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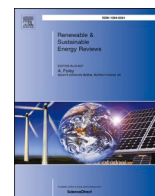
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Carbon binder domain networks and electrical conductivity in lithium-ion battery electrodes: A critical review

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ABSTRACT

In a drive to increase Li-ion battery energy density, as well as support faster charge discharge speeds, electronic conductivity networks require increasingly efficient transport pathways whilst using ever decreasing proportions of conductive additive. Comprehensive understanding of the complexities of electronic conduction in lithium-ion battery electrodes is lacking in the literature. In this work we show higher electronic conductivities do not necessarily lead to higher capacities at high C-rates due to the complex interrelation between the electronically conducting carbon binder domain (CBD) and the ionic diffusion within electrodes. A wide body of literature is reviewed, encompassing the current maxims of percolation theory and conductive additives as well as the relationships between processing steps at each stage of electrode manufacturing and formation of electronic conduction pathways. The state-of-the-art in electrode characterisation techniques are reviewed in the context of providing a holistic and accurate understanding of electronic conductivity. Literature regarding the simulation of electrode structures and their electronic properties is also reviewed. This review presents the first comprehensive survey of the formation of electronic conductivity networks throughout the CBD in battery electrodes, and demonstrates a lack of understanding regarding the most optimum arrangement of the CBD in the literature. This is further explored in relation to the long-range and short-range electrical contacts within a battery electrode which represent the micron level percolation network and the submicron connection of CBD to active material respectively. A guide to future investigations into CBD including specific characterisation experiments and simulation approaches is suggested. We conclude with suggestions on reporting important metrics such as robust electrical characterisation and the provision of metrics to allow comparison between studies such as aerial current density. Future advances in characterisation, simulation and experimentation will be able to provide a more complete understanding if research can be quantitatively compared.

1. Introduction

Lithium-ion batteries (LIBs) are almost universal in our portable electronic devices and demand is projected to increase significantly due to electric vehicle applications. Since their introduction to the market in 1990, energy and power density of these devices have undergone significant improvement [1–3]. The decarbonisation and electrification of transport will be driven using lithium-ion batteries in electric vehicles, and high specific energy densities are desirable for these applications

[1]. In addition, high-power charging of batteries is a clear objective for electric vehicles, both increasing desirability to consumers and increasing vehicle efficiency. It is expected that charging times of 10–15 min for energy dense cells is needed to achieve the widespread adoption of electric vehicles [2,4].

As many readers are already likely very familiar with the architecture of a Li-ion battery we will not labour this point, but a Li-ion battery typically comprises a graphite anode, a lithium metal oxide cathode, a liquid electrolyte with a mixture of organic carbonates, salts, and

Abbreviations: LIB, Lithium-ion battery; CA, Conductive Additive; CBD, Carbon Binder Domain; SEI, Solid Electrolyte Interphase; NMC, Nickel Manganese Cobalt Oxide; PVDF, Polyvinylidene fluoride; SEM, Scanning Electron Microscopy; TEM, Transmission Electron Microscopy; FIB, Focused Ion Beam; xCT, X-ray Computed Tomography; MIP, Mercury Intrusion Porosimetry; EIS, Electrochemical Impedance Spectroscopy; EC, Equivalent Circuit; PITT, Potentiostatic Intermittent Titration Technique; GITT, Galvanostatic Intermittent Titration Technique; DEM, Discrete Element Method; FEA, Finite element analysis; MD, Molecular Dynamics; CFD, Computational Fluid Dynamic; PBM, Population Balance Modelling; RN, Resistor Network.

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additives, as well as copper/aluminium current collectors and a porous separator. Processes that take place within the battery, whether within electrodes or at key interfaces, are central to enabling optimal operation.

A key target for much of the industry is to enhance the cell energy density, usually achieved by limiting the fraction of inactive components during cell assembly such as current collectors, conductive additives (CA), polymer binders and electrolyte [5]. To further improve energy content, thicker electrodes provide a better ratio of electrode to passive component (i.e. current collector and separator) in a cell [6–8]. There is, however, a dilemma in designing cells which require both high energy density and high power density, such as those required for electric vehicles with fast charge capabilities [9]. High resistance electrodes hinder the electro-kinetics of thick electrodes by limiting electron and mass transport. Not only does this lead to capacity loss, but Galvani potentials arising across both electrodes can lead to electrolyte decomposition at the positive electrode and lithium plating at the negative. Therefore, without specific consideration of these parameters, improvements in cell energy density often comes at the expense of power density and vice versa. In addition, lithium-ion cells with higher internal resistance lead to ohmic losses and heat generation which can potentially compromise safety.

In all electrode formulations, there is a conductive additive to improve the electronic conduction. We will describe its role in more detail below but, put simply, the primary purpose of the conductive material is to facilitate better electronic conduction throughout the electrode. Despite the widespread use of conductive additives, there is very little information about the optimal amount needed for a particular cell chemistry or electrode architecture. As a result, there are no targets for cell component specification, such as individual electrode resistance, which makes cell design more challenging.

The formation of electrical conductivity networks via active materials and conductive additives has a direct effect on pore structure, tortuosity, and electrolyte interactions [10]. This contribution will mainly focus on the electrical conductivity networks and the factors that govern their formation and properties. Based on this objective, manufacturing techniques of dry electrodes, characterisation techniques of carbon binder domain (CBD) and numerical modelling approach are all reviewed. The mass transport mechanism of Li ions in electrodes is primarily governed by pore properties and tortuosity. Substantial review works on ionic diffusion and relevant tortuosity factors have been widely published. For instance, a comprehensive review work of the fundamentals of ionic conduction is presented by Park et al. [11]. Ionic transport properties could be affected by advanced electrolyte material, electrode design and tortuosity. The recent progress in electrolyte materials and tortuosity calculation approach has been presented in previous review papers [12,13].

It is expected that this review can be used in conjunction with the existing knowledge of ionic conduction for a comprehensive understanding of complex transport mechanisms within electrodes.

1.1. Electrode structure and performance

Conductivity networks (both ionic and electronic) are of great importance to make a complete circuit and allow correct battery function. There is increasing scientific evidence that high performance electrodes have a mixture of short-range and long-range pathways [14–18]. A schematic representation of a battery electrode cross section is presented in Fig. 1. The active material particles (shown in orange) are embedded within a network of conductive additive and polymeric binder; the so-called carbon-binder domain, CBD (black particles), with interstitial pores are filled with liquid electrolyte. We define long-range electronic contacts as the interconnected percolation network that span between the active material particles and are in the 0.1–10 μm range. Short-range contacts refer to the nearest neighbour interactions between CBD and active material on the 1–100 nm length scale, and are schematically represented in Fig. 1. The interplay of these two forms of electrical contact and their effect on electrode rate capabilities and increased electrode thickness is currently an active area of research [16, 17,19,20].

For anode electrodes, although the graphite active material has higher electronic conductivity than typical cathode active materials, the consequence of Galvani potentials can be severe, potentially leading to lithium plating and dendrite growth. Understanding of conductivity networks is therefore important for both anode and cathode applications.

Carbon conductive additive materials are used in both positive and negative lithium-ion electrodes to decrease electrical resistance. Since conductive additives do not play a significant role in the electrochemical redox process their presence reduces the total energy density, and their content is kept below 10 wt% in electrodes produced for academic research. In commercial electrodes the carbon content is typically below 2 wt%. However, there is currently no fundamental insight into the minimum quantity of conductive additive, where it should be located in the electrode, or what combination of long or short pathways lead to the best cell performance.

The incorporation of conductive additives invokes secondary implications on the electrode structure which have important effects on performance. These secondary effects include changes to electrode porosity and tortuosity, electrode compressibility and mechanical properties, active material and binder interactions, electrolyte reservoirs and wettability, solid electrolyte interphase (SEI) formation, and electrode thermal conductivity [21–23]. These secondary parameters are

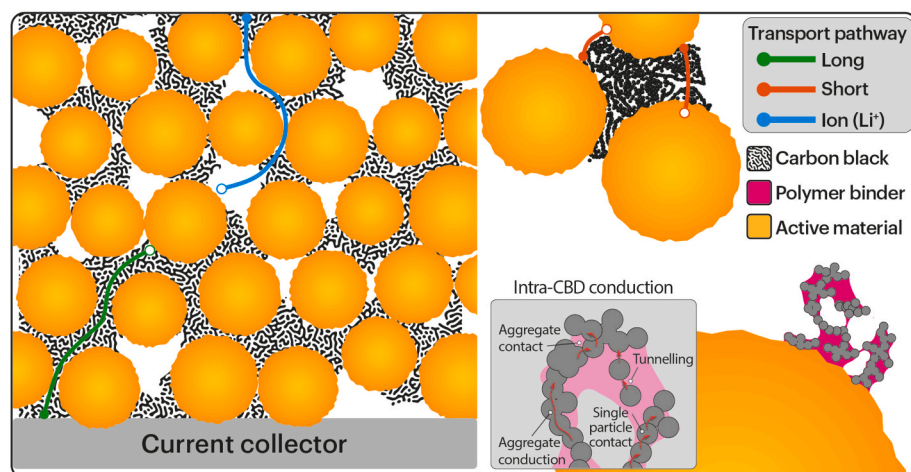


Fig. 1. Highlights the range of electronic conduction pathways length scales, from ultrashort carbon black clusters to long, electrode-wide links. In this figure cathode active material (NMC is shown here) is connected by a microporous carbon black/binder composite, also known as CBD. White space is open pores. The nature of the structure of the carbon black in the binder determines the electronic properties of the composite, shown in the expanded panels on the right, where long and short pathways develop during processing. Furthermore, the complex, microporous structure of the CBD also influences the ionic conductivity, frustrating the pathway of ions (leading to higher tortuosity) and acting as electrolyte reservoirs.

important to consider when incorporating electrode conductive additives.

1.2. Electronic conduction fundamentals

Electrical properties of materials fall broadly into three groups: insulator, conductor or semiconductor. These properties originate from their band structure as described by quantum theory [11,24]. The band gap for a number of widely used lithium-ion battery materials can be found here [11].

The electrical conductivity of binary mixtures of powders each with significantly different conductivity can be described by percolation theory [25–27]. According to percolation theory, the electronic conductivity of a composite above the percolation threshold is expressed by Equation (1), where $\sigma_{c,0}$ is the electronic conductivity of the conductive additive, ν is the volume fraction of the conductive additive, ν_c is the percolation threshold and t is the critical exponent [28]. In this way the electronic conductivity of an electrode is determined based on the volume fraction of conductive additive in the electrode. S. Mandal et al. [29] reported values of 0.03 and 1.7 for the percolation threshold and critical exponent respectively, for LiMn_2O_4 with carbon black conductive additive.

$$\sigma = \sigma_{c,0}(\nu - \nu_c)^t \quad (1)$$

Other equations have been used to simulate the electronic conductivities of positive electrodes, predominantly based upon the work of Newman [30,31]. This pseudo 2D model uses a constant electrical conductivity value to describe the conductivity of the whole electrode [28,32].

As an example, consider a series of lithium-ion battery cathode composed of semiconducting cathode active materials, insulating polymer binder and increasing amounts of conductive additive carbon black. The electrical percolation network is established when the electronically conducting conductive additive has reached its percolation threshold (T_c). Fig. 2a depicts a typical profile of resistivity as a function of conductive material content. The percolation threshold (T_c , Fig. 2a) is clear by the sharp decrease in resistivity when a critical fraction of the electronic conductor is reached. This threshold can be considered as the point at which sufficient high conducting material is present to form the conducting path through the entire electrode. This path may form from direct electrical contact between conductors or through electron tunnelling when distances are allowable [33]. The tunnelling component is important for battery electrodes where insulating polymer binder may be adsorbed between the surfaces of contacting conductive additive (also shown in Fig. 1) [34,35]. It should be noted that the percolation threshold depends on the type of conductive additive. It is much lower

for carbon nanotube (CNT) due to higher aspect ratio (Fig. 2b).

Percolation theory is useful for understanding the long-range conductivity pathways within battery electrodes. However, the component contributions to overall conductivity such as carbon black conductivity, number and physical nature of direct electrical contacts and the number of and nature of tunnelling contacts are difficult to accurately determine in real structures [37]. In addition, the nature of the short-range electrical contacts that might help facilitate reactions on active material sites is not described by percolation theory but may influence electrochemical performance. The discussion herein provides a comprehensive understanding of the complex interactions within battery electrodes which must be considered when trying to understand the intricacies of battery electrode structures.

1.3. Additive materials

1.3.1. Conductive additive structure

Typical carbon-based conductive additive properties are strongly dependent on the carbon structure and physical properties. The most common structures of carbon conductive additives can be broken down into two families, graphite and carbon black (CB). Graphites are used to enhance conductivity, in both the positive and negative electrodes. Graphite conductive additives differ in structure from the sphericalised graphite, mesocarbon and hard carbon coated graphite powders which are also used as active materials. The primary use of graphite conductive additive in the negative electrode is to aid electron percolation pathways and reduce the high contact resistance between the surface-treated graphite active material. However, graphite conductive additives can contribute some reversible capacity within the negative electrode which has led to the term ‘conductive, active additives’ [22]. The addition of graphitic conductive additives can lead to increased electrode density after calendaring and improved electrical conductivity by reducing the spring back effect during calendaring [22,23].

