates, agglomerates of up to 15 crystals in radius are fully utilised without any increase in electronic conductivity. This has implications for LiFePO$_4$ synthesis methods and carbon content, namely, that if the expected discharge rate of a cell is low, less effort could be placed in reducing agglomerate formation during the synthesis phase.

The model presented above does not have the ability to simulate different carbon coating scenarios such as “point-contact”, like those shown in Gaberscek et al. [88], although given that we can show that even relatively small agglomerates are electronically limited at 200 mA/g, it seems reasonable to assume that anything less than full electronic coating of crystals would not be sufficient to assure sufficient electronic transport.

In addition, there is some question as to the validity in varying the transport parameters for electrons and lithium ions independently of each other since in many semiconductors there is an ambipolar coupling between these charges. We note however, that the values of $D_{\text{Li}}$ and $\sigma_{s(p)}$ used in this work are consistent with the experimental literature and as such, any charge coupling in the oxide may already be accounted for in these values. In any event, it is planned that the question of ambipolar effects in LiFePO$_4$ and their impact on crystal scale intercalation modelling will be considered by the authors in future work.

### 2.3.3 Cathode scale

On the cathode scale, the assumption that individual LiFePO$_4$ particles are electronically connected to the current collector by a continuous graphite phase means that we consider only ionic limitations in the electrolyte on this scale, and the affect that
Cathode Thickness ($\mu$m) | $C_0|_{x=x_0}$ (mol/m$^3$) at EOD
---|---
0 | 1000
20 | 800
40 | 600
60 | 400
80 | 200
100 | 0

(a) Effect on $C_0$ (mol/m$^3$) at $x = x_0$ at the end of discharge.

Cathode Thickness ($\mu$m) | Utilisation (% Active Material)
---|---
0 | 100
20 | 80
40 | 60
60 | 40
80 | 20
100 | 0

(b) Effect on cathode-scale utilisation.

Figure 2.4: Effect of changing the cathode thickness for different discharge rates.
- ●: 34 mA/g
- ■: 85 mA/g
- ▲: 171 mA/g
- ▼: 342 mA/g
- ♦: 500 mA/g
- ♠: 855 mA/g
these have on cathodic discharge capacity. We could consider the effect of cathodic-scale parameters like porosity and global carbon content, however these are explored by Srinivasan and Newman [21, 117] and the optimised cathodic designs outlined by these authors would be similar to those produced by our work. Johns et al. [118] recently showed that the electrolyte can limit utilisation at high discharge rates in LiFePO$_4$ cells. Transport in the liquid phase must be sufficient to supply the active material with Li$^+$ ions. The form of the function used to determine the electronic conductivity of the electrolyte ($\kappa_e$) (see Table 2.3) means that as the Li$^+$ concentration approaches zero the conductivity drops, significantly hampering discharge.

Fig. 2.4 shows the effect of increasing the thickness of the cathode (again, $w_{\text{LiFePO}_4}$ and $I$ differ from the values listed in Table 2.2), given the discharge rates used in Fig. 2.2.

Fig. 2.4a shows the concentration of electrolyte at the cathode/current collector interface ($x = x_o$) at the end of discharge, while Fig. 2.4b shows the corresponding active material utilisation. We can see in Fig. 2.4a that at low discharge rates, the concentration of electrolyte is still high at $x = x_o$, even as the electrode thickness is increased. As the discharge rate increases, we can see the concentration at $x = x_o$ decrease due to transport limitations and the cathode must be made thinner to ensure that there is sufficient Li$^+$ remaining in the electrolyte to facilitate discharge. However, at a cathode thickness of 60 $\mu$m, when the discharge rate is 855 mA/g, we observe a minimum in the concentration curve so that as the electrode thickness increases beyond 60 $\mu$m the concentration at $x = x_o$ increases. The reason for this behaviour is that at this high rate, the electronic and ionic limitations on the particle scale (as discussed in Section 2.3.2), become more important than the transport limitations in the electrolyte on the cathode scale and cause the potential to drop below the voltage cutoff before the lithium concentration in the electrolyte can reach zero.

In Fig. 2.4b we can clearly see the utilisation decrease as the thickness increases, across all discharge rates. The sharp decrease in utilisation for the discharge rates of 342 and 500 mA/g is particularly notable and is caused by the drop in $\kappa_e$ when $C_e < 200$ mol/m$^3$. For these two cases the Li$^+$ deficiency in the electrolyte causes the discharge to end. The drop in utilisation is far less pronounced with the 855 mA/g rate for cathode thickness above approximately 50 $\mu$m, as discharge ends (due to particle scale limitations as discussed above) before the remaining Li$^+$ in the electrolyte can be depleted.

These results show that the electrolyte can become important at higher discharge rates, with a cathode thicker than approximately 50 $\mu$m. Indeed, if the recommendations
Figure 2.5: Effect of changing parameters with DR = 855 mA/g. Each curve includes the change from the previous curve.

- Model output from Fig. 2.2, •: \( r_o = 26 \) nm, ☉: \( \sigma_s(p) = 1 \times 10^{-6} \) S/m, +: \( C^0_e = 2 \) M, ♦: \( R_o = 250 \) nm.
given in Section 2.3.2 for high discharge rates were implemented (namely, small crystals either embedded within small agglomerates or entirely surrounded with graphite, as they are in more modern oxides) the electrolyte would become the primary factor in determining the end of discharge. This notion is tested in Fig. 2.5, where particle scale parameters have been modified to increase material utilisation. In Figs. 2.5a and 2.5b we consider a discharge rate of 855 mA/g. The corresponding 855 mA/g curve from Figs. 2.4a and 2.4b have been reproduced in Fig. 2.5a and 2.5b respectively as a “base case” discharge scenario and to provide easy comparisons for the effect that changing particle and crystal parameters in a cumulative manner have on this “base case”.

We note that in Fig. 2.5a, all the curves show that the electrolyte concentration at \( x = x_o \) approaches zero when the cathode thickness is approximately 50 to 70 \( \mu m \). Beyond this range the electrolyte concentration increases. Following on from our observation from Section 2.3.2, the radius of the crystals \( (r_o) \) was halved (to 26 nm) and then the electronic conductivity of the oxide, \( \sigma_{s(p)} \), was increased by an order of magnitude (to \( 1 \times 10^{-6} \) S/m) from the base case scenario. Fig. 2.5b shows that these two modifications result in utilisation that increases to almost 90% for cathodes \( \leq 40 \) \( \mu m \). This scenario is representative of modern oxides, where small crystals (or small agglomerates of crystals) are encased in carbon. We note that in this case, as the cathode thickness increases there is still a large drop off in utilisation, corresponding to \( C_e \rightarrow 0 \) in Fig. 2.5a. The electrolyte concentration remains low compared to the base case as the thickness increases. In this case, the particle-scale electronic and ionic limitations that lead to the end of discharge in the base case, have been reduced and the electrolyte is the only factor constraining discharge.

We now consider what happens if we increase the concentration of the electrolyte to 2 M (whilst maintaining the previous \( r_o \) and \( \sigma_{s(p)} \) modifications to the base case). From Fig. 2.5b we observe that for thin cathodes \( (\leq 40 \mu m) \) this makes little difference to the utilisation. However at cathode thicknesses above 40 \( \mu m \), the utilisation of active material increases by approximately 10 to 15% (in relation to the + curve), even at a thickness of 100 \( \mu m \). Finally the particle size was decreased to 250 nm (whilst maintaining all the previous modifications to the base case). This is largely superfluous, as the electronic limitations of the particle have already been removed by increasing \( \sigma_{s(p)} \). This is evident in Fig. 2.5b, as the utilisation barely increases (compared to the + curve).

These results above clearly infer that for modern oxides, where considerable efforts have been made to decrease crystal size and reduce the formation of agglomerates
of crystals, the transport of LiPF$_6$ electrolytes does limit the discharge of LiFePO$_4$ cathodes. This effect is exacerbated for thicker cathodes (> 50 to 60 $\mu$m in the above case) and higher discharge rates (5C in the above case). This qualitatively matches with the work of Johns et al. [118], who in experiments, utilised approximately 50% of the active material in a LiFePO$_4$ cell, while discharging at 10 C in 1 M LiPF$_6$. After changing the electrolyte to an aqueous electrolyte with 1 M Li$_2$SO$_4$, which has a diffusion coefficient 2 orders of magnitude higher than a non-aqueous LiPF$_6$ electrolyte (and a slightly higher $t_{Li}$ value) the utilisation was still approximately 25% at the greatly increased rate of 900 C.

2.4 Conclusions

The multi-scale model presented above compares well to the experimental data of Srini-vasan and Newman [21], across a range of discharge rates. The results from the particle scale show why minimising the formation of agglomerates and shrinking the size of individual crystals is so successful at increasing the performance of a LiFePO$_4$ cell. We note that the particle-scale configuration in a battery should be directly tailored to the application; low-drain applications (1 C) can tolerate moderately sized crystals (50 nm radius) agglomerated into secondary particles (500 nm radius), whereas a higher discharge rate requires smaller crystals (20 nm radius) either directly coated in carbon (so no agglomerates form) or present in small agglomerates but with increased electronic conductivity (even an improvement of 1 order of magnitude increases performance considerably). In the low-drain case, the benefit of such targeting would centre around increased energy density (as crystal sizing and agglomerates are often controlled by increasing carbon content) and without the need for fine-grain morphology control, reduced costs.

Many of these recommendations have already been implemented in modern oxides, and in these cases, with higher discharge rates, the transport of Li$^+$ ions in the electrolyte becomes important. Doubling the concentration of Li$^+$ in the electrolyte can increase capacity by up to 15%, though effort should be placed in seeking an electrolyte with better transport parameters (e.g. aqueous Li$_2$SO$_4$). The suitability of an electrolyte for use in a Li-ion cell is naturally dependant on other factors like commercial safety, though the results presented here suggest that the ionic diffusivity in a LiPF$_6$ electrolyte can limit the discharge of a modern LiFePO$_4$ cell.
3. A FVM for the Cahn-Hilliard-reaction IBVP

For this chapter, the associated reference is:


Additional numerical detail has also been included below.

3.1 Introduction

The Cahn-Hilliard (CH) equation was first proposed to model the quenching of binary alloys [69], but has found uses for modelling many types of phase separation behaviour. Numerically, the CH equation is difficult to solve accurately, especially in two or three dimensions; it is very stiff and possesses multiple time and space scales. Our interest in CH problems is motivated by semi-conductor intercalation processes, such as those that occur in LiFePO$_4$ batteries and other electrochemically active porous media. LiFePO$_4$ is a promising battery material [7] that undergoes phase-separation during charge and discharge to form highly and lowly lithiated phases [7, 22]. Recently, Singh et al. [76] used the CH equation to model phase separation in this material. Previously, a Stefan problem [55] (which produces isotropic “shrinking-core” behaviour on a spherical domain) has been used to model this phenomenon [21, 82]. However, such a mechanism does not reflect the experimentally observed anistropy of Li$^+$ diffusion in LiFePO$_4$ [57] and it is this acute anistropy that motivates the CH approach of Singh et al. [76].

Traditionally, a no-flux boundary condition (BC) is applied to the CH equation. Singh et al. [76] however, used an anisotropic, two-dimensional CH equation coupled with a flux BC derived from electrochemical relations to simulate the intercalation of Li$^+$ into FePO$_4$ material. The authors then depth-average their CHR initial boundary
value problem (IBVP) over the spatial coordinate corresponding to the direction of rapid diffusion in LiFePO$_4$, to obtain a one-dimensional IBVP (also known as the “Allen-Cahn-reaction” (ACR) model [54]). This one-dimensional IBVP is second-order (compared with the original fourth-order two-dimensional CHR IBVP) and is more amenable to examination using analytic and numerical methods. Burch [71] extends this work (and examines the assumptions necessary to depth-average in more detail) and shows that the introduction of Cahn-Hilliard dynamics coupled with a reaction term appears to explain recent results from the experimental literature, including the observed reduction of the miscibility gap between phases with decreasing crystal size [24, 77]. Burch [71] also presents a numerical method for solving the full one and two-dimensional CHR IBVPs, though we note that there are errors in their numerical approach that we examine below.

A variety of different numerical techniques have been employed to solve the CH equation, including finite element [119, 120], finite difference [121, 122], spectral [123], boundary integral [124], level set [125], discontinuous Galerkin [126] and multigrid methods [127]. To our knowledge, only Cueto-Felgueroso and Peraire [128] and Burch [71] have investigated the use of the finite volume method (FVM) [49] for solving the CH and CHR equations, respectively. Equations discretised with the FVM obey conservation laws, which make the method well suited to solving CH equations, though including BCs for higher-order PDEs can be difficult.

Cueto-Felgueroso and Peraire [128] use a “dual continuous/discontinuous” moving-least-squares (MLS) approach to estimate information at quadrature points on an unstructured (cell-centred) grid. The MLS method comprises a set of basis functions that are fit (in the least-squares sense) locally using a series of neighbouring node points. These locally fit approximations are then smoothed together to form a globally continuous solution (that includes BCs by using an analogue to “ghost-nodes” [129]). This global solution is evaluated to obtain flux terms on control volume (CV) faces, though only for elliptic/parabolic terms. For hyperbolic terms, the global solution provides derivative estimates directly at node points, and these are then used to build a separate approximation (based on Taylor series) over a single control volume. It is in this sense that the solution technique is continuous/discontinuous, as the Taylor series used over a single CV will not necessarily be continuous with its neighbours. This is a sophisticated approach that was originally used to tackle shallow water problems [130].

Burch [71] adopts a simpler approach and constructs difference equations to represent the derivatives required at CV mid-points on a (cell-centred) grid. This approach is
simple to perform on a linear, orthogonal grid in one dimension, but becomes signifi-
cantly more difficult in higher dimensions on unstructured grids. Importantly though,
the difference equations used near boundaries include the variational boundary condi-
tion (VBC). This ensures that all the BCs are included in the discretised fourth-order
problem, though again we note that outcomes from this scheme are not presented.

In this work, we present a method for the numerical solution of the CH and CHR
problems that incorporates the VBC into a local least-squares approximation based on
Taylor series to use with the (vertex-centred) FVM. This simple approach is flexible
enough to compute derivatives on an unstructured grid without the need to build a
global solution that includes BCs. We then solve the CH and CHR equations in both
one and two dimensions applied to Li$^+$ intercalation in LiFePO$_4$ as a relevant case
study, and investigate the role that including the VBC in the least-squares problem has
on the numerical solution.

3.2 Model equations

3.2.1 Cahn-Hilliard equation

We adopt the notation of Burch [71] and assume that the free energy of mixing in our
system is given by the CH functional [69] $G[c(x, t)]$ (J), where $c(x, t) \in [0, 1]$ is the
nondimensional concentration of Li$^+$ in a LiFePO$_4$ crystal, with spatial coordinates $x$
(m), through time $t$ (s). This concentration has been nondimensionalised by $\rho$ (m$^{-3}$),
the constant site density (number of molecules per unit volume in the lattice) of Li$^+$
in a single crystal. For a more detailed derivation of the following model equations,
please see [69, 71]. On an $N_D$-dimensioned domain $\Omega$ with boundary $\Gamma$ the free energy
of mixing in a CH model can be written as

$$G(t) \equiv G[c(x, t)] = \int_\Omega \left[ g_{\text{hom}} + \frac{1}{4} (\nabla c)^T K (\nabla c) \right] \rho \, d\Omega, \quad \text{(3.2.1)}$$

where $g_{\text{hom}}$ (J) is the free energy per molecule of a homogeneous system at a uniform
concentration and $K$ (J m$^{-2}$) is a gradient penalty tensor that we have assumed is
symmetric positive definite, isotropic and constant. We assume $g_{\text{hom}}$ obeys a regular
solution model [46, 69, 71] and is written as

$$g_{\text{hom}}(c) = \Omega m c (1 - c) + k_B T \left( c \ln(c) + (1 - c) \ln(1 - c) \right), \quad \text{(3.2.2)}$$
where $k_B$ (J K$^{-1}$) is Boltzmann’s constant, $T$ (K) is the temperature and $\Omega_m$ (J) is the enthalpy of mixing per site. The chemical potential $\mu$ (J) per molecule of Li$^+$ in the crystal, written with respect to the reference chemical potential $\mu^\Theta$ (J), is given by the variational derivative of (3.2.1) (written with respect to the same reference chemical potentials) [54, 131]

$$\mu - \mu^\Theta = \frac{\partial g_{\text{hom}}}{\partial c} - \nabla \cdot (K \nabla c), \quad (3.2.3)$$

which, given the form of (3.2.2), can be written as

$$\mu - \mu^\Theta = \Omega_m (1 - 2c) + k_B T \ln \left( \frac{c}{1 - c} \right) - \nabla \cdot (K \nabla c). \quad (3.2.4)$$

The mass flux $j$ (m$^{-2}$ s$^{-1}$) per molecule is proportional to a gradient in chemical potential, namely

$$j = \rho c M \nabla \mu, \quad (3.2.5)$$

where $M$ (m$^2$ J$^{-1}$ s$^{-1}$) is a mobility tensor. Finally, as mass is conserved in this system, the Cahn-Hilliard equation is given by

$$\frac{\partial c}{\partial t} + \frac{1}{\rho} \nabla \cdot j = 0, \quad x \in \Omega. \quad (3.2.6)$$

The CH equation (3.2.6) can also be rewritten directly in terms of the concentration $c(x, t)$ and using the Einstein relation to write the mobility as $M = D/(k_B T)$, where $D$ (m$^2$ s$^{-1}$) is a diffusion tensor, we have

$$\frac{\partial c}{\partial t} + \nabla \cdot \left( D \left\{ \left[ 2\Omega_m c - \frac{1}{1 - c} \right] \nabla c + c \nabla [\nabla \cdot (\tilde{K} \nabla c)] \right\} \right) = 0, \quad (3.2.7)$$

where the tilde notation represents a scaling by $k_B T$ (i.e., $\tilde{\Omega}_m = \Omega_m / k_B T$, $\tilde{K} = K / k_B T$).

The solution to (3.2.7) is the concentration distribution of Li$^+$ that minimises the free-energy functional (3.2.1) at any time. The initial concentration of Li$^+$ in a crystal is given by some function $f(x)$, such that

$$c(x, 0) = f(x), \quad \text{at } t = 0, \quad (3.2.8)$$

and the boundary conditions for the problem are [71]

$$\hat{n} \cdot (\tilde{K} \nabla c) = 0, \quad \text{on } \Gamma \quad (3.2.9)$$

$$\hat{n} \cdot (\nabla (\nabla \cdot (\tilde{K} \nabla c))) = 0, \quad \text{on } \Gamma \quad (3.2.10)$$
where \( \hat{n} \) is an outward facing unit normal on \( \Gamma \). We note that (3.2.7) together with (3.2.8) to (3.2.10) represent the Cahn-Hilliard initial boundary value problem, which we shall refer to as the CH IBVP throughout this work.

Equation (3.2.9) is often known as the variational boundary condition (VBC), and Burch [71] emphasises that this condition must be satisfied for (3.2.3) to be valid. Together, the boundary conditions (3.2.9) and (3.2.10) imply the no-flux condition \( \hat{n} \cdot j = 0 \) on \( \Gamma \). This, along with the form of (3.2.6) enforces conservation of mass on the system, or

\[
\frac{dM}{dt} = \frac{1}{\Omega} \frac{d}{dt} \left( \int_{\Omega} c(x, t) \, d\Omega \right) = 0, \tag{3.2.11}
\]

where \( M(t) \) is the dimensionless mass fraction (or average concentration) of Li\(^+\) in the system at time \( t \). In addition, the total free energy of the system must decrease through time [132] and hence

\[
\frac{d\tilde{G}}{dt} = \int_{\Omega} \tilde{\mu} \frac{\partial c}{\partial t} \rho \, d\Omega < 0. \tag{3.2.12}
\]

Equations (3.2.11) and (3.2.12) represent physical conditions that should be satisfied by any solution of the CH equation; a numerical scheme that satisfies (3.2.12) is known as gradient stable [122, 132].

### 3.2.2 Cahn-Hilliard-reaction equation

Singh et al. [76] modify the traditional CH system described in Section 3.2.1 by including a reaction condition on the boundary. The VBC (3.2.9), however, must still be applied, giving the boundary conditions for the CHR problem to be

\[
\hat{n} \cdot (\hat{K} \nabla c) = 0, \quad \text{on } \Gamma
\]
\[
\hat{n} \cdot j = \rho_s R(c), \quad \text{on } \Gamma \tag{3.2.13}
\]

where \( \rho_s \) (m\(^{-2}\)) is the surface site density and \( R(c) \) (s\(^{-1}\)) is a reaction term that determines the number of molecules of Li\(^+\) that intercalate into the crystal. Equations (3.2.7) to (3.2.9) and (3.2.13) represent the IBVP that we shall refer to as the CHR IBVP throughout this work. The reaction term \( R(c) \) is a Butler-Volmer expression [42], defined in terms of the chemical potential (3.2.3) at the surface of the crystal. Burch and Bazant [77] write the general form of this equation as

\[
R(c) = R_{\text{ins}} \left[ 1 - \exp \left( \tilde{\mu}(c) - \tilde{\mu}_e \right) \right], \tag{3.2.14}
\]
where $\tilde{\mu}_e$ is the nondimensional chemical potential of the electrolyte surrounding the crystal and $R_{\text{ins}} \, (s^{-1})$ is the rate for the insertion reaction. For our numerical tests, we keep the general form of (3.2.14), but we note that if the CHR IBVP were used in a traditional battery model, (3.2.14) could be rewritten to explicitly contain an external overpotential and electrolyte concentration. If this is the case, (3.2.1) should also include the reference chemical potential of the electrolyte [54], which is set to zero in this work.

### 3.3 Finite volume discretisation

The finite volume method [49] (FVM) discretises the integral form of a conservation law over a set $\mathcal{V}$ of non-overlapping control volumes (CVs, see Fig. 3.1); the resulting discrete equations satisfy the original conservation laws exactly. On the $i$th CV in $\mathcal{V}$, $V_i$, we define the set of $j$ faces (edges) that border the CV as $\mathcal{E}$, with individual elements in $\mathcal{E}$ written as $E_{ij}$. The centroid node point in $V_i$ is denoted as $x_i$ and the set of quadrature points on the $j$th element of $\mathcal{E}$ as $X_q$, with individual quadrature points written as $x_{qjk}$. As an example, if we define $i = 2$ for the shaded control volume in Fig. 3.1, with borders that include the edges $E_{2,1}$ and $E_{2,2}$, $x_2$ is the centroid node point. Fig. 3.1 also shows two quadrature point $x_{q1,1}$ and $x_{q1,2}$, defined on the edge $E_{2,1}$. 

![Figure 3.1: Example unstructured grid near a boundary in 2D. CVs (vertex-centered) are bordered with a dashed line and have node points defined at their centre. Node $x_5$ is the only node not lying directly on a boundary. $x_{q1,1}$ and $x_{q1,2}$ are quadrature points on the face $E_{2,1}$ and $x_{q2,1}$ is a quadrature point on face $E_{2,2}$, which also lies on a boundary.](image)
We note that (3.2.7) is defined in conservative form, so we can integrate over the $i$th (vertex-centered) CV, $V_i$, and apply the divergence theorem to obtain

\[
\frac{d}{dt} \int_{\Omega_{V_i}} c \, d\Omega_{V_i} = - \int_{\Gamma_{V_i}} (\mathbf{j} \cdot \hat{n}) \, d\Gamma_{V_i},
\]

where $\hat{n}$ is an outward facing normal on $\Gamma_{V_i}$. We then define an average concentration over the $i$th CV as

\[
\bar{c}_i = \frac{1}{\Omega_{V_i}} \int_{\Omega_{V_i}} c \, d\Omega_{V_i},
\]

and recover the exact form

\[
\frac{d\bar{c}_i}{dt} = -\frac{1}{\Omega_{V_i}} \int_{\Gamma_{V_i}} (\mathbf{j} \cdot \hat{n}) \, d\Gamma_{V_i}.
\] (3.3.1)

We can then discretise the line integral in (3.3.1) to obtain

\[
\frac{d\bar{c}_i}{dt} \approx -\frac{1}{\Omega_{V_i}} \sum_{j \in E} \sum_{k \in X_q} (\mathbf{j} \cdot \hat{n})_k w_k,
\] (3.3.2)

where $w_k$ are quadrature weightings at the $k$th quadrature point in $X_q$ on the $j$th edge in $E$. We choose to approximate $\bar{c}_i$ with the value at the $i$th CV centroid, which we designate as $c_i$. This then leaves us to approximate $\mathbf{j} \cdot \hat{n}$ at each of the quadrature points on any given CV face. We use the least-squares technique described in the next section to accomplish this.

### 3.4 Least-squares

Since $\mathbf{j}$ is a function of $c$ and its derivatives (see (3.2.4) & (3.2.5)), then in order to implement the FVM as described in Section 3.3 we require the value of $c$ and its derivatives at quadrature points on CV faces. For a general unstructured grid, this can be quite challenging. Pasdunkorale and Turner [133] use a least-squares approach to estimate first derivatives in order to solve a highly anisotropic diffusion problem on an irregular grid. We adopt this basic approach here and a brief overview is given below (see also [134, 135]).

For any node point $\mathbf{x}_i$, we can write a truncated $p$th order Taylor expansion of the function $f$, centred about any quadrature point $\mathbf{x}_{qjk}$ as

\[
f(\mathbf{x}_{qjk} + \mathbf{h}_k) \approx \sum_{d=0}^{p} \frac{1}{d!} (\mathbf{h}_k \cdot \nabla)^d f(\mathbf{x}_{qjk}),
\] (3.4.1)
where \( h_k = x_i - x_{qjk} \). The number of unknown components in (3.4.1) we require at \( x_{qjk} \) (\( f \) and its derivatives) is given by

\[
m(p) = \sum_{d=0}^{p} \binom{N_D + d - 1}{d},
\]

\[
= \frac{(N_D + p)!}{N_D!p!}.
\]

(3.4.2)

For any given quadrature point, we can apply (3.4.1) to a spread of \( r \) nearby node points, contained in the set \( \mathcal{X}_s \), whose \( i \)th element we refer to as \( x_{si} \). We then form an over-determined linear system \((r > m(p))\) for \( f(x_{qjk}) \) and its derivatives, namely

\[
WHg = Wf.
\]

(3.4.3)

where \( H \in \mathbb{R}^{r \times m(p)} \), \( f \in \mathbb{R}^{r \times 1} \) and \( g \in \mathbb{R}^{m(p) \times 1} \) contains \( f(x_{qjk}) \) and its derivatives. The matrix \( W \in \mathbb{R}^{r \times r} = \text{diag}(w_1, w_2, \ldots, w_r) \), weights nodes closest to the quadrature point, where typically \( w_r = ||h_k||^{-\gamma} \) with \( \gamma \in \{1, 2\} \). (Belward et al. [134] note that this weighting does not change the solution, but it improves the numerical conditioning of the system). The least-squares solution of (3.4.3),

\[
\hat{g} = \arg \min_{g \in \mathbb{R}^{m(p)}} ||WHg - Wf||_2,
\]

(3.4.4)

and \( S\hat{g} \) then gives us our approximations at \( x_{qjk} \). In Eq. (3.4.4) we introduced a scaling matrix \( S \in \mathbb{R}^{m(p) \times m(p)} = \text{diag}(1, ||h_{\max}||^{-1}, \ldots, ||h_{\max}||^{-2}, \ldots) \) where \( h_{\max} = \arg \max ||h_k||_2 \) is the maximum distance between \( x_{qjk} \) and any of the node points used to build \( H \). We also use the scaled \( \tilde{h}_k = h_k/||h_{\max}|| \) to build \( \tilde{H} \) and \( \tilde{W} \). This scaling effectively applies a nondimensionalisation to the least-squares problem, in an attempt to improve the conditioning of (3.4.4).

For the CH equation, we require estimates of up to third derivatives (i.e., \( p \geq 3 \)) and we would like these derivatives to be at least second-order accurate (i.e., \( p \geq 4 \)). In general, as we increase \( p \) to improve the accuracy of our approximations, we are also solving for higher derivative terms that go unused. As such, if we use a given \( p \) value in (3.4.1), but strictly only need a value of \( p_o \) to recover the derivatives we use in the discretisation, we follow Belward et al. [134] and remove the unused \( m(p) - m(p_o) \) higher-order derivative terms from our system. Rewriting (3.4.3) as

\[
WH^*g^* = Wf - WMz.
\]

(3.4.5)
gives $H^* \in \mathbb{R}^{r \times m(p_o)}$, $M \in \mathbb{R}^{r \times (m(p) - m(p_o))}$, $z \in \mathbb{R}^{(m(p) - m(p_o)) \times 1}$ and hence $g^* \in \mathbb{R}^{m(p_o) \times 1}$ only contains the information we explicitly use. We then perform an orthogonal reduction (QR factorisation [136]) on $WM$, namely $Q^TWM = T$, where $Q^T \in \mathbb{R}^{r \times r}$ and $T \in \mathbb{R}^{r \times (m(p) - m(p_o))}$ is upper trapezoidal [129]. This allows us to write (3.4.5) in terms of the unused higher-order derivatives by applying $Q^T$ on the left and hence,

$$Q^TWH^*g^* = Q^TWh - Tz.$$  \hspace{1cm} (3.4.6)

The upper trapezoidal form of $T$ allows us to discard the first $(m(p) - m(p_o))$ equations in (3.4.6) to obtain

$$P^*g^* = f^*.$$  \hspace{1cm} (3.4.7)

where now $P \in \mathbb{R}^{(r-(m(p) - m(p_o))) \times m(p_o)}$ and $f^* \in \mathbb{R}^{(r-(m(p) - m(p_o))) \times 1}$. Again, using a scaled version of $P$ and hence $S$, the least-squares solution of (3.4.7)

$$\hat{g}^* = \arg\min_{g^* \in \mathbb{R}^{m(p_o)}} ||\hat{P}g^* - f^*||_2,$$  \hspace{1cm} (3.4.8)

and $S\hat{g}^*$ gives us our high-order derivative approximations, where now $S \in \mathbb{R}^{m(p_o) \times m(p_o)}$ ((3.4.7) will always be over-determined). Belward et al. [134] showed that the solution to this reduced system is identical to the solution of (3.4.3). The benefit of this reduction is that the size of the least-squares problem we must solve has been reduced and hence the solution can be computed more efficiently. This is especially significant as $(m(p) - m(p_o))$ grows, which is the case when we are computing higher order derivatives to high accuracy (and also as $N_D$ increases). We compute the solution to (3.4.7) by performing a QR factorisation and solve the resulting (determined) upper triangular system. Both $\hat{P}$ and its QR factorisation at every quadrature point can be precomputed (as they only depend on the mesh), and hence $g^*$ can be obtained relatively cheaply.

To illustrate the algebra performed above, let us consider a specific example with $N_D = 2$, $p = 4$. For simplicity, we use the unscaled $h_k = (\Delta x_k, \Delta y_k)^T$ and $W = I$ in this example. Hence (3.4.3) becomes

$$\begin{pmatrix}
1 & \Delta x_1 & \Delta y_1 & \frac{\Delta x_1 \Delta y_1}{6} & \frac{\Delta y_1}{24} \\
1 & \Delta x_2 & \Delta y_2 & \frac{\Delta x_2 \Delta y_2}{6} & \frac{\Delta y_2}{24} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
1 & \Delta x_{sr} & \Delta y_{sr} & \frac{\Delta x_{sr} \Delta y_{sr}}{6} & \frac{\Delta y_{sr}}{24} \\
\end{pmatrix}
\begin{pmatrix}
\frac{f(x_{qjk})}{\partial x} \\
\frac{\partial f(x_{qjk})}{\partial y} \\
\vdots \\
\frac{\partial^2 f(x_{qjk})}{\partial y^2} \\
\end{pmatrix}
= \begin{pmatrix}
f(x_{s1}) \\
f(x_{s2}) \\
\vdots \\
f(x_{sr}) \\
\end{pmatrix}.$$  \hspace{1cm} (3.4.9)
where $H \in \mathbb{R}^{r \times 15}$, $g \in \mathbb{R}^{15 \times 1}$ and $f \in \mathbb{R}^{r \times 1}$. If we wish to eliminate the fourth derivatives from the system, we set $p_0 = 3$, giving $m(p_0) = 10$, and the reduction (3.4.5) gives

$$M = \begin{bmatrix}
\Delta x_1^4 / 24 & \Delta x_1^3 \Delta y_{1,1} / 6 & \Delta x_1^2 \Delta y_{1,1} / 4 & \Delta x_1 \Delta y_{1,1}^3 / 6 & \Delta y_{1,1}^4 / 24 \\
\Delta x_2^4 / 24 & \Delta x_2^3 \Delta y_{2,2} / 6 & \Delta x_2^2 \Delta y_{2,2} / 4 & \Delta x_2 \Delta y_{2,2}^3 / 6 & \Delta y_{2,2}^4 / 24 \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
\Delta x_r^4 / 24 & \Delta x_r^3 \Delta y_{r,r} / 6 & \Delta x_r^2 \Delta y_{r,r} / 4 & \Delta x_r \Delta y_{r,r}^3 / 6 & \Delta y_{r,r}^4 / 24
\end{bmatrix}; \quad z = \begin{bmatrix}
\frac{\partial^4 f}{\partial x^4} (x_{ijk}) \\
\frac{\partial^4 f}{\partial x^3 \partial y} (x_{ijk}) \\
\vdots \\
\frac{\partial^4 f}{\partial y^4} (x_{ijk})
\end{bmatrix},$$

(3.4.10)

where $M \in \mathbb{R}^{r \times 5}$ and $z \in \mathbb{R}^{5 \times 1}$. After performing the orthogonal reduction and removing the first $m(p) - m(p_0) = 5$ equations from (3.4.6), our smaller least-square problem (3.4.7) now has dimensions of $P \in \mathbb{R}^{(r-5) \times 10}$, $g^* \in \mathbb{R}^{10 \times 1}$ and $f^* \in \mathbb{R}^{(r-5) \times 1}$.

