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Roadmap on Li-ion battery manufacturing research

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Revised Draft - Roadmap on Lithium Ion Battery Manufacturing, JPhys Energy

2022 Roadmap on Li-ion Battery Manufacturing Research

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Contents

Introduction

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All mass market Li-ion battery electrodes are fabricated by casting of a viscous slurry comprising an electrochemically active material, a binder, conductive additives and a fugitive liquid onto a metallic foil current collector. The solvent/suspension mixture dries (evaporation of the solvent) to produce an electrode structure that is a random mixture of the constituent particulate materials adhered together and to the current collector by the binder, and residual porosity. Both anodes (typically graphite-based) and cathodes (typically Li-oxide-based) are made this way. The anodes and cathodes are then calendered (rolled under compression) to reduce thickness and to increase density, a porous polymer separator is introduced, and the arrangement packaged together with a liquid Li-ion containing organic electrolyte into cylindrical, pouch or other cells, and then into battery packs.

Because of its high productivity, robustness and scalability to the gigafactory, slurry casting has become embedded as the cornerstone of industrial Li-ion battery fabrication and the reason for the extraordinary and continuing decrease in Li-ion battery costs over the last decade or so. However, because of the growing installed capital base and its ubiquity, it is easy to forget that slurry casting has restrictions and produces reliable electrodes only over a narrow range of thicknesses (tens to a few hundreds of microns), porosities (approximately 30 vol%) and formulations (up to 96 wt% active material). At the industrial scale, electrode innovations tend to be restricted to those that can “drop-in” to existing manufacturing lines, and consequently the trade-off space for cell performance, such as energy density at the expense of power density and vice-versa, remains relatively constrained. Slurry casting also has a propensity for defects such as agglomerates that can act as nucleation points for premature degradation. Surprisingly and despite their widespread use, there are also gaps in the understanding of electrode structural evolution during the critical steps of slurry formulation and casting, drying and calendering. Consequently, the tuning of the many parameters for each of these steps is largely empirical, time-consuming, and wasteful. Until very recently, the development and optimisation of Li-ion battery electrodes has had relatively little up-front design and predictive capability, or in-line metrology, and has relied largely on trial and error.

Alongside the growing installed capacity of slurry casting, there has been an accelerating emergence from the research base of alternative, and in some ways, more capable manufacturing processes, that produce structured or “smart” electrodes. Here the objective is to arrange the materials of the electrode more elegantly and according to a design intended to exploit the intrinsic properties of the electrochemically active material more widely. Increasingly these approaches are guided by modelling and simulation insights. For example, there are now a number of demonstrated approaches to pore engineering where templates or other techniques are used to contrive the interconnected electrode porosity into a more advantageous morphology, such as through electrode thickness pore channels. While capacity at slow charge/discharge rates is usually unaffected by this type of pore structuring, the electrodes can show much improved capacity at faster rates because electrode-scale Li ion diffusion is made easier. Other developments include a growing interest in manufacturing routes that reduce or remove the need for the liquid solvent used in slurry casting, with potentially very significant beneficial impacts on the sustainability of electrode manufacture, as well as possible performance benefits.

In response to these trends and the associated diverse set of challenges, the Faraday Institution, the UK's independent institute for electrochemical energy storage research, established the NEXTRODE (Next generation electrodes) project in September 2019. We have since assembled a multidisciplinary team of experimentalists and modellers from both within and beyond the battery field. Our aim is to realise improvements in battery performance by smarter assembly of the different materials based on investigation, understanding and exploitation of the science of electrode manufacture. In this roadmap article, we outline our view of the opportunities to increase the scientific understanding of the key steps in current Li ion electrode and battery manufacture, and how this understanding might be used to improve manufacturing (for example by reducing excessive trial-and-error optimisation) and battery performance (for example by expanding the range of performance trade-offs available). We also consider some of the emerging new approaches in electrode manufacture, including increased use of in-line metrology, solvent-free or dry processing, how to manipulate electrode structure, and novel approaches to electrode design and analysis. Finally, we are using machine learning and correlative techniques based on manufacturing data at all stages and scales to investigate how manufacturing innovations at the laboratory scale, whether for conventional or new processes, can be translated to the commercial scale more quickly and effectively.

UK Strategy and Ecosystem for Batteries

David Greenwood, The University of Warwick

The UK has identified battery technology, and particularly the industrialisation of batteries as being of strategic national importance, and as a result we have one of the best designed ecosystems in the world for the development and commercialisation of batteries.

Decarbonisation is now clearly embedded within UK government policy, having been the first country (in 2019) to legally commit to achieve net zero by 2050. This has been followed up in November 2020 by the 10-point plan for a green industrial revolution (banning sales of petrol and diesel vehicles by 2030/2035), Transport Decarbonisation Plan, and more recently with the Net Zero Strategy: Build Back Greener and UK Net Zero Research and innovation Framework. All these documents recognise the significant role played by battery energy storage, and the need to build scientific and industrial capability and capacity for their development and manufacture.