Carbon black has a hierarchical structure built from primary particles typically ranging from 30 to 40 nm and are fused together to form larger CB secondary particles (Fig. 3). The primary particles have turbostratic graphitic surface characteristics and amorphous cores, shown in Fig. 3b. The ‘structure’ of an aggregate describes the morphology which can vary from being fibrous to clustered in nature (examples are shown in Fig. 3 right). The structure of an aggregate therefore considers the inter-aggregate spaces and number of interstices within [38]. Hence aggregates with ‘high’ degrees of structure, pore nano/micro-porous, will contain larger internal porosity and surface area which can affect electrolyte uptake and SEI formation. In addition, higher degrees of structure adsorb more polymeric binder onto their internal surfaces, where it is less likely to perform its mechanical function and bind

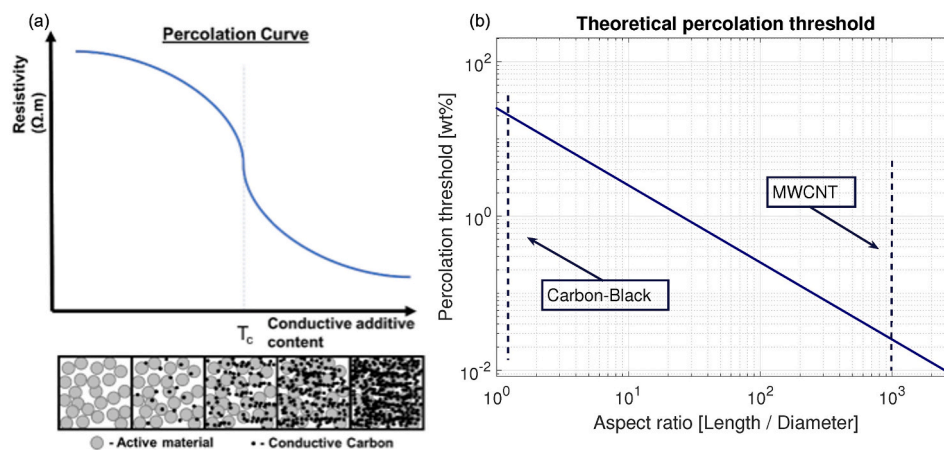


Fig. 2. (a) Depiction of a percolation curve for binary mixture of insulating active material particles and conducting carbon. (b) Percolation threshold decreases with increasing aspect ratio of conductive additives [36].

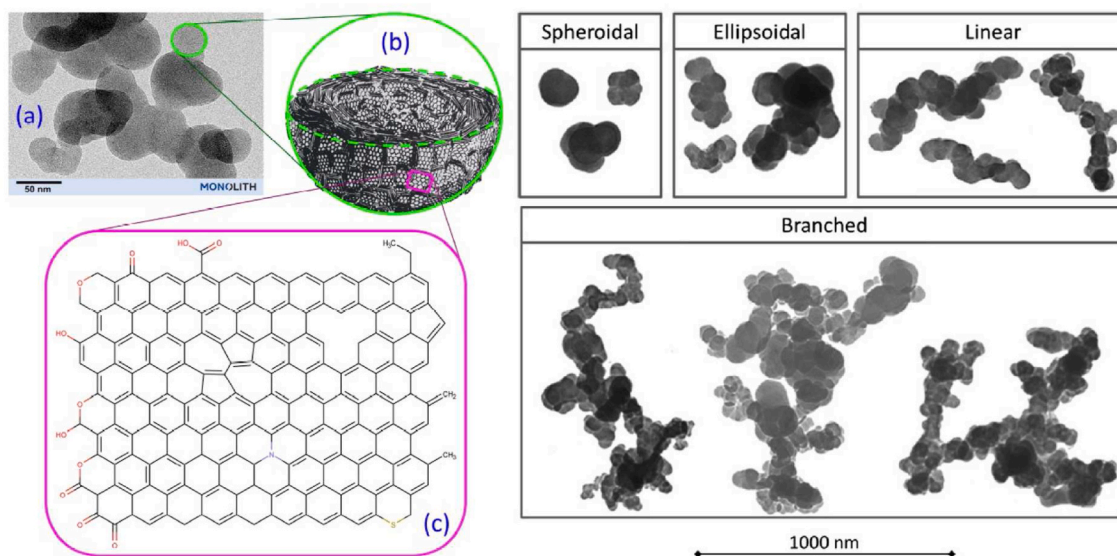


Fig. 3. (a) TEM micrograph of a branched carbon black aggregate. (b) Carbon black primary particle highlights the turbostratic graphite layers. (c) Surface structure and functionalized surface. Right: Various morphological categories of carbon black types. From Refs. [41,42].

individual particles together. Finally, the higher surface area CBs have been shown to accelerate metal ion dissolution at the positive electrode [39]. Spahr et al. highlight the importance of primary particle surface chemistry, aggregate size and structure, and the surface area on the rationale of conductive additive decision making for battery electrodes. It is a common for a combination of CB and graphite conductive additives to be used, drawing on the benefits of both additives, to produce low resistivity and mechanically robust electrodes [22,23,40].

1.3.2. Unconventional conductive additives

Particulate carbon (carbon black, acetylene black, graphite powder) is the conventional conductive additive of choice for LIBs. Alternative conductive additives exist in terms of metal powders [43], metal fibres [44], vapour grown carbon fibres [45], carbon nanotubes [20,46,47], graphene [48–50], and conducting polymers [47,51,52].

Addition of copper or silver metal powders in low concentrations (<1%) to the LFP cathode resulted in improved capacity delivery and cycle life performance. This enhancement is achieved due to increased electronic conductivity offered by the metal powders [43]. Similarly, stainless steel fibres as conductive additives have been shown to provide low electrode resistances and high rate capabilities [44]. Carbon nanomaterials exhibit superior properties compared to metal powders or

fibres in terms of low weight, high chemical resistance and high specific surface area [53]. Fibrous carbon such as vapour grown carbon fibres and carbon nanotubes (CNTs) have high aspect ratio (>100) compared to the particulate carbon. As shown in Fig. 2b, high aspect ratio conductive additives like CNT are more efficient in increasing overall electronic conductivity for a given weight fraction [36]. Due to high flexibility and tensile strength of the fibrous carbon, it can maintain long range contacts between AM particles after long-term cycling, thus improving the cyclic performance of the battery [53,54]. Whereas long-range connectivity can degrade for particulate carbon after long-term cycling (Fig. 4a).

Performance of carbon black, graphene, and carbon nanotubes has been compared in terms of out of plane electronic conductivity (σ_{OOP}) and characteristic time (τ). For CNT, high values of σ_{OOP} and low values of τ are possible, implying good rate performance as compared to carbon black and graphene [56]. Although fibrous carbon has better long-range connectivity, the ability to effectively manipulate the short-range contact points between these conductive additives and active material surface hinders their electrochemical performance [53]. Fibrous CNTs can entangle each other resulting in poor slurry dispersion and therefore non-uniform distribution in the dry electrode [48]. For more information on fibrous carbon readers are referred to respective review studies

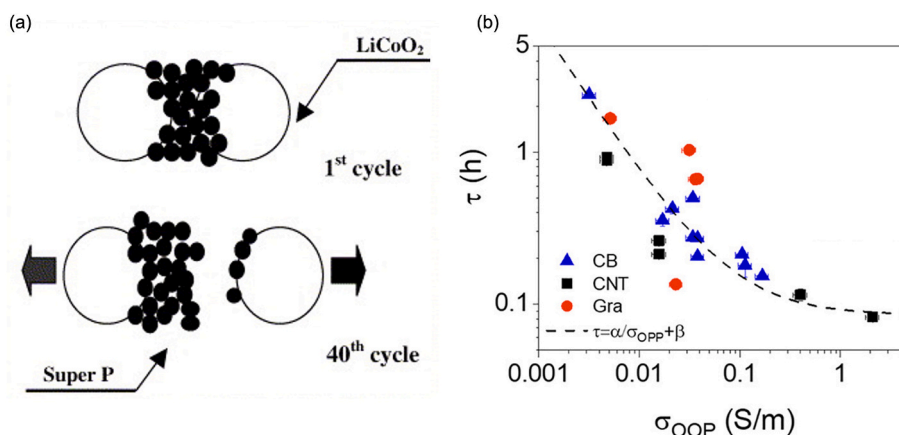


Fig. 4. (a) Schematic showing intact long-range connectivity of CNTs as compared to super P after long-term cycling [55]. (b) Characteristic time (τ) and out-of-plane electronic conductivity comparison of different conductive additives [20].

[53,57,58].

Graphene provides another alternative as a conductive additive. Graphene is a two-dimensional single atomic layer of sp^2 hybridised carbon. Graphene is an excellent conductor due to the shared electronic orbitals throughout its structure, and is a promising candidate as a conductive additive. Graphene can provide a combination of long and short-range contacts to electrodes, due to its high aspect ratio able to span an electrode and planar structure to contact with active material particles [50]. However, it has been shown that wrapping of large graphene sheets over active material surfaces blocks Lithium-ion transport, hindering performance at high C-rates [49,50]. Therefore in addition to the electronic conductivity, surface chemistry and size ratio of graphene to AM particle is also important in building an effective conductivity network [50]. The scalability and high price of graphene as a conductive additive is to also be considered when compared to the low cost of particulate carbon [58].

Researchers have investigated use of multiple conductive additives together to synergise respective strengths [53]. The use of mesoporous carbon along with acetylene black resulted in improved performance of LCO cathode. Adsorption of the electrolyte by micrometre size mesoporous carbon allows intimate contact between lithium ions and AM particles [59]. Use of fibrous carbon along with particulate carbon improves both short and long range connectivity [53]. Binary conductive additives consisting CNTs and graphene nanosheets showed improved performance of LFP cathode compared to cathode made up of single conductive additive [60]. Three different conductive additives, carbon black, graphene sheets, and CNTs have also been combined for better electrode performance [61].

Conducting polymers (CPs) present another alternative for conventional conductive additives [47,52]. Good electronic conductivity, mechanical flexibility, and strong adhesiveness of CPs make them suitable for LIB electrodes. CPs can play a dual role as binder and conductive additive in the electrode matrix. Various studies related to the performance of CPs have been collated [51]. Due to processing difficulties, use of CPs in the LIB industry has been restricted.

Although the non-conventional conductive additives offer various advantages, incorporation in commercial LIBs has been slow mainly due to higher cost. This review focuses on lower cost conventionally used particulate conductive additives. The experimental and simulation methodologies can be extended to non-conventional conductive additives.

1.3.3. Interaction of CBD with other cell components

In addition to improve electronic conductivity of the electrode, conductive additives absorb electrolyte and provide intimate contact between the lithium ions and the AM particles [53]. The extent of

electrolyte uptake depends on the binder properties. Electrolyte uptake causes physical swelling of the binder (Fig. 5a) [62]. For example, electrolyte uptake causes 4% volume expansion of the AM particles whereas binders can expand up to 50% [63]. High values of swelling above 40% lead to a disruption of the conductive network in the CBD phase, which affects the cyclability of the battery and results in capacity fade [62]. Low value of swelling hinders the access of Li ions to the different parts of the electrode composite, leading to an increase of the electrical resistance. Moderate swelling values between 10 and 20% are preferred facilitating lithium ion transport within the CBD [64].

Such binder swelling can change the overall porosity of the CBD phase, affecting Li ion transport through the CBD [65–67]. Existence of electrolyte and corresponding binder swelling deteriorates the electronic conductivity of the composite electrode. Overall electrode resistance can be 3.5 times higher compared to dry electrode. Detailed comparison of physical swelling of different binders have been collated by previous researcher [62,68–71].

Such swelling induces stresses on the CBD phase causing delamination from the AM particle and current collector surface (Fig. 5b). CBD is also stressed by the expansion and contraction of the AM particles during cycling. But such stresses are one order of magnitude lower than stresses caused by the binder swelling [63]. Different modelling studies are available in the literature for investigating the effect of changes in the CBD microstructure on effective porosity, tortuosity, SEI contact area, electronic, and ionic conductivity [65,67].

Conductive additives are considered ‘inactive’ components in the electrode, but recent studies on interaction of super P with electrolyte suggest that even the carbon black actively interacts with the electrolyte. A passivation layer containing inorganic salts was formed at the surface of carbon black, whereas at higher operating voltages, the conductive additive was found to degrade due to formation of organic species on the surface of super P [72].