### 3.4.1 Variational boundary condition

For quadrature points away from the boundaries of the domain, the method described in Section 3.4 works well. However, near boundaries, we face challenges in implementing the BCs. Namely, in a finite volume framework we impose conditions directly on the boundary fluxes, and so it can be difficult to include BCs that are not in this form. We face additional difficulties given the fourth-order CH equation described in Section 3.2. For example, in one dimension using planar coordinates, the CH flux (3.2.5) takes the form

$$j_x = \mathbf{D}_{xx} \left( 2\tilde{a}c - \frac{1}{1 - c} \frac{\partial c}{\partial x} + c\mathbf{K}_{xx} \frac{\partial^3 c}{\partial x^3} \right),$$

(3.4.11)

and on $\Gamma$, (3.2.9) and (3.2.10) reduce to

$$\mathbf{K}_{xx} \frac{\partial c}{\partial x} = 0; \quad \mathbf{K}_{xx} \frac{\partial^3 c}{\partial x^3} = 0.$$  

(3.4.12)

which, of course implies $j_x = 0$ on $\Gamma$, but imposing $j_x = 0$ on (3.4.11) does not necessarily imply (3.4.12).

Burch [71] tackled this problem by substituting the VBC into the standard analytic difference equations used to evaluate information at CV faces near boundaries. Any face whose spread includes a node point that lies on the boundary must use these new difference equations. Quantities evaluated at these faces therefore explicitly include the VBC and Burch [71] is then free to set a flux condition at the boundary of the domain in the standard manner.
The difference equations given by Burch [71] can be derived analytically in traditional ways; perhaps the easiest in this circumstance is to construct an interpolating polynomial using the Newton divided difference form [137]. For a face near a boundary in one-dimension, an extra row is added to the linear system expressing that the derivative of the polynomial is zero at the boundary. The resulting polynomial can then be evaluated/differentiated at CV faces. We note this must be performed for all the quantities \((c, \nabla c, \ldots)\) required at every face that uses boundary node information. This is relatively simple in one-dimension with a linear mesh, however in higher dimensions and with unstructured grids this process becomes difficult. We also note that the difference equations constructed by Burch [71] for mixed higher derivatives in two-dimensions are incorrect, as successive univariate approximation [137] cannot be applied near corners in two-dimensions when including the VBC.

Cueto-Felgueroso and Peraire [128] use a cell-centred FVM to solve the CH equation. They overcome the BC problem by creating extra node points on the boundary of the domain (that would already exist in a vertex-centred approach) whose function values are extrapolated from the BCs (similar to “ghost nodes” [129]). These extra nodes are then included in the spread used to construct the global MLS approximation in order to give “stronger enforcement of the BCs”. As mentioned in Section 3.1, Cueto-Felgueroso and Peraire [128] evaluate hyperbolic terms by using the global MLS approximation to calculate derivative values at node points. Taylor series are then evaluated to compute values at quadrature points on each CV (which makes it easier to apply limiting schemes [110, 130]). Given that the global MLS approximation includes the BCs, and the derivatives used to build the Taylor series are evaluated using this global MLS, the hyperbolic terms should include the BCs, though to what degree is unclear.

The approach we take includes the VBC (3.2.9) explicitly in our (local) least-squares approach (which, as we have seen in the previous section, is built using Taylor series) at quadrature points near the boundary. In a general sense, BCs are often included in least-squares approximations (see [133, 138] for example). This is normally done when solving advection-diffusion problems in order to apply BCs that are not necessarily in “flux-form” (like (3.2.13)). These conditions are included in the LS system at quadrature points that lie directly on a boundary, which we will denote as \(x_{ijk}^b\) (e.g., \(x_{q2,1}^b\) in Fig. 3.1). We explicitly include (3.2.9) in this manner by adding a single additional equation to (3.4.3), namely

\[
\hat{n} \cdot \left( \tilde{K} \nabla f(x_{ijk}^b) \right) = 0. \tag{3.4.13}
\]
This equation is easily added to the linear system, as it is expressed directly at the quadrature point.

Only including (3.4.13) in our approximation, however, is not enough to ensure enforcement of the VBC (3.2.9) for our 4th-order PDE (3.2.7). When constructing the linear system for quadrature points near a boundary, we note that \( r_b \) of the \( r \) nodes used to build the linear system lie on \( \Gamma \) (the grey nodes in Fig. 3.1). We denote one of these \( r_b \) points as \( x_b \), and note that we must express the VBC (3.2.9) at each of these boundary nodes, namely

\[
\mathbf{n} \cdot \left( \bar{K} \nabla f(x_b) \right) = 0. \tag{3.4.14}
\]

We cannot, however, directly include (3.4.14) in our LS system like (3.4.13), as it does not apply at the quadrature point. We therefore express (3.4.14) as a Taylor series centred at the quadrature point of interest, which we denote as \( x_q \) (which could be \( x_{q,jk} \) or \( x_{q,jk}^b \)) and so we can write

\[
\mathbf{n} \cdot \left( \bar{K} \nabla f(x_b) \right) \approx \left( \mathbf{n} \cdot (\bar{K} \nabla) \right) \left( \sum_{d=0}^{p-1} \frac{1}{d!} (\mathbf{h}_b \cdot \nabla)^d f(x_q) \right) = 0, \tag{3.4.15}
\]

where \( \mathbf{h}_b = x_b - x_q \). We are now free to include (3.4.15) in (3.4.3) for each of the \( r_b \) boundary points (taking care to use the scaled \( \hat{\mathbf{h}}_b = \mathbf{h}_b / ||\mathbf{h}_{max}|| \) where applicable for consistency). For the CH IBVP, we also include (3.2.10) in this manner. We note that this approach would still be applicable if the VBC were non-homogeneous. For example, concentration dependent surface effects, \( \gamma(c) \), (like surface “wetting” [139]; see also [71]) are often included in (3.2.1), resulting in (3.2.9) taking the form \( \mathbf{n} \cdot (\bar{K} \nabla c) = \gamma'(c) \).

To illustrate the above approach, let us consider the specific example where we are computing information at the quadrature point \( x_{q2,1} \) in Fig. 3.1 and we include a single boundary node in the least-squares system, say \( x_4 \). Equation (3.4.14) reduces to

\[
- \frac{\partial f}{\partial x} = 0 \quad \text{at } x_4, \tag{3.4.16}
\]

which we can express using (3.4.15) as

\[
- \frac{\partial f}{\partial x}(x_4) \approx - \left( \frac{\partial f}{\partial x}(x_{q2,1}) + \Delta x_4 \frac{\partial^2 f}{\partial x^2}(x_{q2,1}) + \ldots + \frac{\Delta y_4^3}{6} \frac{\partial^4 f}{\partial y^3 \partial x}(x_{q2,1}) \right) = 0. \tag{3.4.17}
\]
If we consider our example system (3.4.9), (3.4.3) now becomes

\[
\begin{pmatrix}
1 & \Delta x_1 & \Delta y_1 & \ldots & \frac{\Delta x_1 \Delta y_3}{6} & \frac{\Delta y_3^4}{24} \\
1 & \Delta x_2 & \Delta y_2 & \ldots & \frac{\Delta x_2 \Delta y_3}{6} & \frac{\Delta y_3^4}{24} \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
1 & \Delta x_r & \Delta y_r & \ldots & \frac{\Delta x_r \Delta y_3}{6} & \frac{\Delta y_3^4}{24} \\
0 & -1 & 0 & \ldots & -\frac{\Delta y_3^2}{6} & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & -1 & \vdots & 0 & 0
\end{pmatrix}
\begin{pmatrix}
f(x_{s1}) \\
f(x_{s2}) \\
\vdots \\
f(x_{sr})
\end{pmatrix} =
\begin{pmatrix}
f(x_{q2,1}) \\
\frac{\partial f}{\partial x}(x_{q2,1}) \\
\vdots \\
\frac{\partial^4 f}{\partial y^4}(x_{q2,1})
\end{pmatrix}, \quad (3.4.18)
\]

where \( \mathbf{H} \in \mathbb{R}^{(r+r_b+1)\times 15} \) and \( \mathbf{f} \in \mathbb{R}^{(r+r_b+1)\times 1} \). The first \( r \) rows in (3.4.18) still express (3.4.1) for the spread of \( r \) node points that we choose to build the least-square system. The next visible row includes (3.4.17) in the linear system, and we note as mentioned above, extra rows (that express (3.4.15) like (3.4.17)) must be included for each of the \( r_b \) boundary node points used. The last row in (3.4.18) implements (3.4.13), as \( x_{q2,1} \) lies on a boundary, specifically

\[
-\frac{\partial f}{\partial y} = 0, \quad \text{at } x_{q2,1}.
\]

This final equation would not be included if we were estimating quantities, for example, at \( x_{q1,1} \) in Fig. 3.1, though the \( r_b \) equations representing (3.4.15) at each boundary node point would be. Furthermore, we note that in this work, we solve the equations given in Section 3.2 on a rectangular domain, and so at a corner node (for example \( x_1 \) in Fig. 3.1) we apply (3.4.15) in both the \( x \) and \( y \) directions separately.

To solve the modified least-squares problems that occur near the boundaries and of which (3.4.18) is a specific example, we use two approaches. The first is known as equality-constrained least-squares [140], and involves removing the boundary condition information from \( \mathbf{WH} \) and instead writing these conditions as the separate linear system

\[
\mathbf{B} \mathbf{g} = \mathbf{d}, \quad (3.4.19)
\]

where \( \mathbf{B} \in \mathbb{R}^{r_t \times m(p)} \), \( \mathbf{d} \in \mathbb{R}^{r_t \times 1} \) and \( r_t \) is the total number of boundary equations we have applied (which depends on the position of the quadrature point, whether we have included a corner node, and the specific IBVP we are solving). We then seek the
least-squares solution to (3.4.3), but constrained such that (3.4.19) is satisfied exactly, or
\[ \hat{g} = \arg \min_{Bg=d} ||\tilde{W}\hat{H}g - \tilde{W}f||_2, \]  
(3.4.20)

where again we have introduced the scaling matrix $S$ and hence $S\hat{g}$ gives us our approximations. In solving this constrained system, we do not apply the reduction described by (3.4.5), instead we retain the $m(p) - m(p_o)$ higher order terms in the system and apply the nullspace method, which uses a QR factorisation (see [140, 141] for details) to solve the complete higher-order system in (3.4.20). The constrained system is only solved at the (small number of) quadrature points near the boundary, and hence the added cost from solving the full system is not great.

The second approach we use notes that the solution to (3.4.20) can be approximated [140] by leaving the $r_t$ boundary equations in $\tilde{W}\tilde{H}$ and applying a large weighting to these equations. The boundary constraints in (3.4.19) are already weighted by $||\tilde{h}_b||^{-\gamma}$, so we multiply this weighting by a constant $\lambda$. For large $\lambda$, the solution of this weighted least-squares problem approximates the solution given by the nullspace method (as long as the size of $\lambda$ does not significantly affect the conditioning of $\tilde{W}\tilde{H}$). The benefit of this weighted approach is that it enables us to easily use the reduction in (3.4.5).

The numerical approach introduced in this section for the application of non-standard BCs in the solution of higher-order PDEs shares similarities with that used in immersed (or embedded) boundary methods (see [142] for a recent review), where BCs must be imposed on the boundary of a domain that does not lie on grid lines. Often, an interpolating function that includes the BC is used to approximate values near a boundary [143, 144]; our need to impose boundary conditions in this fashion results from a 4th order PDE, as opposed to a nonbody conformal boundary, though our approach could most likely be used in that context.

3.4.2 Test functions

Theoretical error bounds for estimating gradients using the weighted least-square approach are given in Turner et al. [135], and both Belward et al. [134] and Turner et al. [135] provide numerical evidence of second order accuracy in estimating first derivatives for a series of test functions on unstructured grids. In order to confirm the accuracy of
our method for computing up to third derivatives with the VBC (3.2.9) included, we
tested the derivative estimation on two simple test functions in one-dimension, namely

\[ f(x) = \sin(x) \quad \text{for} \quad x \in [-10, 10], \quad (3.4.21) \]
\[ f(x) = 0.1 + 0.8 \exp(-x^2) \quad \text{for} \quad x \in [-10, 10]. \quad (3.4.22) \]

Here, (3.4.22) is the initial condition that we apply in Section 3.5 and was used by
Singh et al. [76] in their work on the CHR IBVP. We tested the least-squares approach
described in Section 3.4 on (3.4.21) and as (3.4.22) (numerically) satisfies (3.2.9) on
the boundaries of the test domain, it provides a convenient way to test the addition of
the VBC described in Section 3.4.1. We impose a linear mesh on the one-dimensional
domain, and used the weighted least-squares approach (with boundary weighting \( \lambda = 10 \)
for (3.4.22)) to calculate the value of \( f(x) \) and up to third derivatives at the CV faces
half-way between each node. As we require third derivative terms, we set \( p_o = 3 \) and to
ensure these derivatives are second order accurate, we let \( p = 4 \). We also assign \( r = 6 \),
so that the nearest six node points are used to build the linear system (\( m(p) = 4 \) in
this case). We computed the relative error for \( f \) and its derivatives as the grid spacing
decreases, and for example, the error in \( f \) is measured by

\[ \text{Rel. Error} = \frac{||f_{\text{exact}} - f_{\text{approx}}||_{\infty}}{||f_{\text{exact}}||_{\infty}}. \]

The results of this test are shown in Fig. 3.2, with Fig. 3.2a being a plot of the error
for (3.4.21) and Fig. 3.2b being the same, but for (3.4.22). We see that in Fig. 3.2a
the relative error in the approximations is decreasing at the expected rate; the 5th
order convergence for \( c \) aligns with \( p = 4 \) and \( p_o = 3 \) (as the elimination of the fourth
derivatives should push the remainder term in the Taylor series to 5th order). Each
of the higher-order derivative terms lose an order of accuracy, and we see that upon
reaching the third derivative our approximation is second order, as desired.

Similar results are shown in Fig. 3.2b, where the VBC is included at faces near the
boundary. We note that both the weighted and equality-constrained least-squares ap-
proaches described in Section 3.4.1 produce identical results for this test. We again see
that the third derivatives are approximated to second order. Given these results, we
now proceed to investigate the solution of the CH and CHR IBVPs using the least-
squares method described above.
Figure 3.2: Relative error of approximations versus the maximum distance between a face and the node points used to construct the linear system. Solid lines are least-squares fit to the numerical results and are used to determine the order of each approximation.

(a) \( \sin(x) \).

Order: +: 5.04, \( \times \): 4.04, \( \Box \): 3.04, \( \# \): 2.04.

(b) \( 0.1 + 0.8 \exp(-x^2) \).

Order: +: 5.97, \( \times \): 3.97, \( \Box \): 3.97, \( \# \): 1.98.
3.5 Results

The results presented in this section were computed in C++ and the Intel Compiler (Version 12.0.3.174) was used to compile the code on an Intel Xeon X5650 processor (64-bit with 6 cores running at 2.66 GHz) with the optimisation level set at -O3 and the compiler flag “fp-mode strict”.

We used the SPQR package in SuiteSparse [145] to perform QR factorisations and used the Intel MKL (BLAS, LAPACK and VML) whenever possible. No direct effort was made to parallelise the software produced, however both the SuiteSparse package and the Intel MKL are heavily multi-threaded.

The coupled set of ODEs (in time) generated by the FVM discretisation were solved using the IDA module from Sundials [108]. IDA provides adaptive time stepping with error control using a backward differentiation formula (BDF) (of up to order 5). There have been a number of papers in the literature exploring various time-stepping schemes for the CH equation (see [128, 146–148] for example), most based on the work of Eyre [132] who showed that unconditionally gradient-stable time-stepping is possible. Here, we are primarily concerned with the spatial discretisation of the CH and CHR equations and as such we do not examine the efficiency of the time-stepping scheme. We set IDA to use a maximum of 2nd order time-stepping to ensure that the numerical solution remains gradient-stable. We also use the sign of $\frac{dG}{dt}$ as a recoverable error, which forces IDA to use smaller (order and size) time-steps if gradient-stability is violated. The Jacobian resulting from the numerical approach described in this chapter is naturally banded and so we use the globally convergent, banded Newton solver in IDA to solve the nonlinear system. Overall, computing the numerical solution to the CH and CHR IBVPs takes a few seconds in one dimension, and several hours in two dimensions, with moderate tolerances.

We imposed a linear, orthogonal mesh in both one and two dimensions. Fig. 3.3 shows an example of a linear, orthogonal mesh in two-dimensions, where the quadrature points have been set to lie at the midpoint of control volume faces. The “east” faces have been plotted in Fig. 3.3, though the principles outlined below were also applied for the “north” faces, along with the one-dimensional results shown below. In two-dimensions, a rectangular spread of the nearest 30 node points ($r = r_x r_y = 30$) was used to generate the least-squares matrix $\tilde{W} \tilde{H}$. For symmetry, a rectangular spread with 6 node points in the direction of the faces and five in the perpendicular direction...
Figure 3.3: Linear rectangular mesh in two-dimensions with “east” finite volume faces shown. Function values and gradients must be computed at each of the green highlighted faces separately. Within the other highlighted regions, the least-squares system can be solved with multiple RHS, as $\mathbf{WH}$ (or equivalent) does not change.

was used (i.e., for the “east” faces, 6 node points were used in the $x$ direction and 5 in the $y$ direction, or $r_x = 6, r_y = 5$).

A careful balance is required when choosing the spread of points to include, as enough node points must be used to accurately estimate the information required. This balance is quantified by Turner et al. [135], who showed that the error bound for estimating $\nabla f$ with a weighted least-squares method (that does not include the VBC like in this work) behaves like $||h_{\text{max}}||^p w_{\text{max}} / \tilde{\sigma}_1$, where $w_{\text{max}}$ is the largest weight in $\mathbf{W}$ and $\tilde{\sigma}_1$ is the smallest singular value of $\mathbf{WH}$. A large $p$ implies $\tilde{\sigma}_1 \ll 1$, while decreasing $||h_{\text{max}}||$ affects both $\tilde{\sigma}_1$ and $w_{\text{max}}$. Turner et al. [135] found that in 2D, using between 20-30 of the nearest neighbours to construct the least-squares system performed the best for estimating $\nabla f$; we use this to inform the spread of node points used in this work. Please see Turner et al. [135] for a thorough examination of the error in computing $\nabla f$ for different values of $||h_{\text{max}}||, p$ and $\gamma$ using a series of scattered data points. We should also note that highly scattered data points can harm the performance of a least-squares based method, though Pasdunkorale and Turner [133] showed good results when using a weighted least-squares method to solve a highly anisotropic, diffusion-advection problem in 2D on an increasingly unstructured grid. We however, require higher order derivatives than [133] and hence our results may be impacted by highly irregular grids; we plan to examine this in future work.
The least-squares matrix \( \tilde{W} \tilde{H} \) includes BC information for quadrature points that use a boundary node point in their spread. For quadrature points away from the boundaries, denoted by the blue-shaded region in Fig. 3.3, \( \tilde{W} \tilde{H} \) does not include any BC information and is the same at all the faces in the blue-shaded region. A single least-squares matrix \( \tilde{W} \tilde{H} \) can therefore be generated for the blue-shaded region. This matrix, along with \( \tilde{P}^* \) and its QR factorisation were precomputed and stored before time-stepping began. The gradients at all of the faces in the blue-shaded region were then computed by first assembling the RHS, which has dimensions \( f^* \in \mathbb{R}^{(r-(m(p)-m(p_o))) \times u} \), where \( u \) is the number of faces in the blue-shaded region. Each column of \( f^* \) therefore includes the function values for the spread of node points used at a single face.

The UNPACK/PACK methods from the Intel MKL were used to fill \( f^* \), where the indices used to access the node points in \( f^* \) were precomputed and stored along with \( \tilde{P}^* \) and its QR factorisation. The precomputed QR factorisation of \( \tilde{P}^* \) was then applied on the left of \( f^* \) and the triangle solve \texttt{dtrsm} was used to solve the resulting upper-triangular system. The solution at all of the faces in the blue-shaded region was therefore recovered, with dimension \( Sg^* \in \mathbb{R}^{m(p_o) \times u} \), where the function values and derivatives for each face are stored in the columns of \( Sg^* \).

This approach allowed the solution at the faces in the blue-shaded region to be computed efficiently, as the total cost involves a small matrix multiply, and a triangle solve that uses multiple RHS. For realistic mesh sizes (i.e., bigger than the example mesh pictured in Fig. 3.3), the blue-shaded region typically contains > 90% of the faces in the mesh, increasing the efficiency of this approach.

For faces that include a boundary node point in their spread, the mesh is further partitioned. Faces away from the corners of the domain that still include BCs in the least-squares system, namely the grey and purple shaded regions in Fig. 3.3, can again use multiple RHS to efficiently compute the solutions to the least-squares system (that includes BCs) in each of the individual shaded regions. Depending on solution technique used to impose the BCs (weighted or equality-constrained), the various matrices and their QR factorisations were precomputed for each individual shaded regions. The number and size of these regions depends on the spread of node points used to build the least-squares system. For example, there are six purple-shaded regions shown in Fig. 3.3, with \( r_x / 2 = 3 \) regions close to each boundary in the \( x \) direction. Faces closer to the centre of the mesh do not include a boundary node point in their spread, and hence are included in the blue-shaded region. Each of the purple and grey-shaded regions have separate precomputed matrices, given that the BC information is included at
different relative positions. Considering the three purple-shaded regions closest to the left boundary and moving towards the centre of the mesh, BCs are imposed one, two and three node points away from the faces respectively. Within each of these purple and grey-shaded regions, multiple RHS were used in $f^*$ and once again, the size of the purple and grey-shaded regions grows as the size of the mesh increases.

Fig. 3.3 also shows green shaded regions near the corners of the domain, where $\tilde{W} \tilde{H}$ (or equivalent) must be computed at each face individually. Multiple RHS cannot be used in the least-squares system in these regions, as $\tilde{W} \tilde{H}$ is different at each of the green-shaded faces.

As mentioned, the same approach was used to efficiently compute function values and derivatives for the “north” faces. When solving the CHR IBVP we require the value of the chemical potential $\bar{\mu}$ at node points on the boundaries to compute the reaction boundary condition (3.2.14). This is given by a suitably scaled version of (3.2.4). Furthermore, we note that, given our vertex-centred approach, the only unknown quantity in (3.2.4) is the Laplacian of $c$. We use the least-squares method described above to approximate this value, whereby the boundary conditions are implemented in the same manner as in Section 3.4.1 for a quadrature point that lies on the boundary. When estimating the Laplacian at one of these boundary node points, a Taylor series approximation (3.4.1) is not required to express the node value at this point, as it can be expressed directly in the linear system. We set the weighting at this point to be equal to the weighting at the nearest neighbour multiplied by 100 (as $h_k = h_b = 0$). For symmetry, $r = 25$ node points were used to build $\tilde{W} \tilde{H}$ in this case, with $r_x = 5$ and $r_y = 5$. For node points away from the corners of the domain, the Laplacian at these points was computed using multiple RHS in a similar fashion to that outlined above for faces.

The use of a structured grid is motivated by our case study of CHR dynamics as applied to LiFePO$_4$ and requires efficient solutions on regular domains. As we have emphasised however, the least-square technique discussed in Section 3.4 can be used without modification on unstructured grids. With efficiency in mind, we also set quadrature points in our discretisation to lie at the midpoint of CV faces, which results in (3.3.2) being second-order. Higher-order approximations to the line integral in (3.3.1) rapidly become more costly as the number of quadrature points on a CV face grows, since a least-square problem must be solved at each of these.
A minimum value of $p = 4$ and $p_o = 3$ was used throughout the simulations presented to ensure that our third-derivative approximations stay second-order (unless otherwise noted). We set $\gamma = -2$, $\lambda = 10$, and note that this weighting significantly affects the conditioning of $WH$. This weighting becomes particularly important when solving the CHR IBVP because numerical errors in derivative approximations are exacerbated by the exponential form of the BC (3.2.13). In an attempt to minimise this numerical error, we also investigated using a truncated SVD decomposition to construct a pseudo-inverse \cite{136} ($\text{pinv}$ in MATLAB) in order to solve the least-squares problem. The results of those tests are not shown here, as the pseudo-inverse did not perform as well as the weighted approach. We also set $\tilde{K} = D = I$ and note that for LiFePO$_4$, these tensors may be highly anisotropic. As such, the results presented are not strictly representative of Li$^+$ intercalation into LiFePO$_4$. We chose to keep the tensors symmetric as again, the exponential form of the BC (3.2.13) exacerbates any numerical error and if care is not taken at the boundaries, particularly for the CHR IBVP, asymmetric behaviour results. The results shown below are perfectly symmetric about the centre of the domain, but if any asymmetry were present, this would be obscured by anisotropic tensors.

### 3.5.1 One-dimensional results

**CH IBVP**

Fig. 3.4 shows the results from solving the CH IBVP with 150 node points using the equality-constrained, least-squares method. Fig. 3.4a shows the dimensionless concentration profile through time. We can see that the solution evolves from the symmetric initial condition (3.2.8) to form a narrow band of phase separated material that is symmetric about $x = 0$. The solution at $t = 179.6s$ represents the steady state of the problem, where the material has phase separated as much as possible. Fig. 3.4b shows the absolute value of the relative mass balance error, which is computed by

$$|\text{RMBE}| = \frac{|M(0) - M(t)|}{|M(0)|}.$$  

The mass is computed numerically by using the trapezoid rule to evaluate the integral in (3.2.11). We can see that the mass balance error is very close to machine precision throughout the entire simulation; this confirms that our numerical method is conservative, as is expected when using the FVM. We are aware of only one numerical paper for the CH equation that approaches (or shows evidence of) this level of conservation \cite{124}. In contrast, papers on “conservative” finite difference schemes for the CH equation often plot the total mass in the system with very large axis scalings, obscuring the
Figure 3.4: CH IBVP solution computed in one dimension \((x \in [-10, 10])\) with 150 nodes using equality-constrained least-squares. Relative and absolute tolerances were set at \(1 \times 10^{-6}\).

\(\hat{\Omega}_m = 5, \hat{K} = I, \hat{D} = I\).
degree to which these schemes conserve [121, 122, 149].

The other physical condition our numerical scheme should satisfy is that of gradient stability, given by (3.2.12). Fig. 3.4c plots the change in free energy over time, $d\tilde{G}/dt$, and we see that $\tilde{G}(t)$ is always decreasing throughout the simulation. We note that at no point in Fig. 3.4c does $d\tilde{G}/dt$ become positive, although the rate of decrease in the free energy slows towards the end of the solution (and approaches zero while still remaining negative) as the material phase separates and reaches equilibrium. Papers in the literature often plot the value of $G(t)$, as opposed to $d\tilde{G}/dt$. We chose to plot the rate of change as it is obvious when $d\tilde{G}/dt$ changes sign. Unless the authors explicitly note that their solutions do not stay strictly gradient stable (like Cueto-Felgueroso and Peraire [128]), small increases in free energy are not always evident in a plot of $G(t)$.

Finally, Fig. 3.4d shows the size of the time-steps taken. The adaptive time-stepping of IDA is clearly evident, as the size of the time-step increases over 7 orders of magnitude throughout the simulation. Again, as mentioned previously in Section 3.5, the objective of this paper is not to investigate different time-stepping schemes, and we acknowledge that there are schemes that achieve solutions using a smaller number of time-steps than the 550 shown in Fig. 3.4d (for example [128]).

Now that we have shown that the numerical solution satisfies the relevant physical conditions, we turn to Fig. 3.5 that shows the convergence rates of the our scheme. Specifically, Fig. 3.5a plots the relative error of the solution as the grid spacing decreases. We measure the relative error by

$$\text{Rel. Error} = \frac{||c_{\text{rep}} - c_{\text{approx}}||_{\infty}}{||c_{\text{rep}}||_{\infty}},$$

where the representative solution $c_{\text{rep}}$ is computed with the equality-constrained least-squares method on a linear mesh with 1000 node points, relative and absolute tolerances set to $1 \times 10^{-12}$, $p = 5$ and $p_o = 4$. Node points at the same spatial coordinate in the representative solution are then used in the error calculation. We also tested linearly interpolating the representative solution onto the courser mesh and found that the greatest error always occurs at the boundaries of the domain, and so both methods produce the same error. In Section 3.4.2, we verified that setting $p = 4, p_o = 3$ produces second-order accurate third derivatives, and so we expect the numerical solution to the CH equation should be at least-second order accurate. We see, however in Fig. 3.5a that the solution is converging at a third order rate. We also computed the error for the higher-order case, with $p = 5, p_o = 4$ and we note this solution is approximately fourth-
Figure 3.5: Convergence rates (with respect to a reference solution) for the 1D CH IBVP vs the maximum distance between a face and the node points used to construct the linear system. Relative and absolute tolerances were reduced to $1 \times 10^{-12}$. Closed shapes (□, ◦) use equality-constrained least-squares near boundaries, open shapes (+, ×) use weighted least-squares. Solid lines are least-squared fit to the weighted least-square results to determine the order of each approximation.

+a: $p = 4, p_o = 3$, ×, ○: $p = 5, p_o = 4$. 
order. Fig. 3.5a also shows that the solutions produced by the equality-constrained and weighted least-square methods are identical and converging at the same rates.

Importantly, Fig. 3.5b and 3.5c show the degree to which the numerical solution satisfies the BCs. Fig. 3.5b plots the value of the gradient at the left boundary, which was measured using a simple sixth order difference equation [150], while Fig. 3.5c plots the third derivative at the same boundary, measured using a second order difference equation [150]. We only plot the values at the left boundary as they are identical to the values on the right boundary, given the symmetric initial condition. In a general sense, how well the BCs are satisfied depends on the grid spacing, as we are including the BCs in the least-square problem using a Taylor series centred away from the boundary.

In Fig. 3.5b we see that, for the $p = 4$ case, we satisfy $\partial c/\partial x = 0$ to approximately fourth order for the weighted least-squares (the fit lines for equality-constrained are not shown, they give very similar rates of convergence). The equality-constrained and weighted least-squares approximations also give slightly different values as the grid spacing becomes small (near 600 nodes). This is also the case for $p = 5$, where we see that the weighted least-squares method converges at a rate of around 3. The equality-constrained least-squares however, performs better in this circumstance.

The behaviour shown in Fig. 3.5b, where the satisfaction of the BC begins to vary as the grid spacing decreases is due to the singular nature of the problem as both $p$ increases and the grid spacing decreases (as mentioned in Section 3.5). An example of this singular behaviour can be observed by computing the condition number of the unscaled $\mathbf{W} \mathbf{H}$ (with boundary conditions included as per the weighted least-squares). With 150 node points and $p = 4$ the condition number is $6.67 \times 10^4$, whereas for $p = 5$, it increases to $1.17 \times 10^6$. This shows that the system becomes increasingly ill-conditioned at higher orders. This is also true as the number of node points increases, as we would expect.

Fig. 3.5c shows that $\partial^3 c/\partial x^3 = 0$ is satisfied to slightly over third order for $p = 4$ and second order for $p = 5$ (though the second-order difference equation used to measure the third derivative may be masking a slightly higher-order convergence rate). Again, as the grid spacing becomes small (near 900 nodes), we see the data points become slightly erratic, though it appears that the weighted least-squares performs better than the equality-constrained in this case.

In summary, it appears that for the CH IBVP, our numerical method performs well for low to moderate grid spacing (up to approximately 600 nodes), in that it satisfies all
of the relevant physical conditions (such as mass conservation and gradient stability), along with implementing the BCs in a high-order manner. The weighted least-squares method also appears to perform slightly better than the equality-constrained method. We now investigate the solution to the CHR IBVP.

**CHR IBVP**

Fig. 3.6 shows the results from solving the CHR IBVP with 150 node points using the equality-constrained least-squares method. We can see in Fig. 3.6a that initially (up to $t = 266s$), the solution profile phase-separates in a similar manner to the no-flux case (though the removal of the condition on the third derivative means a small hump forms at $x = \pm 6$ before fully phase-separating). A travelling wave then forms and moves through the domain, before impacting the boundaries, and filling to a uniform concentration. Interestingly, Fig. 3.6b shows that the total mass of the system decreases initially (the 500th time-step corresponds to $t \approx 266s$), before increasing for the rest of the simulation. The behaviour of the CHR IBVP is extremely complex; this deintercalation for example, is driven by the form of (3.2.13). The chemical potential at the boundaries of the solid $\mu_s$, must be greater than the external chemical potential $\mu_e$ to drive flux into the solid.

Burch [71] notes that unlike the CH equation there is no analytic proof that the solution to the CHR IBVP should remain gradient-stable. However, our numerical evidence seems to suggest that under normal circumstances, with the initial condition we used, the CHR IBVP does indeed remain gradient-stable, as is evident in Fig. 3.6c. This figure shows that the free-energy is always decreasing, though between time-steps 500 through 1500 (which corresponds to the existence of the travelling wave), the free energy is decreasing very slowly, at a rate of approximately $-10^{-4}$. Once the concentration wave reaches the boundaries of the domain, the free energy can be decreased significantly (see time step 1750 in Fig. 3.6c) by raising the concentrations at the boundary, before the simulation ends.

A greater number of time-steps are required when solving the CHR IBVP compared to the CH IBVP, as shown in Fig. 3.6d. Again, the adaptive time-stepping is extremely useful, especially when the travelling wave is propagating. The size of the time-step taken during this period is around $10^1$, before reducing as the concentration wave approaches the boundary.
(a) Solution profile, dashed line is the initial condition: \( 0.1 + 0.8 \exp(-x^2) \).
\( t \text{ (s): } + 4.72, \times 266, \Box 3920, \bigcirc 6010, \bigodot 6515.194, \bigcirc 6515.197, \bigtriangleup 6515.8 \).

(b) Proportion of mass in the system over time. The solid line corresponds to the bottom \( x \) axis (time step), while the dashed line corresponds to the top \( x \) axis (\( t \)).

(c) Change in free energy over time.

(d) Size of the time steps taken.

Figure 3.6: CHR IBVP solution computed in one dimension (\( x \in [-10, 10] \)) with 150 nodes using equality-constrained least-squares. Relative and absolute tolerances were set at \( 1 \times 10^{-6} \).
\( \tilde{\Omega}_m = 5, \tilde{K} = I, \tilde{D} = I, \rho_s R_{\text{ins}} / \rho = 1, \tilde{\mu}_e = 0.5 \).
Figure 3.7: Convergence rates (to a reference solution) for the 1D CHR equation vs the maximum distance between a face and the node points used to construct the linear system. Relative and absolute tolerances were reduced to $1 \times 10^{-12}$. Closed shapes (□, ○) use equality-constrained least-squares near boundaries, open shapes (+, ×) use weighted least-squares. Solid lines are least-squared fit to the weighted least-square results to determine the order of each approximation.