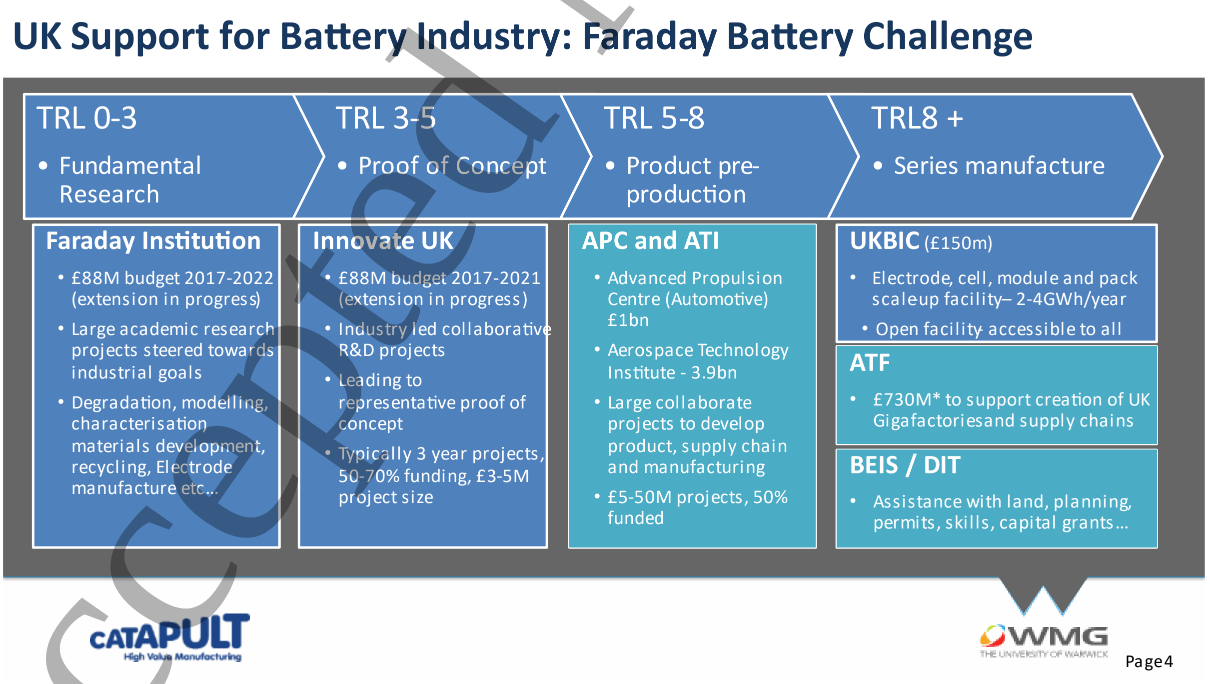
In part the current UK approach has been driven by lessons of the past where the UK produced great science in this field (such as the work of John B Goodenough on cobaltate cathode materials at Oxford in the 1980s) but saw its exploitation take place overseas. It would be easy to put this down to a lack of UK commercialisation capability but, in reality, it was due to not having applications for the technology in the UK economy. In a world before laptops and mobile phones, Sony's camcorder was the first portable electronic device to deliver a business case for the use of Lithium-Ion batteries. To be truly successful at exploiting battery technology, the UK needs to focus as much on applications as it does on science and technology.

Whilst many market sectors have needs for batteries, in the UK it was the automotive sector which provided the initial business case for change. Successive automotive technology roadmaps [ref: NAIGT 2009, APC Electrical Energy Storage Roadmap 2020] have identified the rise of electrified vehicles since the late 1990s, but in the mid 2010's the trajectory took a step change as climate change, air quality (brought into sharp focus by "dieselgate" in 2015) and energy security came together as policy drivers, resulting in a succession of regulations and policy committing the industry to an accelerated path towards electrification.

The UK Auto sector is the largest export sector in the UK, employing 800,000 people and generating £60bn of turnover in 2020. In 2020 we made 1.8M engines manufactured 1M cars per year (down from a peak of 1.8M in 2016) [ref SMMT motor industry facts 2021]. The electrification of this sector represented both an opportunity and a threat, as the battery represents around half of the "bill-of-materials" cost for an electric vehicle, and batteries are expensive and hazardous to ship long distances. If the UK makes batteries for electric vehicles then this opens up a new market opportunity of £9bn per year by 2040 [ref Faraday Institution "UK electric vehicle and battery production to 2040"] and anchors the auto sector in the UK. If we do not then it is likely that car manufacturing will migrate to locations where batteries are made – losing out not just in the missed opportunities of batteries, but also seeing the atrophy of supply chains for the rest of the vehicle.

In response, the Automotive Council and Academic community proposed to government in 2016 an initiative now known as the Faraday Battery Challenge. This proposed a mission-led approach with common governance for all stages of battery development and commercialisation, from fundamental research through to investment in gigafactories and their supply chains. In 2017 the Faraday Battery challenge was launched, with £246M committed to support the first four years of activity, which has subsequently been extended, and additional activities aligned to it. This ecosystem now includes:

- The Faraday Institution – with a remit to fund large-scale, highly collaborative academic research to answer critical industrial questions. This operates a more closely managed programme than most academic funding mechanisms, with regular review and the ability to dynamically redirect funding and resources according to ability to deliver impact
- Collaborative R&D programmes (through Innovate UK) support business led collaborations to get to proof-of-concept with new technologies – with typical projects size £3-5M and 2-3 years' duration
- Collaborative R&D programmes (through the Advanced Propulsion Centre) support industrialisation of vehicles, components and systems, through to the point of pre-production – with typical projects up to £40M in size and around 3 years' duration
- The High Value Manufacturing Catapult – in particular, its centres at WMG (Warwick) and CPI (Teeside) which host pilot lines and scale up facilities
- The UK Battery industrialisation Centre – an internationally unique open access facility for high volume manufacturing scale-up of electrodes, cells and batteries. Opened by the Prime Minister in 2021, the facility hosts production facilities capable of 4GWh/year electrode manufacturing rates, and the ability to assemble cells to pouch and cylindrical forms, as well as semi-automated module and pack build
- The Automotive Transformation fund – currently standing at £750m, with the ability to de-risk capital investments in major manufacturing facilities for batteries and their supply chain
- The Faraday Battery Challenge – a co-ordinating function hosted by UKRI, connecting all of the above mechanisms, with deep links into UK government, including BEIS, DIT, DEFRA, Cabinet Office



UK Support for Battery Industry: Faraday Battery Challenge

TRL 0-3
- Fundamental Research

TRL 3-5
- Proof of Concept

TRL 5-8
- Product pre-production

TRL8 +
- Series manufacture

Faraday Institution
- £88M budget 2017-2022 (extension in progress)
- Large academic research projects steered towards industrial goals
- Degradation, modelling, characterisation materials development, recycling, Electrode manufacture etc…

Innovate UK
- £88M budget 2017-2021 (extension in progress)
- Industry led collaborative R&D projects
- Leading to representative proof of concept
- Typically 3 year projects, 50-70% funding, £3-5M project size

APC and ATI
- Advanced Propulsion Centre (Automotive) £1bn
- Aerospace Technology Institute - 3.9bn
- Large collaborate projects to develop product, supply chain and manufacturing
- £5-50M projects, 50% funded

UKBIC (£150m)
- Electrode, cell, module and pack scaleup facility– 2-4GWh/year
- Open facility accessible to all

ATF
- £730M* to support creation of UK Gigafactoriesand supply chains

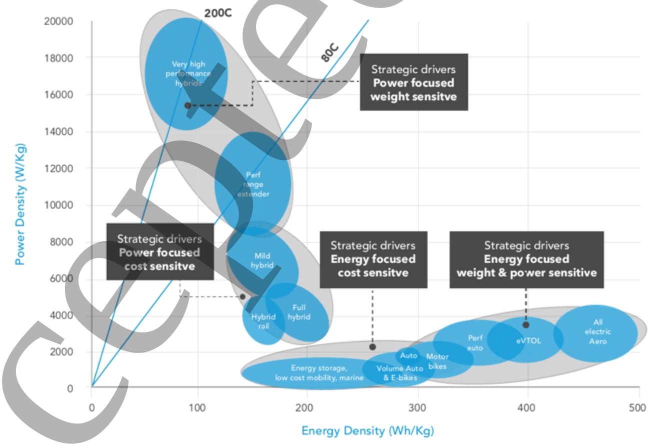
BEIS / DIT
- Assistance with land, planning, permits, skills, capital grants…

For the automotive sector, a key milestone has been the announcement of battery "gigfactories" (battery factories producing gigawatt hours of batteries per year) in the UK – as these will anchor the automotive sector in the UK. At the time of writing, two such factories have been announced, and further announcements are anticipated. As importantly these factories provide the direct market pull for upstream materials manufacturers to respond to – and this will be a major focus for the Faraday Battery Challenge in the future. Further, this market growth improves the business case for battery recycling in the UK, as it delivers both feedstock and customers for end product. At present several initiatives [ref: APC project RECOVAS, Recyclus] are underway to deliver kiloton per year capacity for battery materials recovery, but as yet there remains a gap in the UK capability around conversion of "black mass" to precursors for electrochemical material manufacture

Whilst devised originally to support an automotive requirement, The UK ecosystem provides an excellent base around which to grow UK battery capability into other sectors as their energy storage needs become clearer. These now include all forms of surface transport, aerospace, marine, domestic electricity storage and grid scale storage of renewable energy.

Work by WMG and the Faraday Battery Challenge has studied these future cross sectoral needs and has proposed four "families" of applications which share similar technical requirements, and which could therefore be addressed by similar battery technologies [see figure below – credit WMG / Faraday Battery Challenge 2021]:

1. Power focus / Weight sensitive – batteries with very high charge and discharge power to weight ratio (80-200C rate). Typically used in high value applications such as aerospace and motorsport, where cost may be less of a constraint, and often in a hybridised application.
2. Power focus / Cost sensitive – batteries with relatively high charge/discharge capability (10-50C rate) for use in hybrid applications in higher volume (and more cost sensitive) markets, generally alongside a fuel cell or combustion engine.
3. Energy focus / power and weight sensitive – for use in EV applications from ebikes through electric motorcycles, cars, electric buses and into eVTOL aircraft. These are the primary energy source for the vehicle, so energy density is critical, but power and weight must be adequate for the application.
4. Energy focus / cost sensitive – generally for use in non-transport applications such as grid support where weight and volume are relatively unconstrained, but typically very large (MWh) scale applications, so cost per kWh is a major driver



With these families in mind, it is possible to guide emerging technologies towards their most likely applications and vice-versa, as well as to commission research in areas which will strengthen the market position of UK technologies.

Over the next 5 years the UK has specific opportunities, coming from both research and industrialisation, around electrochemical materials (including NMC, solid state, sodium ion, lithium sulfur and silicon anodes), high power density batteries for aerospace and motorsport, and recycling of battery materials.