1.4. Summary

In addition to the chemical nature and structure of the conductive additives there are several factors which significantly affect the electrical conductivity of the final electrode. Surface modification of both negative and positive active materials has been studied and is used commercially [73,74]. Additionally increasing electrode density through calendaring is employed extensively and improves electrical resistance losses as well as increasing volumetric energy density [75–77]. Finally processing of the electrode powders such as dry mixing, slurry formation and electrode drying, as well as passive component modification like current collector surface treatment are also used commercially, and are discussed in detail in section 2 [5]. This review

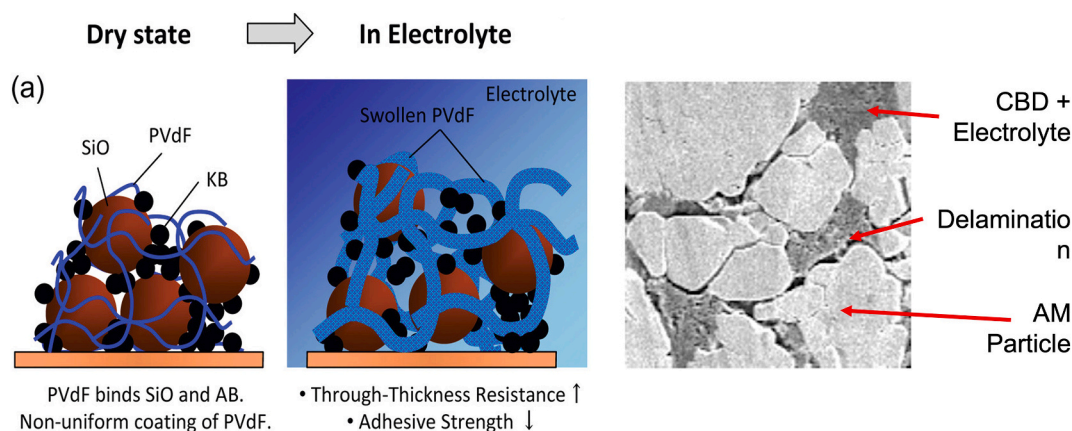


Fig. 5. (a) Schematic showing swelling of the binder due to electrolyte uptake [62]. (b) Delamination of the CBD from AM particle surface due to stresses induced by physical swelling of the binder from electrolyte uptake [63].

aims to summarise these approaches and to investigate recent advances in these fields in relation to the electrical conductivity networks within electrodes.

The nature of the electronic conductivity networks, although initially represented by percolation theory are not fundamentally understood, leading to the question of “What is the optimum electrical conductivity network within a lithium-ion battery?”. Studies have approached this question mathematically and computationally with several simulation methods being employed [65,78–80]. These methods are also reviewed below. Accurate characterisation of the CBD and of electrical conductivity measurements are needed to validate all approaches to understanding and improving this parameter. There are several approaches employed within literature and these will be investigated.

2. Processing, characterisation and modelling of carbon binder domain

2.1. Effects of processing parameters on CBD distribution

Manufacturing processes have an enormous impact on the final structure and arrangement of the components that comprise an electrode. State-of-the-art slurry processing takes a series of powders and, through a wet mixing and coating process, powdered active material, binder and conductive additive are suspended/dissolved to make a slurry mixture which has the correct rheological properties to form into a film, at speed, without defects. Because the slurry mixing and forming process is typically optimised for coating rheology, the location and

morphology of the resultant CA and binder can be difficult to control precisely during fabrication.

For academic researchers to remain relevant the quality of research grade electrodes should be as close to those used industry as possible [81,82]. This means high active material loadings, relevant mass loadings, and commercially relevant electrochemical performance. Without precisely controlled processing protocols the reproducibility of CBD is difficult to control. In addition, it has been shown that each step in electrode processing such as pre-handling of powders, sequential addition, slurry coating, drying, and calendaring, all contribute to the final coating structure and hence electrical, electrochemical, and mechanical properties [83–86].

Of principle concern for this review is the impact the mixing, coating, drying and calendaring processes have on the structure and electronic properties of the conductive additive and the final network formed after manufacture [82,87].

2.1.1. Wet mixing

The wet processing of electrodes slurries affects the final electrical conductivity of an electrode by controlling the degree of dispersion and deagglomeration in the CA. The degree to which this occurs largely determines the slurry viscosity and processability [87–89]. There is a wide variety of mixing and dispersing machines employed during mixing to provide mechanical stress on the fluid and particles (See Fig. 6) [90]. The nature of the stress is usually defined by the direction, compressive and/or shear, and the nature of transfer, via a fluid or between two solid surfaces [91]. Hydrodynamic shear mixing and ball

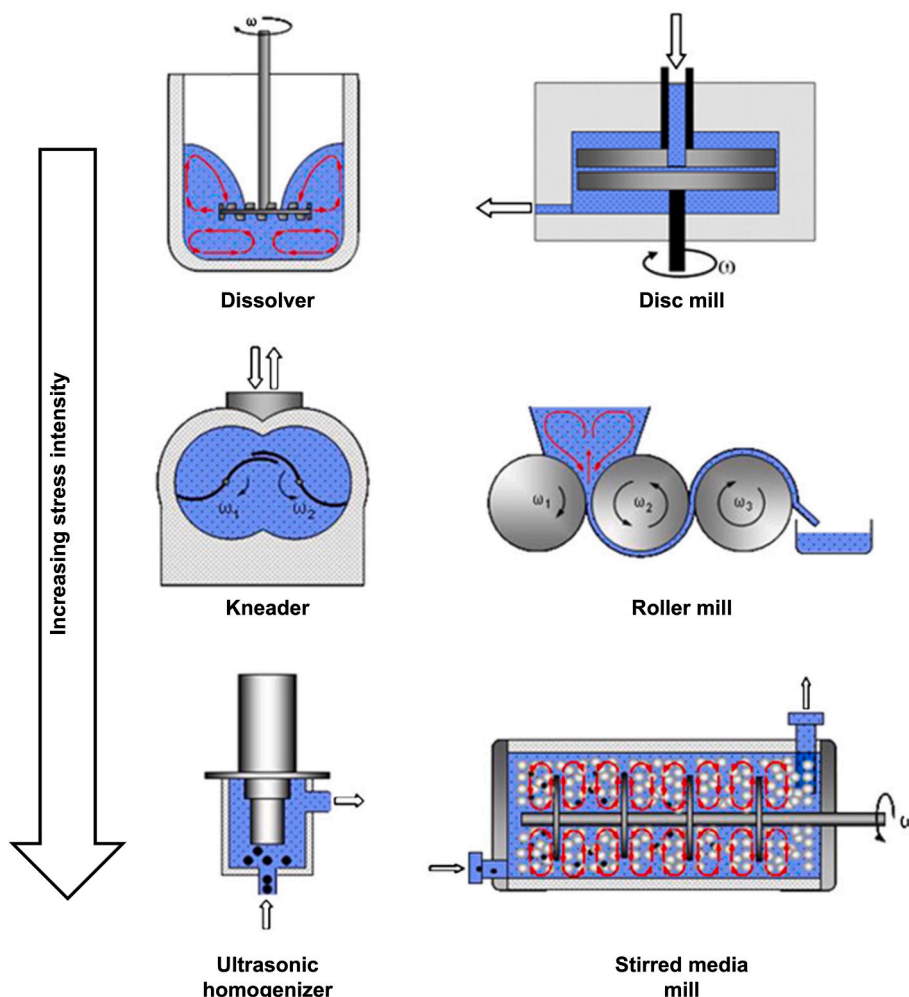


Fig. 6. Schematic representations of dispersing machines arranged in ascending order of stress intensities applied on the slurry [91].

mixing are those most commonly employed in the laboratory and industrial scale [92].

Bauer et al. [93] propose their idealised model for binder distribution which is surmised as: Firstly the CBD requires conductive carbon particles in a less dispersed form or as bound agglomerates [34] which can form long-range electrical contacts, as opposed to perfectly dispersed CB aggregates which can become ‘wrapped’ in insulating binder. Secondly, interpenetration of carbon and binder domains is necessary to prevent a stacking configuration where insulating binder interrupts electronic contact at particle interfaces [82]. Thirdly, surplus binder deposition on the surface of AM is reduced as it is both electronically insulating and blocks ion transport [82,94]. This should be considered alongside the work of G. Liu et al. [95] which also showed the important relationship between conductive additive and binder ratio (CB:PVPDF), they show 1:2 ratios provided close affiliation between CB and active material particles, lowering interfacial resistance through better mechanical strength of the CB-AM bond.

Wet processing of electrode slurries also affects the final electrical conductivity of an electrode. In addition, carbon black and binder distribution largely determine slurry rheology, and hence affect processability. Slurry processing and slurry modulus related to CB aggregate content, have been studied alongside dry mixing [14,16,83,93]. An advantage of dry mixing, where CB agglomerates are broken down before slurry formation, is that significantly lower viscosities can be achieved. Highly porous CB agglomerates absorb solvent within their structure, therefore prior break-up of agglomerates allows more free solvent available between particles, ultimately allowing for higher solid contents [96,97]. The use of higher solid contents brings environmental and economic advantages associated with lower drying energies and solvent use [98,99].

Slurry viscosity measurements have been used to infer the extent of CB deagglomeration. However Haselrieder et al. have shown that rheological changes cannot be used to imply the same degree of deagglomeration between different formulations [14]. In addition, the shear stresses upon mixing are a function of both shear rate (mixer speed) and slurry viscosity. Generally, in lower viscosity slurries CB agglomerates are not broken down effectively [100]. Larger conductive graphite addition to the slurry doesn't increase viscosities as much as CB due to its much lower specific surface area [83,93].

Kremer et al. [101] demonstrated the effect of slurry mixing rate on the electrochemical performance of ultra-thick NMC622 cathodes. High shear mixing caused extensive deagglomeration of carbon black and increased migration during drying (See 2.1.4). It was observed that the porosity of CBD in high shear mixed cathodes were lower than low shear mixed cathodes. These factors resulted in poor capacity of high shear mixed cathodes at high C-rates. Low shear mixing was concluded to be the better option of wet slurry processing.

The inherent nature of electrode slurries, being highly concentrated mixtures of solids in solvent, results in almost no transmission of visible light. This has hindered scattering and diffraction-based analysis of particles within electrode slurries. Recently work by Dreger et al. [100, 102] has shown stabilisers can be used on slurry suspensions and allow sufficient dilution to study the particle sizes of active material and carbon black agglomerates and aggregates. This method opens the ability to further investigate the effects of processing parameters on conductive additives. The power of this technique was demonstrated by Griebel et al. [103] who were able to verify and extend a model for carbon black agglomerate breakdown during dissolver mixing.

2.1.2. Slurry coating

Whilst the shear rates during coating are typically lower than mixing, there is some influence on the conductivity networks during the coating stage. Saraka et al. [17] recently showed that the shear rate at which the slurry is coated on the current collector has an impact on the electrode microstructure and hence the electrode performance. They observed that coating at high shear rates produced electrodes with higher

discharge capacities. This is particularly important for academic researchers who tend to use low shear rate blade coating (speeds ~1–2 m/min) compared to the industrial slot-die processes (10–30 m/min) [104]. Their analysis showed that high coating shear rates result in better long-range connectivity of the CBD. When lower coating rates are used densification of the CBD structure occurs and reduces the long-range connectivity with CBD. Coating a primer layer on the current collector before coating the slurry has been shown to be beneficial by Diehm et al. [105] The strong adhesion of the primer layer allows subsequent coating of a slurry with low binder content. This low binder content allows for increased conductive additive content for the same CBD to AM ratio. It was experimentally observed that such procedure increased the electrical conductivity, rate capability, and capacity retention of the cell. The use of primer layer allowed faster drying of electrode coatings and easy scale-up without compromising the performance.

2.1.3. Electrode drying

During slurry formation binder can be described as ‘free’ in solution meaning polymer material is dissolved in the carrier liquid. During drying polymers then deposit on to the surfaces of active material and conductive additive particles. As the conductive additive dominates the available particulate surface area in an electrode slurry the interaction of binder and conductive carbon is important [94,106]. The implication of this is that the insulating polymer binder can deposit on the interfaces between ‘active material - conductive additive’ and ‘conductive additive - conductive additive’, this is depicted in Fig. 7. Such ‘wrapping’ of active material or conductive additive creates insulating regions of polymer binder between particles, hindering the electronic transport processes within an electrode.

In a study of film drying, insights into AM and pore formation could be gleaned from understanding the shrinking nature of an electrode film. This study highlights how understanding the immobilisation of binder and fine conductive carbon species is lacking during this process [84]. A further study allowed the inference of binder migration during electrode drying [107]. They showed that binder migrates to the electrode surface during drying, leading to effective demixing of the electrode slurry. Higher drying temperatures lead to increased binder migration. Migration of binder to the electrodes surface decreased the adhesion strength of the electrode film and simultaneously increased the resistance. These effects are exacerbated for higher mass loaded, thick, electrodes which require longer drying times. In the case of more intensive mixing it has been shown that both CB and binder migration occurs to a greater extent with more intense mixing processes. This effect is driven by more CB deagglomeration and damage to the binder polymers, both effects contributing to the settling of denser AM to the current collector and increased migration of smaller species to the surface [108]. Such effects have been shown to hinder electrolyte accessibility into the electrode structure close to the separator and reducing the rate capabilities [108]. For a comprehensive overview of drying processes in LIB electrodes the reader is directed to Ref. [109]. Further studies have gone on to show that lower drying rates and higher drying temperatures result in increased demixing and reduced electrochemical performance [17,101]. However it is still unclear to what extent the ionic and electronic conductivity components of the electrode contribute to this factor.