Fig. 3.7 shows the convergence of the numerical solution for the CHR IBVP (the relative error is measured in the same manner as the CH IBVP in Section 3.5.1). In Fig. 3.7a, we can see the rate of convergence is significantly lower when compared to the CH IBVP; the only solution that converges above second order is the equality-constrained case with \( p = 5, p_o = 4 \). In general, we can see that the equality-constrained method outperforms the weighted least-squares. Fig. 3.7b shows the value of the first derivative at the left-hand boundary (again the RHS is identical). We can see that all of the solution methods employed satisfy \( \partial c/\partial x = 0 \) to an order of approximately 1.6.

As we can see, the CHR IBVP is much more difficult to solve than the CH IBVP. Fig. 3.8 shows the concentration profile at the boundary over time (computed with equality-constrained least-squares with \( p = 5, p_o = 4 \)). We can see that compared to the reference solution, the 150 node case raises the boundary concentration slightly slower (the time span between step 3000 to 3500 is quite small, around \( t \approx 20 \text{s} \)). Initially, we were concerned that this was due to the coarse solution incorrectly capturing the travelling wave seen in Fig. 3.6a. This however, was not the case; the coarse solution matched the reference solution very well. The exponential terms in the flux BC appears to exacerbate any small numerical errors in the estimate of the Laplacian at the boundary, and hence the value of \( t \) that corresponds to the concentration wave hitting the boundary. Due to the large miscibility gap between the phases (i.e., the concentration difference between the phases), this causes large relative errors, as shown in Fig. 3.7a. As such, we note that high order approximations should be used near the boundaries whenever possible. We found that computing the Laplacians at the boundary with \( p = 5, p_o = 4 \) while using \( p = 4, p_o = 3 \) for interior faces performed very similarly when compared to using the higher-order approximation throughout the domain.

We should also note that in Fig. 3.7, for simulations that use greater than approximately 300 nodes with the equality-constrained least-squares, and for all simulations using weighted least-squares, the recoverable error condition for IDA had to be disabled to ensure convergence. This results in a small number of time-steps violating gradient-stability. Fig. 3.9 shows an example of this behaviour, where 79 time-steps violate strict gradient-stability and these have been highlighted. The values of \( d\tilde{G}/dt \) at these time steps are in fact quite small, the largest that occurs is \( d\tilde{G}/dt = 1.11 \). Nonetheless, it appears that the best method to solve the CHR problem is to use a high-order approximation at the boundaries, coupled with a small to moderate number of node points to ensure an accurate, strictly gradient-stable solution. As noted above, there is no guarantee that the solution to the CHR IBVP will remain gradient-stable. The
Figure 3.8: Concentration at $x = -10$ over time. The solid line is from the reference solution (computed with 1000 nodes), the dotted line uses 150 nodes. The reference solution has been linearly interpolated to be at the same time points as the coarser solution.

Figure 3.9: Free energy over time with 400 nodes using equality-constrained least-squares with $p = 5$, $p_o = 4$ and the recoverable error disabled. There are 79 time steps that violate gradient-stability and these have been highlighted in red.
dependence of gradient-stability on mesh spacing and solution methodology (along with the resulting small violation) shown in Fig. 3.9, however, seem to suggest that numerical errors inherent in the discretisation are causing this behaviour, rather than the intrinsic behaviour of the CHR IBVP causing a large, positive increase in $d\tilde{G}/dt$, given our initial condition.

3.5.2 Two-dimensional results

We were unable to compute a “reference” solution for the two-dimensional CH and CHR IBVPs, due to the substantial increase in runtime given the large number of nodes and small tolerances required. As such, the following section does not include plots that show evidence of the convergence of the numerical methods in two-dimensions. We did, however, compute the values of the derivatives $\mathbf{n} \cdot (\tilde{K}\nabla c)$ and $\mathbf{n} \cdot (\nabla(\nabla \cdot (\tilde{K}\nabla c)))$ at $x = -10$ across $y$ (which are identical to the values on other boundaries given the symmetry in our domain and IC), in order to verify our solutions satisfy the BCs. The maximum absolute value of these derivatives are tabulated in Table 3.1. Also, given the results in the previous section, all the solutions shown in this section were computed using $p = 5$ and $p_o = 4$.

CH IBVP

Fig. 3.10 and 3.11 show the results from solving the CH IBVP in two dimensions, with $150 \times 150$ node points using the equality-constrained least-squares method. There is, however, one key difference in the solution methodology when compared with Section 3.5.1. When solving the least-squares problem described in Section 3.4 with the equality-constrained method, the number of boundary equations we apply, $r_t$, is greater than $m(p)$. This is because we include both the VBC (3.2.9) and (3.2.10) in the least-squares problem for the CH IBVP. We cannot, therefore, use the nullspace method to solve the constrained system (3.4.20), as it involves partitioning the QR factorisation of $\mathbf{WH}$ into two matrices of size $r_t \times m(p)$ and $(m(p) - r_t) \times m(p)$. When solving the CH IBVP in two-dimensions with the equality-constrained method, $r_t > m(p)$, and as such we only constrain the least-squares system to satisfy the VBC (3.2.9), rather than both (3.2.9) and (3.2.10). This problem does not occur when using the weighted least-squares method, and there was no visible difference in the solutions when comparing this modified equality-constrained method with the weighted least-squares method.

Fig. 3.10 shows that the solution behaves in a similar manner to the one-dimensional solution shown in Fig. 3.4a. The symmetric initial condition again evolves to a steady
Figure 3.10: CH IBVP solution computed in two dimensions ($x, y \in [-10, 10]$) with 150 $\times$ 150 nodes using equality-constrained least-squares. Relative and absolute tolerances were set at $1 \times 10^{-6}$.

$\tilde{\Omega}_m = 5$, $K = I$, $D = I$, $p = 5$, $p_o = 4$. 

(a) $t=0$s. Initial condition: $0.1 + 0.8 \exp(-x^2 + y^2)$.)

(b) $t=4.94$s

(c) $t=66.7$s

(d) $t=180$s
Figure 3.11: CH IBVP solution statistics for the simulation shown in Fig. 3.10.
state at \( t = 180s \) where the material has phase separated as much as possible. The numerical solution conserves mass to near machine precision and remains strictly gradient stable, as shown in Fig. 3.11a and 3.11b. Fig. 3.11c plots the size of the time-step taken with time and we can see that the adaptive time-stepping scheme increases the size of the step throughout the simulation. We also note that it takes approximately 50 more time steps than the one-dimensional simulation (see Fig. 3.4d) in order to reach a steady state.

In terms of satisfying the BCs, Table 3.1 shows that for the CH IBVP solved using the weighted least-squares method, (3.2.9) is satisfied to approximately third order. The condition (3.2.10) however, is only satisfied to first order. The equality-constrained method performs even worse, with the VBC (3.2.9) being satisfied to below third order and the maximum absolute value of the derivatives in (3.2.10) increase with decreasing grid spacing. This is due to our inability to include (3.2.10) in the least-squares system when using the equality-constrained method, as described above. The solution produced does not visibly change, but these results suggest that the weighted least-squares method should be used to solve the CH IBVP in two-dimensions to ensure both BCs are satisfied as the grid spacing decreases.

**CHR IBVP**

The solution to the CHR IBVP is shown at several time points in Fig. 3.12, with associated statistics shown in Fig. 3.13. Like the one-dimensional solution shown in Fig. 3.6a, the solution profile phase-separates as much as possible, up to \( t = 807.7s \). We can see in Fig. 3.13a that this process is associated with a loss of mass (\( t = 807.7s \) roughly corresponds to time step 500). Mass then begins to enter the system, and a travelling wave spreads from the circular phase-separated region in the centre of the domain, towards the boundaries. This travelling wave propagates from \( t = 807.7s \) through to approximately \( t = 5660s \), which corresponds to time steps 500 through 1500. The phase-separated region then impacts the boundaries of the domains around \( t = 5679.6s \), and the rest of the domain is completely phase-separated a short time later at \( t = 5708.1s \). This small time period between \( t = 5679.6s \) and \( t = 5708.1s \) is responsible for increasing the total proportion of mass in the system from 0.6 to 1, as shown in Fig. 3.13c.

The movement of the travelling wave occupies the majority of the simulation time, and the adaptive time-stepping takes large time-steps during this period, as shown in Fig. 3.13c. Interestingly, Fig. 3.13b shows us that many of the time-steps taken during
| No. of Nodes | $||h_{\text{max}}||$ | $\hat{n} \cdot (\overline{K} \nabla c)$ | $\hat{n} \cdot (\nabla (\nabla \cdot (\overline{K} \nabla c)))$ | $\hat{n} \cdot (\overline{K} \nabla c)$ | $\hat{n} \cdot (\nabla (\nabla \cdot (\overline{K} \nabla c)))$ |
|--------------|----------------|------------------|------------------|----------------|------------------|
| **CH IBVP**  |                | Weighted         | Equality         |                |                  |
| 75 × 75      | 0.8653         | $1.43 \times 10^{-5}$ | $1.31 \times 10^{-3}$ | $1.46 \times 10^{-5}$ | $1.25 \times 10^{-3}$ |
| 100 × 100    | 0.6468         | $5.92 \times 10^{-6}$ | $8.97 \times 10^{-4}$ | $5.98 \times 10^{-6}$ | $1.2 \times 10^{-3}$ |
| 125 × 125    | 0.5164         | $3.15 \times 10^{-6}$ | $7.53 \times 10^{-4}$ | $3.21 \times 10^{-6}$ | $1.6 \times 10^{-3}$ |
| 150 × 150    | 0.4297         | $1.83 \times 10^{-6}$ | $6.22 \times 10^{-4}$ | $2.42 \times 10^{-6}$ | $2.0 \times 10^{-3}$ |
| Order        |                | 2.92             | 1.04             | 2.62           | -0.69            |

| **CHR IBVP** |                | Weighted         | Equality         |                |                  |
|--------------|                |                  |                  |                |                  |
| 100 × 100    | 0.6468         | $6.6 \times 10^{-2}$ | -                | $7.9 \times 10^{-2}$ | -                |
| 125 × 125    | 0.5164         | $4.5 \times 10^{-2}$ | -                | $5.4 \times 10^{-2}$ | -                |
| 150 × 150    | 0.4297         | $2.9 \times 10^{-2}$ | -                | $3.9 \times 10^{-2}$ | -                |
| Order        |                | 2                | -                | 1.73           | -                |

Table 3.1: Maximum absolute value of the derivatives on the $x = -10$ boundary across $y$ for the CH and CHR IBVPs in two-dimensions, with $p = 5$ and $p_o = 4$. Runtime constrains meant we could not run enough test cases to justify a plot like Fig. 3.7b.
the simulation violate strict gradient-stability. Indeed, it appears that the majority of these steps occur when the travelling wave is moving (between steps 500-1500). In the one-dimensional solutions, this is the period when the value of $d\tilde{G}/dt$ is extremely small (though still negative). The largest positive value of $d\tilde{G}/dt$ that occurs in Fig. 3.13b during this process is 2.98, which is small given the larger scale of $d\tilde{G}/dt$ in the two-dimensional simulation when compared with the one-dimensional (-22500 in Fig. 3.13b compared with -100 in Fig. 3.6c). Given the large time-steps taken during the wave propagation and the observed violation of gradient-stability, we restricted the maximum size of the time-step IDA takes to $10^0$. Unfortunately this made no difference to the gradient stability of the solution, though it did increase the runtime of the problem considerably. As such, we believe that this behaviour is most likely related to that seen in Fig. 3.9, where an increase in the number of nodes saw a gradient-stable solution (Fig. 3.6c) become one that violates gradient stability. In two-dimensions, the least-squares matrix $H$ is more singular than its one-dimensional equivalent (as $||h_{\text{max}}||$ is larger in two-dimensions) and any significant decrease in the number of nodes ($75 \times 75$ for example) in an attempt to ameliorate this behaviour results in the solution not converging. The recoverable error described in Section 3.5 also had to be disabled to ensure the solutions to the two-dimensional CHR IBVP shown in Fig. 3.12 converged. Unfortunately, we were unable to find any combination of grid spacing, time-step restrictions, $p$ and $p_o$ value, recoverable error criteria, or least-squares solution methodology to give a perfectly gradient-stable solution to the two-dimensional CHR IBVP.

Table 3.1 shows that the weighted least-squares method satisfies the VBC (3.2.9) to second order when solving the CHR IBVP in two-dimensions, compared with slightly below second order for the equality-constrained method. Given that our discretisation in two-dimensions should be second-order, the weighted least-squares method should be used to solve the CHR IBVP to ensure the VBC (3.2.9) is satisfied to the same order.

### 3.6 Conclusions

The least-squares method presented above for solving the CH and CHR IBVPs performs well in both one and two-dimensions. The problem of applying multiple BCs with a fourth-order PDE is handled by incorporating the variational BC into the least-squares system that is used to evaluate information at CV faces.
Figure 3.12: CHR IBVP solution computed in two dimension \((x, y \in [-10, 10])\) with 150 \(\times\) 150 nodes using equality-constrained least-squares. Relative and absolute tolerances were set at \(1 \times 10^{-6}\).

\[ \tilde{\Omega}_m = 5, \ K = I, \ D = I, \ \rho_s R_{\text{ins}}/\rho = 1, \ \tilde{\mu}_e = 0.5, \ p = 5, \ p_o = 4. \]
Figure 3.13: CHR IBVP solution statistics for the simulation shown in Fig. 3.12.

(a) Proportion of mass in the system over time. The solid line corresponds to the bottom $x$ axis (time step), while the dashed line corresponds to the top $x$ axis ($t$).

(b) Change in free energy over time. There are 1100 time steps that violate gradient-stability and these have been highlighted in red.

(c) Size of the time steps taken.
For the CH IBVP in one-dimension, up to fourth-order convergence is reported, using either a weighted or equality-constrained least-squares method. The solutions produced are gradient-stable and satisfy mass conservation laws to near machine precision. Using no more than 600 node points on a linear grid ensures that the BCs are applied in a high-order manner. The CHR IBVP in one dimension, however, requires the use of high-order Taylor series in the least-squares system, solved using the equality-constrained method to ensure greater than second-order convergence is maintained. Satisfying strict gradient-stability however, requires balancing the conditioning of the least-squares system with the high-order Taylor series required and hence less than 400 node-points with lower-order Taylor approximations should be used.

As might be expected, the two-dimensional IBVPs were more difficult to solve numerically. The solution to the CH IBVP remains gradient stable while satisfying mass conservation laws, whereas no solution to the CHR IBVP could be found that remains strictly gradient-stable. The exponential form of the BCs in the CHR IBVP increase the stiffness of the problem considerably when compared to the CH IBVP, making the gradient-stable solution a challenge to compute. Also, the weighted least-squares methods should be used in two-dimensions, in order to satisfy the BCs sufficiently.

In general, given the lack of an analytic proof that the CHR IBVP should remain gradient-stable, we do not expect our numerical solution to always satisfy this constraint. Our numerical results however, seem to suggest that the initial condition tested in this work could represent an excellent test case for the CHR IBVP, possibly admitting gradient-stable solutions. Indeed, the CHR IBVP represents a test for discretisation schemes that are currently used to solve the CH IBVP, as our scheme conserves and is perfectly gradient-stability in one and two dimensions for the CH IBVP, but fails for the CHR IBVP in two-dimensions. Given the extensive literature on numerical solutions of the CH IBVP and the comparative lack on the CHR IBVP, we believe this offers an exciting opportunity to not only test discretisation methods like this work, but time-stepping schemes on the more difficult CHR IBVP.
4. THE EFFECT OF TWO-DIMENSIONAL Li\textsuperscript{+} TRANSPORT

For this chapter, the associated reference is:


Additional numerical detail has also been included below.

4.1 Introduction

In recent years, phase-field models have been used to simulate various properties of LiFePO\textsubscript{4} material [28, 30, 34, 76, 81, 85, 139]. These phase-field models typically result in the concentration distribution of Li\textsuperscript{+} being represented by the solution of the fourth-order Cahn-Hilliard (CH) equation. The CH equation is a thermodynamically consistent approach to modelling phase-separating materials, where the phase interface is “diffuse”. This is in contrast to the sharply defined interface assumed in Stefan equation models that have traditionally been used to represent phase-separation in LiFePO\textsubscript{4} [21, 64, 82]. The CH equation is normally closed with no-flux boundary conditions, however Singh et al. [76] coupled a reaction condition to the boundary of a crystal, which drives Li\textsuperscript{+} intercalation in the material, to arrive at the so called Cahn-Hilliard-reaction (CHR) system. Singh et al. [76] then examined the properties of a simplified second-order, depth-averaged equation (also known as the “Allen-Cahn-reaction” (ACR) model [54]) derived from the CHR system. In particular, Bai et al. [28] showed that applying a large fixed current to the depth-averaged equation results in LiFePO\textsubscript{4} material that fills homogeneously, which helps explain the high-rate behaviour of nanoscale LiFePO\textsubscript{4}. Cogswell and Bazant [30] also included coherency strain to this model system, and found that this further suppresses phase-separation.
Up to this point, analysis of the phase-separating behaviour of LiFePO$_4$ under a fixed current has been performed on the simplified depth-averaged equation. Tang et al. [85] for example, investigated the use of the full CHR system in LiFePO$_4$, though not under a fixed current and hence no connection was made to the suppression of phase-separation. The depth-averaged equation is derived by assuming Li$^+$ transport in the crystal is one-dimensional, in the $y$ direction. For small, defect-free nanocrystals, this is likely to be an excellent approximation. In this work, we examine the behaviour of the full CHR system under parameter regimes where the depth-averaged equation is no longer valid. The numerical solution of the fourth-order, nonlinear CHR system is however, very difficult to compute. Previously, we presented a general numerical method for solving the CHR system on an unstructured grid [151]. We use this numerical approach to solve the CHR IBVP, and validate our numerical solution against the depth-averaged equation by assuming one-dimensional Li$^+$ transport. We then alter both the gradient penalty and diffusivity tensors ($\bar{K}$ and $D$, respectively).

In a one-dimensional regime, the gradient penalty in the $y$ direction, $\bar{K}_{yy}$, is assumed to be large, given that phase-boundaries in the $y$ direction have not been observed experimentally. We examine the behaviour of the CHR system as this parameter is decreased. We then modify $D$, altering the Li$^+$ transport in the crystal from a one-dimensional process to a two-dimensional process. This is motivated by recent experimental and theoretical [116, 152] work that shows Li$^+$ transport in LiFePO$_4$ material that contains antisite defects is at least a two-dimensional process. Examining the phase-change behaviour at high currents with two-dimensional Li$^+$ transport reveals complex dynamics that cannot be captured by a depth-averaged equation.

### 4.2 Model Equations

We begin with a brief overview of the phase-field equations [28, 76, 81] used to model the intercalation of Li$^+$ into a crystal of LiFePO$_4$. Fig. 4.1 shows a schematic of a single crystal of LiFePO$_4$ of length $F_x, F_y$ and $F_z$ in each of the spatial dimensions, which has undergone phase-separation. The phase-boundary in Fig. 4.1 is aligned parallel to the $z$ axis, which is indicative of phase separation without the inclusion of anisotropic strain [30]. A region of highly lithiated material ($\text{Li}_{1-x_i}\text{FePO}_4$, where $x_i \ll 1$) is moving throughout the crystal in the $x$ direction. A “mushy” region of length $\lambda_x$ separates the
Li$_{1-x}$FePO$_4$ phase from the lowly lithiated phase (Li$_{\gamma}$FePO$_4$, where $\gamma \ll 1$) and it is in this region where charge is inserted into the crystal according to the reaction,

$$\text{FePO}_4 + \text{Li}^+ + e^- \xrightarrow{\text{charge}} \text{LiFePO}_4.$$  \hspace{1cm} (4.2.1)

We will also refer to $\lambda_y$ and $\lambda_z$ as the length of the phase-separated region in the $y$ and $z$ direction, respectively, though Fig. 4.1 does not show phase-separation in either of these directions.

At early and late times with a low applied current, the crystal fills homogeneously. This process is not shown in Fig. 4.1 and involves Li$^+$ intercalating into the empty crystal to form Li$_{\gamma}$FePO$_4$ before phase-separating. The phase boundary then moves throughout the crystal as shown in Fig. 4.1, until the entire crystal is composed of Li$_{1-x}$FePO$_4$. Homogeneous filling then continues until the crystal reaches the fully lithiated state LiFePO$_4$. The dynamics of a phase-field model capture all of this behaviour without assuming that a phase-boundary exists (which is unlike a shrinking-core model [21, 82]).

We assume that the crystal shown in Fig. 4.1 is comprised of an ordered series of unit lattice cells of volume $V_{\text{cell}}$ (m$^3$) with $N_{sv}$ individual Li$^+$ intercalation sites per unit cell.

We can write the exposed area of a unit cell on the $xz$ plane at $y = F_y$ as $A_{\text{cell}}$ (m$^2$), with $N_{ss}$ of the $N_{sv}$ sites in the unit cell directly exposed to the reaction on the surface.
The average area of a single intercalation site can then be written as \( A_s = A_{\text{cell}}/N_{ss} \) (m\(^2\)). The constant site density is given by \( \rho = N_{sv}/V_{\text{cell}} \) (m\(^{-3}\)), and the surface site density by \( \rho_s = N_{ss}/A_{\text{cell}} \) (m\(^{-2}\)). Each surface site is associated with an ion channel along which Li\(^+\) is transported from the surface of the crystal to the interior. As shown in Fig. 4.1 the ion channels extend in the \( y \) direction and are associated with a single reaction site, with \( N_H = \rho A_s F_y \) lithium sites in each channel. Over both of the \( xz \) facets at \( y = 0 \) and \( y = F_y \), we have \( N_{As} = 2F_x F_z/A_s \) active surface sites (or twice the number of ion channels).

The distribution of Li\(^+\) in the crystal can be described by the Cahn-Hilliard-reaction equation and a depth-averaged version of the CHR equation [28, 76, 77, 81]. The following sections briefly describe the CHR and depth-averaged equations, and comment on the assumptions necessary (as outlined in detail by Burch [71]) to derive the depth-averaged equation.

4.2.1 Cahn-Hilliard-reaction equation

We adopt the notation of Burch [71] and assume that the free energy of mixing in our system is given by the CH functional [69] \( G[c(x, t)] \) (J), where \( c(x, t) \in [0, 1] \) is the concentration of Li\(^+\) in a LiFePO\(_4\) crystal (nondimensionalised by \( \rho \)) in contact with a reservoir of Li\(^+\) in the electrolyte, with spatial coordinates \( x \) (m), through time \( t \) (s). For a more detailed derivation of the following model equations, we refer the reader to the references [54, 69, 71]. On an \( N_D \)-dimensioned domain \( \Omega \) with boundary \( \Gamma \) the free energy of mixing in a CH model can be written as

\[
G(t) \equiv G[c(x, t)] = \int_\Omega \left[ g_{\text{hom}}(c) + \frac{1}{2} (\nabla c)^T K (\nabla c) + \frac{B(\hat{n}_0)}{2\rho} (c - c_{\text{avg}})^2 \right] \rho \, d\Omega, \tag{4.2.2}
\]

where \( g_{\text{hom}} \) (J) is the free energy per molecule of a homogeneous system at a uniform concentration and \( K \) (J m\(^{-2}\)) is a gradient penalty tensor, which we have assumed is symmetric positive definite, orthotropic and constant (where the diagonal elements of this tensor follow from the width of the phase-boundaries in each direction). The final term in the free energy functional isotropically approximates the effect of coherency strain in the crystal [30, 153, 154], where \( B(\hat{n}_0) \) (Pa) is the elastic energy in the minimizing direction \( \hat{n}_0 \) and \( c_{\text{avg}} \) is the average concentration of Li\(^+\) over \( \Omega \). In Section 4.4, we examine the phase-separation dynamics in both the simple strain-free case and with isotropic coherency strain included.
We assume $g_{\text{hom}}$ obeys a regular solution model \[28, 46, 69, 71\] and is written as

$$g_{\text{hom}}(c) = \Omega_m c(1-c) + 2k_B T (c \ln(c) + (1-c) \ln(1-c)),$$  \hspace{1cm} (4.2.3)

where $k_B$ (J K$^{-1}$) is Boltzmann’s constant, $T$ (K) is the temperature and $\Omega_m$ (J) is the enthalpy of mixing per site. Writing (4.2.1) as

$$\text{LiFePO}_4 - \text{FePO}_4 \leftrightarrow \text{Li}^+ + e^-,$$  \hspace{1cm} (4.2.4)

the chemical potential of the LHS of (4.2.4) is called the diffusional chemical potential $\mu$ (J). This is the potential of $\text{Li}^+$ in the lattice, per molecule. Noting (4.2.3), the variational derivative of (4.2.2) (written with respect to the same reference chemical potentials) \[54, 131\] gives us the diffusional chemical potential, $\mu(x,t) - \mu^\Theta = \Omega_m (1-2c) + 2k_B T \ln \left( \frac{c}{1-c} \right) - \nabla \cdot (K \nabla c) + \frac{B(\hat{n}_0)}{\rho} (c-c_{\text{avg}}) = k_B T \ln a(x,t),$  \hspace{1cm} (4.2.5)

where $a$ is the activity of the $\text{Li}^+$ in the lattice and $\mu^\Theta$ (J) is the reference chemical potential.

The mass flux $j$ (m$^{-2}$ s$^{-1}$) per molecule is proportional to a gradient in chemical potential, namely

$$j(x,t) = \rho c M \nabla \mu,$$  \hspace{1cm} (4.2.6)

where $M$ (m$^2$ J$^{-1}$ s$^{-1}$) is a mobility tensor. As mass is conserved in this system, the Cahn-Hilliard equation is given by

$$\frac{\partial c}{\partial t} + \frac{1}{\rho} \nabla \cdot j = 0, \quad x \in \Omega.$$  \hspace{1cm} (4.2.7)

The CH equation (4.2.7) can also be rewritten directly in terms of the concentration $c(x,t)$ and using the Einstein relation to write the mobility as $M = D/(k_B T)$, where $D$ (m$^2$ s$^{-1}$) is a diffusion tensor, we obtain

$$\frac{\partial c}{\partial t} + \nabla \cdot \left( D \left\{ \left[ 2\tilde{\Omega}_m c - \frac{2}{1-c} \right] \nabla c + c \nabla [\tilde{B}(\hat{n}_0) c - \nabla \cdot (\tilde{K} \nabla c)] \right\} \right) = 0,$$  \hspace{1cm} (4.2.8)

where $\tilde{\Omega}_m = \Omega_m / k_B T$, $\tilde{K} = K / k_B T$ and $\tilde{B}(\hat{n}_0) = B(\hat{n}_0) / \rho k_B T$. The solution to (4.2.8) is the concentration distribution of $\text{Li}^+$ that minimises the free-energy functional (4.2.2) at any time. In (4.2.8) we assume $D$ is constant. As we are considering $\text{Li}^+$ movement on a lattice, $D$ is often taken to be dependant on concentration (and this dependence can be calculated by considering different models for diffusion on a lattice, see \[53, 155\]).
Relations of the form $D = D_0(1 - c)$ are often used (see [156], where this is known as the “modified Cahn-Hilliard” equation; see [54] for a more general derivation), though experimental measurements [157] suggest that the diffusivity does not vary greatly with Li$^+$ concentration. Simulations using $D = D_0(1 - c)$ show the same qualitative results for all cases given in Section 4.4 and as such, we simply assume $D$ is constant. Increasingly nonlinear forms of $D$ may, however, change some of the results given in this work.

The initial concentration of Li$^+$ in a crystal is given by some function $f(x)$, such that

$$c(x, 0) = f(x), \quad \text{at } t = 0. \quad (4.2.9)$$

The boundary conditions for (4.2.8) are [71]

$$\hat{n} \cdot (\mathbf{K} \nabla c) = 0, \quad \text{on } \Gamma \quad (4.2.10)$$
$$\hat{n} \cdot \mathbf{j} = \rho_s R(x, t), \quad \text{on } \Gamma \quad (4.2.11)$$

where $R(x, t)$ ($s^{-1}$) is a reaction term that determines the number of molecules of Li$^+$ that intercalate into the crystal. We note that (4.2.10) is known as the variational boundary condition (VBC) and that $\rho_s$ in (4.2.11) should be dependant on which facet (4.2.11) is applied to (and hence so should $A_s, N_{ss}$, etc). We neglect this dependence however and continue with our definition of $\rho_s$ as the surface density of Li$^+$ sites on the $xz$ surface. We discuss this further in Section 4.2.2. We should also note that [139] introduced concentration-dependent surface effects, $\gamma(c)$, to (4.2.2) (and hence (4.2.10)) that are neglected here.

The current-overpotential form of the Butler-Volmer equation [28, 51, 53] allows us to define $R(x, t)$ as

$$R(x, t) = \frac{(k_a^0 a_e^0)^\alpha (k_c^0 a_0^0)^{1-\alpha}}{\gamma^*_t} \left[ \frac{a_e}{a_e^0} \exp\left(\frac{-\alpha \eta(t)}{k_B T}\right) - \frac{a(x, t)}{a^0} \exp\left(\frac{(1-\alpha) \eta(t)}{k_B T}\right) \right], \quad (4.2.12)$$

where $a_e$ is the activity of the Li$^+$ in the electrolyte (which we set to 1 [28], therefore assuming that Li$^+$ diffusion in the electrolyte is rapid), $a_e^0$ and $a_0$ are the activities of Li$^+$ in the electrolyte and the solid, respectively, at $t = 0$, and $k_a^0$ and $k_c^0$ ($s^{-1}$) are the forward and backward rate constants, respectively, for (4.2.4) (these contain the various reference potentials). These rate constants are related to the mean reaction
time for a single reaction step, $\tau_0$ (s) [28] via the expression $(k_0^a)^\alpha (k_0^c)^{1-\alpha} = 1/\tau_0$. We note that Bai et al. [28] set $\tau_0 = 1$. Thus in order to compare our work with the results of Bai et al. [28], we set $(k_0^a)^\alpha (k_0^c)^{1-\alpha} = 1$. As such, the timescales shown in Section 4.4 should not be taken as representative of discharge times. The activity coefficient of the activated state is denoted by $\gamma^\ddagger$ (which Bai et al. [28] take to be $(1-c)^{-1}$), $\alpha$ is the symmetry factor for (4.2.4) and $e$ (C) is the elementary charge on a proton. Crucially, (4.2.12) uses the Li\textsuperscript{+} activity in the solid, not the concentration. When using a phase-field model to determine the transport of Li\textsuperscript{+} in the solid, the activity (given by (4.2.5)) depends on both the concentration and concentration gradients (specifically $\nabla^2 c$). This dependence would be neglected if concentrations were used in (4.2.12) under a dilute solution limit. This form of the Butler-Volmer expression in connection with phase-field models was first used by Bai et al. [28] (see also [53, 54]).

Given the form of (4.2.12), we write the surface overpotential as $\eta(t) = \Delta \Phi_c(t) - E_{\text{ref}}$ (V), where $\Delta \Phi_c(t) = \Phi_c(t) - \Phi_e(t)$ (V) is the averaged potential difference over the entire solid/electrolyte interface of an individual crystal. If we consider a complete LiFePO\textsubscript{4} cell (anode and cathode), rather than the individual crystal described above, we can write the OCV of a cell, $E_{\text{cell}}$ (V), with respect to Li\textsuperscript{+} metal, as

$$E_{\text{cell}} = \Delta \Phi_{\text{cath}} - \Delta \Phi_a. \quad (4.2.13)$$

Here $\Delta \Phi_{\text{cath}}$ and $\Delta \Phi_a$ (V) are the potential differences across the cathode and anode respectively, written with respect to Li\textsuperscript{+} metal. In this work we are modelling the discharge of a single crystal, though we still wish to plot the potential of an individual LiFePO\textsubscript{4} crystal on a voltage scale representative of a LiFePO\textsubscript{4} cell. As such, we replace $\Delta \Phi_{\text{cath}}$ in (4.2.13) with the potential drop across an individual crystal, $\Delta \Phi_c$ (V), to obtain the voltage of our LiFePO\textsubscript{4} crystal, $E_c$ (V), which we define as

$$E_c = \Delta \Phi_c - \Delta \Phi_a. \quad (4.2.14)$$

We write the overpotential $\eta$ with respect to $E_{\text{ref}}$ (V), the reference voltage of our crystal “half-cell” at $t = 0$, which is given by the Nernst equation, namely

$$E_{\text{ref}} = \Delta \Phi_c^0 = \frac{k_B T}{e} \ln \left( \frac{k_0^c}{k_0^a} \right) + \frac{k_B T}{e} \ln \left( \frac{a_0^c}{a_0^a} \right). \quad (4.2.15)$$

Given that $\Delta \Phi_a$ (and the ratio of our rate constants) is undetermined, we follow Bai et al. [28] and consider the potential drop across an individual crystal relative to the open circuit voltage plateau in a LiFePO\textsubscript{4} cell, which is 3.42 V versus Li\textsuperscript{+} metal.
Previously we set \((k_a^0)^\alpha(k_c^0)^{1-\alpha} = 1\), but for consistency with the crystal voltage defined by Bai et al. [28], we must also set \(k_c^0 = k_a^0 = 1\) and assume that the potential drop across the anode is constant and equal to \(-\Delta \Phi_a = 3.42\) V. With our definition of \(\eta\) we can write (4.2.14) as

\[
E_c = \eta + E_{\text{ref}} - \Delta \Phi_a.
\] (4.2.16)

The OCV of our “cell” at \(t = 0\) with no applied current is therefore \(E_c^0 = E_{\text{ref}} - \Delta \Phi_a \approx 3.477\) (given \(\eta = 0\)). Normally, when modelling a complete LiFePO\(_4\) cell, we would determine \(E_c^0\) experimentally by measuring the OCV of a LiFePO\(_4\) cell at \(t = 0\), without assuming that the rate constants are equal.

Writing the overpotential and reaction term in this fashion is algebraically equivalent to the definition used by [28], however given uniform initial conditions and therefore reference activities, \(E_{\text{ref}}\), as given by (4.2.15), is a constant. Importantly, this means that our overpotential \(\eta\) is only a function of time. This makes coupling crystal-scale models to a (possibly multi-scale) porous electrode model much simpler. We should note that the definition of the overpotential given here is very similar to that given in our previous paper [82]. In [82], we included \(\Delta \Phi_a^0\) in \(E_{\text{ref}}\) (making our reference potential the OCV of a complete LiFePO\(_4\) cell at \(t = 0\), where the notation for the reference potential \(E_{\text{ref}}\), has been changed from \(E^0\) in [82] to avoid confusion with standard potentials) and absorbed the rate constants, reference activities and anodic potential difference at \(t = 0\) into the exchange current density \(i_0\), which follows from the treatment of the Butler-Volmer equation given by Farrell et al. [48].