So with a world class research and development ecosystem and a clear technology strategy, the UK has the best possible basis for innovation in batteries. For those of us in the research community, our job is now to deliver against that vision.

Synthesis of cathode active materials and scale-up challenges

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Status

Nickel-rich cathode materials, such as layered $LiNi_xMn_yCo_zO_2$ (NMCXYZ), present nearest-stage opportunities for high energy density lithium-ion batteries due to their high practical capacities and market maturity.[1] At present, the cost of the raw materials represents the most expensive part of the process, with the synthesis and processing of the cathode powder bearing a high price factor.[2] Sustainably scaling up the synthesis of high-nickel NMC-type cathodes in a reliable, efficient and cost-effective way is crucial to the long-term manufacture of large-scale, high-energy Li-ion batteries, and to meeting the proposed 300-mile range for electric vehicles.

Traditional routes to inorganic oxide materials include ceramic solid-state syntheses, where high reaction temperature and long reaction times afford thermodynamic products in the bulk form. Control over primary (or secondary) particle morphology is very difficult, since the high temperatures required to overcome diffusion barriers make it challenging to selectively control reaction progress. Alternative synthetic approaches can offer advantages including a degree of control over particle morphology. Solventothermal methods, for example, can provide a route to tailoring particle size and shape through judicious selection of solvent or capping agent. Sol-gel routes can be fine-tuned via starting alkoxides to facilitate size and shape design. The synthetic route employed can therefore play a role not only in guiding the resulting crystal structure obtained but also in determining the resulting particle morphology which itself can have significant implications on resulting performance.[3]

However, when moving to a larger scale, it can be difficult to maintain reproducibility and consistency between batches when using these more traditional methods. One commonly applied synthetic route, which allows fine-tuning of particle morphology and affords materials at larger scale, is the co-precipitation process. In the case of NMC cathodes, salt solutions (typically MSO$_4$, M = Ni, Mn, Co) are mixed together in the desired stoichiometry with ammonium hydroxide acting as a chelating agent and a hydroxide base as a precipitating agent. After precipitation of the desired transition metal hydroxide, the dried precursor is mixed and calcined with a lithium source at an elevated temperature (typically an oxygen-rich environment).[4] A general schematic for this process, performed using a stirred tank reactor, is depicted in Figure 1. Careful monitoring and manipulation of reaction conditions such as pH, temperature, stirring, feed rate, concentration of reacting species and counter ions, and the presence of chelating agents, provide a means to controlling precursor particle nucleation and growth.[5] Many existing chemical companies have access to CSTR equipment, meaning it is a readily available, non-disruptive technology. Combining the CSTR method with robust analytical tools, it is possible to maximise reproducibility between batches in the end product. This is a scalable method provided physical characteristics such as reactor geometry and stirring shear forces are considered when increasing throughput.

Current and future challenges

Careful consideration of the co-precipitation synthesis parameters for Ni-rich materials can provide a means for optimising primary particle size, particle density, and the assembly of these primary particles (typically several 100's nm in diameter) into larger secondary structures which can range from 5 to 15 µm in diameter. Control over these morphological attributes can have significant implications for the resulting specific capacity and capacity retention of Ni-rich cathode materials.[6] For example, ammonia is often applied as a chelating agent for nickel-rich layered NMC materials. Fine-tuning the ratio of transition metal reactants to such a chelating agent can directly influence the resulting secondary particle morphology. The ability to direct secondary assembly formation becomes increasingly important when one considers the anisotropic lattice changes at potentials above 4.2 V in nickel-rich NMC cathodes.[7] The contraction/expansion which accompanies this can lead to microcracking of the secondary particle and this exposure of fresh cathode surface to electrolyte can lead to diminished capacity retention.[8] Controlling this secondary particle assembly formation to reduce the occurrence of voids between primary particles could thus influence these cracking phenomena. Continuous stirred tank reactors, of the type illustrated in Figure 1, provide a means for synthesising these NMC hydroxide precursors, but care must be taken in controlling reaction parameters and conditions to minimise any resulting variations in secondary particle sizes and distributions, tap density and eventual electrochemical performance as well as maintain an appropriate atmosphere for the desired transition metal oxidation state. Recently work from Guo *et al.* details the application of a continuous stirred tank reactor for the continuous hydroxide precipitation of a Ni-rich NCA-type cathode precursor.[9] Here, the synthesis parameters were systematically optimised and experiments reveal an optimum pH level and ammonia to transition metal ratio of 11.0 and 1.0 respectively.