2.1.4. Electrode calendaring

Calendaring is commonly used to increase the volumetric energy density of electrodes by removing internal porosity. The calendaring process compacts electrode components therefore increasing the number of electrical contacts and increasing conductivity. However, the reduction in porosity can significantly inhibit ionic conductivity due to loss of porosity and increase in tortuosity. The calendaring process requires a careful trade-off between energy density, electrical conductivity and ionic conductivity [110,111].

With respect to conductive additives calendaring has been shown to

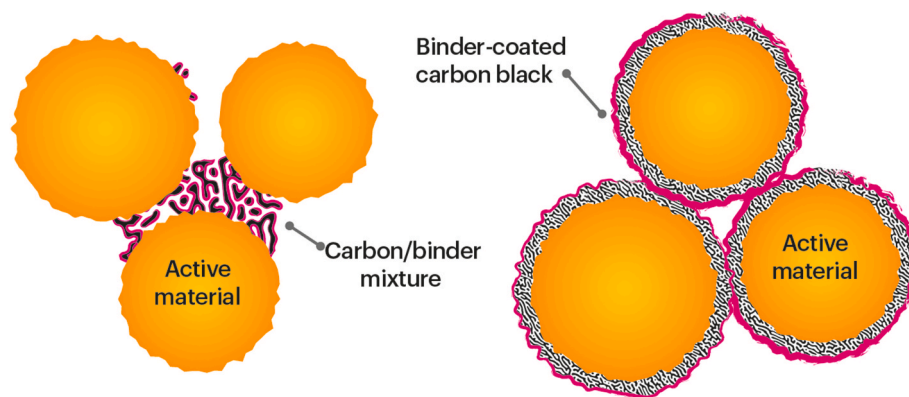


Fig. 7. Shows a schematic representation of interpenetrating CBD network between AM particles (left) and (right) active material particles wrapped in insulating layer of polymer binder. (Key: Orange – AM, pink – binder, black – carbon black).

be most effective at increasing electrical conductivity in electrodes with homogeneously distributed CB aggregates due to the large number of new electrical contacts which can be formed when compressing such structure [93]. Graphitic conductive additives are important during calendaring as their flaky nature improves the compressibility of electrodes by reducing the spring back effect [23]. Regarding the mechanofusion of CB and NMC active materials discussed above, calendaring was shown to be a necessary step in increasing conductivity by increasing contact areas between particles [83,96]. This stands as an example as to the importance of understanding conductive networks in relation to every step of the electrode manufacturing process.

The calendaring process also affects the interaction between electrode and current collector. It has been shown that after calendaring cathode active material can indent into the current collector, reducing contact resistance [18]. However the adhesive strength of the electrode to the current collectors is negatively affected by this process [100,112]. The calendaring process can induce defects into electrodes, ranging in scale from cracks in individual active material particles up to whole coating detachment [83,113]. What is less well understood is the effect of interaction between the CBD and current collector during calendaring, undoubtedly an important contact resistance within electrodes requires further work.

2.1.5. Emerging processes

2.1.5.1. Dispersants. An area of note is the use of dispersants and surfactants to affect slurry properties and CB agglomeration during processing. Several polymeric surfactants are now used commercially to lower slurry viscosity through dispersion of CB agglomerates. Within the literature dispersants have the ability to evenly breakdown agglomerates of CB and homogeneously distribute carbon throughout the electrode which provides good long-range electrical contacts [114–116]. The surfactants act by interacting with CB surfaces via various functionalities and then repelling interparticle interactions via steric hindrance [117,118].

An inherent drawback for dispersants is they remain in the final electrode, detracting from the energy density and requiring very high stability for the lifetime of the cell. Additionally and not dissimilar to polymer binder, if excess dispersant is present then due to its insulating nature it can form conduction barriers [117]. The effect high energy mixing may have on the structure and function of such dispersants in relation to dry and wet processes discussed above requires further research.

2.1.5.2. Dry and low solvent processing. Dry mixing of electrode components is of specific interest to manufacturers as it reduces the time-consuming and costly drying process in the manufacturing line.

Removing the role of solvents has additional economic and environmental benefits as well as potential performance benefits [98,99]. A number of dry and low solvent powder processing procedures have been studied including: low energy drum mixing [97], mechanofusion mixing [83,97], dissolvers, extruders, and kneading processes [108], planetary mixers [119] and ball milling [16]. These processing measures can have unique effects on the deagglomeration and dispersion of the conductive additive and significantly affect conductivity networks.

The study of Bockholt et al. [97] compared drum mixing, mechanofusion, ‘intensive’ mixing and planetary mixing. This study showed that drum mixing is able to effectively mix CB and Active material at a meso scale, but breakdown of CB agglomerates is limited. This was compared to more intensive planetary type mixing where agglomerates of CB were fragmented and more finely distributed between active material. Further mechanofusion was shown to breakdown CB agglomerates efficiently and attached the CB to the surface of the active material. Mechanofusion involves a rotating vessel where powders are forced outward to stator vessel walls and forced between a small gap between rotor and stator [120]. As demonstrated in Fig. 8 (left), intense planetary mixing of CB agglomerates was shown to increase powder conductivity when compared with rotary drum homogenisation, however the use of mechanofusion to adhere CB to the surface of active material did not achieve the highest electrical conductivity or rate capability in electrodes. As can be seen in Fig. 5 for the mechanofusion process, compared with all other mixing methods an extended CBD network is absent from the electrode, and the primary electrical contacts are directly between active material particles. This study highlighted the important relationship of long and short range electrical contacts within electrodes. Short range contact and intimacy between the active material and carbon black is clearly enhanced by mechanofusion mixing and this technique may provide a useful tool for the introduction of short range contacts within electrodes. However, if this enhancement comes at the detriment of long range electrical contacts overall conductivity is significantly reduced.

Kneaders are used for highly viscous suspensions, ensuring good dispersion despite lack of flow. Longer kneading times have demonstrated improved CB deagglomeration and increased contact points to the active material surface (Short-range electrical contacts) [100,108]. Kneading increased electrical conductivity of all electrodes compared with a traditional dissolver slurry formation, this translated to greatly improved capacities at high discharge rates. It is noteworthy that the best rate capability did not directly correspond to the highest electrode electrical conductivity, a phenomenon to be discussed further in section 3. This study particularly highlights how the proportion of short range and long range electrical contacts within the CBD also influences ion diffusion [100]. The very high solid contents reported in this kneading study (>75 wt%) required dilution in order to be incorporated into a conventional comma bar coating step. However the use of a screw

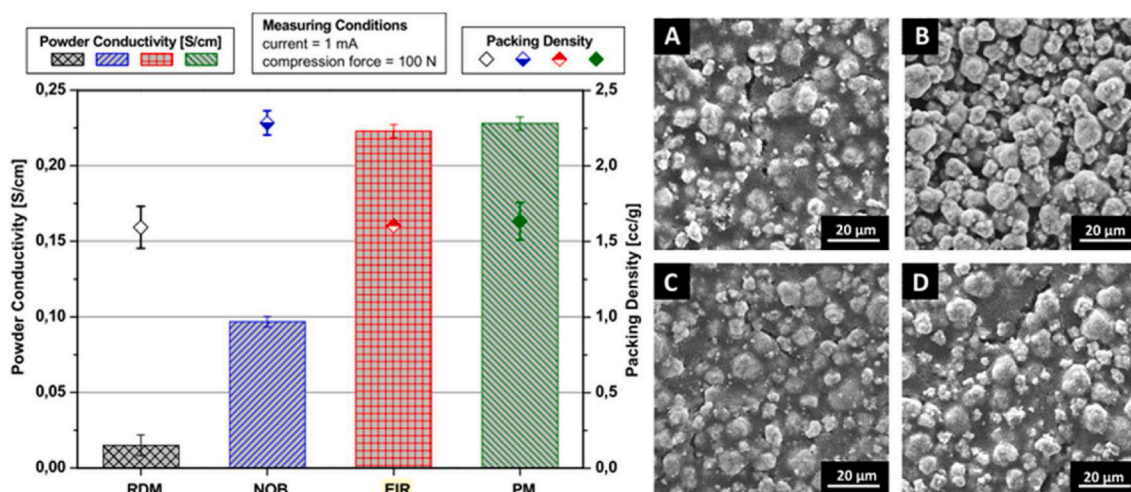


Fig. 8. (left) Diamonds packing density and bars powder conductivity of cathode mixtures. (Right) SEM images of cathode electrodes, A: Rotary drum mixer (RDM), B: Nobilta mechanofusion mixer (NOB), C: Eirich intensive mixer (EIR). D: Planetary Mixer (PM) [100].

extruder was explored for the high solid content slurry and could produce electrodes with improved electronic conductivity from high solid content slurries [108]. The use of electrode extrusion may offer a significant advancement in low solvent electrode processing, and no doubt new coating technologies will be required for dry processed electrodes.

2.1.6. Summary

The processing of electrode powders has a significant effect on the formation of CBD and hence the formation of electronic and ionic conductivity networks. With regards to the CA: The breakdown of agglomerate and aggregate structure during slurry processing will affect the long-range electrical contacts. In conjunction the intensity of the processing and the intimacy of the CA and active material surface contacts determines the short-range electrical contacts. A number of these processing methodologies have been reviewed all of which affect the nature of the short and long-range contacts and in turn the LIB performance.

Additional phenomena have been highlighted during the electrode processing which affect the long and short-range electrical conductivities, primarily demixing which causes inhomogeneity within the CBD and the deposition of the electrode binder which can block both the long-range contacts between sections of the CBD and the short-range surface contacts between AM and CA.

Electrode processing methodology significantly impacts CBD special arrangement and the formation of electrical contacts, it thus provides a further tool for the manipulation and investigation of short and long-range contacts. There is great potential to use processing techniques and operating parameters to manipulate the CBD phase and provide holistic understanding of electrical conductivities within electrodes, and tailor CBD microstructures for given applications.

2.2. Characterisation of conductivity networks

To understand electrical conductivity networks, and to investigate the short- and long-range components it is crucial to identify their structural features and quantify their electrical properties. The conductivity network's primary component is conductive carbon which is to varying degrees amorphous, small in dimension and low in density. These properties which are intrinsic to conductive additives have brought significant challenges to characterisation. Likewise, the ability to accurately measure electrical properties of electrodes across the multiple length scales has many challenges.

2.2.1. Structural characterisation

Characterising structures from the scale of the conductive carbon primary particles 30–50 nm to the larger aggregate sizes 200–400 nm and then onto the aggregate/agglomerate network 1–10 μm requires characterisation techniques which operate across multiple length scales. Here we review microscopic and tomographic characterisation tools for the carbon conductive network, as well as average structure techniques such as mercury intrusion porosimetry, X-ray scattering and dynamic light scattering.

2.2.1.1. Electron microscopy. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) of LIB electrodes and materials can provide microstructural information down to the nanometer scale. In addition, surface properties as well as 3D structure of active material and CA particles can be obtained. Cross sectional SEM can quantify the CBD, active particles and pore spaces within electrodes. To achieve this information careful sample preparation is required, typically involving impregnation of an electrode with resin and ion milling to reveal a polished cross section [121–123].

Taking cross-section micrographs of electrodes in SEM can provide 2-D information of the conductive carbon networks. The technique is visualised in 7. In Fig. 9a, trenches are milled into an electrode surface using focused ion beam (FIB) milling allowing high-resolution cross-sectional images to be obtained (Fig. 9b). Using focused ion beam milling a serial sectioning approach can be adopted where a 3-D reconstruction of the electrode can be performed, with recent resolutions achieving voxel sizes down to 5 nm [124–128]. The processing of the 2-D images to represent 3-D structures requires statistically robust image analysis regimes and can require a large amount of manual data processing [66,124,129].

The sectioning approach of FIB-SEM can provide an unparalleled insight into electrode microstructure and in particular the CBD [66]. The major drawback of quantitative 3-D microscopy is representativity which requires image volumes to be adjusted accordingly to the feature size of interest. Another drawback is the destructive and ex-situ nature of the analysis and the time consuming and expensive sample preparation, image collection and processing [129]. Experimentally there can also be issues in FIB-SEM with obtaining contrast between the FIB milling plane and the solid behind pore openings as well as damaging fine CBD features. Very low currents must be used to overcome these issues as well as impregnation of electrodes with epoxy resin.