The total current entering or leaving the crystal, \(I_c(t)\) (A), is given by

\[
I_c(t) = \frac{e}{A_s} \int_{\Gamma} R(x, t) \, d\Gamma,
\] (4.2.17)

where (4.2.17) can be used to determine the overpotential \(\eta(t)\) when a fixed current is applied to the crystal.

Finally, the dimensionless mass fraction (or average concentration, \(c_{\text{avg}}\)) of Li\(^+\) in the system, \(M(t)\), is given by

\[
M(t) = \frac{1}{\Omega} \int_{\Omega} c(x, t) \, d\Omega.
\] (4.2.18)
4.2.2 Depth-averaged equation

Equation (4.2.8) is a stiff, three-dimensional fourth-order PDE whose solution can be challenging to compute. As such, Singh et al. [76] depth-average (4.2.8) and recover a second-order PDE that represents the concentration distribution in the \(xz\) plane. The assumptions needed to justify this averaging are examined in detail by Burch [71], and we outline these below.

The depth-averaging procedure considers the fluxes across the boundaries of rectangular parallelepipeds of width \(\epsilon\) (using the integral form of (4.2.8), similar to the discretisation of a PDE with the Finite Volume Method) as \(\epsilon \to 0\). If we assume one-dimensional transport in the system (motivated by \textit{ab initio} calculations that show transport in \(y\) is orders of magnitude easier than in \(x\) or \(z\) [90, 157, 158]), namely that

\[
\frac{D_{xx}}{\lambda_x^2} \ll \left(\frac{\rho_s}{\rho F_y}\right) R_y, \quad \text{and} \quad \frac{D_{zz}}{\lambda_z^2} \ll \left(\frac{\rho_s}{\rho F_y}\right) R_y, \tag{4.2.19}
\]

where \(R_y\) (s\(^{-1}\)) is a typical reaction rate on the \(xz\) plane, then we can set the fluxes across the boundaries of the parallelepipeds in the \(xy\) and \(yz\) directions to be zero. We note however, that setting these fluxes to zero using (4.2.19) only applies for parallelepipeds in the bulk of the crystal. The reaction condition applied to the boundary of the crystal, (4.2.11), is applied across the entire crystal surface, and regardless of the size of \(\epsilon\), the fluxes on the surface of the \(xy\) and \(yz\) planes will be nonzero. Given the assumption of one-dimensional transport, \(\text{Li}^+\) will not diffuse into surrounding parallelepipeds from those exposed to the surface reaction, but it will still intercalate, especially at early times before a concentration gradient has had time to establish and affect the reaction rate. As such, we note that for the CHR system and the depth-averaged equation to be equivalent, no-flux boundary conditions should be applied to the CHR equation, on every exposed facet apart from those in the \(xz\) plane. This makes our previous definition of \(\rho_s\) as the surface density on the \(xz\) plane clearer, as for the most part, we don’t actually apply flux conditions to any other surface in the CHR system, and hence don’t require \(\rho_s\) to be dependent on the surface orientation.

The other assumption necessary for the depth-averaging procedure is a uniform concentration field in \(y\). Thus, we require that

\[
\frac{F_y^2}{D_{yy}} \ll \frac{\rho F_y}{\rho_s R_y}, \quad \text{and} \quad \lambda_y \gg F_y, \tag{4.2.20}
\]
or that the diffusion time in $y$ is much smaller than the reaction time on the $xz$ plane, and that the width of a possible phase boundary in $y$ is much greater than the facet width in that dimension. Given the assumptions outlined above, we recover the depth averaged version of (4.2.8), namely

$$\frac{\partial c(x, z, t)}{\partial t} = \frac{2\rho_s R(x, z, t)}{\rho F_y}. \tag{4.2.21}$$

In the absence of anisotropic strain, the concentration variation in $z$ can be neglected [28, 76], resulting in a one-dimensional depth-averaged equation in $x$, namely,

$$\frac{\partial c(x, t)}{\partial t} = \frac{2\rho_s R(x, t)}{\rho F_y}. \tag{4.2.22}$$

As the reaction boundary condition (4.2.11) is used during the averaging process we are left with a single boundary condition for (4.2.22), namely the VBC (4.2.10), or

$$\tilde{K}_{xx} \frac{\partial c(x, t)}{\partial x} = 0.$$

Given the definitions of $\rho$ and $\rho_s$, we can then write

$$\frac{\partial c(x, t)}{\partial t} = \frac{2R(x, t)}{N_H}. \tag{4.2.23}$$

4.2.3 Nondimensionalisation

In order to compare the solution of the CHR problem to that of the depth-averaged equation, we choose to simplify the three-dimensional CHR problem to two dimensions, and simulate only the $xy$ plane. Previously, analysis of elastic effects concluded that phase boundaries always align with the $yz$ planes [29, 159], which suggests a phase-transformation as pictured in Fig. 4.1. A more sophisticated analysis by Cogswell and Bazant [30] suggests that phase boundaries form in diagonal stripes on the $xz$ plane (the $\{101\}$ plane), though in this paper we choose to focus on the simpler case, with isotropic coherency strain (and hence isotropic $B$), which does not change the orientation of the phase-boundary, or energy penalties associated with phase-boundary formation in various directions. This is an important point as Cogswell and Bazant [30] showed that elastic strain favours phase-separation in the $[101]$ and $[100]$ directions given a coherent and semicoherent interface, respectively. The goal of this work was to examine the behaviour of the CHR IBVP when the assumptions necessary for depth-averaging are not satisfied, which requires resolving transport in the $y$ direction. The
Further inclusion of anisotropic elastic strain would require a 3D simulation, increasing the numerical stiffness of the problem considerably. We believe quantitatively modelling LiFePO$_4$ crystals would require 3D simulations, but as a first attempt at examining the role of transport in the $y$ direction, we simplify the problem to two dimensional planar coordinates $\mathbf{x} = [\tilde{x}, \tilde{y}] \in [0, F_x/L_x] \times [0, F_y/L_y]$ where we have applied the nondimensionalisations

$$\tilde{x} = \frac{x}{L_x}; \quad \tilde{y} = \frac{y}{L_y}; \quad \tilde{t} = \frac{t}{t_0}; \quad \tilde{\eta} = \frac{\eta_e}{k_B T}.$$ (4.2.24)

Here $L_x$ and $L_y$ are representative length scales in the $x$ and $y$ direction respectively, and $t_0$ is a representative time scale for the problem. Also, the dimensionless chemical potentials that follow have been scaled by $k_B T$. At the cost of notational simplicity, we have specified a different characteristic length scale in both the $x$ and $y$ directions (that isn’t necessarily the facet lengths $F_x$ and $F_y$). The orthotropy of the parameters used to generate the results in Section 4.4 make this a necessity, and we discuss the values for $L_x$ and $L_y$ in Section 4.3. Following Bai et al. [28], we also add a Langevin noise term $X_n$ [160] to (4.2.8). This noise is sampled from a normal distribution with zero mean of the form

$$X_n \sim \mathcal{N}\left(0, \sqrt{2k_B T \frac{a_e^{1-\alpha} a^n}{\gamma^{\frac{1}{\alpha}}}}\right).$$ (4.2.25)

Writing Eq. (4.2.7) as

$$\frac{\partial c}{\partial \tilde{t}} + \nabla \cdot \tilde{j} + X_n = 0,$$ (4.2.26)

where $\tilde{j}$ is the dimensionless mass flux, setting the time scale to be $t_0 = L_y^2/D_{yy}$ and assuming $D$ is orthotropic, we recover the dimensionless form

$$\frac{\partial c}{\partial \tilde{t}} + \nabla \cdot \left(2\tilde{\Omega}_m c - \frac{2}{1-c}\right) \left(k_1 \frac{\partial c}{\partial \tilde{x}} \hat{i} + k_4 \frac{\partial c}{\partial \tilde{y}} \hat{j}\right) + c \left(k_{13} \frac{\partial^3 c}{\partial \tilde{x}^3} - k_{2} \frac{\partial^3 c}{\partial \tilde{x}^2 \tilde{y}} - k_{3} \frac{\partial^3 c}{\partial \tilde{y}^2 \tilde{x}} \right) \hat{i} + \left(k_{14} \frac{\partial c}{\partial \tilde{y}} - k_{5} \frac{\partial^3 c}{\partial \tilde{x}^2 \tilde{y}} - k_{6} \frac{\partial^3 c}{\partial \tilde{y}^2 \tilde{x}} \right) \hat{j} + X_n = 0.$$ (4.2.27)

In order to compare the numerical solution of the two-dimensional CHR equation to the depth-averaged equation, we apply a no-flux boundary condition on the $y$ boundaries
as discussed in Section 4.2.2, or,
\[
\hat{n} \cdot \left( k_7 \frac{\partial c}{\partial \tilde{x}} \hat{i} + k_8 \frac{\partial c}{\partial \tilde{y}} \hat{j} \right) = 0, \quad \text{on } \Gamma, \quad (4.2.28)
\]
\[
\hat{n} \cdot \hat{j} = \hat{n} \cdot (k_9 \hat{i} + k_{10} \hat{j}) \tilde{R}, \quad \text{on } \tilde{y} = 0, \tilde{y} = F_y/L_y, \quad (4.2.29)
\]
\[
\hat{n} \cdot \hat{j} = 0, \quad \text{on } \tilde{x} = 0, \tilde{x} = F_x/L_x. \quad (4.2.30)
\]

We have included a generic normal \( \hat{n} \) in (4.2.29) instead of simply using \( \hat{j} \), as in Section 4.4 we briefly investigate the differences between the two-dimensional CHR IBVP and the depth-averaged equation if (4.2.29) is applied to \( \Gamma \).

The dimensionless reaction term is given by
\[
\tilde{R} = \left( \frac{a_0^0}{a_e} \right)^{\alpha} \left( \frac{a_0^0}{a_e} \right)^{1-\alpha} \frac{a_e}{a_0^0} \exp \left( -\alpha \tilde{\eta} \right) - \frac{a_e}{a_0^0} \exp \left( \left( 1 - \alpha \right) \tilde{\eta} \right) \right]. \quad (4.2.31)
\]

The dimensionless chemical potential is given by
\[
\tilde{\mu} - \tilde{\mu}^\Theta = \tilde{\Omega}_m (1 - 2c) + 2 \ln \left( \frac{c}{1-c} \right) - \left( k_{11} \frac{\partial^2 c}{\partial \tilde{x}^2} + k_{12} \frac{\partial^2 c}{\partial \tilde{y}^2} \right) + \tilde{B}(\hat{n}_0)(c - c_{\text{avg}}) = \ln a. \quad (4.2.32)
\]

The dimensioned crystal voltage can be written as
\[
E_c = \frac{k_B T}{e} \left( \tilde{\eta} + \ln \left( \frac{a_0^0}{a_e} \right) \right) + 3.42. \quad (4.2.33)
\]

The dimensionless parameters in (4.2.27) to (4.2.32) are given by
\[
\begin{align*}
&k_1 = \frac{D_{xx} L_y^2}{D_{yy} L_x^2}; \quad k_2 = \frac{D_{xx} \tilde{K}_{xx} L_y^4}{D_{yy} L_x^4}; \quad k_3 = \frac{D_{xx} \tilde{K}_{yy} L_y^2}{D_{yy} L_x^2}; \quad k_4 = 1; \quad k_5 = \frac{\tilde{K}_{xx}}{L_x^2}; \\
&k_6 = \frac{\tilde{K}_{yy}}{L_y^2}; \quad k_7 = \frac{\tilde{K}_{xx}}{L_x}; \quad k_8 = \frac{\tilde{K}_{yy}}{L_y}; \quad k_9 = \frac{\rho_s t_0}{\rho L_x \tau_0}; \quad k_{10} = \frac{\rho_s t_0}{\rho L_y \tau_0}; \quad k_{11} = \frac{\tilde{K}_{xx}}{L_x^2}; \\
&k_{12} = \frac{\tilde{K}_{yy}}{L_y^2}; \quad k_{13} = k_1 \tilde{B}(\hat{n}_0); \quad k_{14} = k_4 \tilde{B}(\hat{n}_0).
\end{align*}
\]

In order to compare the results from the CHR system with those from the depth-averaged system, we apply the same nondimensionalisation to the total current entering/leaving a LiFePO₄ crystal, \( I_c(t) \), as Bai et al. [28] apply to the depth-averaged
system, and hence $I_c$ is given by

$$I_c = \frac{\tau_0 I_c(t)}{eN_{As}} = \frac{1}{2F_x} \left( L_y \tilde{I}_{ce} + L_x \tilde{I}_{cn} \right), \quad (4.2.34)$$

where $\tilde{I}_{ce}$ is the dimensionless current on the $\tilde{x} = 0$ and $\tilde{x} = F_x/L_x$ boundaries of the crystal and $\tilde{I}_{cn}$ is the dimensionless current on the $\tilde{y} = 0$ and $\tilde{y} = F_y/L_y$ boundaries. These are given by

$$\tilde{I}_{ce} = \frac{\tilde{y} = F_y/L_y}{\tilde{y} = 0} \int \tilde{R}_{\tilde{x} = F_x/L_x} + \tilde{R}_{\tilde{x} = 0} \, d\tilde{y}, \quad (4.2.35)$$

and

$$\tilde{I}_{cn} = \frac{\tilde{x} = F_x/L_x}{\tilde{x} = 0} \int \tilde{R}_{\tilde{y} = F_y/L_y} + \tilde{R}_{\tilde{y} = 0} \, d\tilde{x}. \quad (4.2.36)$$

For the depth-averaged equation (4.2.23) we nondimensionalise with $\tau = t N_{H\tau_0}; \quad \tilde{x} = \frac{x}{L_x}$; where $L_x$ is some representative length scale (which is the same as that used to nondimensionalise $x$ in the CHR system). This, along with the addition of the noise term defined previously, gives the dimensionless depth-averaged equation as

$$\frac{\partial c}{\partial \tau} = 2 \tilde{R} + X_n. \quad (4.2.37)$$

We note that there is a factor of two in (4.2.37) when compared to the depth-averaged equation presented by Bai et al. [28]; this explicitly shows that both the top and bottom $xz$ facets are included in the reaction, and we therefore include the factor of two in $N_{As}$. This ensures the dimensionless current used to generate the results in Section 4.4 remains consistent with that of Bai et al. [28].

The dimensionless form of the VBC (4.2.10) is given by

$$k_i \frac{\partial c}{\partial \tilde{x}} = 0, \quad \text{on } \tilde{x} = 0, \tilde{x} = F_x/L_x \quad (4.2.38)$$
with the dimensionless chemical potential

\[ \tilde{\mu} - \tilde{\mu}_\Theta = \tilde{\Omega}_m (1 - 2c) + 2 \ln \left( \frac{c}{1 - c} \right) - k_{11} \frac{\partial^2 c}{\partial \tilde{x}^2} + \tilde{B}(\tilde{n}_0)(c - c_{\text{avg}}) = \ln a. \]  

Finally, the dimensionless current entering/leaving the crystal \( \tilde{I}_c \) for the depth-averaged equation is written as

\[ \tilde{I}_c = \frac{\tau_0 I_c(t)}{e N_{\Lambda s}} = \frac{L_x}{F_x} \int_{\tilde{x}=0}^{\tilde{x}=F_x/L_x} \tilde{R} \, d\tilde{x}. \]  

### 4.3 Numerics

Table 4.1 lists the equation systems we solve in this work, along with each of the auxiliary equations and definitions necessary to close the systems. In terms of the dimensionless length scales used for both problems, we set the length scale in the \( x \) direction to be the width of the phase-boundary, \( L_x = \lambda_x \). For the \( y \) direction in the CHR system, we used the facet length, \( L_y = F_y \), which makes the time scale, \( t_0 \), the diffusion time in the \( y \) direction. We should note that using different length scales in each direction is essential to ensure convergence of the CHR equation. The form of the initial condition (4.2.9) used was \( f(x) = 0.01 \). For all comparative simulations shown, given the noise term outlined in Section 4.2, we deliberately perturbed the initial condition by \( 1 \times 10^{-6} \) at \( \tilde{x} = 6 \). This perturbation overwhelms the presence of the noise term (which at early times is of the order \( 1 \times 10^{-10} \)) and forces the crystals to phase-separate at \( \tilde{x} = 6 \) when the composition enters the spinodal region. This allows us to directly compare the behaviour of the CHR and depth-averaged models in the presence of noise. There is no visible difference in solution behaviour of either the CHR
or depth-averaged problems when this perturbation is included or not. Strictly speaking however, any non-uniform initial condition makes our formulation of the overpotential and reaction term incorrect. As such, outside of the comparisons shown in this paper, a uniform initial condition should be used.

In terms of solving the equation systems listed in Table 4.1, the two-dimensional, CHR system is by far the more challenging to solve numerically. We use the method outlined in Dargaville and Farrell [151] to solve the system. Briefly, the Finite Volume Method (FVM) is used to discretise the system, with a least-squares method used to estimate derivatives at quadrature points. Importantly, this least-squares method includes the VBC, so that we are free to set the flux-condition (4.2.29) as required. This ensures all of the boundary conditions are satisfied when solving the fourth-order system. The results presented were computed in C++, with the least-squares systems solved using routines from the LAPACK library provided in the Intel MKL (in contrast to using the SPQR package as in Dargaville and Farrell [151]). Time stepping was provided by the IDA module from Sundials [108]. The orthotropy of the parameters used to generate Fig. 4.3c allowed us to use a (linear) mesh with $80 \times 25$ nodes, in the $x$ and $y$ directions, respectively.

For regions away from the boundaries of the domain, we also used difference approximations to calculate the function value and gradients at finite volume faces. High-order difference approximations are easy to form explicitly on a rectangular mesh and do not include BC information. This restricted their use to the blue-shaded region in Fig. 3.3, but as mentioned in Chapter 3, this is the majority of the faces in the mesh. The difference approximations used were taken from Table 1 in Hyman et al. [150], and in the $x$ and $y$ directions, values at the faces were calculated with fourth-order approximations for both the function values and first derivatives, with a second-order approximation used for the third derivatives. Successive univariate approximations [137] were used to calculate the mixed derivative terms required. This involved calculating the Laplacian at node points, which were compute with second-order approximations taken from Table 2 in Hyman et al. [150]. The values of the Laplacians were then differentiated once using a second-order approximation, in order to obtain the mixed derivative terms at the faces.

Function values and derivatives as estimated by simple difference equations (at both the faces and nodes as required) can be computed efficiently by constructing access patterns stored in sparse matrices. These patterns are precomputed at the start of the simulation and the function values and derivatives at all of the faces in the blue-shaded
region in Fig. 3.3 can then be calculated by a single sparse matrix-multiply for each quantity estimated. The Sparse BLAS routines in the Intel MKL was used for these calculations (namely mkl_dcsrmv). Careful use of zero and one-based indexing in the sparse matrix-multiply routines also allowed the removal of any explicit transposition of the access patterns. In summary, for the results shown in this chapter, difference equations were used to estimate function values and derivatives in the blue-shaded region in Fig. 3.3, with the least-squares method used in the remaining purple, grey and green-shaded regions as described in Chapter 3.

In Dargaville and Farrell [151] the reaction term in the boundary condition, (4.2.29), was defined generically in terms of exterior chemical potential. In this work, we consider the galvanostatic discharge of a LiFePO$_4$ crystal, which requires us to set a fixed value for $I_c(t)$ (in (4.2.17)), which corresponds to setting a fixed $\bar{I}_c$ in (4.2.34). We then solve the integral equation (4.2.34) (using a discrete form via the application of the trapezoid rule) for the overpotential $\bar{\eta}$. This increases the bandwidth of the Jacobian considerably, making the use of a banded Newton solver computationally unfeasible. As such, in this work we used a Jacobian-Free Newton-Krylov (JFNK) method [161] to solve the nonlinear system. The IDA module provides a JFNK solver with several different Krylov methods for solving the linear system, and we used GMRES with the built-in block-banded preconditioner.

The preconditioner applied in this solver was constructed with the same function $F$ that was evaluated to determine the nonlinear residuals. In an attempt to construct a “cheap” function $G$ that could be used to build the preconditioner, the difference equations mentioned above were used to approximate information in $G$ at all of the faces shown in Fig. 3.3, not just the blue-shaded region. This results in $G$ not including the VBC. Unfortunately, this resulted in the nonlinear solver not converging and hence $G$ was required to contain all the BC information.

Using the difference equations in the blue-shaded region and the least-squares functions on the remaining faces was however, an excellent cheap preconditioner if the least-squares method were used to estimate values at every face in $F$, as in Chapter 3. In a further attempt to reduce the cost of computing the preconditioner, lower-order difference equations were used in the blue-shaded region, reducing the size of the sparse access patterns and therefore reducing the cost of the sparse matrix-multiply. There was no significant difference in the runtimes with this modification, as computing information in the purple, grey and green-shaded regions in Fig. 3.3 using the least-squares method dominated the cost of constructing $G$. 

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We also note that as mentioned in Chapter 3, analytic difference equations can be derived in one dimension that include the VBC. These equations can be used in two dimensions on a structured (orthogonal) mesh to calculate information in the grey and purple regions shown in Fig. 3.3, leaving the least-squares method to approximate information in only the green regions. Again, this would result in $G$ being cheaper to compute. Using this approach however, resulted in severe convergence failures. Hence, $G$ was required to not only contain all the BC information, but it must be computed using the least-squares method (i.e., the same as $F$). Therefore, for the results shown in this chapter, $G = F$. A preconditioner with reduced bandwidth was used though.

The use of difference approximations and a JFNK solver in this fashion resulted in a considerable decrease in run time when compared with Dargaville and Farrell [151]; the solution to the low current case ($\tilde{I}_c = 0.01$) shown in Fig. 4.3c took around 5 minutes to compute, with the higher current cases only taking several seconds.

4.3.1 Depth-averaged equation

The one-dimensional depth-averaged equation is simpler to solve than the CHR equation in two dimensions, though there are still several points worth discussing. Firstly, we used the Finite Difference method to discretise (4.2.37) with 100 node points in the $x$ direction. The integral equation (4.2.40) was discretised with the trapezoid rule (as with the two-dimensional CHR equation), and the resulting system was advanced in time with IDA. Given the small size of the discretised system, a dense Newton solver was used to solve the nonlinear system. The run time for the one-dimensional depth-averaged equation was several seconds.

Equation (4.2.37) does not look like a traditional second-order PDE, however $\tilde{R}$ is dependent on the second derivative of $c$ through (4.2.39). As such, it can be difficult to include the VBC in the discretised system. We evaluated the second derivative at node points on the boundary with our least-squares method, which includes the VBC. These values are then used to construct the reaction term at the boundary node points. This is identical to the approach we used to calculate the reaction term for the two-dimensional problem above, and in [151].

Interestingly, neglecting to include any boundary conditions in the discretised system resulted in a qualitatively correct solution. Fig. 4.2a shows the results from solving the depth-averaged equation with the VBC included with the least-squares method (the solid lines) and without (the dashed lines). The dashed lines are computed by
(a) Depth-averaged solution profiles for $\tilde{I} = 0.01$. The solutions given by the dashed line have been linearly interpolated to be at the same time points as the solid lines.
$t (s)$: $+ 0.31 \times 10^4$, $\times 0.34 \times 10^4$, $\Box 0.38 \times 10^4$, $\bigcirc 0.83 \times 10^4$, $\Diamond 1.28 \times 10^4$, $\bigcirc 1.59 \times 10^4$, $\triangle 1.63 \times 10^4$.

(b) Maximum of the first derivative at the boundaries throughout the simulations. Lines are least-squared fit to the results to determine the order of each approximation. The relative tolerance was set at $1 \times 10^{-10}$, the absolute tolerance at $1 \times 10^{-8}$.
Order: $+: 2.8894$, $\times: 0.99519$.

Figure 4.2: Differences between solving the one-dimensional depth-averaged equation with (solid lines) and without the VBC (dashed lines).
naively discretising the depth-averaged equation and solving the discrete equations at every node point, without applying any conditions or constraints on the boundary node values (i.e., the least-squares method which includes the VBC is not used to estimate second derivatives at the boundaries). For the majority of time points, the solutions are nearly identical. It is only when the phase-changed regions approaches the boundary of the domain that the solutions differ significantly.

For the majority of the simulation, \( \partial c / \partial \tilde{x} = 0 \) seems to be satisfied by both methods. Further examination of this behaviour is shown in Fig. 4.2b. Fig. 4.2b plots the maximum size of the first derivative (as measured with a fourth-order difference equation) at either of the boundaries for both of the simulations shown in Fig. 4.2a, as the number of node points in the mesh is increased. Fig. 4.2b shows that the value of the first derivative at the boundaries is always smaller when the VBC is included, by at least an order of magnitude. The solution without the VBC included does seem to satisfy \( \partial c / \partial \tilde{x} = 0 \), though only to first order. Using the least-squares method to explicitly include the VBC, \( \partial c / \partial \tilde{x} = 0 \) is satisfied to almost third order.

The aim of Fig. 4.2 was to examine the possible impact of different numerical approaches in solving the depth-averaged equation, given that the existing literature sometimes does not include detail of how the VBC is applied to the depth-averaged equation. All the results in this thesis were computed with the VBC applied, as outlined in Chapter 3.

4.4 Results

For all the results in the following section, unless otherwise stated, the parameter values used for the simulations are shown in Table 4.2. Importantly, the parameters \( \tilde{\Omega}_m \) and \( \lambda_x \) were taken from Bai et al. [28], though we should note that more accurate parameter estimates are available in the recent work of Cogswell and Bazant [30]. Preliminary investigations (not shown here) using parameters from Cogswell and Bazant [30] show qualitative results similar to those outlined below, though the use of the updated parameter may affect some results.

4.4.1 Comparing depth-averaged and two-dimensional CHR solutions

We begin by attempting to match the results from the two-dimensional CHR system with the depth-averaged results of Bai et al. [28] in order to confirm that our
Figure 4.3: Comparisons between the depth-averaged and two-dimensional CHR equations without coherency strain, given highly anisotropic $D$ and $\tilde{K}$. Selected concentration profiles (a) and (c) are shown for the depth-averaged equation, the equivalent plots for the full CHR system are shown in Fig. 4.4 and 4.5, respectively.
two-dimensional numerical solution is consistent with the previously reported depth-averaged results in the literature. It is a necessary condition on the two-dimensional CHR model that it reproduces one-dimensional depth-averaged results in the appropriate parameter limits. We use an experimentally measured value for the diffusivity in the $y$ direction, $D_{yy} = 1.6 \times 10^{-13}$ m$^2$ s$^{-1}$ [116] and, based on $ab$ initio calculations of diffusivities and energy barriers that suggest Li$^+$ transport in the $x$ direction is unlikely [90, 157, 158], we set the diffusivity in the $x$ direction to be 8 orders of magnitude smaller, or $D_{xx} = 1.6 \times 10^{-21}$ m$^2$ s$^{-1}$. For both the depth-averaged and CHR systems, we set the length of the phase boundary in the $x$ direction to be $\lambda_x = 5$ nm (and hence $\tilde{K}_{xx} = 25$ nm$^2$) [28, 84], and for the CHR system, we set the phase boundary length in the $y$ direction to be much larger than that in the $x$ direction, namely $\tilde{K}_{yy} = 300\tilde{K}_{xx}$.
or $\lambda_y \approx 86$ nm.

Fig. 4.3 shows the results from comparing the depth-averaged equation with the two-dimensional CHR equation, without strain and given the parameters outlined above. Fig. 4.3c in particular shows a plot of the potential against the mass fraction of Li$^+$ through time. We can see that the solution to the CHR equation matches the depth-averaged results very well across the range of nondimensional currents. The large drop in potential at a mass fraction of 0.2 with $\tilde{I}_c = 0.01$ is due to the formation of a separate phase in the crystal. The small humps at a mass fraction of approximately 0.55 and 0.95 are caused by the release of interfacial energy when the phase-boundaries reach the edges of the domain. At higher currents, the crystals do not phase-separate and from $\tilde{I}_c \sim 2$, the potentials decrease monotonically. Fig. 4.3c essentially replicates Figure 4a from Bai et al. [28], with the small hump that occurs at a total mass fraction of approximately 0.55 in Fig. 4.3c at a different position compared with Bai et al. [28] because of our initial condition (as outlined in Section 4.3). Figures 4.3a and 4.3b show the concentration profiles from the depth-averaged solution with $\tilde{I}_c = 0.01$ and $\tilde{I}_c = 2$ respectively, again replicating Figures 4b and d from Bai et al. [28]. The lower current case (Fig. 4.3a) shows that phase-separation has occurred in the crystal, whereas the higher current case (Fig. 4.3b) shows that phase-separation is completely suppressed.

The equivalent concentration profiles for the two-dimensional CHR system are shown in Figures 4.4 and 4.5. We can see that the behaviour of the two-dimensional solutions is identical to that produced by the depth-averaged equations (which is implied by Fig. 4.3c, as the concentration profiles in the crystal strongly affect the overpotential). In the low current case shown in Fig. 4.4, we see no concentration gradients in the $y$ direction, essentially mimicking the one-dimensional transport shown in Fig. 4.3a. Similarly, Fig. 4.5 shows that phase-separation is suppressed in the high current case, with no concentration gradients evident in either the $x$ or $y$ directions. These results provide confidence in our numerical solution of the two-dimensional CHR system as well as provide guidance on the magnitude of the components of $\mathbf{D}$ and $\tilde{\mathbf{K}}$ needed to satisfy the assumption of one-dimensional transport (and hence the use of the depth-averaged equation). We should note that the potentials for the CHR and depth-averaged systems with coherency strain also matched well (replicating Figure 5c from Cogswell and Bazant [30]), and as such are not shown here.

As mentioned in Section 4.2.2, the depth-averaging process enforces a no-flux boundary condition along all of the crystal facets, except those in the $xz$ plane. As such, we impose a no flux condition on the $y$ faces at $x = 0$ and $x = F_x$ when solving the
Figure 4.4: CHR IBVP solution computed in two dimensions with $\tilde{I}_c = 0.01$ and without coherency strain.
Figure 4.5: CHR IBVP solution computed in two dimensions with $I_c = 2$ and without coherency strain.
two-dimensional CHR system in order to compare the solution with the depth-averaged equation. Fig. 4.6 shows the results from imposing the original flux boundary condition on all boundaries in the two-dimensional CHR system, with $I_c = 0.01$. In doing this we did not modify the value of $\rho_s$ for the different site density on the $yz$ face; indeed there is a question of whether lithium even intercalates on this surface. We see that the only difference between Figures 4.4 and 4.6 is that, initially, the phase-separation occurs at the boundaries of the domain. Qualitatively, this is very similar to the results shown by Bai et al. [28], where they note that [22] suggests that the lithiated phase perfectly wets the inactive facets. Bai et al. [28] subsequently apply wetting boundary conditions [164] on the depth-averaged equation that allows heterogeneous nucleation at $x = 0$ and $x = F_x$. In the two-dimensional simulations, some Li$^+$ ions intercalate into the crystal via the boundaries at $x = 0$ and $x = F_x$. Given the small $D_{xx}$ value, these ions are not significantly transported in the $x$ direction, however their inclusion at the $x = 0$ and $x = F_x$ faces is enough to overwhelm the noise term $X$ in (4.2.27) and cause phase-separation to always be initiated adjacent to these faces. Furthermore, given the orthotropy in the $D$ and $\tilde{K}$ values listed in Table 4.2 we observe similar trends at low and high currents for the case where (4.2.29) is applied to all boundaries of the domain compared to Figs. 4.4 and 4.5 where (4.2.29) is applied to the boundaries at $y = 0$ and $y = F_y$, namely, that high current suppresses phase separation.

Now that we have established the parameter values necessary to satisfy the assumptions given by (4.2.19) and (4.2.20) we turn our attention to investigating parameter regimes that cannot be simulated by the depth-averaged equation. In the simulations that follow we adopt more isotropic parameters and these affect the phase-separation behaviour in both the $x$ and $y$ directions. Given this, and the fact that the aforementioned perturbation of the initial Li$^+$ concentration profile was only implemented to allow the direct comparisons in Fig. 4.3c, we remove this perturbation and begin our simulations with a uniform Li$^+$ concentration profile.

4.4.2 Investigating values for $\tilde{K}_{yy}$

When a component of the gradient penalty tensor $\tilde{K}$ is large, this reflects a physical condition where concentration gradients in the respective direction cause an increase in the free energy of the system. Such gradients are consequently penalised in the minimisation of the free energy that occurs in the models introduced in Section 4.2. The value of the diagonal elements of $\tilde{K}$ can be inferred from the experimentally observed length of the phase-boundary in each direction. The lack of evidence of a phase-boundary forming in the $y$ direction leads to the assumption that $\lambda_y$ and hence $\tilde{K}_{yy}$
Figure 4.6: CHR IBVP solution computed in two dimensions with $\hat{I}_c = 0.01$, without coherency strain and (4.2.11) applied to all of the boundaries.
must be much larger than the values in any other direction. In the previous section, we set $K_{yy}$ to be 300 times greater than $K_{xx}$ that gives a phase-boundary length in the $y$ direction of $\lambda_y \approx 86$ nm. We note however, that this value does not actually satisfy the bound given in (4.2.20), which requires $\lambda_y \gg F_y$. Numerically, it is difficult to solve the two-dimensional CHR system with a value of $\lambda_y$ that satisfies (4.2.20). This is unsurprising, as $K$ multiplies the highest-order derivatives in the system, and these are the derivatives that are estimated numerically with the lowest order [151]. It is clear from Fig. 4.3c that in practice, requiring $K_{yy} \gg K_{xx}$ is sufficient to ensure equivalence between the two-dimensional CHR and the depth-averaged systems.