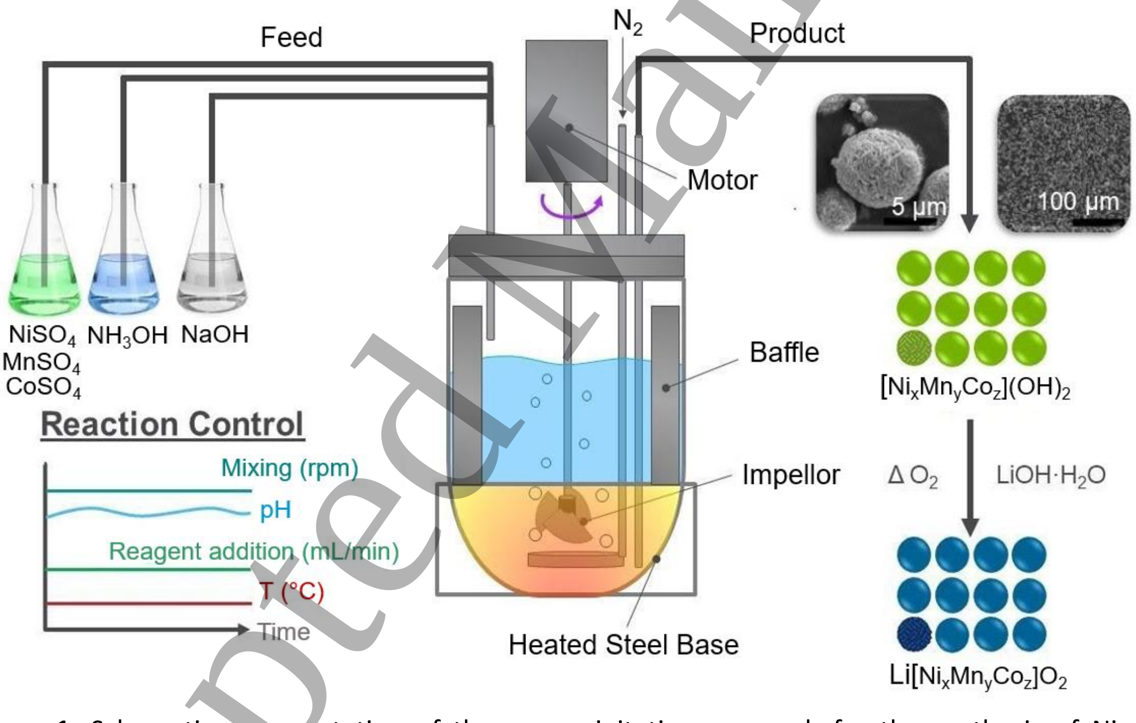

Figure 1. Schematic representation of the co-precipitation approach for the synthesis of Ni-rich cathode materials, using a continuous stirred tank reactor. Transition metal sulfate solutions are pumped into the reactor with ammonia hydroxide and sodium hydroxide to control the pH. Once the reaction is complete, spherical secondary particles of NMC hydroxide are collected (green), and subsequently, calcined under oxygen at high temperatures to form the layered oxide (blue).

Advances in science and technology to meet challenges

Although secondary particle size is critical for governing the electrochemical performance of the cathode powder, primary particle size is also important. While the secondary particle assemblies are governed by the co-precipitation process, the primary particles which make these up are particularly susceptible to the calcination conditions. A recent study has looked in detail at calcination conditions of $Ni(OH)_2$ with LiOH precursors and how these manifest in resulting physicochemical properties for the high nickel content cathode $LiNiO_2$.[10] Through the application of automated SEM image analysis, the authors have demonstrated the influence of calcination temperature and Li precursor concentration on the resulting primary particle size. The interface area between the $LiNiO_2$ particle surface and the electrolyte has been monitored by a capacitance method and demonstrates a decrease in first cycle capacity loss with increasing interface area. These findings highlight the critical role particle morphology has to play on resulting performance parameters and a deeper understanding of this influence is of increasing interest with the advent of single crystal morphologies, doped variants and concentration gradient materials. In particular, single crystal morphologies offer the potential for longer lifetime performances due to the lack of grain boundaries that can propagate particle cracking during cycling.

One significant challenge in synthesis and subsequent storage of ever-increasing nickel content cathodes is the inherent surface instabilities which can result in subsequent capacity limitations. Coating methods afford a route to protecting the underlying cathode particles. Wet process methods offer a route to scaled-up coating, but may have an uneven distribution of coating depth across the surface of the particles. Chemical vapour deposition (CVD) and atomic layer deposition (ALD) methods can produce ultrathin and uniform layers on high nickel cathode particles, which act as a barrier to unwanted electrode-electrolyte side reactions. Depending on the coating used, it is possible to additionally tune the resulting cathode electronic, structural and thermal properties.

The co-precipitation method itself allows a variety of chemistries and reaction conditions to be manipulated to produce a range of different morphologies and compositions. For example, core-shell or concentration gradient particles can be applied to try to alleviate these deleterious surface reconstructions.[11] These usually consist of a Ni-rich centre, with a more stable (e.g. higher Mn-content) surface. Judicious selection of gradient conditions may improve resulting thermal stability, alleviate unwanted surface phase transformations, and stem transition metal dissolution that occurs over time. A continued challenge is in the scale-up of such concentration gradient particles, as careful control of synthesis conditions is vital to maintain structural control as the concentration varies across the assembly.

Future Comments and Concluding Remarks

There is an increasing focus on manipulating particle morphologies as these significantly influence key electrochemical performances. For example, the application of in-line monitoring methods such as dynamic light scattering (DLS) of focused beam reflectance measurement (FBRM) can allow for accurate particle sizing information during synthesis.[12] The further application of multiscale computational modelling is providing phase maps to calculate the most accurate reaction conditions required in order to produce the desired particle specifications.[13] Deepening our synthetic understanding and developing controlled and scalable processes to such tailored particle morphologies remains an ongoing challenge.