2.2.1.2. X-ray computed tomography. X-ray computed tomography (xCT) has revealed detailed 3-D properties in composite electrodes down

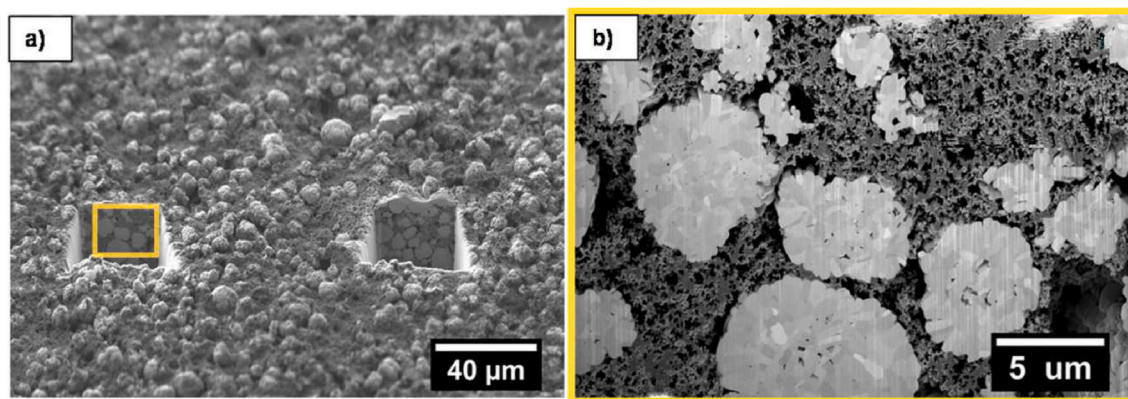


Fig. 9. SEM micrograph (a) showing two trenches milled into NMC cathode. (b) a cross section of cathode clearly visualising active material particles and CBD [127].

to the 100 nm scale [130]. For higher spatial resolutions ~ 15 nm to be achieved increasingly longer temporal acquisition and the use of synchrotron x-ray sources are required [130,131]. To resolve features of electrodes over multiple length scales the resolution requirement has been shown to be very specific to the size of the physical parameter under investigation within a LIB electrode. This means that the representative volume element varies and that 3D data must be collected at more than one length scale to remain accurate [131]. The CBD of electrodes remains difficult to characterise with xCT due to its small size and low atomic number and absorbance. However, xCT can be used in conjunction with modelling where the xCT measurements make up the basis for electrode macro structure and carbon and binder components are modelled around these structures. Many studies have utilised this approach [67,79,132–134]. Daemi et al. [127] combined analysis of CBD porosity obtained from FIB-SEM and interpolated this with a 3D microstructure obtained for NMC particles within an electrode to understand how CBD may be distributed. More recent developments in Zernike phase contrast based xCT measurements have been able to

distinguish some morphological features of the CBD with 50 nm resolution and quantify the contact areas with active materials [135]. Using this method electrode tortuosity and pore properties from 100 to 2000 nm could be inferred. S. Hein et al. [79] combined xCT with cross sectional SEM and electrochemical impedance spectroscopy to produce model electrode CBDs. This study linked the characterisation methods with the electrochemical performance of the cell via simulation of CBD structure, it showed that CBD situated at the contact points between active materials was the most likely configuration in their studied electrode. In addition incorporation of iron nanoparticles in the CBD can greatly enhance the phase contrasts within xCT and SEM techniques [136]. In general, characterisation and reconstruction of nano-porous CBD phase via xCT is challenging. Fig. 10 illustrate different CBD phase reconstruction approach. In Fig. 10a–b, virtual CBD structures were reconstructed between active material particle phase [67]. Recently some novel approach has been proposed to segment and reconstruct the CBD phase from Xct scans, e.g. deep learning segmentation (Fig. 10c–d) [137] and so-called dual-scan superimposition

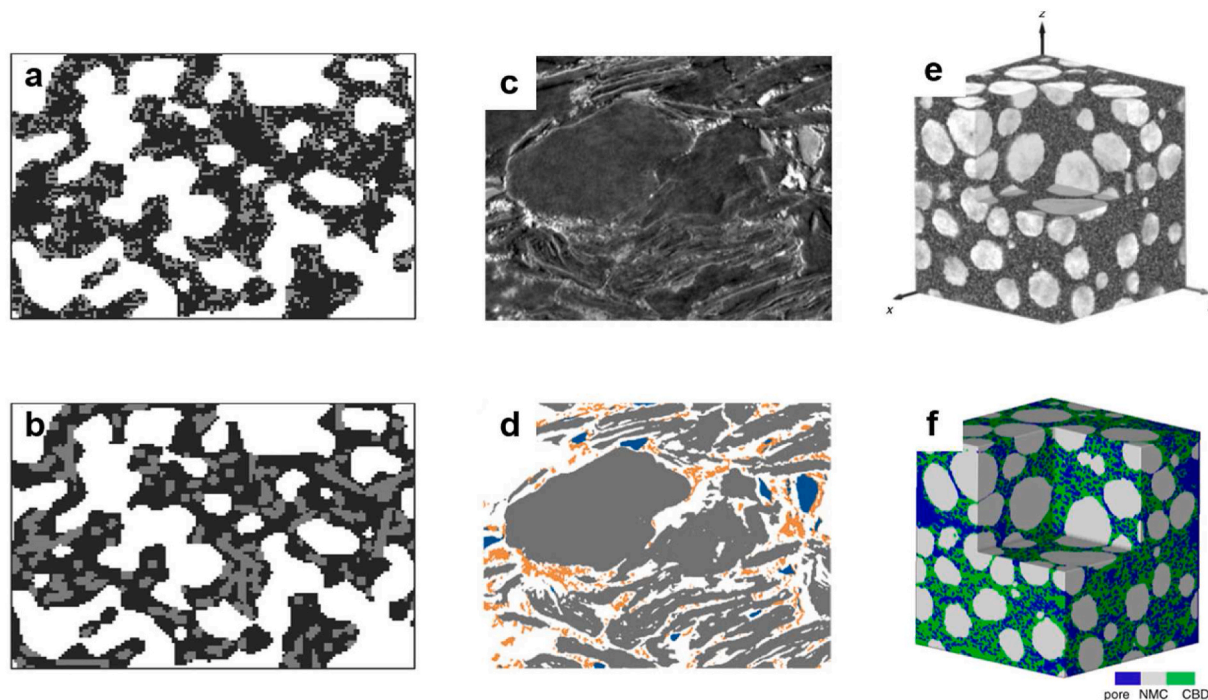


Fig. 10. Electrode structure characterised using X-ray tomography and CBD phase reconstruction (a–b: inserted CBD clusters using random cluster model and fiber model [70] c–d: tomography scan of anode structure and segmentation via deep learning [139] e–f: reconstructed cathode structure via micro xCT and nano xCT, and segmented three phases [140].

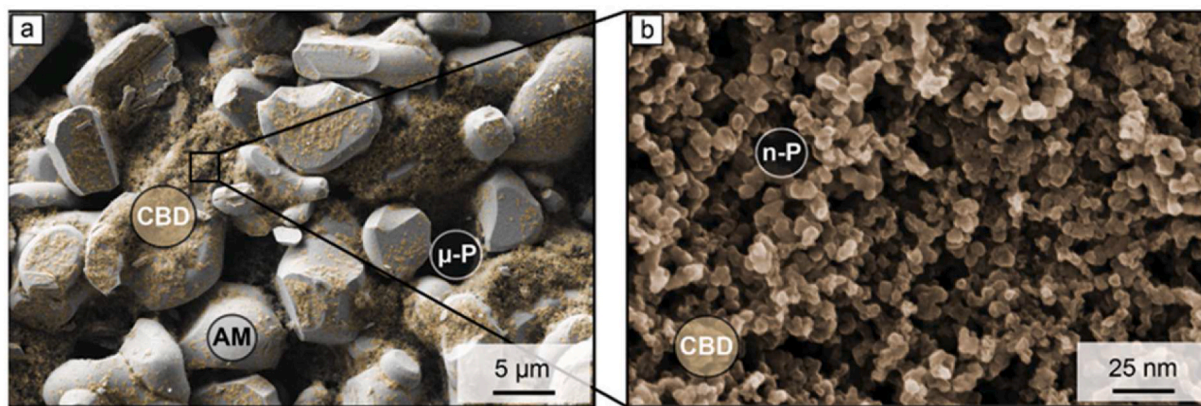


Fig. 11. Coloured SEM images of the different length scales of pores in a LiCoO₂ electrode. Grey is active material particles and other the CBD. (a) Shows the μm pore (μ-P) space between larger AM particles and (b) the nm pores (n-P) within the CBD [69].

technique (Fig. 10e–f) [138] (see Fig. 11).

The prominence of smaller lab scale devices is increasing accessibility of xCT to researchers, however to access smaller spatial resolution required for CBD analysis brighter synchrotron sources are required [141]. The appropriate preparation of electrode samples for xCT measurement has been well reviewed and highlights the complexity of obtaining a representative sample with appropriate dimensions for analysis [139]. Although xCT is an excellent tool for characterising microporosity and space between active material particles, detailed characterisation of CBD requires tandem studies with SEM and MIP [66, 130].

2.2.1.3. Mercury intrusion porosimetry. The structure of an electrode contains regions of porosity between the solid components. These pores can range from a few nm to 10 μm in scale, as depicted in the SEM images of Fig. 11. The pore structure of the electrode is crucial to allow electrolyte wetting of the active materials and for lithium-ion diffusion to the redox active sites. The size shape and interconnectivity of these pores are vital to allow the mass transport of lithium-ions within the electrode. The nature of the electrode pores is governed by the arrangement of active material particles and the CBD.

As discussed, both SEM and xCT can be used to measure pore structures, however both have limitations. Traditionally gas adsorption is used to characterise porous structures [140], however the thin nature of electrodes and low amount of sample mass make this technique difficult to perform and it's use is very limited within the literature. Mercury intrusion porosimetry (MIP) has been successfully performed on electrodes and has been shown to provide useful pore properties over a wide range (4 nm–10 μm) [110]. MIP infiltrates porous structures with liquid mercury, and the size of pores can be determined by the Washburn equation (equation (2)), knowing the contact angle (θ) and surface tension (γ) of mercury (140° and 0.48 N/m respectively). The technique has been successfully applied to lithium-ion battery electrodes in a number of studies [14,68,96,110].

$$\Delta P = \frac{2\gamma \cos \theta}{r_p} \quad (2)$$

MIP has been shown to be a useful tool in studying the deagglomeration of conductive additives and the breakage of aggregates [119]. The breakdown of large agglomerates affects micro-pore distribution in the electrode, and the dispersion or breakdown of CB aggregates affects the nano-pore distribution, from these pore distributions inferences to the long and short range conductivity structures can be made [83,96]. There is a question of whether or not this technique damages the true pore structure of an electrode. In theory MIP applies pressure isometrically to the sample and therefore should not destroy the electrode structure but this is still to be confirmed. Froboese et al. [110] report

that CB agglomerates should also be able to withstand the applied pressure of MIP due to the interaction of CB and binder within the electrode. MIP does not measure closed pores which may be present in the electrode so this must be considered. Further validation of the accuracy of MIP for assessing electrode porosity and the effects of closed pores would be useful.

2.2.2. Electrical characterisation

Within electrodes the long-range electronic percolation networks are comprised of many contacting materials with varying degrees of resistance. It is difficult to deconvolute these specific contributions of a given electrode component, and often bulk measurements are made. Ultimately it is the bulk conductivities which determine the rate at which electrons can percolate through the electrode to partake in redox reactions. Characterisation of the electrical conductivity is therefore important when optimising electrodes for given applications. However, accurate and reliable data collection which is truly relevant to electrode performance is difficult to obtain.

2.2.2.1. Four-point probe conductivity. Four-point probes are commonly employed in materials science for measuring thin film sheet resistances and have been applied to lithium-ion battery electrodes. The four-point probe method allows measurement of film resistivity (ρ) without interference from probe contact resistance according to equation (3). Typically, the correction factor G is a function of the sample geometry [85, 142]. Traditionally these probes have been used to characterise thin film (<1 μm) resistivity and operate under the assumption of uniform film resistivity. A schematical representation of probe field lines is shown in 10(a). The concern with this measurement technique for LIB electrodes is that conductivity measurements taken in plane at an electrode surface may not accurately represent the resistivity of the electrode.

$$\rho = G \frac{V}{I} \quad (3)$$

The reason why the four-point probe method is preferred to determine absolute values, is that four-point probe avoids contact resistance between the sense probe and the specimen points. Thus, it is applicable to determine absolute electrical resistances of the coating. However, the four-point probe method was developed to determine conductivities of thin films and when applied to electrodes provides a resistivity of the upper film and in addition a measurement of conductivity parallel to the current collector termed the 'in plane' resistivity. Not only is this resistivity out of plane with the primary direction of electron transfer, but it disproportionately conducts at the electrode surface and is therefore less sensitive to any potential compositional changes through the electrode plane [143]. When applying four-point probe measurement of an electrode it is also important to remove contributions from the current

collector. This can be achieved by producing electrode coatings on non-conductive medias such as mylar film, or removal of the current collector [144].

Several four-point probe geometries have been developed to effectively measure absolute electrode conductivities over a range of length scales. The line probe in Fig. 12b was used to measure the conductivity over the millimeter scale for commercially relevant electrodes. Due to the large displacement between the sensing probes relative to the electrode thickness, confidence in the accuracy of the measurement is improved as the effect of inhomogeneous phenomena or defects are greatly reduced [144].