Given this behaviour, we investigate the dynamics of the CHR system as $K_{yy}$ is decreased. Fig. 4.7 shows the results from setting $K_{yy} = 50K_{xx}$ with a nondimensional current of $\tilde{I}_c = 0.01$. We see that at early times (before $4.37 \times 10^3$ s), a phase-boundary forms that has a distinct gradient in the $y$ direction. As time progresses, the phase-boundary smooths out parallel to the $y$ axis, before moving throughout the domain in a similar manner to that shown in Fig. 4.4. This shows that for low values of $K_{yy}$ with small currents, as long as the phase-boundary forms parallel to the $y$ axis, it tends to remain that way as the wave propagates.

Higher current cases on the other hand, show complex dynamics that are qualitatively different to the low current cases, especially when compared with the results shown in Section 4.4.1. Fig. 4.8 shows the results from discharging a crystal at $\tilde{I}_c = 8$, again with $K_{yy} = 50K_{xx}$. We can see that at $t = 5.60$ s, several phase boundaries are beginning to form, however in Fig. 4.8d, we can see that the individual peaks in Fig. 4.8c have formed a single phase-boundary in the $y$ direction, parallel to the $x$ axis. This phase-boundary then continues to move parallel to the $x$ axis until discharge finishes. This is in contrast to the results shown in Section 4.4.1, where higher currents suppress phase-separation.

Fig. 4.9a shows the corresponding potentials from Figs. 4.7 and 4.8. We can see that for $\tilde{I}_c = 0.01$, the potential looks much like that in Fig. 4.3c, as a phase-boundary still forms parallel to the $y$ axis before propagating. We should note that the spinodal gap decreases slightly as the current increases, as evidenced by the mass fraction at which the material phase separates. This corresponds to the small vertical jump in the potential at a mass fraction of 0.3 with $\tilde{I}_c = 0.25$, compared with the jump at 0.2 for $\tilde{I}_c = 0.01$. The point at which the phase-boundary forms parallel to $x$ instead of $y$ is also visible in Fig. 4.9a. Around a nondimensional current of $\tilde{I}_c = 2$, we can see that the potential decreases once the phase-boundary has formed (at a mass fraction of 0.3), instead of increasing as at lower currents.
Fig. 4.9b shows the same results as Fig. 4.9a, but with coherency strain included. The crystals now fill homogeneously for all currents, except $I_c = 0.01$, like Fig. 4.3c. As Cogswell and Bazant [30] note, the addition of coherency strain suppresses phase-separation, and decreases the critical current at which the material fills homogeneously. We should also note that the phase-boundary that forms in the low current case, $I_c = 0.01$, forms parallel to the $y$ axis. The concentration profiles given the addition of coherency strain are almost identical to those shown in Fig. 4.4 for $I_c = 0.01$, and Fig. 4.5 for higher currents, and as such are not shown.

From these results it is clear that without isotropic coherency strain, the phase-separation behaviour is sensitive to the choice of $K_{yy}$, especially for higher currents. We observe that materials for which $K_{yy} \sim O(10) K_{xx}$ display a tendency to phase-separate, forming a phase boundary parallel to the $x$ axis at high currents. Such behaviour cannot be observed from a one-dimensional model. However, with the addition of isotropic coherency strain, it appears that there is no qualitative difference in phase-separation with a less orthotropic $K$. We now turn to investigating the effect of reducing the orthotropy in $D$.

### 4.4.3 Investigating values for $D_{xx}$: two-dimensional transport and defects

In Section 4.4.1 we used a highly orthotropic $D$ in the two-dimensional CHR equation in order to match the results from the one-dimensional depth-averaged equation; the diagonal elements of $D$ differed by 8 orders of magnitude. We used an experimentally derived value of $D_{yy}$ and based the value of $D_{xx}$ on ab initio calculations [157, 158] that suggest Li$^+$ transport is one-dimensional in $y$. A closer examination of diffusion coefficients (and energy barriers) from the literature is given in Table 4.3. Collated in Table 4.3 are values determined both experimentally and from ab initio methods, though only for analyses that investigate the individual components of $D$. We have deliberately excluded any measurements of “total” (isotropic) diffusion coefficients, such as those obtained from PITT or GITT measurements.

The ab initio calculations shown in Table 4.3 [90, 157, 158] calculate energy barriers for Li$^+$ transport. The energy barriers in $y$ are much smaller than those in any other direction, which again suggests a large degree of anisotropy in $D$. Table 4.3 however, shows that the diffusion coefficients and energy barriers in $x$ and $z$ that have been determined experimentally exhibit far less anisotropy than those calculated theoretically, often differing by only 1 to 2 orders of magnitude. A number of authors [58, 116, 152, 165, 166]
Figure 4.7: CHR IBVP solution computed in two dimensions with $K_{yy} = 50K_{xx}$, $\bar{I}_c = 0.01$ and without coherency strain.
Figure 4.8: CHR IBVP solution computed in two dimensions with $K_{yy} = 50K_{xx}$, $\bar{I}_c = 8$ and without coherency strain.
Figure 4.9: Potentials from the two-dimensional CHR system with $\tilde{K}_{yy} = 50 \tilde{K}_{xx}$. The small increases/decreases in the potential that are separate from the distinct jumps when phase-boundaries form (e.g., at a mass fraction of 0.2 to 0.3 in Fig. 4.9a), result from phase-boundaries interacting in some other way, e.g., colliding with other phase-separated regions or the edges of the domain. Selected concentration profiles for Fig. 4.9a are shown in Figures 4.7 and 4.8.
have suggested this is due to antisite defects blocking lithium channels, and hence causing the one-dimensional transport of Li$^+$ to become essentially two-dimensional in the $yz$ plane, as Li$^+$ crosses into neighbouring channels. Malik et al. [152] notes that this crossing process involves a net displacement in $<101>$, which is the primary mechanism for diffusion in [100] and [001] directions. Indeed, the crystals synthesised by Amin et al. [116] and used to measure Li$^+$ diffusivities were observed to contain around 2.5-3% antisite defects (specifically Fe$^{2+}$ on Li$^+$).

Table 4.3 also lists diffusion coefficients calculated with an *ab initio* method that include antisite defects [8] and we see that the diffusion process is far more isotropic, with transport in $x$ still being slower than in $y$ or $z$, but now only by a factor of approximately two. Malik et al. [152] also used *ab initio* calculations to simulate the diffusion coefficients of Li-vacancies (which can be related to the Li$^+$ diffusivity) given certain concentrations of antisite defects. The presence of a small concentration of antisite defects at $T = 440$ K decreases the diffusivity in $y$ by around 2 orders of magnitude, while increasing the diffusivity in $x$ and $z$ by roughly the same amount. The work by Malik et al. [152] also suggests that Li-vacancy diffusion in $z$ is roughly an order of magnitude smaller than in $x$. Given that we solve the two-dimensional CHR equation in the $xy$ plane, we cannot examine the effect of increasing transport in $z$, or the fully anisotropic [101] direction. However, as a first-attempt at quantifying the effects of what is possibly a three-dimensional transport regime, we continue to assume that $D_{zz}$ remains small and apply our two-dimensional CHR model where we increase the transport of Li$^+$ in $x$ by increasing $D_{xx}$. For consistency, we set $D_{xx}$ to be two orders of magnitude smaller than $D_{yy}$, based on the value measured by [116], which suggests that Li$^+$ transport in the $x$ direction is at least an order of magnitude smaller than in $y$.

Table 4.3 shows that the reported values of $D$ vary between approximately two to three orders of magnitude. Similar results to those shown below can be obtained with diffusion coefficients taken from references other than [116], as given in Table 4.3. We note however, that if $D_{yy}$ is modified, given that we do not have a value of $\tau_0$ that reflects the reaction (4.2.4) ($\tau_0$ is set to unity for this analysis), we may inadvertently move from a surface-reaction-limited (SRL) [71] regime (i.e., one that satisfies the first assumption in (4.2.20) given that $\rho F_y/\rho_s R_y \sim N_H \tau_0$), to one that is limited by bulk transport (BTL) in the $y$ direction. Tang et al. [85] examined the effect of a BTL regime on the inclination angle of phase-boundaries in LiFePO$_4$, but no connection was made to the suppression of phase-boundaries in the material. There is still some question of whether LiFePO$_4$ crystals operate in an SRL or BTL regime and we could
have examined the appearance/suppression of phase-boundaries in a BTL regime. In this paper we focus on the effect of isotropic diffusion in a parameter regime limited by the timescale of the surface reaction (i.e., SRL). Our own numerical experiments (not shown here) with $D$ values taken from Table 4.3 and $\tau_0 = 1$ (i.e., within an SRL regime) indicate that there is a range of (realistic) values $\tau_0$ can take while still remaining SRL and displaying behaviour qualitatively similar to that shown below.

Fig. 4.10 shows the potential that results from discharging the two-dimensional CHR equation given $D_{xx} \sim O(10^{-2})D_{yy}$. Fig. 4.10a shows the results without coherency strain, and we can see that for an applied current of $\tilde{I}_c = 0.01$, the potential looks like that seen in Fig. 4.3c, although the potential as the phase-boundary is propagating is closer to the open circuit plateau of 3.42 V. The material does phase separate, as evidenced by the increase in potential when the mass fraction is approximately 0.2. Again, we have not plotted the corresponding concentration profile for this case as they are very similar to those shown in Fig. 4.4. Although we are approaching diffusivities that allow two-dimensional transport, phase-boundaries still form parallel to the $y$ axis and thus the resulting concentration profiles appear to be very similar to those with one-dimensional transport like Fig. 4.4.

Similar to the results outlined in Section 4.4.2, at higher currents the material displays qualitatively different behaviour when compared with Fig. 4.3c. In particular, as the current is increased, it appears that the material is still phase-separating, though the increase in potential becomes less visible, especially for $\tilde{I}_c = 8$. Curiously, the potential for $\tilde{I}_c = 8$ looks almost indistinguishable from the sloping potentials shown in Fig. 4.3c that characterise homogeneous filling at higher currents. Fig. 4.11 shows the concentration profiles corresponding to the $\tilde{I}_c = 8$ curve shown in Fig. 4.10a. We can see that although the $\tilde{I}_c = 8$ profile in Fig. 4.10a looks like that for a crystal that is filling homogeneously, the material is still phase-separating. The profiles shown in Fig. 4.11 would normally imply that we are in a one-dimensional regime where phase boundaries always form parallel to the $y$ axis and the Li$^+$ concentration profiles and associated voltage curves could be modelled using a depth-averaged equation. Remarkably, this is clearly not the case here, as not only do we not satisfy assumption (4.2.19) that facilitates depth-averaging, we also recall that at high currents the depth-averaged model suppresses phase change (see Fig. 4.3).

The reduction in the gap between the open circuit voltage (3.42 V) and the potential as the phase-boundary is propagating, shown in Fig. 4.10a with $\tilde{I}_c = 0.01$, looks very similar to that of a very low current discharge in a one-dimensional regime. This is
<table>
<thead>
<tr>
<th>Ref.</th>
<th>$D_{xx}$</th>
<th>$D_{yy}$</th>
<th>$D_{zz}$</th>
<th>Experiment</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>[157]</td>
<td>-</td>
<td>$10^{-12}$</td>
<td>$10^{-50}$</td>
<td>N</td>
<td>Li$^+$ diffusion coefficient in LiFePO$<em>4$. Diffusion in the [101] direction $D</em>{xx} \approx 10^{-14}$.</td>
</tr>
<tr>
<td>[116]</td>
<td>$&lt; 10^{-23}$</td>
<td>$1.6 \times 10^{-13}$</td>
<td>$2.4 \times 10^{-13}$</td>
<td>Y</td>
<td>T $\approx 420$ K. Chemical diffusion coefficient (Li$^+$ + e$^-)$</td>
</tr>
<tr>
<td>[86]</td>
<td>$2.5 \times 10^{-13}$</td>
<td>$1 \times 10^{-12}$</td>
<td>$1 \times 10^{-12}$</td>
<td>Y</td>
<td>Fig. 3b at $2.075 \times 10^{3}$ T$^{-1}$/K. Chemical diffusion coefficient.</td>
</tr>
<tr>
<td>[8]</td>
<td>-</td>
<td>$1.3 \times 10^{-11}$</td>
<td>$1 \times 10^{-12}$</td>
<td>N</td>
<td>Li$^+$ diffusion coefficient at $T = 700$ K.</td>
</tr>
<tr>
<td>[8]</td>
<td>$4 \times 10^{-11}$</td>
<td>$8.2 \times 10^{-11}$</td>
<td>$6.6 \times 10^{-11}$</td>
<td>N</td>
<td>Li$^+$ diffusion coefficient at $T = 600$ K with antisite defects.</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Energy barriers</th>
<th>[100]</th>
<th>[010]</th>
<th>[001]</th>
</tr>
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<tbody>
<tr>
<td>[157]</td>
<td>-</td>
<td>0.27</td>
<td>2.5</td>
</tr>
<tr>
<td>[86]</td>
<td>0.96</td>
<td>0.7</td>
<td>0.75</td>
</tr>
<tr>
<td>[167]</td>
<td>0.636</td>
<td>0.54</td>
<td>0.669</td>
</tr>
<tr>
<td>[90, 158]</td>
<td>-</td>
<td>0.55</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Table 4.3: Anisotropic diffusion coefficients ($m^2 \ s^{-1}$) and energy barriers (eV) from the literature. The “Experiment” column marks “Y” if the values were measured experimentally and “N” if ab initio calculations were used.
evident in Fig. 4.12c, where the potential for the depth-averaged equation at the very low current of \( \tilde{I}_c = 0.001 \) is plotted, and we can see that the potential is close to 3.42 V for most of the discharge. This suggests that the behaviour in a two-dimensional regime may be like that seen in a one-dimensional regime with a lower applied current. Given that all of the simulations shown in Fig. 4.10a phase separate, even with currents as high as \( \tilde{I}_c = 8 \), this hypothesis would require that currents between \( 0.01 \leq \tilde{I}_c \leq 8 \) with two-dimensional transport be similar to currents between \( 0.001 \leq \tilde{I}_c \ll 0.25 \) with one-dimensional transport (i.e., below that required to see homogeneous filling in a one-dimensional regime).

In addition to showing a very low current discharge (\( \tilde{I}_c = 0.001 \)), Fig. 4.12 also shows the results from solving the depth-averaged with \( \tilde{I}_c = 0.0325 \) and \( \tilde{I}_c = 0.065 \), where phase-separation still occurs. Burch et al. [81] note that as the current is increased, the spinodal gap shrinks (also see Bai et al. [28]), until it disappears completely, which leads to homogeneous filling. We can see this is the case in Fig. 4.12c, as the shrinking of the spinodal gap with increasing current is clearly visible. We recall this is evident from the mass fraction at which phase-separation occurs. The phase-boundary appears at a mass fraction of approximately 0.375 with \( \tilde{I}_c = 0.0325 \), whereas with \( \tilde{I}_c = 0.065 \), phase separation does not occur until a mass fraction of around 0.6. The corresponding concentration profiles are shown in Figures 4.12a and 4.12b, where the shrinking of the spinodal is clearly visible, as the phase-boundaries only appear at longer times when an increasing mass of Li\(^+\) has intercalated into the crystal.

We see that in the two-dimensional regime shown in Fig. 4.10a, the spinodal gap only shrinks slightly with increasing current. At a current of \( \tilde{I}_c = 0.01 \), the crystal phase separates at a mass fraction of approximately 0.2, whereas at the very high current of \( \tilde{I}_c = 8 \) phase-separation occurs at a mass fraction of around 0.25. Given that in a one-dimensional regime, the spinodal gap decreases to the point where phase-separation first occurs at 0.6 with \( \tilde{I}_c = 0.0625 \), and we only see a small decrease in the spinodal gap with two-dimensional transport for such a large range of currents, it appears unlikely that the two-dimensional simulations are equivalent to the depth-averaged simulations at lower currents. If the two regimes were equivalent, the small decrease in the spinodal suggests that an extremely large current would be required to suppress phase-separation with two-dimensional transport. We however, could not find a current high enough to suppress phase-separation in the two-dimensional regime, and unfortunately, analytic analysis of the spinodal gap with a non-zero current is very difficult, even for the depth-averaged equation [81]. We also note that for the voltage curves shown in Fig. 4.12c, the potentials do not decrease monotonically like those in Fig. 4.10a, though both
Figure 4.10: Potentials from the two-dimensional CHR system with $D_{xx} = 1.3 \times 10^{-15}$ m$^2$ s$^{-1}$. The small increases/decreases in the potential that are separate from the distinct jumps when phase-boundaries form (e.g., at a mass fraction of 0.2 with $\tilde{I}_c = 0.01$ in Fig. 4.10a), result from phase-boundaries interacting in some other way, e.g., colliding with other phase-separated regions or the edges of the domain. Selected concentration profiles for Fig. 4.10a are shown in Fig. 4.11, those for Fig. 4.10b are given in Fig. 4.13.
Figure 4.11: CHR IBVP solution computed in two dimensions with $D_{xx} = 1.3 \times 10^{-15}$, $I_c = 8$ and without coherency strain.
(a) Depth-averaged concentration through time with $\tilde{I}_c = 0.0325$. $t$ (s): $+ 0.965 \times 10^3$, $\times 1.751 \times 10^3$, $\Box 1.92 \times 10^3$, $\bigcirc 3.19 \times 10^3$, $\Diamond 4.1 \times 10^3$, $\bigcirc 4.94 \times 10^3$.

(b) Depth-averaged concentration through time with $\tilde{I}_c = 0.0625$. $t$ (s): $+ 0.505 \times 10^3$, $\times 1.15 \times 10^3$, $\Box 1.44 \times 10^3$, $\bigcirc 1.56 \times 10^3$, $\Diamond 2.14 \times 10^3$, $\bigcirc 2.53 \times 10^3$.

(c) Potential from depth-averaged system for different fixed currents without strain

Figure 4.12: Potential and concentration profiles from the depth-averaged system without coherency strain and with $\tilde{I}_c$ below that necessary to see homogeneous filling.
represent solutions that phase-separate. As such, it appears that for cases without strain, the two-dimensional regime characterised by an isotropic $D$ is fundamentally different to a one-dimensional regime described by the depth-averaged equation, as might be expected.

Given that two-dimensional transport seems to promote phase-separation and the addition of coherency strain suppresses phase-separation, including coherency strain with the modified value of $D_{xx}$ may alter the phase-separating behaviour in a two-dimensional regime. Fig. 4.10b shows the results from including coherency strain with $D_{xx} \sim O(10^{-2})D_{yy}$. We can see that apart from the upward sloping voltage profile at $\tilde{I}_c = 0.01$ that is characteristic of including coherency strain, the voltage curves at higher currents look almost identical to those in Fig. 4.10a. Again, in a one-dimensional regime, the voltage curve with $\tilde{I}_c = 8$ would imply homogeneous filling. Phase-boundaries however, still form at all of the currents tested in Fig. 4.10b. An example of this is shown in Fig. 4.13, which depicts the concentration profile corresponding to the $\tilde{I}_c = 8$ case in Fig. 4.10b. Again, phase-separation is clearly visible.

It appears from Fig. 4.10b that the spinodal gap is decreasing at a higher rate than that in Fig. 4.10a, though the small increase in voltage as the phase-boundary forms with $\tilde{I}_c = 8$ is barely visible. This increase in voltage occurs around a mass fraction of 0.35, and given the results shown in Fig. 4.12 and the discussion above, this indicates that at the high current of $\tilde{I}_c = 8$, simulations with two-dimensional transport and coherency strain are still well within the region where we see phase-separation occur. Again, we could not find a large enough current to suppress phase-separation with both two-dimensional transport and coherency strain. The CHR IBVP, where $\text{Li}^+$ transport is two-dimensional, even with coherency strain, is therefore not equivalent to the depth-averaged system discharged at lower currents.

### 4.5 Discussion and conclusions

In this work, we examined the differences in phase-change behaviour between the full two-dimensional CHR equation and the simplified depth-averaged equation presented by Bai et al. [28]. For small, defect-free nanoparticles where $\text{Li}^+$ is transported in a purely one-dimensional fashion along ion channels in the $y$ direction, the depth-averaged equation is an excellent approximation to the full CHR system in a parameter space that is surface-reaction limited (SRL). This is unsurprising given the assumptions required to derive the depth-averaged equation. Our numerical results revealed that for the
Figure 4.13: CHR IBVP solution computed in two dimensions with \( \mathbf{D}_{xx} = 1.3 \times 10^{-15} \), \( \bar{I}_c = 8 \) and with strain included.
two-dimensional CHR equation to produce solutions that match the depth-averaged, the diffusion coefficient in $y$ must be approximately 8 orders of magnitude larger than the diffusion coefficient in $x$. The gradient penalty in $y$ must also be at least 300 times bigger than that in $x$, and no-flux conditions should be applied on facets of the crystal apart from those in the $xz$ plane. These results help to quantify the transport parameters required to justify a depth-averaged approximation to Li$^+$ transport in LiFePO$_4$.

We then examined the behaviour of the two-dimensional CHR system as the orthotropy of $\tilde{K}$ and $D$ was reduced. We found that reducing the orthotropy of the gradient penalty tensor $\tilde{K}$ did not significantly affect the solution at low currents when compared with the fully orthotropic $\tilde{K}$, but at high currents, phase-boundaries formed parallel to the $x$ axis when $\tilde{K}_{yy}$ was reduced to only 50 times $\tilde{K}_{xx}$. This behaviour was completely suppressed by the addition of isotropic coherency strain, as the crystal began filling homogeneously at high currents, in a manner similar to that predicted by the depth-averaged equation. While the appearance of phase-boundaries parallel to the $x$ axis, as opposed to $y$, in solutions without coherency strain is interesting, in an experiment where coherency strain is working to suppress phase-separation, our results show that it is unlikely that this behaviour could be observed. As mentioned previously, our work did not include anisotropic elastic strain, which Cogswell and Bazant [30] showed also penalised phase-boundary formation normal to the [010] direction. As such, the appearance of phase separation parallel to the $x$ direction in LiFePO$_4$ crystals seems very unlikely.

More interesting behaviour resulted from decreasing the orthotropy of Li$^+$ diffusivity in the crystal. Reducing $D_{xx}$ to be only 2 orders of magnitude smaller than $D_{yy}$ resulted in the formation of phase-boundaries parallel to the $y$ axis even at very high currents. Of particular interest however, was that the discharge curves associated with this two-dimensional transport decreased monotonically, in a manner that is normally characteristic of homogeneous filling. Furthermore, the addition of isotropic coherency strain did not suppress this behaviour, with distinct phase-separation still visible at high currents. In a practical sense, this makes determining the nature of phase-separation in LiFePO$_4$ very difficult, as simply examining the voltage curves of individual LiFePO$_4$ crystal (if possible) is not enough to determine if a crystal is filling homogeneously.

In recent years it has become clear that the presence of antisite defects in the crystal can disrupt the strictly one-dimensional transport of Li$^+$, possibly decreasing the effective diffusivity in the $y$ direction and forcing a more isotropic transport regime. We should
note that given a fixed probability of defect formation, a reduction in crystal size will significantly reduce the number of defects per ion channel, and hence the number of blocked Li$^+$ sites [152]. Defect formation is a complicated phenomenon, driven by many parameters during material synthesis. At a crystal size of 100 nm$^3$ (as used in this work), the work of Malik et al. [152] suggests that the large majority of lithium sites in a channel should be accessible; Malik et al. [152] for example note that for crystals smaller than 60nm, the presence of defects results in no blocked Li$^+$ sites.

Although Li$^+$ transport in small crystals may be orthotropic given low concentrations of antisite defects, we chose to investigate the implications of isotropic transport in small crystals. This is because homogeneous filling becomes more favourable as crystal size decreases, given a reduction in the crystal size reduces the miscibility gap [77]. Small crystals tend to suppress phase-separation, with high-current discharges and the addition of averaged coherency strain only exacerbating this tendency. Given that we still find phase-separation occurring at all of the discharge rates tested, this shows that isotropic Li$^+$ transport heavily encourages phase-separation, even in a parameter regime deliberately designed to promote homogeneous filling.

With one-dimensional Li$^+$ transport, phase-separation only occurs at very low discharge rates. Given that crystals fill homogeneously at higher currents, it seems natural that in a one-dimensional regime, suppression of phase-separation could be held partially responsible for the observed increase in the high-rate performance of LiFePO$_4$. Our results however, indicate that when considering a single discharge cycle, the suppression of phase-separation is in itself not enough to explain this phenomenon. In a two-dimensional regime, the voltage curves shown in Fig. 4.10 are all associated with solutions that phase-separate, and upon reaching the voltage cutoff of 3.2 V, the crystals are almost completely discharged, like those seen in a one-dimensional regime in Fig. 4.3c. Given that crystals that undergo phase separation in a two-dimensional regime perform almost identically to crystals that fill homogeneously in a one-dimensional regime, there appears to be no fundamental disadvantage to phase-separation during a single discharge.

This of course neglects any consideration of deformation effects that may occur during phase-separation, which could lead to capacity fade in heavily cycled material [28]. If significant deformations form during phase-separation, then the appearance of phase-separation at high currents in the presence of defects, as shown above, could limit the cycling performance of LiFePO$_4$ material. Decreases in the performance of LiFePO$_4$ material with defects has previously been associated with a decrease in Li$^+$ transport in
the $y$ direction, caused by blocked lithium channels [152, 157, 168]. Our results however, show that defects fundamentally affect the phase-separating behaviour of LiFePO$_4$, and this may also contribute to decreased cycling performance.

The phase-change behaviour of LiFePO$_4$ as modelled by a phase-field model is very complicated, and is affected by particle size, strain, rate of discharge, and as this work shows, the dimensionality of Li$^+$ transport in the material. Two-dimensional Li$^+$ transport produces results that differ significantly from those produced by one-dimensional Li$^+$ transport, even in a parameter regime that is limited by the timescale of the surface reaction. We would expect the nature of phase-separation in LiFePO$_4$ to change given diffusion limitations in $y$, but it is surprising that altering $D_{xx}$ affects the suppression of phase-boundaries to such a large degree when the crystal is surface-reaction limited. Also, simply inspecting the concentration profiles produced in this work would suggest a one-dimensional transport process (e.g., Fig. 4.13 certainly looks one-dimensional, even though $D$ is isotropic). The sloping voltage curves produced by phase-separating materials at high currents are also unusual, and contradict the common belief that monotonically decreasing voltages imply homogeneous filling.

Given that we only simulated Li$^+$ concentration in the $xy$ plane and included isotropic coherency strain, we believe there would be significant merit in examining the fully anisotropic, three-dimensional transport of Li$^+$ in the material during fixed-current discharge, as modelled by the CHR system. This transport should be governed by an understanding of the anisotropy of diffusion in the presence of defects, along with the inclusion of fully anisotropic strain (such as that included by Cogswell and Bazant [30] in the depth-averaged equation governing the $xz$ plane or Tang et al. [85] in the full CHR system in 3D), deformation effects and electrochemical boundary conditions that apply a fixed current to a crystal. Our work shows that examining solutions of the full CHR system under fixed current can reveal novel phase-change dynamics. In particular, it appears that LiFePO$_4$ material with antisite defects may behave very differently at high currents when compared with defect-free material, and this may help further the theoretical understanding of phase-change behaviour in modern, high-rate LiFePO$_4$ cathodes.
5. Model comparisons for high-rate LiFePO$_4$ cathodes

For this chapter, the associated reference is:

S. Dargaville, T. W. Farrell, A comparison of mathematical models for phase-change in high-rate LiFePO$_4$ cathodes. Under Review.

Additional numerical detail has also been included below.

5.1 Introduction

Since Padhi et al. [7] first investigated the use of LiFePO$_4$ as a battery material, there has been a marked increase in the capacity of LiFePO$_4$ cathodes discharged at high currents. Padhi et al. [7] achieved a capacity of 120 mAh/g with a discharge rate (DR) of just 1.85 mA/g. Recently, papers in the literature have been routinely reporting similar discharge capacities at rates of 3400 mA/g or higher [17, 105, 169, 170]. This improvement is mainly based around decreasing the cathode thickness (to improve transport of Li$^+$ in the electrolyte) along with enhancing the electronic conductivity of the cathode in some fashion (typically through enhanced carbon coating of crystals).

Mathematical models of LiFePO$_4$ cathodes [21, 65–68, 82, 171] have found considerable success in validating against experimental discharge curves, though most of the cathodes used to validate these models were only discharged at rates less than 5C (Kasavajjula et al. [64] is an exception, discharging at up to 20C). These works also use simple models to represent the concentration distribution of Li$^+$ in individual crystals of LiFePO$_4$, namely, shrinking-core based models [21, 64, 82], homogeneous diffusion equations [65–68] and simply assuming a constant Li$^+$ concentration [171]. Recent experimental and theoretical work has shown that the behaviour of LiFePO$_4$ material during charge/discharge is very complex and this complexity is not captured in
such models. In particular, the diffusivity of Li\(^+\) in LiFePO\(_4\) material can be highly anisotropic [157, 158, 167], with anisotropic elastic strain also playing an important role [30]. The phase-transition that occurs between highly and lowly lithiated forms of LiFePO\(_4\) in individual crystals has also shown to be suppressed under certain discharge conditions [27, 28, 30, 78].

Previously [82], we presented a multi-scale cathodic model of LiFePO\(_4\) material that used a shrinking-core to represent the phase-transition that occurs on the crystal scale. This paper is a continuation of that work, where we now replace the shrinking-core based model on the crystal scale with a phase-field model [28, 30, 76, 81, 85]. Phase-field models minimise the free energy of the system through time, which allows the formation (or suppression) of phase-boundaries if energetically favourable. These models require the solution of the fourth-order Cahn-Hilliard-reaction (CHR) initial-boundary-value problem (IBVP) (based off the seminal work of Cahn and Hilliard [69]), which can be difficult to solve. As such, most of the existing phase-field work applied to LiFePO\(_4\) simplifies this equation [28, 30, 76, 81, 84, 139, 165] in various limits, including the limit of highly orthotropic diffusivity in order to recover a second-order, depth-averaged equation (also known as the “Allen-Cahn-reaction” (ACR) model [54]). Recently [172], we showed that solving the full 2D CHR system with isotropic diffusivity (caused by the presence of antisite defects) can result in the existence of phase-separating regions that are normally suppressed in (defect-free) crystals governed by the depth-averaged equation.

As mentioned, the ability of modern LiFePO\(_4\) cathodes to achieve high discharge capacities at high rates is dependant on the elimination of the electronic and electrolytic limitations that constrain low-rate material [82], making the crystal-scale model used (and its behaviour at high currents) a key factor in matching experimental discharge curves. The recent work of Ferguson and Bazant [53] examined the use of a phase-field model (namely the 1D depth-averaged equation) on the crystal scale of a porous cathode model, though they did not attempt to validate against experimental discharge curves. In this paper we consider the impact of several crystal-scale models on the ability of a two-scale cathode model to validate against discharge curves from modern, high-rate (> 5 C) LiFePO\(_4\) material. We examine the use of both the 1D, depth-averaged and the 2D CHR system in a two-scale cathodic model of LiFePO\(_4\) material and compare the results against the three-scale, shrinking-core based model presented previously [82]. Many-particle effects [79] also affect the discharge when using phase-field models on the crystal scale of a cathodic model and are examined. The primary aim of this paper is to provide a snapshot on the current ability of theoretical modelling to accurately
predict LiFePO$_4$ cathode discharge and to ascertain if adopting crystal scale models of increasing physical complexity affords greater predictive ability.

### 5.2 Model development

In this section we develop a two-scale model based on our previous work [48, 82] (please see these papers for more detail on the derivation of these equations). In Dargaville and Farrell [82], we used a three-scale model to represent the distribution of active material and carbon within a porous LiFePO$_4$ cathode. Outputs from this model were validating using data from Srinivasan and Newman [21]. It is possible to construct LiFePO$_4$ cathodes that do not contain agglomerates, using synthesis techniques designed to coat individual LiFePO$_4$ crystals in carbon [105, 173]. In this work, we assume that all LiFePO$_4$ crystals are well-coated in carbon, sufficient to provide a conductive electronic network throughout the cathode. This eliminates the “particle” scale from the model in Dargaville and Farrell [82].

Fig. 5.1 shows a schematic of the size-scales used in this work. The smallest size scale, denoted as the “crystal scale” (Fig. 3a), represents a small rectangular crystal of LiFePO$_4$ material, with dimensions $F_x$, $F_y$ and $F_z$ (m). We choose to simulate the crystal scale on a rectangular domain, given that synthesis techniques for creating nano-sized LiFePO$_4$ material have now advanced to the point of creating very regular,
rectangular “platelets” or “nanorods” [174–176] with various orientations. The “cathode scale” is then made up of many crystals, each coated in highly-conductive carbon. The cathode scale is porous, and consists of several phases, namely binder (inert), carbon and a well-stirred, binary electrolyte composed of LiPF$_6$ that fully saturates the porous region. We assume that the inner boundary of the cathode ($X = X_i$) is in contact with a reservoir of excess electrolyte solution and the outer boundary ($X = X_o$) contacts the current collector. We should note that the cathodic spatial variable, $X$, in Fig. 1b has been changed from $x$ in Dargaville and Farrell [82] to avoid confusion with the crystal scale spatial variables $x$ shown in Fig. 1a, which corresponds to the $a$ crystallographic direction (with the $y$ spatial variable equivalent to the $b$ crystallographic direction).

Overall, the reaction that occurs during charge/discharge in a LiFePO$_4$ battery [7] is

$$
\text{FePO}_4 + \text{Li}^+ + e^- \xrightleftharpoons{\text{discharge}}^{\text{charge}} \text{LiFePO}_4.
$$

(5.2.1)

This reaction occurs on the surface of the crystals pictured in Fig. 1a, with the crystal shown as having undergone phase separation into highly ($\xi \ll 1$) and lowly lithiated ($\gamma \ll 1$) states. Previously [82], we used a shrinking-core model (a one-phase Stefan problem [55] based on that presented by Srinivasan and Newman [21]) to describe this phase-separation. Recently, the Bazant group, in particular, has been using phase-field models [28, 30, 71, 76] to represent the concentration of Li$^+$ in LiFePO$_4$ material. These models have the advantage that phase-boundaries only form when it is energetically feasible, as opposed to a shrinking-core, where a phase-boundary is always present. Prior to the possible phase-separation, it is generally accepted that there is a small concentration region (in Li$_v$FePO$_4$, between $0 < v < \gamma$ and $1 - \xi < v < 1$) where LiFePO$_4$ crystals fill homogeneously [21, 24, 177]. In a shrinking-core based model, the size of this miscibility gap must be set explicitly, whereas in a phase-field model they arise naturally and are dependant on several factors, including crystal size and temperature [77], consistent with experimental reports [24, 177]. Importantly, the addition of anisotropic elastic strain [30] to a phase-field model resulted in simulations that show qualitative agreement with experimentally observed phase-boundary orientations in nano-sized LiFePO$_4$ crystals. In this work, we use these phase-field models to simulate the concentration distribution on the crystal scale, given the now considerable evidence indicating that a shrinking-core based model is a poor representation of the behaviour of LiFePO$_4$ material.
5.2.1 Crystal scale

Outlined in this section is the phase-field model we use to simulate Li$^+$ intercalation into LiFePO$_4$ material. The notation used below is taken directly from Dargaville and Farrell [172], based on the phase-field model mentioned previously [28, 76, 81]. We consider the 2D CHR IBVP and the simplified 1D depth-averaged equation on the crystal scale, with isotropic coherency strain, as in Dargaville and Farrell [172]. Section 5.3 examines the differences between using both models in the two-scale framework developed in Section 5.2.2.