Acknowledgements

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Evolution of the Slurry Making Process

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Status

Every stage of the lithium-ion cell manufacturing sequence is important, but the mixing and coating steps arguably have the greatest impact on cell quality [1]. The active materials are mixed with a polymeric binder dissolved in a solvent, and then coated on a thin metal foil, which acts as the current collector. Most cathode and some anode mixes will use one or more carbon additives as conductivity enhancers. Table 4.1 compares the electrode formulations disclosed in an early Sony patent [2] with typical formulations used today (LCO = $LiCoO_2$, NMC-811 = $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, PVDF = poly vinylidene difluoride, CMC = carboxymethyl cellulose, SBR = styrene butadiene rubber, CB = carbon black). The biggest change since 1991 is in the anode, where PVDF has been replaced with CMC and SBR. This has increased the proportion of active material in the electrode and enabled the solvent NMP (N-methyl pyrrolidinone) to be replaced with water. Graphite has replaced hard carbon, ever since ethylene carbonate was introduced as an electrolyte component in place of propylene carbonate.

Table 1 Electrode Formulations (wt%)

	Active	Binder	Carbon
Anode			
1995	Hard carbon 90.0	PVDF 10.0	N / A N / A
2021	Graphite +SiO_x 90.5 + 5.0	CMC + SBR 1.5 + 2.0	CB 1.0
Cathode			
1995	LCO 91.0	PVDF 3.0	CB 6.0
2021	NMC-811 96.0	PVDF 2.0	CB 2.0

The requirements from the mixing process are a homogeneous mix, free from agglomerates, stable for long enough to be coated, and with a viscosity in the correct range for the subsequent coating process. The characterisation and stability of mixes is discussed in greater detail in Section 5. The small scale planetary centrifugal mixers used in laboratory work cannot be scaled up to an industrial scale, but they do produce an idealised version of any given mix formulation. The standard mixer is usually a hydrodynamic shear mixer, with a rotating stirrer head. Kneaders with slower rotation speeds are used for higher viscosity mixes. More specialised mixers are now available, for example, with a rotating mixing tool and counter rotating mixing pan (Eirich, 1 – 12,000 litre mixers), or a rotating thin film mixer with a very high shear rate (Bühler, 11 – 960 litre hour^{-1} flow rate). Some photographs of scalable mixing machines are shown in Figure 4.1. A full sized coating operation would typically require around three litres of mix per minute.

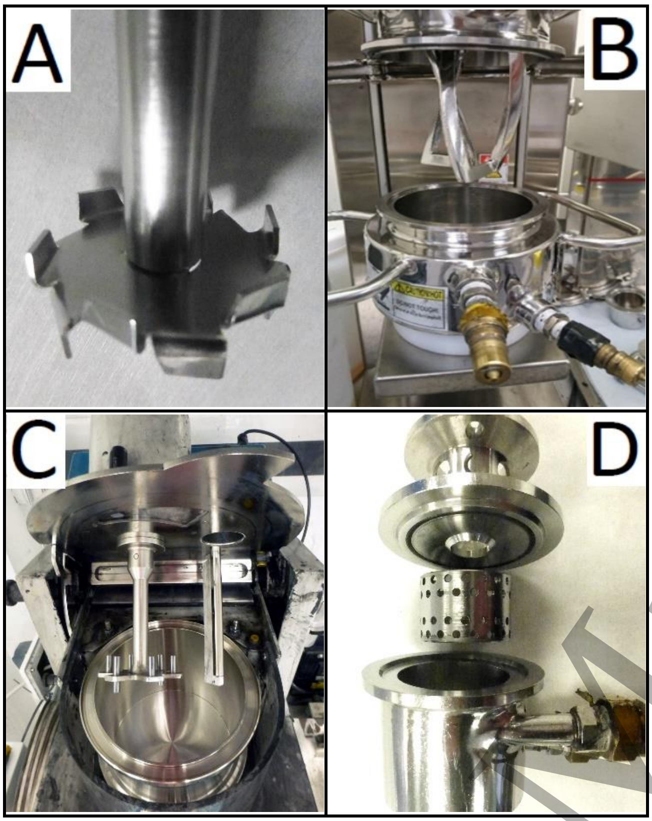

Figure 1. Small scale versions of scalable mixing equipment, A) Hydrodynamic Shear Mixer, B) Kneader, C) Rotating Pan Mixer, and D) Rotating Thin Film Mixer

The coating machine splits into two parts; a high precision coating applicator and a long drying oven, typically with multiple temperature zones. The laboratory “doctor blade” applicator can be scaled up to the reverse comma bar configuration, but industrially slot die coating is the preferred approach [3]. The drying stage ensures that all the solvent is evaporated before the end of the drying oven. However, if drying is too fast, it can lead to increased inhomogeneity, cracking or cratering in the coating.

Current and Future Challenges

Despite many improvements over the past thirty years, there are still several areas where further innovations would be welcome :-

1) **Aqueous cathode coatings**. NMP has been eliminated from anode coatings, but is still just about the only solvent for the PVDF binder in cathodes. NMP is toxic and carcinogenic, uses more energy to evaporate than water, and requires a solvent recovery system in industrial applications. Water would be preferred, but it may hydrolyse cathode materials like LFP ($LiFePO_4$) and NMC-811, and change the morphology of the PVDF binder in the electrode.