Flexible 4-four-line probes reported by Wheeler et al. [146] have been used to measure in homogeneities in electrode conductivity at the sub mm scale, Fig. 12c. This probe with micro meter spacing between probe heads can be moved across an electrode surface to measure changes in local electrical conductivity. However, these probes inherently measured the in-plane resistance and without further detailed measurements into depth profiling of electrodes these methods cannot provide a complete picture of electrode conductivity. It has also been demonstrated that the addition of electrolyte to the composite electrode decreased the electrical conductivity, bringing further concerns to electrical conductivity measurements performed outside of the cell environment [146,147]. In addition due to the relative thickness and the tortuous nature of electrical conductivity networks in battery electrodes only a small proportion of its surface structure will contribute to the resistivity, potentially neglecting structural gradients.

A probe is proposed by Kondo et al. [28] is shown in Fig. 12c, this probe applies the four point method to the measurement of through plane electrical resistance. This probe was used to study electrode density and CA content with results highlighting the weakness of percolation theory to describe battery electrode conductivity. The drawback with this method is the contact resistance introduced between the two electrodes, which are compressed together. Due to the presence of this contact resistance the absolute resistivity cannot be determined, and further experimentation is needed to determine how this contact resistance may vary between electrode formulations. These probes are discussed further in section 2.2.2.3.

The four point probe method is useful for obtaining absolute

resistivity, and these measurements have been put to useful applications such as those displayed by Hong et al. [148] where an in-situ measurement was used to correlate resistivity with temperature fluctuations within a pouch cell. However, a detailed study and further validation of the four-point probe measurements of LIB electrodes is needed.

2.2.2.2. Two-point probe conductivity. For thicker electrodes and high-power applications, through plane electrode resistance is possibly the more important resistance determining rate capabilities. Through plane measurement with two probes depicted in Fig. 13 measures the bulk resistance through the plane of the electrode [18,93]. This relationship is represented in Equation (4), where a resistance (R) is measured over a given sample area (A), through a plane of thickness (t). Commonly this is performed on circular electrodes but any geometry can be measured. However, absolute resistivity's cannot be determined using a two-probe set up. This is due to the inability to separate film resistance from the contact resistance of the probe with the surface and the contact resistance of the electrode with the current collector, all of which are measured in series. The contact resistances added to the system at the probe-electrode interfaces require thorough calibration requiring controlled pressure and surface area contact. Specifically, the rough surface of the upper electrode which contacts the probe can have variable contact resistances. Compressive force is applied to the electrode to increase the consistency of the contact resistances of the probe, and any sample deformation in terms of thickness (t) must be accurately measured to determine electrode thickness.

$$\rho = R \frac{A}{t} = R \cdot \frac{\pi r^2}{t} \tag{4}$$

The two-probe through plane measurement of conductivity is relatively easy to set up and does provide a measure of resistance, which is intuitively most valuable when studying conductivity networks for high power and thicker electrode applications. However reproducible contact between probe and electrode remains a challenge, specifically when comparing between electrodes of different formulation with varying surface roughness's. The 'Powder Probe' depicted in Fig. 13 offers a method of reducing the contact resistance between the electrode surface and contacting stamp. This probe has inherent plasticity and micron size

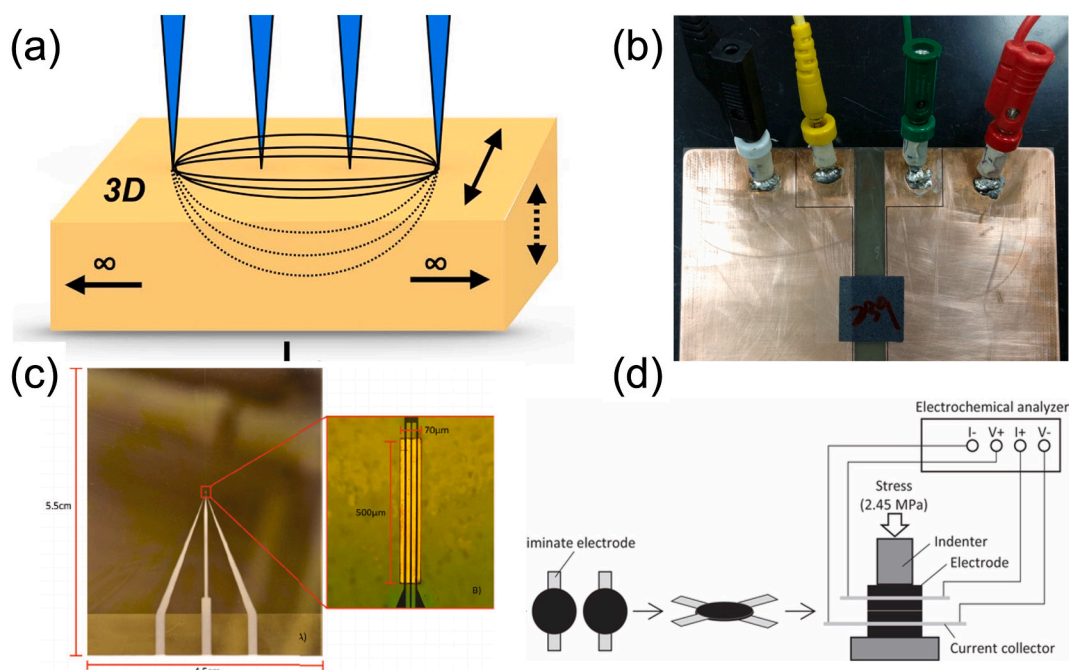


Fig. 12. (a) Schematic of 4 point probe conductivity measurement principle. (b) photo of custom four-line probe design, (c) photo of custom flexible four-line probe, (d) Schematic of four-line measurement applied to through plane resistance of electrodes [28,143–146].

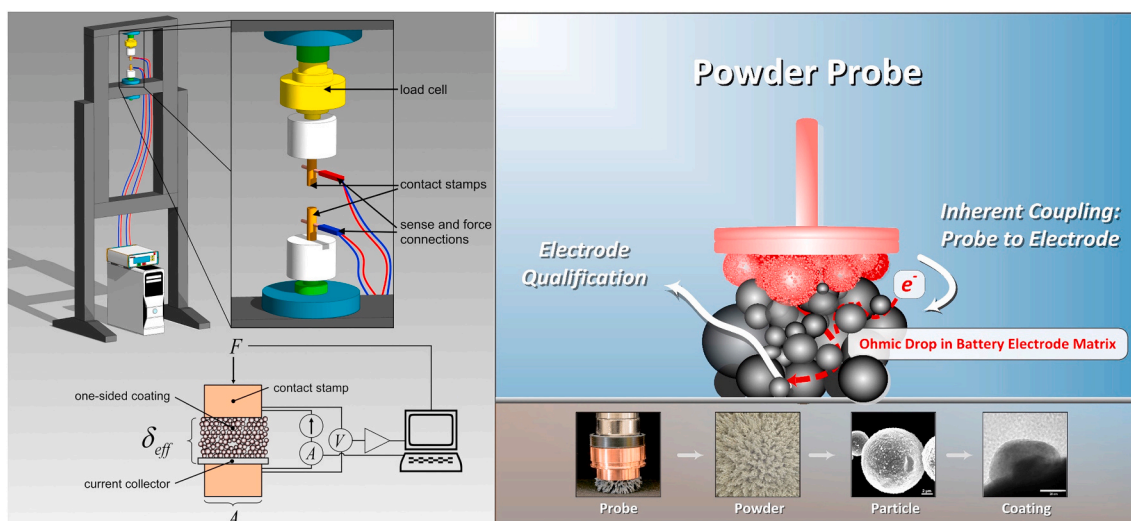


Fig. 13. (Right) typical two-point probe measurement setup using a load cell to reproducibly apply pressure to contact probes. (left) depiction of the powder probe for reduction in contact resistance at electrode surface [17].

particles can couple with the topography of the electrode surface [18, 149].

2.2.2.3. Electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) is commonly used to analyse the impedance response within lithium-ion batteries. It is a non-invasive and relatively simple experiment to perform, however the data interpretation is complex. Within lithium-ion electrodes the overall measured impedance response is composed of the contributions from: the electrical resistance, the ionic resistance of ions within electrode pores, the solution resistance of lithium ions within the electrolyte and charge transfer processes as lithium ions intercalate with active material. These processes are depicted in Fig. 14 [148]. EIS can be used to extract the electrical conductivity of cells, and also relevant information about secondary effects of conductive additive networks, such as tortuosity of electrode structure and ion diffusion coefficients.

To accurately represent the impedance of a whole lithium-ion battery it is essential that the correct equivalent circuit (EC) model is applied. The use of resistive and capacitive components is necessary to describe the charge transfer processes occurring within electrode components [151–153]. Constant phase elements may be used to replace capacitors to account for the real world deviations for ideal behaviour such as electrode roughness [153]. Warburg elements are also used to

represent ion diffusion processes in the electrolyte, separator, and active materials [150]. The series connection of the equivalent circuit elements yields the entire model for a cell. Fitting of the equivalent circuit to the cell yields the resistance values for each component, however as for all impedance fitting, robust equivalent circuits and pore models are required [148,154].

Symmetrical cells are useful to study the effect of conductive carbon in electrode formulation as they remove counter electrode contributions [79,154,155]. The effect of conductive carbon and electrode thickness has been investigated with EIS [156,157]. Y. Itou et al. [156] use EIS to produce a percolation curve of LiNiO_2 electrical resistance for carbon black formulations between 4 and 14 wt%. Although the dependence of resistance on CB ratio showed a typical percolation trend, their model showed how high concentrations of CB negatively affect the tortuosity of pore networks and ionic resistance of lithium ions [156,158]. The relationship between electrical and ionic conductivity and hence the rate capabilities is discussed further in section 3. However, the ability of EIS to provide quantitative analysis of both ionic and electrical conductivity of electrodes in-situ remains unique and very useful.

Impedance spectroscopy remains an important tool in assessing lithium-ion cells in-situ, showing promising prospects for battery management systems and assessing cells' state of health in operation [152, 159]. Better understanding of conductivity networks within electrodes and their effects on EIS response will aid further developments in these applications.

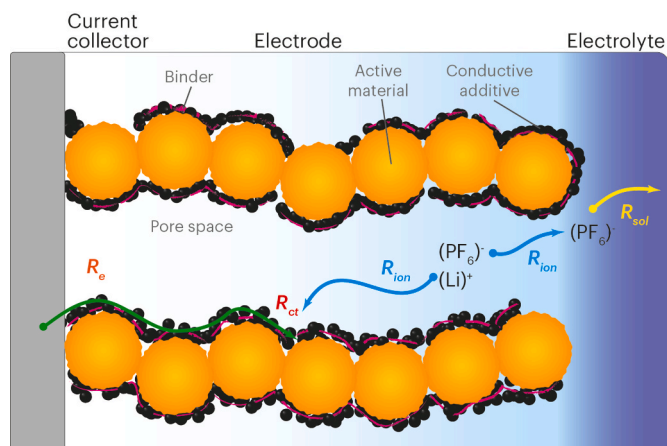


Fig. 14. Schematic illustration of the respective internal resistances of porous electrodes which can be interrogated using EIS. Modified from [150].

2.2.2.4. Titration techniques. Potentiostatic intermittent titration technique (PITT) and galvanostatic intermittent titration technique (GITT) are widely used to determine exchange current density and lithium diffusion coefficients [160,161]. GITT is often applied and considered the most reliable method. However, the reported data for intercalation materials can vary by orders of magnitude for identical materials. This issue arises due to intricate knowledge of the electrode microstructure which is required to accurately calculate the lithium diffusion coefficient such as porosity and pore structure, active material particle morphology and active material surface area in contact with electrolyte [161]. The thorough characterisation of electrode parameters is discussed above in Section 2.2.1 and the challenges for example in determining the active surface area in contact with electrolyte can be envisaged. However, this highlights the importance in understanding the short-range electrical contacts within lithium-ion electrodes, and how the surface covering and intimacy of the short range electrical conductivity network closely affects the ionic conductivity.

2.2.2.5. Rate capability measurements. Rate capability measurements can provide indirect characterisation of the conductive network. Distribution of CBD phase inside electrode affects high C rate performance of the composite electrode. Theoretically, if the effective electronic conductivity decreases, the magnitude of performance deterioration at high C rate is larger than at low C rate (Fig. 15a) [162]. The rate capability performance is also affected by the binder to carbon black ratio in the CBD phase. The characteristic time (τ) defines the rate performance. This parameter is a measure of the C-rate, above which the capacity begins to fall off [56]. Low value of τ implies good performance at high C-rates. As seen in Fig. 15b, rate performance depends on the mass fraction and type of the conductive additive.

Hein et al. [79] have demonstrated that distribution of CBD inside the electrode affects the rate performance. Presence of CBD only in the contact regions of AM particles gives worse rate performance compared to random distribution of CBD on the AM particle surface. Hence rate capability data can provide indirect insights into the electronic conductivity but it should be noted that rate capability measurements are due to combination of multiple factors including ionic and electronic transport.