**CHR equation**

If we assume the free energy in a LiFePO$_4$ crystal with domain $\Omega$ and boundary $\Gamma$ is governed by a Cahn-Hilliard functional [69] with averaged, isotropic coherency strain [30] and neglecting surface effects [139], the concentration of Li$^+$ in the lattice $c(x,t) \in [0,1]$ (nondimensionalised by $\rho$ (m$^{-3}$), the constant density of Li$^+$ sites in the lattice) is governed by

$$\frac{\partial c}{\partial t} + \nabla \cdot \left( D \left( 2\tilde{\Omega}_m c - \frac{2}{1-c} \nabla c + c \nabla \left( \tilde{B}(\hat{n}_0) c - \nabla \cdot (\tilde{K} \nabla c) \right) \right) \right) + X_n = 0, \quad (5.2.2)$$

where $t$ is time (s), $D$ (m$^2$/s) is a diffusion tensor, $\tilde{\Omega}_m$ is the dimensionless enthalpy of mixing per site, $\tilde{K}$ (m$^2$) is a gradient-penalty tensor (orthotropic, constant and symmetric positive definite), $\tilde{B}(\hat{n}_0)$ (Pa/J) is the isotropic, elastic energy in the minimizing direction $\hat{n}_0$ and $X_n$ is a Langevin noise term [160] with zero mean (see also [28, 172]).

For the crystal pictured in Fig. 1a, we assume that the concentration of Li$^+$ in the $z$ direction (not pictured) is constant [172]. We therefore set $x = [x,y]$ (in Cartesian coordinates), where $x$ (m) and $y$ (m) correspond to the $a$ and $b$ crystallographic axes, respectively. The dimensionless chemical potential, $\tilde{\mu}$, of Li$^+$ in the lattice, written with respect to the dimensionless reference potential $\tilde{\mu}^\Theta$, is given by

$$\tilde{\mu}(x,t) - \tilde{\mu}^\Theta = \tilde{\Omega}_m (1-2c) + \ln \left( \frac{c}{1-c} \right) - \nabla \cdot (\tilde{K} \nabla c) + \tilde{B}(\hat{n}_0)(c - c_{avg}) = \ln a(x,t), \quad (5.2.3)$$

where $a$ is the activity of Li$^+$ in the lattice and $c_{avg}$ is the dimensionless average concentration across the crystal. The initial concentration of Li$^+$ in a crystal is given by some function $f(x)$, such that

$$c(x,0) = f(x), \quad \text{at } t = 0. \quad (5.2.4)$$
We apply a flux condition on the \(xz\) surface of the crystal (where \(j (m^{-2} s^{-1})\) is the mass flux of \(Li^+\) per molecule in (5.2.2)) and a no-flux condition on the other surfaces [172]. We should note that the flux condition is applied over the entire \(xz\) surface, whereas mentioned previously, the concentration in \(z\) is constant. This is accounted for in (5.2.11), which integrates the reaction term over the entire surface of each (three-dimensional) crystal. This ensures that (5.2.11) gives the current entering/leaving each three-dimensional crystal, represented by either the 2D CHR equation or the 1D depth-averaged equation.

We must also impose a variational boundary condition (VBC) [81], giving the boundary conditions for (5.2.2) as

\[
\hat{n} \cdot (\mathbf{K} \nabla c) = 0, \quad \text{on } \Gamma \quad \text{(5.2.5)}
\]

\[
\hat{n} \cdot j = \rho_s R(x, X, t), \quad \text{on } y = 0 \text{ and } F_y \quad \text{(5.2.6)}
\]

\[
\hat{n} \cdot j = 0, \quad \text{on } x = 0 \text{ and } F_x \quad \text{(5.2.7)}
\]

where \(R(x, X, t) (s^{-1})\) is a reaction term that determines the number of molecules of \(Li^+\) that intercalate into the crystal and \(\rho_s (m^{-2})\) is the constant \(Li^+\) site density on the \(xz\) surface.

The current-overpotential form of the Butler-Volmer equation [51, 54, 74] allows us to define \(R(x, X, t)\) as

\[
R(x, X, t) = \frac{(k_0 a^0_e)^\alpha (k_0^c a^0_c)^{1-\alpha}}{\gamma^*_{\sharp}} \left[ \frac{a_e(X, t)}{a^0_e} \exp \left( \frac{-\alpha e \eta(X, t)}{k_B T} \right) - \frac{a(x, X, t)}{a^0} \exp \left( \frac{(1-\alpha) e \eta(X, t)}{k_B T} \right) \right], \quad \text{(5.2.8)}
\]

where \(\gamma^*_{\sharp}\) is the activity coefficient of the activated state, \(e \ (C)\) is the elementary charge on a proton and \(k_0^e\) and \(k_0^c \ (s^{-1})\) are the rate constants for the reaction. We assume that both \(a_e(X, t)\), the activity of \(Li^+\) in the electrolyte and \(\eta(X, t) \ (V)\), the surface overpotential, are constant across the surface of any individual crystal and are determined entirely on the cathode scale (see Section 5.2.2). Equation (5.2.8) also contains activities computed at a reference state, taken at \(t = 0\), denoted by the “0” superscript. Please see Dargaville and Farrell [172] for a discussion on this reference state and the resulting definition of \(\eta\) and (5.2.8). Equation (5.2.8) is written in terms of the activities and rate constants at the reference state, instead of explicitly in terms of an exchange
current density, \( i_0 \) (A/m\(^2\)). We can write \( i_0 \) in terms of these variables by using

\[
i_0 = \rho_s e \left( k_{0} a_{c}^{0} \right)^{\alpha} \left( k_{c} a_{c}^{0} \right)^{1-\alpha}.
\]

(5.2.9)

As noted in Dargaville and Farrell [172], we can consider the combination of the rate constants as \( \tau_0 \) (s\(^{-1}\)), the mean time scale of the reaction. We can therefore consider

\[
i_0 = \frac{\rho_s e (a_{e}^{0})^{\alpha} (a_{c}^{0})^{1-\alpha}}{\tau_0},
\]

(5.2.10)

with the understanding that in Section 5.3, when we modify \( \tau_0 \), we are in fact modifying \( i_0 \).

Finally, the total current entering or leaving any individual crystal in the cathode, \( I_c(X,t) \) (A) is given by

\[
I_c(X,t) = \frac{e}{A_s} \int_{\Gamma} R(x,X,t) d\Gamma,
\]

(5.2.11)

where \( A_s \) (m\(^2\)) is the average area of a single intercalation site on the \( xz \) surface. The dimensionless mass fraction of Li\(^+\) intercalated into a crystal in the cathode, \( M(X,t) \) (or the average concentration \( c_{\text{avg}} \), is also given by

\[
M(X,t) = \frac{1}{\Omega} \int_{\Omega} c(x,X,t) d\Omega,
\]

(5.2.12)

**Depth-averaged**

If the time-scale for the reaction on the surface is slow compared with the diffusion in the solid and both \( D \) and \( \tilde{K} \) are highly orthotropic, (5.2.2) can be depth-averaged [76, 81, 172] along the \( y \) direction to recover the one-dimensional equation (in the absence of anisotropic strain [30]) that represents the concentration of Li\(^+\) in the \( x \) direction (see Fig 1a) for an individual crystal in the cathode, namely

\[
\frac{\partial c(x,t)}{\partial t} = \frac{2R(x,X,t)}{N_H} + X_n.
\]

(5.2.13)

Here \( N_H \) is the number of lithium sites in each of the individual channels pictured in Fig 1a. Equation (5.2.13) only applies in a parameter regime that is limited by the timescale of the surface reaction (surface-reaction limited, or SRL). It cannot simulate regimes when diffusion-limitations apply in the crystal (i.e., when the bulk-transport of Li\(^+\) in the crystal limits the discharge, also known as bulk-transport limited, or BTL), as \( D \) has been averaged out of the equation. We must use the full, 2D CHR
equation if either $D$ or $K$ are isotropic, or if diffusion limitations apply (either caused by a small $D$ or a small $\tau_0$). We could simply use the full 2D CHR equation in all simulations (as it is valid across all parameter regimes), however the 2D CHR equation is more computationally expensive to solve, especially when embedded in a two-scale framework. We therefore only use the 2D CHR equation in Section 5.3 when strictly necessary.

The reaction flux boundary condition (5.2.6) is used in the depth-averaging process (with (5.2.7) a consequence of the averaging), leaving the VBC (5.2.5) applied at the boundaries, or

\[
\tilde{K}_{xx} \frac{\partial c(x,t)}{\partial x} = 0, \quad \text{on } x = 0, F_x.
\]  

(5.2.14)

**5.2.2 Cathode scale**

On the cathode scale we consider a porous agglomeration of crystals, graphite and binder flooded with electrolyte, with spatial coordinate $X$ ($X_1 \leq X \leq X_o$) as shown in Fig. 1b. Conservation of volume on the cathodic scale dictates that

\[
\epsilon_{\text{LiFePO}_4} + \epsilon_g + \epsilon_b + \epsilon = 1,
\]  

(5.2.15)

where $\epsilon_{\text{LiFePO}_4}$, $\epsilon_g$, $\epsilon_b$ and $\epsilon$ are the volume fractions of LiFePO$_4$ oxide, graphite, binder and electrolyte, respectively, on the cathode scales. Conservation of charge on the cathode scale requires that

\[
i_e + i_g = \frac{I}{A} \hat{X},
\]  

(5.2.16)

where $i_e$ and $i_g$ ($A/m^2$) are the current densities per total unit area in the electrolyte and the graphite phase, respectively, $I$ (A) is the applied discharge current, $A$ ($m^2$) is the cross-sectional surface area of the cathode and $\hat{X}$ is a unit vector normal to the graphite/electrolyte interface at all points. Equation (5.2.16) states that any charge that enters the crystals through mass transport of species within the electrolyte must exist via the graphite phase.

The local overpotential on the cathode scale $\eta$ (V) (with respect to Li$^+$ metal) is given by the potential difference between the graphite and electrolyte phases, $\Phi_g$ and $\Phi_e$ (V) respectively, in the cathode, relative to a constant, well-defined reference potential, $E_{\text{ref}}$ (V), (which we take to be the open-circuit potential of a LiFePO$_4$ cell, 3.5 V). Thus,

\[
\eta = \Phi_g - \Phi_e - E_{\text{ref}}.
\]  

(5.2.17)
We should note that $E_{\text{ref}}$ is written as $E^0$ in Dargaville and Farrell [82]. Charge is removed from the electrolyte by intercalating into the crystals according to

$$\nabla \cdot \mathbf{i}_e = \frac{\epsilon_{\text{LiFePO}_4} I_c}{V_{\text{LiFePO}_4}},$$

(5.2.18)

where $V_{\text{LiFePO}_4}$ (m$^3$) is the volume of LiFePO$_4$ in the cathode. We can see in (5.2.18) that we must directly compute the current entering/leaving each individual crystal by evaluating (5.2.11) to determine $I_c(X, t)$, as $a(x, X, t)$ depends on $x$. This is different to the approach that we have taken previously [82], where spherical symmetry of the crystals allowed us to obtain a direct expression for $\nabla \cdot \mathbf{i}_e$.

We can describe $\mathbf{i}_e$ using a modified Ohm’s law and $\mathbf{i}_g$ with Ohm’s law and noting (5.2.18), we may then obtain an equation for $\eta$ as follows,

$$\nabla \cdot \left( \frac{\sigma_g \kappa_{\text{eff}}}{\sigma_g + \kappa_{\text{eff}}} \left( \nabla \eta + \frac{2R_gT}{F} (1 - t_{\text{Li}^+}) \nabla \ln a_e + \frac{I}{\sigma_g A} \hat{X} \right) \right) = \frac{\epsilon_{\text{LiFePO}_4} I_c}{V_{\text{LiFePO}_4}},$$

(5.2.19)

where $F$ (C/mol) is Faraday’s constant, $R_g$ (J/(mol K)) is the universal gas constant, $t_{\text{Li}^+}$ is the transport number for lithium in the electrolyte, $\kappa_{\text{eff}}$ (S/m) is the effective conductivity of the electrolyte on the cathode scale (corrected for tortuosity and porosity [106]) and $\sigma_g$ (S/m) is the effective conductivity of the carbon/graphite network.

The intrinsic (averaged over the pores) concentration of Li$^+$ in the electrolyte on the cathode scale, $C_e$ (mol/m$^3$) is given by

$$\frac{\partial \epsilon C_e}{\partial t} = \nabla \cdot (D_{\text{eff}} \nabla C_e) - \frac{(1 - t_{\text{Li}^+}) \epsilon_{\text{LiFePO}_4} I_c}{V_{\text{LiFePO}_4} F},$$

(5.2.20)

where $D_{\text{eff}}$ (m$^2$/s) is the effective diffusivity of Li$^+$ in the electrolyte (again corrected for tortuosity and porosity [106]). The boundary conditions for the cathodic scale are

$$C_e = C^0_e; \quad \text{at } X = X_i,$$

(5.2.21)

$$\mathbf{i}_e = \frac{I}{A} \hat{X}; \quad \text{at } X = X_i,$$

(5.2.22)

$$\nabla C_e = 0; \quad \text{at } X = X_o,$$

(5.2.23)

$$\mathbf{i}_e = 0; \quad \text{at } X = X_o,$$

(5.2.24)

where $C^0_e$ (mol/m$^3$) is the concentration of Li$^+$ in the electrolyte at $t = 0$. We note that the boundary conditions in $\mathbf{i}_e$ can easily be transformed into boundary conditions.
for $\eta$ using Eqs. (5.2.18) and (5.2.19). Initially we assume that the cathode is in a state of equilibrium, thus

$$C_e = C_0, \quad \text{at } t = 0.$$  \hspace{1cm} (5.2.25)

Given that we have assumed a perfectly conductive network of carbon is present through the cathode, the cell potential, $E_{\text{cell}} (V)$, can be well approximated by

$$E_{\text{cell}} = \eta|_{X=X_i} + E_{\text{ref}} - R_c \frac{I}{A},$$ \hspace{1cm} (5.2.26)

where $R_c (\Omega \text{ m}^2)$ represents any contact resistance that may exist at the cathode/current collector boundary.

### 5.2.3 Numerics

The equations along with the boundary and initial conditions (BCs & ICs) that govern the discharge of our two-scale model of LiFePO$_4$ cathodes are listed in Table 5.1. In order to solve these equations, the crystal scale was nondimensionalised and discretised in the same fashion as Dargaville and Farrell [172]. This discretisation uses the least-squares based Finite Volume Method (FVM) [49] detailed in Dargaville and Farrell [151] for the 2D CHR equation. The least-squares matrices used in this FVM method were precomputed based on their position in the crystal-scale mesh and solved using BLAS/LAPACK routines from the Intel Math Kernel Library (MKL). The cathode scale was kept in dimensioned form, and the equations were discretised with the FVM.

Discretising the two-scale model in this fashion produces a large system of stiff differential-algebraic equations. The solution to this system was implemented in C++ and the IDA module from the Sundials library [108] was used to provide time-stepping. IDA uses an (up-to) 5th order backward-differentiation-formula (BDF) to advance in time, with
adaptive time-stepping based on error estimates. The sophisticated time-stepping provided by this library is essential to efficiently capturing the multiple time-scales present in this system. We used an absolute tolerance of $1 \times 10^{-6}$ and a relative tolerance of $1 \times 10^{-8}$.

The nonlinear system that results from the two-scale model outlined in Section 5.2 is very stiff, especially when the 2D CHR IBVP is used on the crystal scale. The multi-scale nature of the model also means the system can grow fairly large (up to a million equations). This is because each discretised node point on the cathode scale has a crystal scale equation associated with it. This results in a system of size $n_t = 2n_{\text{cath}} + n_{\text{cath}}n_c$, where $n_{\text{cath}}$ and $n_c$ are the number of node points on the cathode and crystal scales, respectively. For simulations with the 1D depth-averaged IBVP on the crystal scale, we used $n_c = 40$ and $n_{\text{cath}} = 320$. When using the 2D CHR equation on the crystal scale, we reduced the number of equations on cathode scale to $n_{\text{cath}} = 32$, as we used $n_c = 120 \times 25$.

In order to solve this system efficiently, we used the parallel Jacobian-Free-Newton-Krylov (JFNK) [161] from IDA. This library has support for cluster implementations provided by the message passing library MPI. The parallel implementation provides several inexact Newton-Krylov methods (we used GMRES [178]) and also provides a built-in block-banded preconditioner. This JFNK method was used in Chapter 4 along with the built-in preconditioner by simply setting the number of cores used by MPI to be one, as the $F(t, y, \dot{y})$ routine used in that chapter was not written to support computation in parallel.

When using the parallel implementation of IDA with more than one core, IDA handles the communication between cores when solving the differential-algebraic equations (DAEs), all that is required of the user is to write an $F$ routine that supports computation in parallel. Each core receives a subset of the equations in the system, namely

$$y = [y_0, y_1, y_2, \ldots]; \quad \dot{y} = [\dot{y}_0, \dot{y}_1, \dot{y}_2, \ldots],$$

where the subscript represents the core each subset of equations is associated with (numbered starting from 0). Each core is required to compute the component of the nonlinear residual, $F$, associated with the local section of the DAE system, or

$$F(t, y, \dot{y}) = [F_0(t, y, \dot{y}), F_1(t, y, \dot{y}), F_2(t, y, \dot{y}), \ldots].$$
Each of the local components of the $F$ routines can however, be dependent on equations associated with neighbouring cores. Any equations present on neighbouring cores that are required to build the local $F$ must therefore be sent by the user between cores within the $F$ routine, using MPI. When using the built-in block-banded preconditioner, as mentioned in Chapter 4, the user is required to supply a function $G$ that approximates $F$ ($G = F$ is allowed). In parallel, this results in

$$G(t, y, \dot{y}) = [G_0(t, y, \dot{y}), G_1(t, y, \dot{y}), G_2(t, y, \dot{y}), \ldots].$$

The routine $G$ however, should not perform any communication. $F$ is called once before the preconditioner is constructed, which updates any local copies of equations stored on neighbouring cores. The preconditioner associated with this has the form

$$P = \text{diag}[P_0, P_1, P_2, \ldots],$$

which is block diagonal, where each block is computed locally on the $i$th core using

$$P_i \approx \frac{\partial G_i}{\partial y_i} + \alpha \frac{\partial G_i}{\partial \dot{y}_i}, \quad (5.2.27)$$

where $\alpha$ is a scalar associated with the time-stepping that IDA uses. By default, IDA approximates the derivatives in (5.2.27) using a difference expression, but importantly these derivatives are taken with respect to the local equations $y_i$, not the global $y$. This is a consequence of restricting all communication between cores to $F$, and means the preconditioner neglects any coupling between cores (that would occur in the off-diagonal blocks in $P$). This can become important if the off-block couplings are large, as $P$ would then be a poor approximation to the Jacobian. The neglected couplings are dependent on the domain decomposition used to split the problem across multiple cores. There are many ways generic DAE systems can be partitioned, and the effect of two different domain decompositions was investigated for our two-scale system. For more details on the IDA library and the JFNK/block-banded preconditioner described above, please see the User Guide for IDA [108].

Initially, the solution to the two-scale system presented in this chapter was computed on a single core. As such, the discretised equations in the system were ordered in an attempt to minimise the bandwidth of the Jacobian (and hence the preconditioner). This reduced the runtime, as IDA computes each of the diagonal blocks in the preconditioner using “shift” vectors that decrease the number of function evaluations needed when the system is banded. A simple ordering was used, namely one
of the discretised nodes from each of the equations on the cathode scale was placed before nodes from the crystal associated with that node. For example, if both \( C_e \) and \( \eta \) are solved for on the cathode scale, with the nodes from the discretised system written as \( \eta_1, \eta_2, \ldots \), and the discretised crystal scale equations associated with the first node on the cathode scale labelled as \( c_{1,1}, c_{1,2}, \ldots \), the global vector was ordered like \( y = [C_{e1}, \eta_1, c_{1,1}, c_{1,2}, \ldots, C_{e2}, \eta_2, c_{2,1}, c_{2,2}, \ldots] \). All of the discretised equations for any individual crystal depend only on the values of the cathode scale equations at a single mesh point.

Fig. 5.2a shows an example of the Jacobian that results from this node ordering, on a single core, with 9 mesh points on the cathode scale, and using the one-dimensional depth-averaged equation on the crystal scale with 40 mesh points. This Jacobian was computed using difference approximations in the same fashion as IDA would compute the preconditioner (i.e., using \( G \)). The system is banded, with the larger bandwidth at the ends of the domain corresponding to asymmetric difference equations used on the cathode scale. Importantly, the bandwidth shown in Fig. 5.2a does not increase as the number of mesh points on the cathode scale increases. Using this approach on a single core works very well, and for a small number of mesh points on the cathode scale, the solution is computed relatively quickly. For a higher number of nodes and if the two-dimensional CHR equation is used on the crystal scale, a single core cannot compute the solution within a reasonable runtime.
As such, the domain was partitioned in order to compute the solution in parallel. Fig. 5.3 shows a diagram of the decomposition used, and for illustrative purposes 9 mesh points are shown on the cathode scale (to match Fig. 5.2a), distributed across 3 cores. Each of the coloured shaded regions denotes the node points associated with a specific core. The domain has been split on the cathode scale, with each core responsible for a subset of the cathode scale equations, and hence for a subset of the crystals in the problem. The node ordering chosen makes the domain decomposition very simple, as $y$ can be divided evenly, i.e., if there is a total of $n_t$ equations in the system, each of the $n_p$ cores (or processes) is allotted $n_t/n_p$ equations in sequence. The arrows in Fig. 5.3 show the communication that occurs between cores, and as the cathode scale equations are all solved in one-dimension, very minimal communication need occur. Each core requires the values of each of the equations on the cathode scale at neighbouring node points. Fig. 5.3 only shows the closest nodal value for each equation being communicated, but in practice more than one node is used, depending on the approximations used to estimate function values and derivatives on the cathode scale.

Fig. 5.2b shows the Jacobian that resulted from this domain decomposition. Solid lines have been used to denote the partitions between the nodes associated with each core. The Jacobian is identical when compared with Fig. 5.2a, though any terms in the off-diagonal blocks are neglected. This due to $G$ not performing any communication, as
noted before. This means with the domain decomposition pictured in Fig. 5.3, some of the couplings between node points of $\eta$ and $C_e$ are neglected, while all of the couplings between the cathode scale equations and the crystal scale are retained. This approach however, performs very poorly, often resulting in runtimes orders of magnitude larger than the single processor case. This is because the off-diagonal couplings between $\eta$ and $C_e$ are some of the largest elements in Fig. 5.2a, while the elements coupling the cathode and crystal scales are small.

In order to increase the performance when solving the system in parallel, the ordering of the nodes in the system was altered and hence the domain was partitioned differently. Rather than trying to minimise the bandwidth of the system, the order chosen was designed to minimise the distance between elements of $\eta$ and $C_e$. Simply, all the cathode scale equations were placed at the front of $y$, with all the crystal scale equations following them, i.e., $y = [C_{e1}, C_{e2}, \ldots, \eta_1, \eta_2, \ldots, c_{1,1}, c_{1,2}, \ldots, c_{2,1}, c_{2,2}, \ldots]$. 

Fig. 5.4a shows the Jacobian resulting from this ordering with one core, and it is evident that the bandwidth of the system has increased considerably. The columns of nonzero elements in Fig. 5.4a that increase the bandwidth are the couplings between the cathode and crystal scales, which are small. Importantly, all the couplings between the cathode scale equations are clustered in the top left of Fig. 5.4a. For a single core, this approach converges slightly worse than the previous node ordering, as many of the off-diagonal elements are neglected by using a bandwidth smaller than the true bandwidth shown in Fig. 5.4a.
Given this node ordering, a domain decomposition was required that preserved the cathode/crystal scale couplings. Fig. 5.5 shows the decomposition used, with all of the cathode scale equations stored on the first core. If there are $n_{\text{cath}}$ equations on the cathode scale and hence $n_{\text{cath}}$ individual crystal scale problems, $n_{\text{cath}}/n_p$ crystals were distributed per core. This means that the first core has more equations associated with it than any other core, though for small $n_{\text{cath}}$, this did not affect the performance of the code significantly.

With the domain decomposition shown in Fig. 5.5, all the cathode scale equations were now associated with a single core, and neighbouring nodes on the cathode scale do not need to be communicated between cores. Fig. 5.5 shows that instead, the associated $n_{\text{cath}}/n_p$ nodes for each equation on the cathode scale from core 0 must be sent to every other core. These cores then calculate the current entering/leaving each of the crystals, and send these $n_{\text{cath}}/n_p$ currents back to core 0. The crystals stored locally on core 0 do not have to communicate at all, as they are stored on the same core as the cathode scale equations and so any communication between core 0 and itself would be redundant.

Fig. 5.4b shows the Jacobian that results from the domain decomposition outlined in Fig. 5.5. All of the off-diagonal terms have been neglected, except on core 0 (shown in the diagonal block in the top left). This is because core 0 does not need to communicate
between the cathode and crystal scales equations (and hence the cathode and crystal scale couplings are retained in \( P_0 \)). IDA allows the preconditioner to be applied with a smaller bandwidth than was used to generate it. Any elements outside this smaller bandwidth are discarded. For the problem outlined in this chapter, on core 0, the bandwidth used to generate the preconditioner was set as the true bandwidth of the first diagonal block in Fig. 5.4b. A far smaller bandwidth however, was retained during the application step. Any attempt to reduce the cost of generating the preconditioner by setting the bandwidth to be less than the true value resulted in significantly reduced convergence. This is because the “shift” vectors used to calculate the local banded preconditioner include elements outside of the specified bandwidth within the computed bands, which requires caution. The true bandwidth of the remaining blocks in Fig. 5.4b is small, which makes generating the preconditioner on core 0 the most costly part of forming \( P \).

Due to time constraints, different node orderings were not investigated in any great depth. It may be possible to use a node reordering algorithm that would reduce the bandwidth either on core 0, or the entire problem, without introducing off-block couplings that may harm the convergence of the system. The use of a simple RCM reordering was considered, but this performed very poorly, with little reduction in either the bandwidth of the system, or the location of the largest elements in the Jacobian.

Earlier in this section, it was noted that the node ordering shown in Fig. 5.4a actually resulted in slightly poorer performance on a single core when compared with that pictured in Fig. 5.2a, due to the increased bandwidth. When the domain decomposition shown in Fig. 5.5 was performed however, the performance of the system in parallel, with the Jacobian shown in Fig. 5.4b is significantly enhanced when compared with that in Fig. 5.2b. As the number of cores increases, the runtime of the code scaled reasonably well. This is due in part to the very minimal communication between cores, as shown in Fig. 5.5.

It can be difficult to test the efficiency of the parallel code as described above, given that the entire bandwidth is used when generating the preconditioner on core 0. This requires \( n_0 \) function evaluations, where \( n_0 \) is the number of local equations on core 0. In Fig. 5.5 for example, this is given by

\[
\begin{equation}
  n_0 = 2n_{\text{cath}} + \frac{n_{\text{cath}}}{n_p}n_{\text{crys}},
\end{equation}
\]

(5.2.28)
where \( n_{\text{crys}} \) is the number of mesh points used on the crystal scale. This is in comparison to setting a fixed bandwidth and hence using a constant number of function evaluations as \( n_i \) increases, as is the case on the remaining cores. This means that any increase in the number of cores, without a corresponding increase in the number of mesh points used on the cathode scale will reduce the total number of equations on core 0. This reduces the cost of computing the preconditioner, obscuring the degree that the parallel code scales as the number of cores increases.

The main cost of the solving the two-scale system outlined in this chapter was generating the preconditioner, given the large bandwidth on core 0. Although the preconditioner on core 0 was generated with full bandwidth, only a small fraction of this bandwidth was retained during the application phase. This indicates that system does not require that the off-diagonal terms in the top-left block of Fig. 5.4b are present during the application of the preconditioner to converge. As mentioned above, reducing the bandwidth used to generate the preconditioner on core 0 results in convergence problems, indicating that the inclusion of the off-diagonal elements in the computed bands, caused by the use of “shift” vectors, was at fault. If these terms could be removed from the Jacobian, given that a small bandwidth can be used during the application phase, the application and generation bandwidths could possibly be reduced to a (small) constant value. Remembering that \( G \) does not communicate between cores, the aforementioned “redundant” communication was enabled between core 0 and itself. This results in core 0 using MPI to send the cathode scale nodal values and currents to itself (even though these values are all stored core 0). This has the effect of removing the off-diagonal terms from the Jacobian. In Fig. 5.5, this communication would be
No. cathode scale mesh points \((n_{\text{cath}})\) 6400 6400 6400 6400 6400
No. cores \((n_p)\) 1 2 4 8 16
Runtime (s) 5795 2965 1545 850 502
Speedup factor - 1.95 3.75 6.82 11.54

Table 5.2: Runtime of the parallel code as the number of cores is increased, with core 0 communicating with itself. The one-dimensional depth-averaged equation with 40 mesh points was used on the crystal scale (resulting in a total of approximately 286k nodes). The relative tolerance was set at \(1 \times 10^{-8}\), with the absolute tolerance set at \(1 \times 10^{-6}\).

represented by arrows between the cathode scale and the blue-shaded crystals.

Fig. 5.6 shows the Jacobian associated with this modification and it is clear that the off-diagonal terms on core 0 have been removed. This makes the bandwidth of the Jacobian on core 0 much smaller, allowing a constant bandwidth to be used on core 0. This therefore reduces the number of function evaluations used to build the preconditioner. This does not affect the convergence of the system, as a small bandwidth was already used during the application phase on core 0. This modification also allowed \(n_{\text{cath}}\) to be kept constant while increasing \(n_p\) when timing the parallel code, as the number of function evaluations used to generate the preconditioner remains constant as \(n_0\) grows. Core 0 is still associated with more nodes than any other core, though this is more representative of an equal division of work between cores when compared with constructing a preconditioner based on Fig. 5.4b. With \(n_p = 16\), the runtime when using the decomposition implied by Fig. 5.6 is roughly 10 times smaller compared with the case where communication is disabled on core 0.

Table 5.2 shows the runtime of the code when communication is enabled on core 0. Due to time constraints, runtimes for the disabled case are not shown, though they always perform around an order of magnitude worse than the results shown in Table 5.2. Table 5.2 shows the speedup factor of the code in parallel, which is computed relative to the \(n_p = 1\) case. Using 8 cores results in a 6.82 times reduction in the runtime. A speedup factor less than \(n_p\) as the number of cores grows is fairly typical of solving systems in parallel (see the CPU-only case in [179] for example), with the speedup factor approaching linear values for fewer numbers of cores.

The analysis in this section does not change if the two-dimensional CHR equation were used on the crystal scale. The bandwidth (and size) of the Jacobians pictured in Figures 5.2, 5.4 and Fig. 5.6 increase, but the communication routines do not change. Table 5.3 shows the results with communication enabled on core 0 and it can be seen that the
code scales very similarly when compared with the results shown in Table 5.2, though $n_{\text{cath}}$ is much smaller, given that a two-dimensional equation is used on the crystal scale.

When using either of the domain decompositions described in this section, there are $n_{\text{cath}}/n_p$ individual crystals associated with each core. The mesh on the crystal scale does not change, allowing the use of multiple RHS when performing most of the operations used to compute $\mathbf{F}$ (and $\mathbf{G}$). This is particularly significant when using the two-dimensional CHR equation. As described in Chapter 3, the least-squares system does not change throughout the majority of the linear, rectangular mesh used on the crystal scale. In Chapter 3, this meant multiple RHS could be used to solve for information at a large number of the control volume faces shown in Fig. 3.3 for a single crystal. In this chapter, this approach was extended to all of the crystals stored on any one core. This means information at the control volume faces in any of the shaded regions in Fig. 3.3, for every crystal stored on a core, were computed simultaneously.

In Chapter 4, the least-squares system in the blue-shaded region in Fig. 3.3 was replaced with simple difference approximations that were stored as a sparse matrix pattern. Again, using multiple RHS allowed the function values and derivatives to be computed at all of the $u$ faces in the blue-shaded region, for an individual crystal, with a single sparse matrix multiply for each quantity. In a manner similar to that used for the least-squares system, when using multiple cores, the number of RHS used was extended to include every crystal on a single core, and hence the concentration and derivative values at all of the $u \times (n_{\text{cath}}/n_p)$ faces in the blue-shaded region across any individual core could be computed with a single, sparse matrix multiply.

Most of the BLAS/LAPACK routines used from the Intel MKL are multi-threaded with OpenMP. This means that when using MPI, the number of MPI and OpenMP threads must be balanced. When using both the depth-averaged and CHR IBVP on

<table>
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<th>32</th>
<th>32</th>
<th>32</th>
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<th>32</th>
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<td>4</td>
<td>8</td>
<td>16</td>
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<td>2814</td>
<td>1624</td>
<td>958</td>
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<td>2.03</td>
<td>3.95</td>
<td>6.85</td>
<td>11.61</td>
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Table 5.3: Runtime of the parallel code as the number of cores is increased, with core 0 communicating with itself. The two-dimensional CHR equation with $40 \times 25$ mesh points was used on the crystal scale (resulting in a total of approximately 32k nodes). The relative tolerance was set at $1 \times 10^{-8}$, with the absolute tolerance set at $1 \times 10^{-6}$. 
the crystal scale, setting the number of OpenMP threads equal to 1 (one OpenMP thread for each MPI thread) was optimal. This indicates that the speedup from using multi-threaded operations (like the multiple RHS operations described above) is not greater than the speedup seen from simply decomposing the domain further and using another MPI thread. This may change if the number of nodes on the crystal scale were to increase. Of course, performing a single operation using multiple RHS is still far more efficient than calling the same routine many times, even when using only a single thread for those operations.