2) **Continuous mixing**. Coating is a continuous process, but mixing has traditionally been a batch process. Continuous mixing would reduce the process time and energy consumption, and improve process control, to give a more consistent slurry.
3) **Increased solids content**. The solids content used are typically ~ 50 % in aqueous anode mixes, and ~ 70 % in NMP cathode mixes. If these values can be increased, while maintaining coatability, then the materials and energy costs are reduced [4]. The ultimate limit of this is solvent-less coating (see Section 10 – Dry powder electrode processing).
4) **Thicker electrode**. Using thicker electrodes reduces the amount of metal foil and separator in the cell, and increases the energy density. They can compromise the rate performance of the cell, due to longer electronic and ionic conduction pathways through the electrodes. Moreover, from a practical perspective, it can be difficult to produce thick coatings with acceptable mechanical properties e.g. sufficient flexibility to be wound in cylindrical cells.
5) **Simultaneous double sided coating**. Drying ovens are usually horizontal, with the wet ink on top of the metal foil. Double sided coatings are produced by rewinding the foil, and coating on the other side. Apart from the extra manufacturing time, this means that one side of the coating goes through the oven twice. Simultaneous two sided coating requires a floating drying zone [5].
6) **Porosity gradients**. It is possible to model electrodes, and calculate the optimum porosity as 10 % at the metal foil, and 50 % at the coating surface, rather than a uniform 30 % [6]. In practice, this may require successive coating layers, or a templating technique [7]

Advances in Science and Technology to Meet Challenges

Several of the challenges identified in the previous section have been the subject of laboratory investigations. In studies on aqueous coating of NMC cathode materials, the reaction of the NMC depended on the composition [8]. There was more lithium dissolution for materials with a higher nickel content like NMC-811. Surface exchange of protons and lithium ions produced a high local pH, which could cause corrosion of the aluminium current collector. Potentially, this could be mitigated by a carbon coating on the aluminium. There were also minor changes to the NMC-811 surface, probably due to dissolution of residual Li_2CO_3. Cells achieved a 70 % capacity retention after 1000 cycles, compared to 76 % for an NMC-811 / NMP cathode. Aqueous coating also allows different binder chemistries to be considered [9], provided that they have sufficient oxidation stability for the cathode environment. Surface coatings on active materials, using techniques like atomic layer deposition [10], are also being investigated, to facilitate aqueous processing.

Three different mixing processes were compared on a standard NMC-111 : PVDF : CB = 90 : 4 : 6 wt% mix in NMP; two batch and one continuous [11]. The mixers were a standard stirrer (60 % solids content), a kneader, and co-rotating twin screw extruder (both 75 % solids). The optimum kneading time was 2 – 4 hours. The extruder and optimum kneader coatings gave comparable cycle life to the stirrer coatings, and much better rate performance at 5 C.

Coatings with coat weights of 170 – 660 gsm were prepared from the same NMC-622 : PVDF : Super P : SFG6 = 93 : 4 : 2 : 1 wt% mix [12]. As expected, the performance at high discharge rates was worse for the heavier coatings. Further investigations compared mixing with different solids contents (65 vs. 73 %), and with different drying temperatures.

One topic which can benefit several aspects of the coating process is an understanding of the complicated processes that occur in electrodes during drying. This is based on the dimensionless Peclet numbers, which suggest whether, for example, the binder and conductive carbon will migrate towards the surface of the coating or remain uniformly distributed [13, 14]. A knowledge of the processes occurring can help to increase coating speeds and potentially enable thicker electrodes to be prepared.

As regards mixing, there have been some systematic investigations of different mixing sequences [15, 16]. Historically, PVDF was always pre-dissolved in NMP, and carbon blacks would be de-agglomerated by bead milling. However, dry mixing of all the solid materials is now an option, followed by sequential addition of the coating solvent.

Concluding Remarks

The mixing of slurries and coating of electrodes are important stages within lithium ion cell manufacture, and both require strict process control to achieve a consistent product. New mixing equipment is being introduced, and there will soon be a transition from batch to continuous mixing. There is greater understanding of the science under-pinning the drying phase of coating, and this is helping towards faster coatings and mixes with higher solids contents. The next advance will be the elimination of NMP from cathode mixes, but it remains to be seen whether this will involve aqueous mixes or solvent free coating. Another approach is to adopt a high throughput screening technique, as used successfully in the development of cathode materials and electrolytes [17], to improve electrolyte formulations and mixing approaches, rather than using the existing empirical approach.

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Rheological properties of lithium-ion battery electrode slurries

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Status

The current manufacturing process for lithium-ion batteries (LIB) comprises the deposition of a composite film onto a metallic substrate which contains active, conducting, and binding materials and additives. The deposition is usually via a slurry cast method, and therefore the rheology or flow properties of the slurries is a key parameter considered during manufacturing. It is a function of the formulation and mixing process and can be used to gauge the effectiveness of the mixing, giving important insights into the structure of and interactions in the wet slurry. Finally, it will dictate the behaviour of the slurry during coating and drying, and with optimisation can be used to tailor the microstructure of the electrode produced (Figure 1). [1], [2]

Rheology has typically been used as a quality control indicator, with a shear viscosity measurement performed on a slurry sample at a single or small range of shear rates. There is much to be gained in expanding beyond this, to more thorough characterisation of samples and introducing in-line measurements rather than sampling to capture variations within a batch.

It is an area receiving increased attention, often because of the desire to use new electrode materials, and greener solvents. With rheology being one way the properties of new formulations can be matched to existing slurries and provide drop-in replacements in the manufacturing process (e.g. different active materials [3], green binders[4]). In addition, there has been increased focus on explaining the origins of the rheology, as understanding the impact of the slurry components (e.g. binder [5], carbon black [6]) allows the formulation to be optimised (e.g. maximise amount of active material).