2.2.3. Summary for characterisation

The aim of physical characterisation of the CBD is to understanding the nature of electrical conductivity networks within LIB electrodes, and ultimately to allow an optimum structure to be understood. The local and average structure techniques introduced here represent the current state of the art for studying the CBD. However, it is clear that one single characterisation method cannot provide a complete understanding of the CBD nature. Researchers should therefore employ a holistic approach to electrode characterisation, employing techniques which can provide structural information over multiple length scales at a local and average level. The rubber industry has studied CB extensively as a filler for many decades [165,166]. Useful expertise from this sector could be readily applied to the use of CB as a conductive additive, an example of which could be the use of Ultra small angle X-ray scattering to characterise CB aggregates and agglomerate networks within electrodes [38, 163]. Likewise recent advances in μ CT have been used to characterise CB fillers in rubber composites [164].

Electrical conductivity measurements of carbon black percolation networks have been performed for over 65 years [165]. Although four-point probe measurements have been shown to provide conductivities for LIB [144], recent work has highlighted how the through plane resistances of LIB electrodes cannot be correlated with cell rate capability, a phenomenon which will be discussed in more detail in Section 3.1 [16]. What is apparently missing within the literature is a detailed comparison of electrode conductivities obtained from 4 to 2 point probe methods. It would also be useful to compare ex-situ measurements of conductivities to those obtained from EIS for electrodes in the presence of electrolyte.

The characterisation of CBD and electrical conductivity measurements will not have a one-size-fits-all technique. To truly understand electrode conductivity, researchers in the community will need to combine physical, electrical and simulation approaches in a coordinated manner such that the community can better compare experimental results. These approaches are already being combined in some of the above examples and as such our insight into the CBD will grow.

2.3. Simulation approaches to electronic conductivity

The development of mathematical models which accurately describe the intricacies of electronic conductivity within electrodes is lacking within the academic literature. Partially this is related to the difficult nature of characterising these networks as discussed in section 2.2. However, the simulation of electrode structures offers a method of studying the effect of key parameters such as particle sizes, morphologies and conductivities on electrode electronic conductivity. Numerical simulations will significantly contribute to our understanding of electrode processing, structure and performance, and will enable us to improve our ability to improve electrode manufacture. Previous studies have used a variety of techniques to simulate electrode structures such as Discrete element method (DEM) [167–169], Finite element analysis (FEA) [33] and molecular dynamics (MD) [170] to produce close packed structures of electrode particles.

In the following, the numerical modelling of particulate processes for electrode manufacturing as well as models for the relationships between electrode structures and electrical conductivity are reviewed.

2.3.1. Particle based simulations of electrode manufacturing processes

DEM models the motion and interactions of particulate material, and can be used to describe particulate processes during electrode manufacturing [169,171,172]. Carbon black (CB) networks can be significantly affected by processes such as dry powder mixing and calendaring, and thus affect the final product performance of electrodes. Fig. 16 illustrates typical particulate processes modelled by DEM in our group. Fig. 16a depicts dry powder mixing processes in a mechanofusion mixer and Fig. 16b depicts the calendaring process of electrode microstructures. It is useful to investigate the process variables as well as the corresponding electrode structures by DEM.

2.3.1.1. Mixing process and de-agglomeration of carbon black. The three primary constituents of electrode slurries, binder, active material, and conductive additive have different particle size and physical properties [92]. During the mixing process the carbon black agglomerates need to be de-agglomerated into nano-sized powders and evenly dispersed within the electrode. Ludwig et al. [173] applied DEM method to investigate the mixing uniformity of electrode particles, and studied the effect of adhesive forces, demonstrating the usefulness of DEM as a tool to investigate mixing behaviour of electrode materials using known

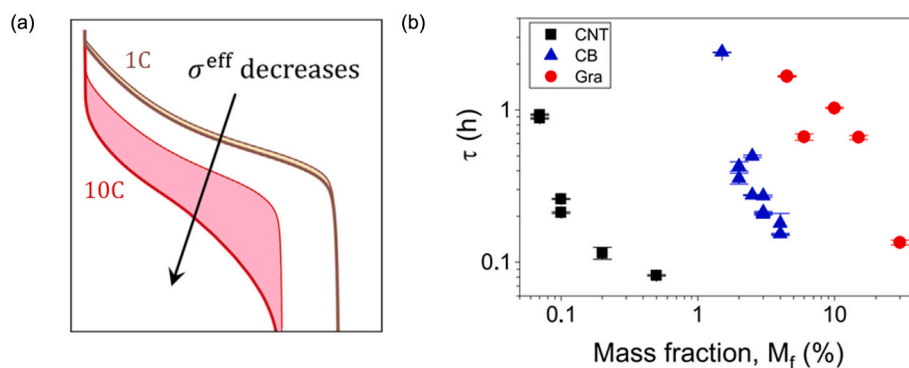


Fig. 15. Reduced performance at high C rate can be due to decreased electronic conductivity resulting from sub-optimal conductive network [163]. (b) Characteristic time constant signifying high C-rate performance decreases with increasing mass fraction of conductive additives [164].

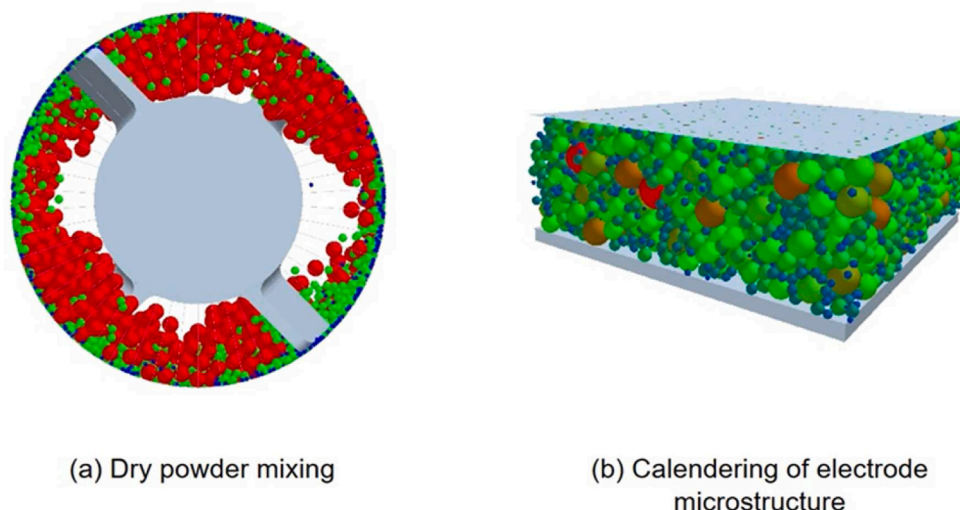


Fig. 16. Particulate process modelling by DEM. (a) a dry mixing mechanofusion process (b) calendaring of active material particles between parallel plates.

surface energy values. Recently, Mayer et al. [119] studied the dispersion and breakage of CB agglomerates using DEM. In their work, hydrodynamic drag forces in a shear flow acting on the nano-sized CB agglomerates were considered. The DEM simulations showed a decrease in agglomerate size with increased shear stress, in line with experimental observations.

For the nano-sized carbon black agglomerates, the correct measurement and calibration of the contact parameters used for DEM simulations are important. Some adhesive contact models based on JKR and DMT theory have been developed to describe the adhesive forces between micro/nanosized powders [174,175]. Due to finite computation resources, most work focuses on single agglomerate breakup. In the future, it is necessary to identify the optimised operation parameters in a full scale mixer with the assistance of numerical modelling [176–178]. The coupling of DEM with other methods e.g. computational fluid dynamics (CFD) and Population Balance Modelling (PBM) is also helpful to fully understand the carbon black de-agglomeration process [177,179].

2.3.1.2. Calendaring process and electrical conductivity changes. The calendaring process can induce electrode microstructure changes and hence influence the carbon conductivity network and enhanced electrode energy density. Experimentally, the mechanical properties of electrode structures can be characterised by monitoring the rolling force during calendaring [77]. The hardness and elastic deformability of electrode structures could be measured via Micro and Nano indentation techniques [180]. The structures can be further characterised by mercury intrusion porosimetry and tomography, as have been presented in section 2.2.1. DEM offers a useful numerical tool to reproduce the particulate structure of electrodes [181] and study the microstructure evolutions during the calendaring process.

The DEM simulation of binder and binder particle interaction has been attempted and considered in relation to the calendaring effect. The mechanical bonding of electrode particles has been simulated by Sangrós et al. [182,183] with a Hertzian bond contact model simulating the AM particle interactions and inter-particle polymer binders. In their research, the bond parameters were calibrated by combining nano-indentation tests and corresponding simulations [182]. During the calendaring process, detailed micro-scale property changes including coordination number, number of bonds and fabric tensors were obtained and analysed via DEM simulation [182]. Afterwards, the correlations between the microstructure and electrode-scale properties are established based on DEM simulation outcomes [184]. A new DEM calendaring model has recently been reported by Ngandiong et al. [168] The relationships between the calendaring pressure, microstructural

evolution and electrochemical performance were evaluated.

Most recently, Srivastava et al. [80] proposed a DEM based method to engineer the electrode mesostructures by controlling the cohesive force of CBD phase and the adhesive force between AM particles and CBD phase. Fig. 17 depicts the DEM simulations of electrode manufacturing considering randomly dispersed CBD particles. By generating the electrode structures with different CBD cohesive forces and Active material-CBD adhesive forces, the electrochemical transport parameters including tortuosity and electronic conductivity were tailored.

Current particle-based simulations are limited in realistic representations of particle morphology and structure, and most focus on spherical approximations. In a more recent work, realistic structures characterised from X-ray tomography were applied for modelling the calendaring process and corresponding transport properties [169]. Further research which can more accurately represent the particle shape, microstructure and interaction of electrode particles is needed. In addition the uptake of binder by different conductive additives will require a more complex understanding of particle bonding [33]. This is discussed further in section 2.3.2.

2.3.2. Correlations of granular electrode structure, carbon networks and electrical properties

Substantial research on the electrical property predictions have been reported using effective medium theory or empirical relations [185–187]. However, the detailed spatially resolved microstructures and inter-particle contacts cannot be considered in these equations. The electrical conduction through a granular material considering inter-particle contacts was represented mathematically by Batchelor and O'Brien in 1977 [188]. Recently, research by particulate modelling [184] have shown that the rate of electrical conductivity perpendicular to the current collector is related to the co-ordination number and the solid fraction of the representative volume, as well as the distribution of particle contacts, intuitively showing that the rate of electrical conductivity is determined not only by the number but the directionality of the contacts. The specific resistance of particle contacts has been approximated but accurate data from direct measurement of contacts is difficult to obtain. The important relationship of these directional long range and direct contact short range electrical contacts is again highlighted by this work, and a better empirical understanding of these contacts will aid more accurate modelling.

Using numerical simulations, detailed granular structures of electrodes can be reconstructed and considered in the electrical conductivity models [110,139]. Awarke et al. [33] developed a

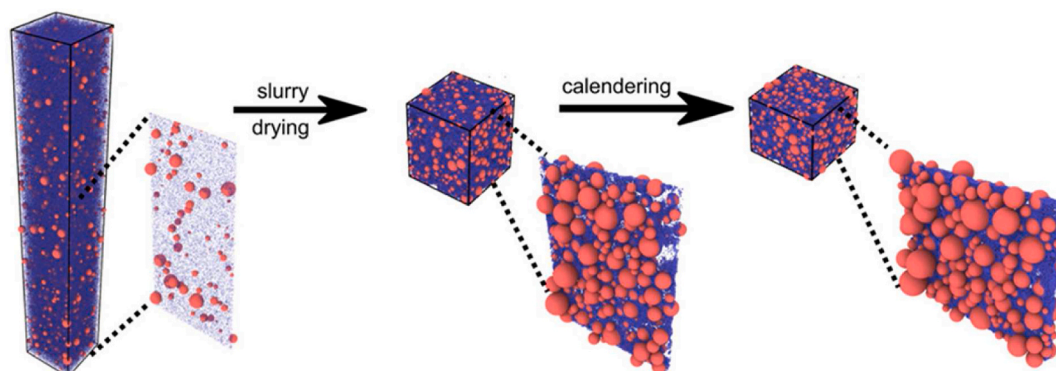


Fig. 17. Schematics generated from DEM Simulations of the three-phase electrode processing [83].

percolation-tunnelling based model using FEA to predict the electrical conductivity of cathodes. The microstructures were randomly generated considering different carbon black and active material (AM) particle size factors. The effect of carbon black addition and carbon black coating was considered in this model. Some works using the DEM method have been used to model electrode conductivity [189,190]. Fig. 18 illustrates a typical Resistor Network (RN) method. For the electrode structure generated from particle packing algorithm using DEM, the conductive pathways are firstly constructed by calculating percolation probability within a particle assembly (Fig. 18a). The percolated clusters are then converted to an equivalent resistor network with defined contact resistance between particle pairs (Fig. 18b). By adding boundary nodes and potentials at the current collectors, a linear system of equations can be created which discretize the particle assembly into a resistor network. After solving the linear equations, the electrical conductivity of electrode structures can be estimated using Ohm's law. This method has been applied to predict the electrical conductivity of electrode structures of solid oxide fuel cells and lithium-ion batteries [189]. Recently, the RN method has been successfully used to predict the effective conductivity and transport properties of pore phases within electrodes [191].