5.3 Results and discussion

In this section, we attempt to validate the results from the model developed in Section 5.2 with experimental data from Zheng et al. [169]. We choose to validate against the [169] data in this work for several reasons. Firstly, the cathodes used by Zheng et al. [169] are discharged at high rates while retaining significant capacity; at 3400 mA/g for example, a capacity of greater than 100 mAh/g is achieved. This is very different to the data [21] that we validated against in Dargaville and Farrell [82], where a capacity of less than 20 mAh/g is observed at a rate of 855 mA/g. Zheng et al. [169] also measured many of the parameters necessary to construct a mathematical model of the porous cathode, including active material loading and importantly, porosity and cathode thickness. The individual LiFePO$_4$ crystals were also coated in carbon (3 wt%), with 7.2% acetylene black distributed throughout the cathode.

Zheng et al. [169] also provided SEM images of the (roughly) rectangular LiFePO$_4$ crystal synthesised (that we estimated as $250 \times 100 \times 100$ nm). The SEM images show LiFePO$_4$ crystals with good carbon connectivity, with a combination of well-connected crystals and small agglomerates of crystals visible (we estimate around 5 crystals in an agglomerate). We would consider this morphology to effectively eliminate the “particle” scale that we used previously to model agglomerates [82]. Though we showed previously Dargaville and Farrell [82] that agglomerates do considerably affect the discharge capacity of a LiFePO$_4$ cathode, the agglomerates modelled in Dargaville and Farrell [82] contained approximately 450 crystals (with a 50 nm crystal size and 500 nm agglomerate radius), with no surface coating of carbon on the crystals.

As discussed in Dargaville and Farrell [82], the ability of a cathode to sustain high rate discharge is highly dependent on the use of agglomerate-free material, along with a cathode designed to promote Li$^+$ diffusion in the electrolyte. The cathodes in Zheng
<table>
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</tr>
<tr>
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<td>[169]</td>
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<td>$C_{\text{solv}}$</td>
<td>$(1 - C_c(\bar{V}<em>{\text{Li}} + \bar{V}</em>{\text{PF}}))/\bar{V}_{\text{solv}}$</td>
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</tr>
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<td>$\bar{V}_{\text{solv}}$</td>
<td>$87 \times 10^{6}$ (in EC:EMC)</td>
<td>m$^3$/mol</td>
<td>[113]</td>
</tr>
<tr>
<td>$w_{\text{LiFePO}_4}$</td>
<td>$3.64 \times 10^6$</td>
<td>kg</td>
<td>[169]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.5</td>
<td>-</td>
<td>[48]</td>
</tr>
<tr>
<td>$\gamma_{\pm}$</td>
<td>$\exp \left(-1.0378 \sqrt{m}/(1 + 3 \sqrt{m}) +3.2796m\right)$</td>
<td>-</td>
<td>[107]</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.35</td>
<td>-</td>
<td>[169, 180]</td>
</tr>
<tr>
<td>$\epsilon_g + \epsilon_b$</td>
<td>0.2455</td>
<td>-</td>
<td>[169, 180]</td>
</tr>
<tr>
<td>$\epsilon_{\text{LiFePO}_4}$</td>
<td>0.4044</td>
<td>-</td>
<td>[169, 180]</td>
</tr>
<tr>
<td>$\kappa_c$</td>
<td>$1 \times 10^{-3} \left(91.1 + 1910.1 C_c - 1052 C_c^2 + 155.4 C_c^3\right)$</td>
<td>S/m</td>
<td>[21]</td>
</tr>
<tr>
<td>$\kappa_{\text{eff}}$</td>
<td>$\epsilon \kappa_c/\tau$</td>
<td>S/m</td>
<td>[106]</td>
</tr>
<tr>
<td>$\sigma_g$</td>
<td>$7 \times 10^8$</td>
<td>S/m</td>
<td>[48]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>$1.83 \epsilon^{0.53}$</td>
<td>-</td>
<td>[106]</td>
</tr>
</tbody>
</table>

Table 5.4: Parameter values used in the model. (a) - Fit to experimental curves in Fig. 5.7a, (b) - Fit to experimental curves in Fig. 5.8a, (c) - Fit to experimental curves in Fig. 5.16.
et al. [169] were formed using a constant weight of active material pressed to a set porosity of 35%, giving a cathode thickness of approximately 25 µm. This significantly reduces diffusion limitations in the electrolyte. This is very important, as this paper focuses on a comparison of how different crystal-scale models of phase-change in LiFePO$_4$ affect cathodic-scale discharge curves. The model presented in Dargaville and Farrell [82] validated well against experimental data from Srinivasan and Newman [21], even though we used a shrinking-core model on the crystal scale. This was because electrical resistance (from the agglomerates) and electrolytic resistance (from the transport of electrolyte in the thick, 62 µm cathodes) constrained the discharge, even at the relatively low rate of 855 mA/g. The ability of the cathodes presented in Zheng et al. [169] to discharge at much high rates means that these resistances are smaller (if not eliminated entirely at the rates tested). In a mathematical model of such a cathode, this makes the choice of a crystal-scale model crucial to the ability of such a model to validate against experimental data. In the absence of discharge data for individual nano-sized LiFePO$_4$ crystals, validating against the cathodic discharge curves of high-rate material where most of the (obvious) resistances have been reduced or eliminated is perhaps the best way to verify the validity of a crystal-scale model. Indeed, in this work we could have attempted to validate against data like that from Srinivasan and Newman [21] as previously, however the choice of crystal-scale model would not have a significant effect on the cathodic-scale discharge curves, given the resistances controlling the discharge.

5.3.1 Shrinking-core

Fitting to Zheng et al. [169] data

Prior to investigating the behaviour of the two-scale model presented in Section 5.2, we investigate the ability of our shrinking-core model to reproduce the data of Zheng et al. [169]. This will provide a baseline to compare with the outcomes of our phase-field models. Given that we have argued the Zheng et al. [169] cathodes would most likely not contain large agglomerates, this required us to adapt our previous three-scale model into one that represented two-scale material. The main difference between the two and three-scale models is that of electrical resistance on the “particle” scale, so we decreased the size of the agglomerates to $R_o = 255$ nm and increased the electrical conductivity of the LiFePO$_4$ material on the particle scale to $\sigma_{s(p)} = 1 \times 10^{-3}$ S/m. This would represent very small agglomerates (with a radius of three crystals) that contain some mix of carbon and LiFePO$_4$ material within the agglomerate. Increasing $\sigma_{s(p)}$ beyond
this point has no effect on the discharge curves, confirming that we have removed any electrical resistance present in the agglomerates, effectively turning the three-scale model into one with two-scales. Our three-scale model also contains another equation on the particle scale (Equation (27) in Dargaville and Farrell [82]) that tracks the concentration of Li\(^+\) in the electrolyte within the porous agglomerates. This equation however, does not affect the discharge curves when validating against the Zheng et al. [169] data. Given the large cathodic porosity and the thin nature of the Zheng et al. [169] cathodes, transport of electrolyte at the individual particle scale is very rapid. This allowed us to run the code used to generate the results in Dargaville and Farrell [82] without modification. We note that we could have embedded a shrinking-core based model in the two-scale work presented in this paper, however given that a shrinking-core is not an accurate description of the phase-change in LiFePO\(_4\) this seems unnecessary. Our goal here is simply to understand how a shrinking-core model, which we know is physically incorrect, validates against the “crystal-centric” discharge data of a modern LiFePO\(_4\) material. We can then compare and contrast this outcome with that obtained from the more physically realistic phase-field models.

Fig. 5.7a shows the results from comparing the shrinking-core based model as described above with the discharge data from Zheng et al. [169]. We can see that the shrinking-core based model results in poor fits to the data. In order to obtain these fits, we varied several parameter from the values used in Dargaville and Farrell [82]. These include the exchange current density \(i_0\), contact resistance \(R_c\) and crystal size (that we chose to match the volume of the crystals estimated in Section 5.2.1). The values for any parameter that were changed from Dargaville and Farrell [82] are given in Table 5.4.

We did not modify the maximum theoretical oxide capacity, \(Q_{\text{max}} = 156 \text{ mAh/g}\), previously used in the shrinking-core based model, given that at low discharge rates both the Zheng et al. [169] and Srinivasan and Newman [21] data displayed a capacity less (approximately 156 mAh/g) than the theoretical capacity (170 mAh/g). In Sections 5.3.2 and 5.3.3, the maximum theoretical capacity is determined by \(\rho (m^{-3})\), the constant density of Li\(^+\) sites in the lattice, which we take from experimental measurements (see Table 5.4). As such, the shrinking-core and phase-field models in this paper display different capacities at low discharge rates, though given the poor fitting results obtained in Sections 5.3.2 and 5.3.3, no effort was made to remedy this difference.

Perhaps the most important parameter modified from Dargaville and Farrell [82] is that of the lithium diffusion coefficient in the isotropic, shrinking-core model, \(D_{\text{Li}}\). As discussed in Section 5.2, we assume a highly conductive carbon network is present on the
(a) Discharge curves from the model (solid) compared to experimental data from Zheng et al. [169] (symbols) for a range of constant DRs.

(b) Concentration of Li\(^+\) in the electrolyte through time for DR = 8500.

\( t \) (s): \( \times 0.78, \square 1.7, \bigcirc 3.88, \bigotimes 7.78, \bigodot 15.01 \)

Figure 5.7: Results from the shrinking-core based model developed in Dargaville and Farrell [82].
cathode scale, so electronic limitations do not constrain the discharge of the cathode. Fig. 5.7b also illustrates that electrolyte diffusion does not limit the discharge, with the concentration of Li\(^+\) in the electrolyte plotted across the cathode for the 8500 mA/g discharge shown in Fig. 5.7a. We can see that even at \(X = X_o\), approximately 450 mol/m\(^3\) of Li\(^+\) remains in the electrolyte at the end of discharge \((t = 15.01)\), confirming that Li\(^+\) transport in the electrolyte does not limit the discharge capacity of a sufficiently porous, 25\(\mu\)m thick cathode.

Lithium diffusion in the crystal is therefore the only mechanism in the model that can significantly reduce the capacity of the cathode as the discharge rate is increased. The value we used to compute the curves in Fig. 5.7a, \(D_{Li} = 9 \times 10^{-17} \text{ m}^2/\text{s}\), is roughly an order of magnitude larger than the \(D_{Li}\) we used in Dargaville and Farrell [82], to accommodate the much higher discharge rates used in Zheng et al. [169]. This isotropic diffusivity is however, up to 6 orders of magnitude smaller than values reported for the \{010\} direction by both experimental and \textit{ab initio} calculations [8, 86, 116, 157]. We have already acknowledged that a shrinking-core is not an accurate model of the discharge behaviour of LiFePO\(_4\) crystals, in particular because it ignores the anisotropy of Li\(^+\) diffusion (in defect-free crystals). It is therefore unsurprising that in order to fit discharge curves, we are forced to use a diffusivity that is inconsistent with previously reported values. PITT, GITT and CITT measurements [9, 83, 102, 181–183] of the lithium diffusivity have reported values from \(10^{-15}\) to \(10^{-21} \text{ m}^2/\text{s}\), though these intermittent titration techniques “measure” the diffusion coefficient by fitting a crystal-scale model to cathodic responses from small variations in potential or current. The crystal scale model chosen is normally a spherical, linear diffusion equation, though both shrinking-core [183] and phase-field [83] models have been investigated.

An argument could be made that the diffusion coefficients reported by GITT and PITT methods, though several orders of magnitude lower than otherwise measured [8, 86, 116, 157], encapsulate all of the neglected processes (like anisotropic diffusivity, phase-change, strain, etc.) that occur in LiFePO\(_4\) material in an “effective”, isotropic diffusion coefficient. However, given the high sensitivity of phase-change in LiFePO\(_4\) to crystal size, discharge rate, strain and defect concentrations [28, 30, 81, 172], we would expect diffusion coefficients measured by PITT and GITT methods to vary considerably between different samples of LiFePO\(_4\) material. The choice of the model applied in the PITT and GITT methods can also significantly alter the diffusivity measured. An example of this is given in Zhu and Wang [183], where the diffusivity of LiFePO\(_4\) was extracted using both a linear diffusion equation and a shrinking-core based model applied to PITT and GITT measurements. The diffusivity reported is almost constant.

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when a shrinking-core is used to fit the data, while varying across 4 to 5 orders of magnitude with concentration when using a linear diffusion equation.

Choosing a simple, isotropic crystal scale model (shrinking-core or linear diffusion equation) and using an “effective” diffusion coefficient in this fashion certainly makes fitting cathodic-scale models to experimental data (like in Fig. 5.7a) easier. However, we would argue that in a model designed to simulate modern, high-rate LiFePO$_4$ material, the inclusion of an isotropic crystal scale equation removes the predictive ability of the model, even if adequate fits to experimental data can be obtained. Our argument in Dargaville and Farrell [82] was that electrical resistance from agglomerated crystals along with electrolytic resistance in the cathode was constraining the discharge, rendering the crystal scale largely unimportant. Figure 5b in Dargaville and Farrell [82] illustrates this, as halving the crystal size with a 60 µm cathode only increased cathodic utilisation by approximately 10%, whereas decreasing the electrical resistance of the agglomerates resulted in a 30% increase in utilisation. This allowed us to justify the use of a simple crystal scale model, as most of the conclusions in Dargaville and Farrell [82] were centred around the electrical and electrolytic constraints. We can not justify such arguments for the discharge curves from Zheng et al. [169]. We could however, have developed mechanisms in the model designed to obtain better fits in Fig. 5.7a. In particular, we note that in Fig. 5.7a, the model over-predicts the utilisation at low discharge rates and under-predicts it at high discharge rates. Srinivasan and Newman [21] encountered a similar problem (see Fig. 4 in Srinivasan and Newman [21]) and used two different crystal sizes to obtain adequate fits. We could have used a similar approach, though this would not address the fundamental limitations of an isotropic, crystal-scale model. As such, we now turn to the results from the more sophisticated phase-field models outlined in Section 5.2.

5.3.2 Depth-averaged

Fitting to Zheng et al. [169] data

Fig. 5.8a shows the results from comparing the two-scale, depth-averaged model described in Section 5.2 with the experimental data from Zheng et al. [169]. To obtain these fits, we have modified both the contact resistance, $R_c$, and exchange current density, $i_0$ (by varying $\tau_0$, see below for a discussion on this parameter), from the values used in Section 5.3.1 (see Table 5.4). Fig. 5.8a shows that the depth-averaged model has fit the experimental data very poorly, indeed worse than the shrinking-core based model shown in Fig. 5.7a. We should note that all the crystals in the cathode, at all
(a) Discharge curves from the 2-scale depth-averaged based model (solid) compared to experimental data from Zheng et al. [169] (symbols) for a range of constant DRs.

(b) Comparison of discharge curves with decreased cathode-scale conductivity. Solid line: $\sigma_c = 7 \times 10^8$ S/m, dashed line: $\sigma_c = 7 \times 10^{-3}$ S/m.

Figure 5.8: Results from the depth-averaged, two-scale model presented in Section 5.2.
discharge rates shown in Fig. 5.8a, fill homogeneously. Importantly, the entire discharge capacity of the cathode has been utilised at all the discharge rates considered (the 8500 mA/g discharge is not visible in Fig. 5.8a with a voltage cutoff of 2.5V, as it plateaus at approximately 2.0V, though it behaves almost identically to the 3400 mA/g discharge, using the entire capacity of the cathode).

This over-utilisation is a direct consequence of using the depth-averaged equation on the crystal scale. In Section 5.3.1, diffusion limitations in the crystal reduced the discharge capacity of the shrinking-core model, however the depth-averaged phase-field model assumes that diffusion is rapid in the solid compared with the reaction. This results in (5.2.13), which does not contain any diffusivities that could be used to limit the discharge. This is in contrast to the 2D CHR equation, which we use in Section 5.3.3, in an attempt to model diffusion-limited crystals. Rather than decrease the experimentally measured diffusivities in the 2D CHR equation, we can instead decrease $\tau_0$, the mean time scale for the reaction on the surface of the crystal, which forms a component of the exchange current density $i_0$ (see (5.2.10)). Reducing $\tau_0$ (which corresponds to increasing $i_0$) however, does not result in a diffusion-limited crystal when using the depth-averaged equation, as the depth-averaging process assumes the crystal is limited by the time scale of the reaction. Care must therefore be taken when using the depth-averaged equation to use $\tau_0$ values (and hence $i_0$ values) that do not violate the depth-averaging assumptions [81]. A range of interesting dynamics emerge from the two-scale, depth-averaged model as $\tau_0$ is modified, and these are discussed later in this section, though none of these dynamics lead to improved fits between the depth-averaged model and the Zheng et al. [169] data.

Given the arguments above on diffusion limitations in the depth-averaged model, there are two remaining possible mechanisms for reducing the discharge capacity of the depth-averaged model and obtaining better fits than those shown in Fig. 5.8a. We showed in Fig. 5.7b when using a shrinking-core based model, that for such thin cathodes, the electrolyte transport does not limit cathodic discharge capacities, even at high rates. We see very similar results when using the depth-averaged equation on the crystal scale. This leaves us with only electrical resistances and kinetic limitations (that are discussed in the next section) on the cathode scale to reduce the discharge capacity.

In Section 5.2, we concluded that electrical resistance was unlikely to play a large role given that each crystal is coated in carbon and agglomerates are small. It is possible however, that the distribution of carbon in the cathode does not form a well-connected network, as assumed in our two-scale model. Fig. 5.8b tests this hypothesis, by reducing
\( \sigma_g \), the conductivity of the carbon network (normally set to the conductivity of carbon, namely \( 7 \times 10^8 \text{ S/m} \)) on the cathodic scale. This has the effect of assuming that electrons are transported through a mix of carbon and LiFePO\(_4\) (with the conductivity of LiFePO\(_4\) at \( \sim 1 \times 10^{-7} \text{ S/m} \)). This forces us to compute the potential in the graphite phase, as the approximation we use to compute the cell potential, Eqn. (5.2.26), is invalid if \( \sigma_g \) is not large. We therefore explicitly solve for \( \Phi_g (V) \), the potential in the graphite phase by using

\[
\nabla \cdot (\nabla \Phi_g) = \frac{\epsilon_{\text{LiFePO}_4} I_c}{\sigma_g V_{\text{LiFePO}_4}}.
\]

(5.3.1)

The cell potential can then be computed as

\[
E_{\text{cell}} = \eta |x=X_i - \Phi_g|_{x=X_i} + \Phi_g |x=X_o} + E_{\text{ref}} - R_c \frac{I}{A}.
\]

(5.3.2)

We can see in Fig. 5.8b however, that increasing the electrical resistance on the cathode scale has very little effect on the discharge curves. We compared discharges for \( \sigma_g = 7 \times 10^{-3} \text{ S/m} \), to those in Fig. 5.8a, where \( \sigma_g = 7 \times 10^8 \text{ S/m} \). This reduced conductivity is very similar to the cathodic-scale conductivity used by Srinivasan and Newman [21] (\( 5 \times 10^{-3} \text{ S/m} \)) to represent the poor electrical conductivity of their mix (which we modelled explicitly with agglomerates [82]). We observe that both the discharges at 340 mA/g and 1700 mA/g with reduced cathode scale conductivity are very similar to the corresponding curves in Fig. 5.8a and show full cathodic utilisation, though the voltage does decrease monotonically as the discharge continues. This is, however, distinctly different to the voltage plateaus and sharp drop-off exhibited by the Zheng et al. [169] data. This shows that poor mixing of the active material and carbon in the cathode cannot account for a reduction in the capacity of the 25 \( \mu \text{m} \) cathodes used by Zheng et al. [169].

**Model outcomes**

Separate to a discussion about the ability of a depth-averaged based model to fit experimental discharge curves, Fig. 5.8a shows behaviour that cannot be observed when using a shrinking-core (or isotropic diffusion-based) model on the crystal scale, especially with a discharge rate of 17 mA/g. We can see in Fig. 5.8a, at a rate of both 17 mA/g and 340 mA/g, small spikes are visible in the voltage profile. These spikes are the result of discharging a “many-particle” system [79, 80] where the equilibrium potential of a single crystal is non-monotonic and hence phase-separates near equilibrium. Several works have been investigating the behaviour of these types of systems with different
Figure 5.9: Discharge curves from the two-scale, depth-averaged based model for different values of $\tau_0$ with DR=17mA/g.

names (including “many-particle” [79], “mosaic effects” [81] and “discrete-filling” [53]) in recent years, governed by the idea that crystals in close proximity can “communicate” by modifying the local electrochemical potential and hence affect the charge/discharge behaviour of each individual crystal in the cathode.

Dreyer et al. [79] used a simple mathematical model based on this idea to explain the fundamental voltage hysteresis between charge and discharge observed in LiFePO$_4$ material. This model predicts that phase-separating crystals in a cathode discharge “one-by-one” through the cathode. During a slow, quasi-static discharge, Dreyer et al. [79] note that phase-separation in many crystals simultaneously is unstable (which was proven rigorously by [80]), which will result in a cathode filled with crystals that are either fully intercalated or deintercalated. This prediction supports the observations of the “domino-cascade” model of Delmas et al. [61]. This does not imply that
crystals do not phase-separate during the discharge of a cathode at normal discharge rates, merely that we if we observed the cathode close to equilibrium (in an \textit{ex situ} experiment for example), any individual crystal that is phase-separating in the cathode would be unstable as part of a “many particle” group (even though the phase-separated state is the equilibrium state in a single crystal) and would transfer lithium (via the electrolyte) to nearby crystals in order to return to a homogeneous state (i.e., fully charged/discharged). The observed cathodes would therefore only be comprised of crystals either fully charged or discharged.

The voltage spikes shown in Fig. 5.8a agree with this result, though we should note that the voltage spikes do not correspond to individual crystals in our simulation discharging. We discretised the cathodic scale equations with 320 node points (as outlined in Section 5.2.3), meaning we have 320 individual crystals that discharge during our simulation, whereas approximately 32 voltage spikes are visible in the 17 mA/g discharge shown in Fig. 5.8a. Ferguson and Bazant [53] discussed this phenomena briefly, which they dubbed “discrete-filling”. We can consider the “one-by-one” discharge of crystals discussed by Dreyer et al. [79] (which was recently confirmed experimentally by Chueh et al. [184]) in fact occurring in small blocks of more than one crystal (which Ferguson and Bazant [53] call active particles), with the size of the block (or equivalently the number of active particles, \(n_{ap}\)) determined by considering an equivalent circuit governed by the timescale of charging a single particle (\(\tau_c\)) and the discharge rate [53]. Ferguson and Bazant [53] give this relation as

\[
n_{ap} = \tau_c I. \tag{5.3.3}
\]

The 32 individual voltage spikes in Fig. 5.8a at a 17 mA/g rate, (shown on a smaller scale in Fig. 5.9a), can be considered as representative of 32 individual blocks of crystals discharging together (i.e., \(n_{ap} = 32\)). Equation (5.3.3) implies that we can decrease the number of active particles by reducing the timescale of charging, which we can accomplish by decreasing the mean time scale of reaction \(\tau_0\) in our model (essentially increasing \(i_0\)).

In Fig. 5.9b, we show the same discharge rate as in Fig. 5.9a, however we have decreased the timescale of reaction to \(\tau_0 = 0.1\) s, and we can see a greater number of voltage spikes occurring. This is closer to the “one-by-one” discharge of crystals in the cathode described by Dreyer et al. [79]. We can observe this directly in Fig. 5.10, where the concentration in a series of adjacent crystals in the cathode is plotted through time, for both of the discharges in Fig. 5.9. We have plotted the concentration at \(x = F_x\) in
each crystal, as all of the crystals fill homogeneously and hence the concentration is the same across the entire crystal. In both Figs. 5.10a and 5.10b, the 16th through 26th crystal concentrations are plotted (corresponding to a dimensionless cathode position of $\tilde{X} = 0.05$ to 0.08125). We can see in Fig. 5.10a, with $\tau_0 = 1$, which for the ten crystals plotted, the discharges are separated into two separate blocks, with the crystals in each block discharging at very similar times. Fig. 5.10b shows that as we decrease $\tau_0$ to 0.1, as implied by the voltage spikes in Fig. 5.9b, we decrease the number of active particles discharging together and there are now 6 distinct groups of crystals discharging.

The concentrations plotted in Fig. 5.10 also show that the mass of lithium in all of the crystals seems to increase linearly for early times ($< 0.6 \times 10^4$ s) before fluctuating around a dimensionless concentration of 0.2. Initially, the entire cathode discharges homogeneously until the concentration in each crystal reaches the lower spinodal point.
at a concentration of 0.2. The crystals then begin to fill discretely across the cathode, from the separator to the current collector, either in small blocks or individually as described above. We can see this in Fig. 5.11a, where we have plotted the concentrations through time, in three crystals distributed throughout the cathode, corresponding to the discharge curve in Fig. 5.9a. We can see that the crystal closest to the separator ($\tilde{X} = 0.05$) discharges first, with the crystal closest to the current collector ($\tilde{X} = 1$) discharging last. The crystals discharging in Fig. 5.11a will, in fact, be discharging together with a series of nearby crystals given the results outlined in Fig. 5.10a, however we have only plotted the concentration from three, non-adjacent crystals in Fig. 5.11a for simplicity. If we consider the crystal at $\tilde{X} = 0.5$, we can see that although the intercalation front does not reach it until approximately $t = 2 \times 10^4$ s, the concentration in the crystal (and all of the remaining crystals in the cathode, including the crystal at $\tilde{X} = 1$) fluctuates around the spinodal point from $0.5 \times 10^4 < t < 2 \times 10^4$ s, before the crystal at $\tilde{X} = 0.5$ finishes discharging.

The timing of these concentration fluctuations matches the voltage spikes in Fig. 5.9a almost exactly. We have also plotted the concentration in the same three crystals when $\tau_0 = 0.1$ in Fig. 5.11b (corresponding to the voltage curve in Fig. 5.9b) and we see similar results. Namely, the concentration fluctuations become more numerous and decrease in size when compared with Fig. 5.11a as $\tau_0$ is decreased. This gives us insight into the cause of the voltage fluctuations seen in Fig. 5.9. As predicted by Dreyer et al. [79], it is the “communication” between crystals in a many-particle system that is responsible. Ferguson and Bazant [53] notes that these spikes are caused by discrete filling, but at a discharge rate of 17 mA/g we notice that it is not the intercalation/deintercalation of an individual crystal (or small number of crystals) near the intercalation front causing the voltage spikes. Instead, the crystals far away from this front (i.e., the remainder of the cathode) are influenced by the potential variation of the crystals that are near the front, and begin to both intercalate and deintercalate around the spinodal point, before fully discharging when the intercalation front reaches them.

We have also examined the behaviour of a many-particle system in a parameter regime where crystals may phase-separate. As noted above, the many-particle model of Dreyer et al. [79] does not suggest that crystals cannot phase-separate, but that phase-separation, if it occurs, will be restricted to one crystal (or given the results outlined above, perhaps in a small number of crystals) at a time, because of discrete filling. Effects associated with phase-separation are not visible in the 17 mA/g discharges examined above (as phase separation does not occur in this case). We note that the combination of coherency strain and moderate currents suppresses phase separation in individual crystal
Figure 5.11: Crystal concentrations at the boundary of a crystal \((x = F_x, \text{ as the crystals all fill homogeneously, so the concentration is the same across } x)\), for three crystals in different dimensionless cathode positions through time, with DR=17mA/g.

In Fig. 5.12 we have plotted the concentration in three adjacent crystals in the cathode through time, during a discharge of 1.7 mA/g. We can see in Fig. 5.12a that at such a low current, the crystal at cathodic position \(\tilde{X} = 0.025\) has phase-separated. Surprisingly, the crystals at positions \(\tilde{X} = 0.0281\) and \(\tilde{X} = 0.0313\) in Figs. 5.12b and 5.12c, respectively, have not phase-separated. The only mechanism that could cause this is a different current entering adjacent crystals, with the crystals shown in Figs. 5.12b and 5.12c subject to a higher current than that shown in Fig. 5.12a. This is indeed the case, as shown in Fig. 5.13, where we have plotted the current entering the discharges [28, 30]. As such, we decided to examine the behaviour of the two-scale, depth-averaged model with coherency strain removed and at a lower discharge rate, namely 1.7 mA/g.
Figure 5.12: Concentration profiles through time for three adjacent crystals between $\bar{X} = 0.025$ to $\bar{X} = 0.0313$ with coherency strain disabled, DR=1.7 mA/g and $\tau_0 = 1$. 
(a) Current entering the three adjacent crystals between $\tilde{X} = 0.025$ to $\tilde{X} = 0.0313$, through time. The black curve (crystal 8) corresponds to the concentration profile in Fig. 5.12a, with the blue and purple curves Figs. 5.12b and 5.12c, respectively (crystals 9 & 10).

(b) Current entering the crystals between $\tilde{X} = 0.9375$ to $\tilde{X} = 1$, through time.

Figure 5.13: Current profiles through time for various crystals in the cathode with coherency strain disabled, DR=1.7 mA/g and $\tau_0 = 1$. 
crystals shown in Fig. 5.12 through time. Initially, crystal 8 (the crystal at $\tilde{X} = 0.025$) is subject to a fairly low current. We can see that between approximately $5.6 \times 10^4$ and $5.7 \times 10^4$ s, a plateau in the current appears, which corresponds to the time during when the phase-boundary in Fig. 5.12a is propagating. At $t \approx 6.35 \times 10^4$ s, crystals 9 and 10 discharge together (a consequence of the many-particle effects as discussed above), but at a current approximately 5 times higher than crystal 8. This pushes crystals 9-10 into a regime where they do not phase-separate, as shown in Figs. 5.12b and 5.12c.

We might normally assume that the current entering each individual crystal would roughly correspond to 1.7 mA/g, given that we are discharging the entire cathode at 1.7 mA/g. This is clearly not the case, as it appears that the behaviour of nearby crystals can significantly influence the local applied current and Fig. 5.10a showed that only a small number of crystals discharge at any one time (and hence take the current load of the entire cathode). Surprisingly, a 1.7 mA/g rate corresponds to an individual crystal discharging at $1.53 \times 10^{17}$ A, which is much lower than the currents observed in Fig. 5.13. Given conservation of charge, this means that we must be removing Li$^+$ from crystals at some point in the cathode. We have already observed in Fig. 5.11 that crystals far from the intercalation front oscillate around their lower spinodal point, both intercalating and deintercalating through time. Fig. 5.13b shows the current entering crystals 300 to 320 (from $\tilde{X} = 0.9375$ to $\tilde{X} = 1$), close to the current collector. At $t = 5.6 \times 10^4$ s, these crystals are far from the intercalation front and are in fact deintercalating (as indicated by $I_c < 0$ for these crystals). At the same time, which as shown in Fig. 5.13, crystal 8 ($\tilde{X} = 0.025$) is intercalating with a current larger than 1.7 mA/g would suggest. We would note that crystals 300-320 ($\tilde{X} = 0.9375$ to $\tilde{X} = 1$) offsets the high rate applied to crystal 8. This process also explains the larger voltage (and concentration) spikes observed in Fig. 5.9 (and Fig. 5.11) towards the end of discharge. As the intercalation front moves through the cathode, there are a smaller fraction of undischarged crystals remaining in the cathode to offset the higher current applied near the intercalation front, resulting in greater amounts of Li$^+$ deintercalating from the remaining crystals.

The idea that adjacent crystals in a cathode could be subject to different current loads could perhaps be expected in the case of poor electrical conductivity, with certain crystals better connected to the carbon network. The results shown here however, are purely driven by the many-particle effects described by Dreyer et al. [79], and occur whenever we constrain the global flux applied to a system made up of many particles with non-monotonic equilibrium potentials. Surprisingly, we did not anticipate such a
large difference between the observed local current ($\sim 10^{-14}$ A) and the average global current ($\sim 10^{-17}$ A at 1.7 mA/g). Not only is the entire current load of the cathode applied to a small number of crystals, but additional current is applied due to the crystals far from the intercalation front deintercalating. This implies that the global current applied in a many-particle system cannot be used as an analogue for the local current applied to individual crystals.

Importantly, a rate of 1.7 mA/g in our model corresponds to a local current that is very close to the point when a crystal governed by the depth-averaged equation without strain will fill homogeneously (as shown in Fig. 5.12). As the phase-separating nature of the depth-averaged equation is very closely linked to the applied current, this means that many-particle effects, by raising the local current applied to an individual crystal, may also work to suppress phase-separation. This is particularly important when considering how individual crystals phase-separate under set currents [28, 30]. It may be that for crystals where phase separation is suppressed at higher currents (i.e., those with 1D Li$^+$ diffusion), phase-separation only occurs at very low cathodic currents, lower than might be implied by individual crystal simulations.

The many-particle effects outlined above are intimately related to both the current and the timescale of the reaction on the crystal scale. Thus far, we have only considered the impact of decreasing $\tau_0$ and the discharge rate. Equation (5.3.3) from Ferguson and Bazant [53] also implies that the number of active particles can increase as either the discharge rate or $\tau_0$ is increased. This is visible in Fig. 5.8a, where the voltage spikes begin to disappear at higher currents. This is because at high rates, all of the crystals in the cathode begin to discharge together (as $n_{ap}$ is large). The disappearance of voltage spikes also implies that each crystal is receiving a local current that is very close to the globally applied discharge rate. Equivalently, we can increase $\tau_0$ and see the same effect. Fig. 5.14 shows the result from discharging a cathode at 17 mA/g with $\tau_0 = 1000$ s, and we can see in Fig. 5.14a that the entire cathode discharges homogeneously. There is no intercalation front moving across the cathode and the individual crystals are also discharging homogeneously, as was the case for $\tau_0 = 1$. The corresponding discharge curve is shown in Fig. 5.14b and we can see that we can see that the potential begins to decrease monotonically. Importantly, this result reflects the comments of Ferguson and Bazant [53], who note that the behaviour of a cathodic-scale discharge curve can be unrelated to whether or not individual crystals in the cathode are phase-separating. We observed flat voltage profiles in Fig. 5.8a as the cathode was “phase-separating”, with an intercalation front moving through the cathode, even though the individual crystals were filling homogeneously.
The nonlinear behaviour observed in these many-particle systems is very interesting and is reflected in the various model outputs from both Dreyer et al. [79] and Ferguson and Bazant [53]. Dreyer et al. [79] make the point that in a normal cathode (made up of $10^{12}$ to $10^{17}$ individual crystals), these voltage spikes would average to a smooth voltage plateau. The nature of our one-dimensional cathodic equations however, means that the size and number of the voltage spikes seen in our simulations are not influenced by the number of node points used in the discretisation of the cathode scale equations. The number of active particles, $n_{ap}$, and hence the number of voltage spikes seen in our simulations is governed by (5.3.3), which does not depend on $n_{cath}$. To test this, we simulated the same discharge as plotted in Fig. 5.9a with $n_{cath} = 6400$, instead of $n_{cath} = 320$ and the cell potential (along with every other variable) did not change. As such, the discrete filling observed should not be confused with a grid-size dependant
discretisation effect. To smooth out the voltage spikes, we likely require a two or three
dimensional distribution of crystals in the crystal (as opposed to the one-dimensional
distribution in this work), which would give an equivalent circuit diagram like that in
Dreyer et al. [79] and Ferguson and Bazant [53], with crystals wired both in series (like
in this work) and in parallel.