In the future it will be useful to investigate the effect of microstructure changes, carbon black dispersion and agglomeration, and particle breakage on electrical conductivity changes. In particular, the amount and distribution of binder domain can have a significant effect on the final product properties. Some algorithms for describing the CBD phase in numerical modelling have already been developed by researchers [15,192]. Since DEM can be used to simulate the electrical properties at the particle scale, in future it will be useful to investigate the effect of structure changes, internal voids and particle breakage on the electrical conductivity changes. In addition, it also offers a method to optimise particle arrangements for improved electrical conductivity.

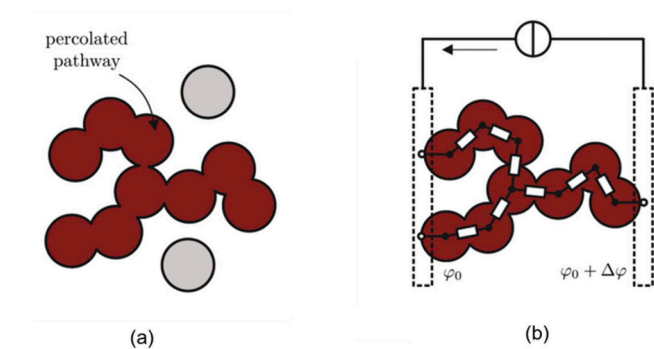


Fig. 18. Resistor network method (a) conductive pathway (b) resistor network by assigning nodes and potentials [191].

3. Perspective and advances

3.1. Experimental

Several studies demonstrated enhanced or optimised electrical conductivity of electrodes by manipulating conductive carbon additive microstructure. Although reducing the resistivity of electrodes is desirable, the rate capabilities of such electrodes will only be improved if the electrical resistance is the rate limiting step. However, both electronic and ionic diffusion determine rate capabilities. Therefore, the development of improved electronic conductivity within electrodes must be considered in conjunction with the properties which affect lithium-ion conductivity, primarily the pore properties and active surface area of an electrode. This is especially true in cases where high electronic conductivities do not correspond to the highest rate capabilities.

Examples where high electronic conductivity did not correspond to the higher rate capability are shown in Fig. 16. The Dreger et al. [102] investigation into high solid content kneader mixing showed that an optimum mixing time of 2 h lead to the highest rate capability and most stable long term cycling capacity. It was shown that longer mixing times further increased the electronic conductivity of the electrodes (measured through plane via two-point probe) but reduced the rate capabilities due to covering of active material surfaces, blocking lithium-ion intercalation to active sites. The study of Morelly et al. [16] is an example of experiments on manipulation of the ratio and multi stage mixing of agglomerated conductive carbon which are at low mass loadings between 2.5 and 3.0 wt%. They suggest that overall the increase in rate capabilities caused by the 0.5 wt% increase in carbon content shows that electronic conductivity was the limiting factor for their study. However, within their four-point probe conductivity measurements of the 2.5 wt% electrode, which is electronically limited, the highest electrical conductivity does not correspond to the electrode with best rate capability and no correlation can be seen between electrode conductivity and rate capability. As a final example, the Haselrieder et al. [14] study, which investigates the combination of multistage mixing and dry powder processing, shows that generally rate capabilities are improved by increasing electrode conductivity via pre-treatment dry mixing. However, in their experiments the electrode with the highest conductance did not correspond to the best rate performance (Fig. 19). In this study, through plane conductivity, MIP and rate capabilities are all used to infer from nano- and micropore size distributions to show how electrode pore structure affected ionic diffusion processes.

The study of Bauer et al. [93] provides resistances (through plane with a two point probe) and rate capabilities of uncalendered electrodes. In this study a clear correlation between high resistance and poor rate capability is presented. Although SEM provides useful characterisation of the CBD in this study, full MIP characterisation of the porous properties would allow better determination of ionic diffusion processes.

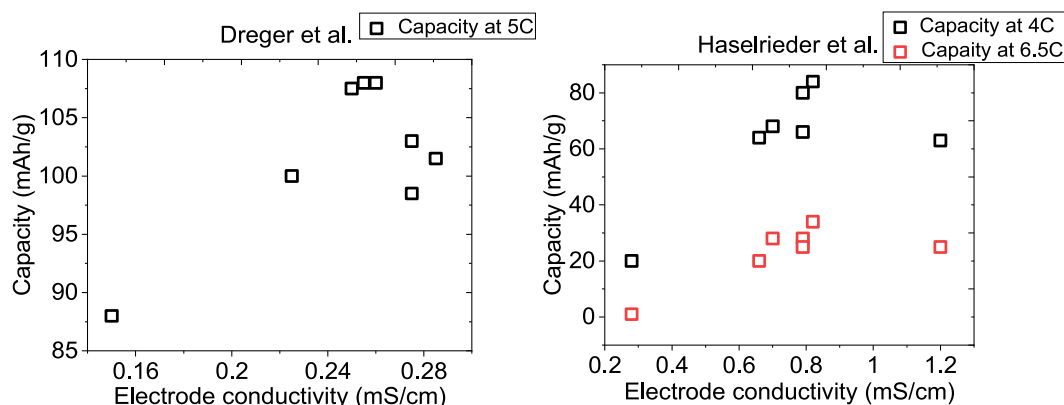


Fig. 19. Compares literature values for electrode conductivity plotted against the reversible capacity available at high C-rates [111].

occurring. The thorough investigations of the effect of carbon black on electrode conductivity presented in the works of the Toyota labs [154, 156, 157] provide useful insight on how CB also affects ionic diffusion processes. However, in these studies' characterisation of the electrochemical performance within a lithium-ion battery performance is missing and would add useful insight.

It is apparent that the long-range electrical contacts within the CBD and the short-range contacts between CBD and active material both play important roles in enhancing electrochemical performance. It is often not clear within studies whether electrodes are limited by their electrical conductivity or ionic diffusion pathways, as demonstrated here with case studies variably showing enhanced or hindered electrode rate performance with an increase in electrical conductivity. More detailed understanding of the long and short-range electrical contacts and the interplay between them is required. Additionally, further work is required to develop understanding of the ionic diffusion processes alongside electrical conductivity networks, as manipulation of CBD to enhance conductivity fundamentally affects ionic diffusion processes.

3.2. Simulation

Electrochemical modelling techniques can provide a useful tool to understand the influence of the CBD morphology, distribution, and network on overall cell performance. Wieser et al. [78] applied the spatial resolving of electrode microstructure approach in their physicochemical simulations. The ionic mass transport resistance due to the presence of nano-porous CBD was reflected in the effective transport properties. It was found that at low C-rates the effect of CBD was negligible but at high C-rates, decrease in the terminal voltage and capacity was observed. It was calculated that more than 60% of the graphite active material surface area was covered by the CBD. This resulted in some local areas of active material with high Li-ion flux. The authors speculated that such high flux areas may increase the probability of Li-metal plating and thus negatively affect the cell life. This study highlights the importance of the short-range electrical contacts on the surface of active material particles and at the interface between CBD and active material.

After reconstructing the electrode meso-structure from experimental image data, Hein et al. [79] investigated the influence of different CBD generation algorithms on overall cell performance. They found that the 'contact' CBD generation algorithm reproduced the experimental results of very high tortuosity and poor rate capabilities. This algorithm generates dense blocking CBD between the contact points of AM particles which hinders the Li-ion transport. Chouchane et al. [65] followed a different approach to understand effect of CBD morphology on overall cell performance. Their electrode meso-structure was obtained through coarse-grained molecular dynamics (CGMD) simulations of the manufacturing processes. An in-house 4D resolved electrochemical

simulator was used to analyse the effect of CBD micro-porosity on the overall cell performance. Three scenarios of CBD were compared, i) Blocking: Li-ions cannot diffuse through CBD, ii) Partially open: Li-ions can diffuse through CBD to some extent, iii) Fully open: Li-ions can diffuse through CBD as if there is no CBD. The transport properties were modified to implicitly consider these three CBD cases in the electrochemical modelling. As expected, the blocking CBD resulted in localized regions of high Li-ion concentration causing high polarization losses and poor electrode utilization. The difference in capacity of blocking and fully open cases increased at high C-rates. Tools such as this will be useful to simulate the effects of CBD morphology on ionic transport, but they must be linked accurately with appropriate electronic conductivity models.

Srivastava et al. [80] generated various CBD networks by tuning the active material-CBD adhesion and CBD-CBD cohesion in a DEM simulation. They introduced a dimensionless figure of merit to quantify the electrode performance. This dimensionless number provides a description of electrochemical transport efficiency within battery electrodes. It was found that the electrode microstructure containing AM particles coated with deagglomerated CBD particles produced highest value for the figure of merit. This is an example of the importance of the short-range connectivity of CBD-CBD and particularly active material-CBD.

These studies highlight the usefulness of predictive modelling techniques to investigate the effect of CBD morphology, distribution, and network on the overall cell performance. With the development of open-source platforms like PyBaMM [193] and Dandeliion [194], running the Newman-type electrochemical models has become much easier. These models do have several limitations including lack of consideration of the SEI layer and volume changes of AM particles during charge/discharge, as well as volume-averaging of transport properties. Still, such electrochemical modelling can be used to analyse the effect of CBD on overall cell performance. A holistic model that can consider short and long-range electrical and ionic conductivity may finally be able to address the question of 'what is the optimal proportion of CBD for a given electrode application'. To increase reliability of such modelling approaches, a thorough validation is of utmost importance.

3.3. Summary

The interplay of electronic and ionic conductivity on electrochemical performance is well known [195]. Hence robust characterisation of the electrode pore properties and the distribution of CBD on active material is critical when optimising the long and short range electronic conductivities of electrodes. The previously discussed characterisation methods of MIP, SEM, x-CT can provide this data. It is equally important that electrode conductivities are performed robustly, and a thorough comparative study of through-plane and in-plane resistances would be

beneficial to the literature. Finally, we propose that when characterising rate capabilities of electrodes that aerial current densities, or relevant information to calculate these, be reported for more reliable comparison of rate capabilities between studies. As Fig. 19 highlights, some papers report relative capacities or C-rates when studying rate capabilities, and without adequate information to determine aerial capacity more accurate meta-analysis can be performed.

The above studies highlight the importance of robust and accurate electrochemical and physical characterisation of electrodes for the advancement of scientific understanding. The combination of this approach and simulation studies will provide more accurate understanding of the interplay between ionic and electronic diffusion processes. Investigations into both LiFePO_4 and NMC rate capabilities at a particle level have shown extremely high rate capabilities of more than $>100\text{C}$ [196,197]. These studies highlight the current lack of conventional electrode structures to facilitate this rate of ionic and electronic diffusion and the huge potential of further research.

4. Conclusion

This review outlines and discusses the current understanding of conventional conductive carbons in lithium-ion batteries and their effect on electrode electrical conductivity. The recent advances in conductive additive and electrode modelling are reviewed, as are the current state of the art characterisation routes including their advantages and disadvantages. In the academic setting typically large 10–20 wt% conductive additive formulations are used to investigate new active material properties. These quantities are significantly higher than the 1–4% used in commercial electrodes. To remain industrially relevant academic researchers should endeavour to study electrode structures with industrially applicable formulations. For commercial applications the CBD content is variable for different applications. Design guidance for thick and thin electrodes and instruction on the manipulation of CBD content for high power or high energy applications is lacking within the literature. This work details the current understanding of electrode preparation techniques for LIBs, and discusses their influence on electronic conductivity networks, which are primarily driven by the manipulation of the carbon and binder domains. Although further understanding of the short and long-range electrical contacts within battery electrodes is needed, characterisation and identification of the interdependent nature of electronic pathways with those of and lithium-ion diffusion is required.

Future advances in characterisation techniques should be focused on better characterising the formation of, as well as micro- and nano-scale structure of the CBD in electrodes. Specifically, being able to distinguish between carbon and binder would be useful to build our understanding of their interaction at contact barriers. Importantly, thorough and robust characterisation of the electrical conductivity and electrochemical performance of electrodes is needed, alongside an increase in our understanding of conductivity measurements and a drive to report all electrode parameters for improved comparison.

Many disruptive electrode technologies have been reviewed, however often such technology cannot be transferred to large scale manufacturing processes. In this regard simulation approaches which describe the multi component steps of electrode manufacture will be extremely valuable. The development of greater experimental understanding and validated computational prediction of optimal CBD structure will enable the design of high energy and high-power electrodes, which can be tailored for specific applications. This is critical to enable the transition from incumbent trial and error approaches of electrode processing, to performance driven electrode manufacturing process design. The future of enhanced conductivity within electrodes will likely be achieved by the combination of the solutions presented herein.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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