Quantifying $\tau_0$

There are a range of dynamics, outlined above, which can occur in the two-scale model
as $\tau_0$ is varied. In general, we observed that a small $\tau_0$ (but not so small as to violate
the depth-averaging assumptions of surface-reaction limited crystals, see Section 5.3.3
where we show that $\tau_0 \lesssim 1 \times 10^{-4}$ results in diffusion-limited crystals) can give dis-
charges that occur “one-by-one”, with individual crystals (or small blocks) discharging
in sequence throughout the cathode (as observed in Fig. 5.10 for example). We could
consider this to be a cathodic discharge that is “phase-separating”, in that there are
regions of the cathode that are either fully lithiated or unlithiated. This is separate to
the phase-separating nature of an individual crystal, and results in discharge curves on
the cathode scale that show voltage plateaus. Large $\tau_0$ gives cathodes that fill homoge-
neously (see Fig. 5.14), in that all the crystals in the cathode discharge simultaneously
(again this is separate to the crystal-scale behaviour). This results in a monotonic
decrease in the cell potential through time.

We can consider $\tau_0$ (s), the mean time scale of reaction, as a component of the exchange
current density $i_0$ (A m$^{-2}$), which is given by (5.2.10). With $\tau_0 = 1$s, the value used
to generate Fig. 5.8a, the equivalent exchange current density is $i_0 = 0.615$ A/m$^2$.
This is quite large, especially when compared to the value obtained from fitting our
shrinking-core based model to the Zheng et al. [169] data in Section 5.3.1, namely
$i_0 = 5 \times 10^{-4}$ A/m$^2$. If we instead calculate the $\tau_0$ that results from an exchange
current of $i_0 = 5 \times 10^{-4}$ A/m$^2$, we recover $\tau_0 = 1228.99$s. This is very similar to
the value we examined in Fig. 5.14, which displayed a monotonic decrease in the cell
potential, somewhat like the Zheng et al. [169] data at high rates.

A large $\tau_0$ implies that the reaction, (5.2.1), is slow, which results in reaction kinetics
limiting the discharge of a cathode. Given Fig. 5.14b, it is therefore possible that slow
reaction kinetics may be responsible for the reduced capacity (and somewhat sloped
discharge curves) at high rates observed by Zheng et al. [169]. As noted, a large $\tau_0$
implies a small $i_0$, and although we may see (slight) slopes in the voltage at low rates,
as the discharge rate is increased, the cell potential exhibits larger voltage drops. This
is even evident at the low rate of 1.7 mA/g, with the voltage curve in Fig. 5.14b decreasing by approximately 0.025 V in early times when compared with Fig. 5.8a. Fig. 5.15 shows an attempt to match the 1700 mA/g curve from Zheng et al. [169] with increasing values of $\tau_0$. We can see there is no value of $\tau_0$ between 1 and $1 \times 10^5$ that matches the experimental data. In particular, the entire discharge capacity of the cathode is used for all values tested in Fig. 5.15. The $\tau_0$ values tested correspond to an exchange current density, $i_0$, between 0.615 and $6.15 \times 10^{-6}$ A/m$^2$ (this range includes the $i_0$ value used in Section 5.3.1).

We can see that at higher $\tau_0$ values in Fig. 5.15, the reaction is too slow to accommodate the discharge rate and the cell potential decreases considerably. Unfortunately, this does not result in better fits of the Zheng et al. [169] data. The cell potentials do begin to curve, (like Fig. 5.14b), which is representative of the cathode filling homogeneously. Given a different voltage cutoff, we could reduce the observed capacity of the model (e.g., a voltage cutoff of 2.7 V in Fig. 5.15 for the $\tau_0 = 1 \times 10^5$ s curve would result in a capacity of approximately 100 mAh/g). This however, would produce a discharge curve very different to those from the Zheng et al. [169] data, where even at a discharge rate of 3400 mA/g (see Fig. 5.8a), there is a distinct voltage plateau and a sharp drop-off (the 8500 mA/g curve however, does not show a voltage plateau and could possibly be explained by kinetic limitations). This result shows that we could not fit the Zheng
et al. [169] data by assuming that the reaction kinetics in the model are slow (i.e., that $\tau_0$ is large).

We would argue that a large $\tau_0$ seems unlikely, especially given that the time scale of a single reaction step given by (5.2.1), if calculated using $i_0 = 5 \times 10^{-4}$ A/m$^2$, is almost 20 minutes. One could also argue that our computation of the activities in both the solid and the electrolyte at the reference state ($t = 0$) in (5.2.9) may be incorrect, resulting in a misleading $\tau_0$ value given a fixed $i_0$. Regardless of the exact value of $\tau_0$ and the fitting observed in Figures 5.8a and 5.15, the results in this section show that $\tau_0$ could be quantified by examining a complete LiFePO$_4$ cathode under different discharge rates. A small $\tau_0$ would result in a cathode filling discretely, with a distinct intercalation front visible. A large value would instead give a cathode where all of the crystals fill simultaneously. These distinct behaviours are a consequence of the many-particle effects described above, which is dependant on the ability of individual crystals to “communicate” with the remaining crystals in the cathode. Low electrical conductivity or electrolyte limitations in the cathode may hamper these effects, though it may be possible to directly observe the lithiation of an entire cathode in a manner similar to that used by Harris et al. [185] to observe a Li$^+$ intercalation front in graphite electrodes, and hence qualitatively determine $\tau_0$.

As mentioned, the depth-averaged model is only valid in an SRL regime (i.e., large $\tau_0$), and given the inability of the two-scale, depth-averaged based model to fit the Zheng et al. [169], we now examine the use of the 2D CHR equation on the crystal scale, given it is valid for all values of $\tau_0$.

### 5.3.3 2D CHR

*Fitting to Zheng et al. [169] data*

When using the 2D CHR equation on the crystal scale, we have a greater number of parameters to set. Namely, both the diffusion and gradient penalty tensors ($\mathbf{D}$ and $\mathbf{K}$ respectively). The diffusivities, $\mathbf{D}$ (m$^2$/s) in particular, have been measured in various crystallographic directions in several studies (see Amin et al. [116] and Amin et al. [86] for examples). In the presence of defects, the diffusivity of Li$^+$ in LiFePO$_4$ material may move from a one-dimensional (anisotropic) process to a possibly three-dimensional (isotropic) process. We have discussed this in a previous paper [172] along with the effect that two-dimensional Li$^+$ transport has on phase-separation in the SRL discharge of an individual crystal.
In this work, we use the same $K$ and $D$ as Dargaville and Farrell [172] (see Table 5.4) and hence consider the cathodic-scale discharge of crystals governed by two-dimensional Li$^+$ transport in the presence of defects. Individual crystals governed by the 2D CHR equation, discharged with the parameters from Dargaville and Farrell [172], phase-separate, even at high currents. Our use of the parameters from Dargaville and Farrell [172] with the 2D CHR equation is in an attempt to examine the impact of phase-separating crystals on cathode scale discharge curves, particularly at high currents, given that the depth-averaged equation used in Section 5.3.2 will never exhibit phase-separation at high currents.

Before setting a small $\tau_0$ and diffusion-limiting the crystals, which the previous sections suggest is necessary to fit the Zheng et al. [169] data, we first decided to examine the effect of two-dimensional Li$^+$ transport in a SRL many-particle cathode. Fig. 5.16 shows the results from comparing the two scale, 2D CHR based model to the experimental data from Zheng et al. [169]. We see that the results are very similar to that shown in Fig. 5.8a, with the full capacity of the cathode used at all discharge rates. We also included the 8500 mA/g discharge in Fig. 5.16 (that is very similar to the 8500 mA/g
discharge in Fig. 5.8a that was not shown) and we see a (slight) monotonic decrease in potential. Given the results of the previous section (see Figures Fig. 5.14b and 5.15), this is due to the cathode filling homogeneously (again, not necessarily the crystals) due to kinetic limitations at such a high discharge rate (even with $\tau_0 = 1$).

In Fig. 5.16, we set $\tau_0 = 1$ (and hence used the same $i_0$) as in Fig. 5.8a. We therefore expected Fig. 5.16 to show similar results to Fig. 5.8a as this is well within a SRL regime, and the only mechanism we have identified to limit the discharge, namely diffusion limitations in the solid, does not occur in this regime. We also note that at discharge rates of 17 mA/g and 340 mA/g, we see the voltage spikes characteristic of many-particle effects as described in Section 5.3.2. These effects are identical to those observed with the depth-averaged system and as such we do not discuss them further here.

We do see one key difference when compared with the depth-averaged discharge of Fig. 5.8a, and that is the presence of phase-separation in every crystal through the cathode, at all discharge rates tested. This shows the effect of using two-dimensional Li$^+$ transport in the solid in an SRL regime and is consistent with the results of Dargaville and Farrell [172]. Fig. 5.17 shows this, with the concentration distribution of Li$^+$ in a crystal at the separator ($X = X_i$) plotted through time, for the 8500 mA/g discharge in Fig. 5.16. Even at this very high rate, phase-separating regions are clearly visible. This is in contrast to the depth-averaged based model, where phase-separation is suppressed at such discharge rates. We should also note that at low-currents, where many-particle effects are increasing the local current applied to a crystal (see Section 5.3.2), we still see phase-separation when using the 2D CHR equation in the crystals. This is because phase-separation in individual crystals with 2D Li$^+$ transport is still prominent at high currents. Again, this emphasises that the voltage plateaus seen in the cell potentials are due to the formation of intercalation waves in the cathode (as discussed in Section 5.3.2). Both Figures 5.8a and 5.16 show voltage plateaus, though the crystals in Fig. 5.8a fill homogeneously, in contrast to the crystals in Fig. 5.16 that phase-separate.

The phase-separation observed across all currents when using the 2D CHR equation on the crystal scale has no effect on the ability of the model to fit the Zheng et al. [169] data. In part, this is because, as noted in Dargaville and Farrell [172], discharging crystals with two-dimensional Li$^+$ transport that phase-separate (in an SRL regime) exhibit voltage curves almost identical to those seen in crystals with one-dimensional Li$^+$ transport that fill homogeneously. Given that, as discussed in Section 5.3.2, electrolytic, electronic and kinetic resistances cannot explain the limited capacity observed
Figure 5.17: Dimensionless Li\textsuperscript{+} concentration in a crystal at the separator ($X = X_i$) through time with DR=8500 mA/g.
by Zheng et al. [169], we now turn our attention to a 2D CHR regime where diffusion limitations in the solid are dominant.

In order to discharge the two-scale model in a regime where the crystals are diffusion-limited, we decrease $\tau_0$, while keeping the diffusivities at the experimentally measured values. Diffusion limitations in the solid become prominent with $\tau_0 \lesssim 1 \times 10^{-4}$ (this is discussed further in Section 5.3.3 and we should also note that $1 \times 10^{-4} < \tau_0 < 1$ results in SRL discharges and hence match the results shown in Fig. 5.16)), however setting $\tau_0$ to be small increases the stiffness of the system considerably and our numerical approach fails to converge (for $\tau_0 \lesssim 1 \times 10^{-4}$). We tried modifying several numerical parameters in an attempt to overcome this, including adjusting the absolute and relative tolerances, increasing the bandwidth of the preconditioner, increasing the dimension of the Krylov subspace used in the JFNK solver and increasing the number of nodes used on the cathode and crystal scales, but could not find an approach that would converge. Unfortunately this means that we could not obtain any fits to the Zheng et al. [169] data using the 2D CHR equation in a diffusion-limited regime.

Given the discussion regarding choices for $\tau_0$ in Section 5.2.1 and possible mechanisms that might explain the reduced capacity observed at high rates in the Zheng et al. [169] data, our argument in this work has been that diffusion-limitations in the crystal seem the most likely to explain the decrease in capacity. There are a range of choices for $D$ (see the table in Dargaville and Farrell [172]), $K$ [28, 30] and $\tau_0$ in the 2D CHR equation that can generate diffusion-limited crystals. Unfortunately, we could not find any combination of these parameters that would result in diffusion-limited crystals and allow convergence when embedded in the two-scale model. We would argue that the validation exercise performed in Fig. 5.16 is therefore not representative of the ability of the 2D CHR equation to represent the discharge of LiFePO$_4$ material, particularly given that the parameter regime where the model may fit the data is to date, numerically inaccessible. Given the range of important processes neglected by our use of the 2D CHR equation, namely anisotropic elastic strain [30], along with the possibility of 3D Li$^+$ transport in the presence of defects, an argument could be made (as we do in Dargaville and Farrell [172]) that full 3D simulations of LiFePO$_4$ may be necessary. This may affect the ability of a two-scale model to fit the experimental data, though moving to three dimensions on the crystal-scale or including equations that govern the anisotropic elastic strain throughout a crystal would only increase the stiffness of the problem, making numerical solutions even more challenging to achieve.
Diffusion-limited single-crystal discharges

In the previous section, we attempted to use diffusion limitations in the crystal scale to reduce the discharge capacity of the two-scale model outlined in Section 5.2, but were unable to simulate this parameter regime due to numerical difficulties. As such, we decided to discharge individual crystals in a diffusion-limited regime to see if the discharge capacity of an individual crystal could be reduced in a manner similar to that seen on the cathode scale in the Zheng et al. [169] data. Previously [172] we discharged individual crystals by applying a fixed current across the surface to illustrate the effect of two-dimensional Li$^+$ transport with $\tau_0 = 1$, which is well within a SRL regime.

We take same approach here, with $\mathbf{D}$ set at the values used in this work and Dargaville and Farrell [172] (see Table 5.4), but with $\tau_0$ small, ensuring that the timescale of the reaction is quicker than that of diffusion. We also modified $\mathbf{K}$ from the value used in Dargaville and Farrell [172]. An orthotropic $\mathbf{K}$ was used in Dargaville and Farrell [172] to enable crystal-scale comparisons to be made with the depth-averaged equation. Without anisotropic elastic strain [30], an anisotropic $\mathbf{K}$ also controls the alignment of the phase-boundaries and promotes phase-separation parallel to the $y$ axis in Fig. 5.17. The parameter $\mathbf{K}$ however, is more likely isotropic (though an isotropic $\mathbf{K}$ does nothing to change the fitting results shown in Fig. 5.16) and so when applying
Figure 5.19: Concentration profile in an individual crystal discharge [172] with $\tilde{I}_c = 8$, $\tau_0 = 1 \times 10^{-4}$ s and $K_{yy} = K_{xx}$.

diffusion-limitations in a single crystal discharge as below, we set $K_{xx} = K_{yy}$.

Fig. 5.18 shows the results from discharging an individual crystal with $K_{yy} = K_{xx}$ and $\tau_0 = 1 \times 10^{-4}$ s. We have used a dimensionless current in Fig. 5.18 (see Dargaville and Farrell [172]) and should note that the nondimensionalisation used for the current in the individual crystal discharges in Fig. 5.18, $\tilde{I}_c$, cannot be compared directly with the dimensionless current in Dargaville and Farrell [172] as the parameter $\tau_0$ is used in the nondimensionalisation (and we use a different $\tau_0$ when compared with Dargaville and Farrell [172]). We can see in Fig. 5.18, that as we increase the dimensionless current, we can successfully constrain the discharge of an individual crystal. The discharge curves in Fig. 5.18 do not feature a voltage plateau like those from the Zheng et al. [169] data, but we would again note that the curves from Zheng et al. [169] are cathodic-scale cell
potentials, with Fig. 5.18 from individual crystal discharges. The potentials on each scale can differ considerably. As an example of this, see Figure 9b in Dargaville and Farrell [172], where the potential is given for individual crystal discharges when using the 2D CHR equation with isotropic Li⁺ transport in an SRL regime. These potentials look very different compared to the cathode-scale discharge curves in Fig. 5.16, even though the cathode in Fig. 5.16 is comprised of crystals governed by the 2D CHR equation, with the same parameters as used in the individual crystal discharges shown in Figure 9b in Dargaville and Farrell [172].

We see in Fig. 5.18 that an individual crystal discharged at \( \tilde{I}_c = 8 \) only utilises approximately 40% of its capacity. This is because significant concentration gradients form in the \( y \) direction near the surface of the crystal, which block the intercalation of further lithium into an ion channel. This is visible in Fig. 5.19, where the concentration of Li⁺ in the crystal is shown through time (with the corresponding mass fractions), for the \( \tilde{I}_c = 8 \) case shown in Fig. 5.18. We can see that throughout time, concentration gradients have formed in the \( y \) direction, as expected. We should note that these concentration gradients are different to the phase-boundaries presented in SRL simulations in Dargaville and Farrell [172]. At a mass fraction of 0.402, the lithium concentration at the \( xz \) surface of the crystal has reached 1. Lithium in the electrolyte therefore cannot intercalate at the surface until the lithium in the solid has diffused away from the surface (this is the definition of a diffusion-limited problem). This shows it is possible to diffusion limit a single crystal with small \( \tau_0 \) and experimentally derived diffusivities using the 2D CHR equation.

5.4 Conclusions

In this work, we examined the ability of several mathematical models of LiFePO₄ cathodes to fit recent experimental data where major electronic and electrolytic resistances have been removed. When validating against such a cathode, the crystal-scale model used becomes the major factor in determining the goodness of fit. In the absence of some unaccounted for physical phenomenon (perhaps surface “wetting” [139] and the role of size-dependent nucleation in a porous cathode model with a distribution of particle sizes, or increasingly sophisticated kinetic models [54]), diffusion limitations in the crystal are the only mechanism that can constrain the discharge capacities of these cathodes at high rate as observed experimentally.
When using a shrinking-core model on the crystal scale, we can obtain moderate fits against the Zheng et al. [169] data by using a very low Li$^+$ diffusion coefficient, consistent with PITT/GITT measurements, but not with measured anisotropic values. Using a simple model, such a shrinking-core, results in fitting with an “effective” diffusion coefficient that encapsulates all of the neglected processes that may occur in LiFePO$_4$. The many-particle effects described by Dreyer et al. [79] also cannot be observed when using a shrinking-core model, as it is not thermodynamically consistent.

Phase-field models of Li$^+$ intercalation into individual crystals offer a great deal more flexibility and display results that match various experimental observations. We examined the use of a depth-averaged and 2D CHR equation on the crystal scale of our two-scale cathodic model. The depth-averaged equation is valid when the surface reaction is the rate-limiting step in a crystal and, perhaps not surprisingly, we found very poor fits to the Zheng et al. [169] data. This was because the depth-averaged equation implicitly assumes diffusion limitations are negligible, whereas we identified diffusion limitations as the most likely way to enable better fits against the Zheng et al. [169] data. As such, we turned to the 2D CHR equation on the crystal scale, with experimentally measured diffusivities based on the presence of defects. The 2D CHR equation is valid under all parameter regimes and when the surface reaction was rate-limiting, we recovered similar results to the depth-averaged case, except that all the crystals phase-separated at all discharge rates tested, in contrast to the depth-averaged equation where homogeneous filling was observed. This is because we used 2D diffusivities that reflect the presence of defects, which suppress homogeneous filling [172]. Regardless of the diffusivities used, in an SRL regime with the 2D CHR equation, as with the depth-averaged, adequate fits could not be obtained.

Moving to a regime where diffusion-limitations become prominent, we could not find a series of parameters that lead to numerical convergence when using the 2D CHR equation on the crystal-scale of the two-scale model, even though we used a numerical scheme designed for stiff problems, with high-order, adaptive time-stepping used in conjunction with a parallel, Krylov-based Newton solver. We were able to discharge individual crystals with the 2D CHR equation and show that diffusion-limitations can limit the discharge of individual crystals, however the two-scale system in a diffusion-limited regime was simply too stiff. We believe that given more advanced numerical techniques, solutions could be obtained with diffusion-limited crystals (as with the shrinking-core model) governed by the 2D CHR equation on the crystal-scale of a two-scale model, while retaining the advantages of a phase-field model and hence provide a better fit to the Zheng et al. [169] data.
In the two-scale model presented, we observed many-particle effects consistent with those reported by Dreyer et al. [79]. Importantly, we found that at low discharge rates, where crystals in the cathode fill discretely throughout the cathode (or in small blocks), the local current applied to individual crystals can be up to three orders of magnitude higher than the global discharge rate would imply. Conservation of charge forces a large number of crystals far from the intercalation front to deintercalate (and subsequently intercalate), resulting in spikes in the cell potential. This difference in local current means the phase-separating behaviour of an individual crystal at a set current may not be indicative of the phase-separating behaviour of a crystal in a many-particle cathode.

These many-particle effects may also allow the determination of \( \tau_0 \), the mean time scale of the reaction, which determines if a crystal is limited by the surface-reaction of diffusion-limitations. Our model results indicate that a qualitative analogue for \( \tau_0 \) is whether the cathode itself discharges homogeneously (separate to the crystal scale behaviour) at various discharge rates. The existence of voltage plateaus in the cell potential is determined by the cathodic scale behaviour, not the phase-separation of individual crystals, as we observed flat discharge curves in the presence of both phase-separating and homogeneously filling crystals. Existing theoretical models like those of Ferguson and Bazant [53] and Dreyer et al. [79], along with this work, show that the discharge behaviour and performance of \( \text{LiFePO}_4 \) is a highly nonlinear function of many variables on several size scales, that couple in unexpected ways.

We believe that phase-field modelling of \( \text{LiFePO}_4 \) has great validity, and in recent years has begun to explain a number of physical processes observed in \( \text{LiFePO}_4 \). If we are to have a truly predictive model of the discharge of \( \text{LiFePO}_4 \) cathodes, this complexity must be brought into a cathodic-scale model. This work has been an attempt at this process and shows the increasing numerical challenges that face multi-scale simulations of battery materials. Alternatively, traditional isotropic models of \( \text{Li}^+ \) intercalation, like shrinking-core based models, can be used to obtain acceptable fits using established mechanisms and extensive parameter fitting. We could have chosen to fit a phase-field based, two-scale model against data with severe electronic or electrolytic limitations. These limitations would overshadow the crystal-scale effects and most likely allow us to match experimental curves. The discharge of low-rate (\(<5\text{C}\)) \( \text{LiFePO}_4 \) cathodes where discharges are largely governed by these limitations are well modelled by existing work and we believe that further advances in modelling \( \text{LiFePO}_4 \) cathodes should be tested on high-rate data.
6. Conclusions

This chapter gives a summary of the research performed, followed by proposals for further work based on the findings presented in this thesis.

6.1 Summary and discussion

In Chapter 1, the objectives of this thesis were outlined. In this section, these objectives are restated and detail provided on how they were achieved throughout the thesis.

Objective 1: Develop a multi-scale mathematical model of LiFePO$_4$ cathodes

Chapter 2 developed a mathematical model of LiFePO$_4$ cathodes with three size scales, based on observed morphologies. The “crystal” size scale represented individual nano-sized crystals of LiFePO$_4$ and their discharge behaviour was modelled by a shrinking-core. The “particle” size scale was formed by considering a porous agglomeration of individual crystals, coated in carbon, with the “cathode” scale representing a porous collection of particles connected by a carbon network. The results from this model were validated against experimental data from Srinivasan and Newman [21] and fit well.

This validated model was then used to examine the effect of changing various manufacturing parameters, including both the size of the agglomerated particles and the cathode thickness. Importantly, at discharge rates of 855 mA/g, large agglomerates and thick cathodes both constrain the capacity of the cathode. This conclusion mirrors the construction of recent LiFePO$_4$ cathodes (i.e., cathodes developed since the publication of Srinivasan and Newman [21] in 2004), which can be discharged at rates much higher than 855 mA/g, as agglomerates are eliminated through the careful introduction of carbon at various stages in the synthesis/manufacturing processes and the cathode thickness is often decreased to around 20 µm.

The success of the multi-scale approach described in Chapter 2 in fitting experimental data, even with a shrinking-core model on the crystal scale is mostly due to the large
agglomerates and thick cathode. These factors impact the discharge curves to a much greater degree than the behaviour on the crystal scale, allowing the use of a simple crystal scale model. For commercial battery materials (as opposed to cutting-edge material produced in small batches in a research laboratory) where the mixing/synthesis of carbon around individual crystals may not be feasible, the multi-scale model outlined in Chapter 2 works well.

**Objective 2: Develop an appropriate numerical method to solve phase-field models**

A least-squares based Finite Volume Method was developed in Chapter 3 to solve the Cahn-Hilliard and Cahn-Hilliard-reaction IBVPs that result from phase-field models of LiFePO$_4$. The FVM was chosen to discretise the equations as charge is conserved in battery systems and the existing numerical literature often does not show evidence of perfect mass-conservation for these equations. The CH and CHR equations are fourth-order PDEs and as such, implementing the BCs in a FVM framework can be difficult. A least-squares method, suitable for use on unstructured meshes, was used to estimate derivative values at quadrature points. This least-squares system explicitly included one of the BCs, which allowed a flux condition to be applied as required with the FVM.

The least-squares based FVM method was tested on both the Cahn-Hilliard IBVP (which enforces no-flux conditions on the boundary of the domain) and the Cahn-Hilliard-reaction IBVP (which enforces a flux condition), in both one and two dimensions. In terms of the relevant physicality constraints, the least-squares based FVM developed in Chapter 3 performed well. For the CH IBVP, in both one and two dimensions, mass conservation of the order of machine precision was observed, with the solution staying perfectly gradient-stable throughout the entire simulation (i.e., the free energy always decreased). The CHR IBVP is much stiffer, and while gradient-stable solutions were observed in one-dimension, the method failed to produce perfectly gradient stable solutions in two-dimensions, though the increase in the free energy was small.

**Objective 3: Apply two-dimensional phase-field models to the crystal-scale discharge of LiFePO$_4$ material and compare the results to existing reduced order models and to recently observed experimental phenomena**
In Chapter 4, a phase-field model was used to simulate the discharge of an individual crystal of LiFePO$_4$. These models were first applied to LiFePO$_4$ by Singh et al. [76] and their use has implicated many factors that modify the phase-separating behaviour of LiFePO$_4$, including current, crystal size and strain. In Chapter 4, the CHR IBVP in two-dimensions was used to examine how isotropic Li$^+$ diffusion may further affect this behaviour. Isotropic Li$^+$ diffusion has been observed experimentally and has been explained in recent years as a consequence of defects forming in the crystal lattice, which block lithium channels (in the $b$ direction) and hence impede the normally orthotropic diffusion of Li$^+$. Simulating this necessitated the use of the full CHR IBVP, as opposed to the simplified depth-averaged equation used by much of the literature. The least-squares based FVM from Chapter 3 was therefore used to obtain numerical solutions.

The inclusion of isotropic diffusion allowed phase-boundaries to form, even at high currents with isotropic coherency strain, which both work to suppress phase-separation. This implies that defects may fundamentally change the phase-separating behaviour of LiFePO$_4$, which is important as phase-separation can cause deformations in crystals, which can affect the cycling behaviour of a cathode. It also has implications for material synthesis and manufacturing (as the defect concentration is often determined by the synthesis method used). This result adds the dimensionality of Li$^+$ transport to the growing list of phenomena that affect the formation of phase-boundaries in LiFePO$_4$ material.

**Objective 4: Develop a mathematical model of modern LiFePO$_4$ cathodes that includes the crystal-scale model developed in Objective 3 and compare the results from such a model against both experimental data and existing models, including that developed in Objective 1**

Chapter 5 took the multi-scale framework outlined in Chapter 2 and removed the particle-scale, based on the elimination of agglomerates in modern, high-rate LiFePO$_4$ cathodes. Two different forms of phase-field models, namely a 1D depth-averaged equation and the 2D CHR equation, detailed in Chapter 4, were used on the crystal-scale of this model.

The results from these models were then compared to discharge curves from Zheng et al. [169] and poor fits were obtained when using both the depth-averaged and 2D CHR equations. This was due to the reduction in discharge capacity at high currents in the experimental curves of Zheng et al. [169]. In Chapter 2, the reduced capacity...
was due to electronic and electrolytic limitations, but in order to facilitate the high-rate discharges of Zheng et al. [169], those limitations have mostly been removed, leaving diffusion-limitations in the solid as perhaps the only common mechanism available to explain this behaviour. Better fits were obtained by using the (modified) shrinking-core based multi-scale model developed in Chapter 2, as diffusion limitations in the solid are easy to enforce, though this does not address any of the drawbacks of a shrinking-core model.

The depth-averaged equation cannot be used in a diffusion-limited regime, as it assumes that the surface reaction is the rate-limiting process (and all diffusivities are averaged out of the problem). The 2D CHR equation can simulate diffusion-limited material, though when embedded in a two-scale cathodic model, this leads to convergence failures in the numerical scheme. As such, with the 2D CHR equation, the validation exercise was performed in a surface-reaction limited parameter regime (though with isotropic diffusivities that the depth-averaged equation cannot simulate), resulting in the poor fits mentioned above.

The crystals governed by the 2D CHR equation in an SRL regime, as part of a two-scale cathodic model, phase-separated at all currents tested. The cathode scale voltage curves however, did not differ from when the depth-averaged equation was used on the crystal-scale and the crystals fill homogeneously. This means that the appearance of voltage plateaus in the cathode scale voltage curves are not influenced by whether the crystals in a cathode are phase-separating during discharge.

“Many-particle” effects were also observed when using phase-field models on the crystal-scale, consistent with those reported by Dreyer et al. [79] and required by any thermodynamically consistent battery model of phase-separating material. In particular, the model suggests that the local current applied to an individual crystal may be very different to the global current applied to the cathode. Given that current is heavily implicated in the phase-separating behaviour of individual crystals, this makes it difficult to infer if individual crystals in a cathode would be phase-separating based purely on the global current. The results presented in Chapter 5 do indicate that many-particle effects could be used to quantify the time scale of reaction in LiFePO$_4$, as at low currents, a small value of $\tau_0$ results in cathodes that discharge through the movement of an intercalation front, whereas a large $\tau_0$ results in a cathode where every crystal fills simultaneously. Quantifying $\tau_0$ is important, as it can be used to determine if LiFePO$_4$ crystals are limited by the rate of the surface reaction or Li$^+$ diffusion and therefore determine whether depth-averaging phase-field models is appropriate in LiFePO$_4$. 
6.2 Directions for further research

The outcomes of this thesis suggest a number of possible directions for future research, which are briefly discussed below.

Direction 1: Include both elastic strain and isotropic diffusivity in a 3D model of LiFePO$_4$ crystals

Chapter 4 showed the importance of considering isotropic diffusion in the presence of defects in LiFePO$_4$, which necessitates finding the solution of the 2D CHR IBVP. Cogswell and Bazant [30] showed that anisotropic elastic strain is also very important in predicting phase-boundary alignment in LiFePO$_4$. The work in Chapter 4 only included averaged, isotropic coherency strain. Combining both these effects would require the solution of the CHR IBVP in 3D, increasing the stiffness of the problem considerably. Tang et al. [85] examined the solution of a phase-field model for LiFePO$_4$ in 3D without applying a fixed current and hence did not examine the suppression of phase-separation. A 3D model of LiFePO$_4$ crystals, based on the CHR IBVP and constrained to discharge at a fixed-current, could simulate crystals across a range of parameter values and possibly shed further light on the phase-change dynamics in LiFePO$_4$ crystals.

Direction 2: Investigate the inclusion of nucleation mechanisms

The role of nucleation in phase-boundary formation, until very recently [139], has been neglected in phase-field models of LiFePO$_4$ material. The work in this thesis neglects any discussion of nucleation and assumes that phase-boundaries form when the concentration of Li$^+$ enters the spinodal gap. The work of [139] shows that nucleation is size-dependent in LiFePO$_4$ and hence a distribution of different crystal sizes in a porous electrode model may behave very differently than one with a single crystal size. These effects are currently being investigated [186], but not in connection with the 2D Li$^+$ transport shown in Chapters 4 and 5.

Direction 3: Investigate the loss of coherency in the lattice with a phase-field model

Coherency strain (as used by Cogswell and Bazant [30] and in Chapters 4 and 5) results from lattice mismatches between different phases in solid material. Cogswell
and Bazant [30] showed that coherency strain further suppresses phase-separation in LiFePO$_4$ during discharge and at equilibrium, the introduction of semicoherent interfaces between the two phases can change the alignment of phase-boundaries. When using this modelling framework, one must choose whether the phase-boundaries are coherent (or not) before the simulation begins. Cogswell and Bazant [30] acknowledge that the mechanism for the loss of coherency is also unknown. This mechanism should be investigated further and the inclusion of some process in a phase-field model that controls how coherent an interface is would be very useful, allowing the thermodynamics of the system to determine whether an interface loses coherency.

**Direction 4: Investigate more advanced numerical techniques for the solution of two-scale cathodic models that include diffusion-limited phase-field models on the crystal-scale**

The high-order, adaptive BDF time-stepping and parallel Jacobian-Free Newton-Krylov scheme used to solve the model presented in Chapter 5 did not converge when the 2D CHR IBVP on the crystal-scale was limited by the rate of Li$^+$ diffusion. As noted, this parameter space is crucial to the ability of the model to fit experimental discharge curves. More sophisticated numerical techniques should therefore be investigated in order to solve this model system. Preliminary investigations seem to suggest that the block-banded preconditioner in IDA should be replaced with a preconditioner that accounts for off-diagonal block couplings.
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