The rheology can also be tuned by changing other process parameters such as solid weight percent [7], mixing methods [8], coating temperature [9] and the incorporation of secondary solvents [10], [11]. The goal in these studies is to achieve higher yield stress to reduce sedimentation, and steepen the viscosity curve, to achieve increased viscosity at low shear leading to less slumping after coating and sharper coating edges, and decreased high shear viscosity, leading to less resistance and more stable flow in the coater.

However, there are significant opportunities for predictive control of the final coating microstructure. Currently, it is difficult to correlate the rheological properties with the electrode performance[12], but with advances in modelling and incorporation of the myriad other factors involved in the creation of coating microstructure, this may be achieved.

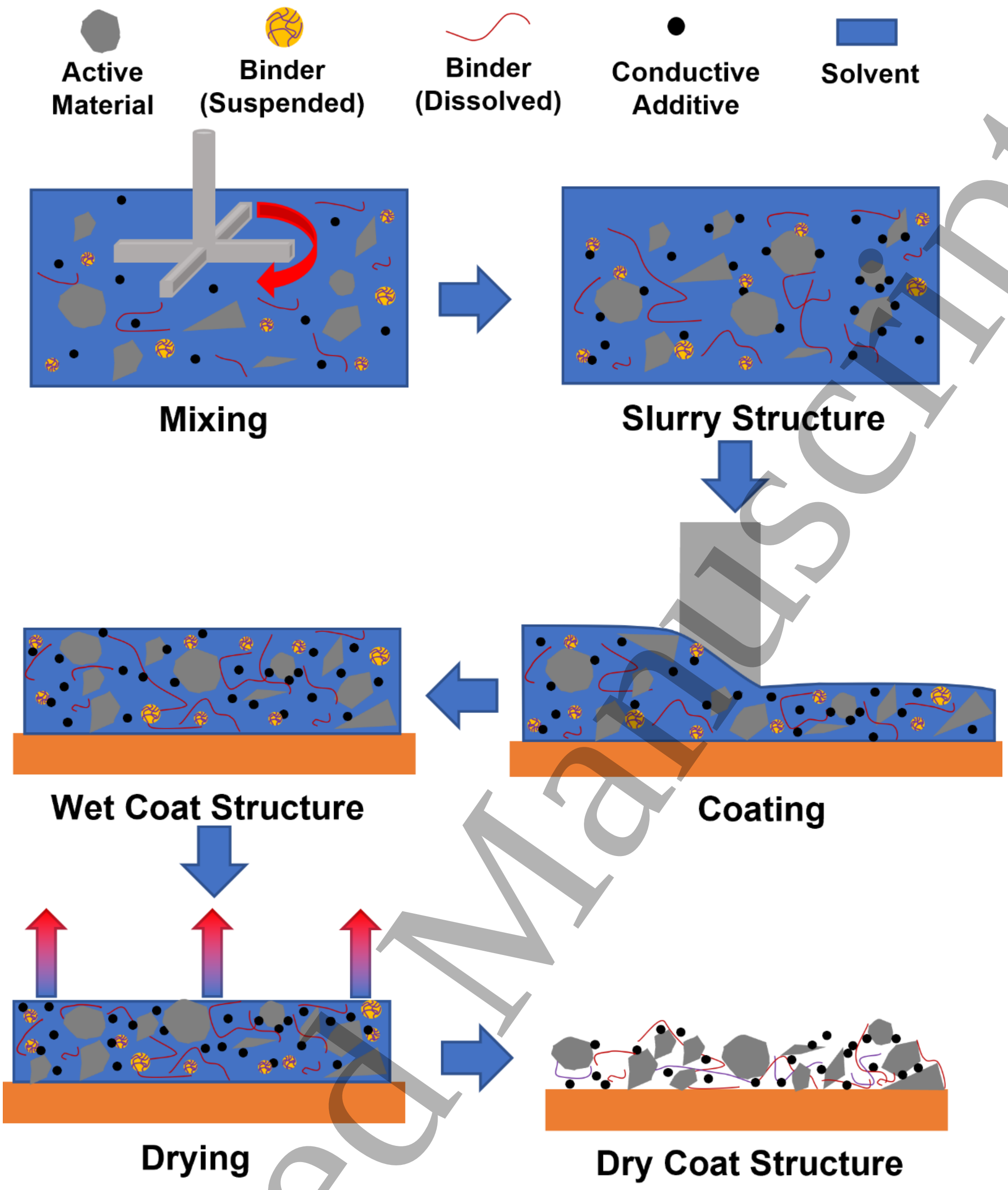

Figure 1. Flow diagram illustrating the creation of microstructure during the electrode manufacture process. Rheology is dictated by the formulation and mixing steps and impacts the coating and resulting wet coat structure, which then has a knock-on effect on the dry coat structure (including changes in the subsequent calendering step)

Current and Future Challenges

There are three major challenges to be addressed, to use rheology as a predictive tool in manufacture. The first is advancing rheological characterisation of electrode slurries with industrially relevant formulations, weight percentages and apparatus (mixers and coaters). The difference between lab-scale and industrial processes can be vast, and currently the relationship between these process changes and key properties (such as rheology) is not understood, making scaleup difficult and limiting the applicability of research. Advanced characterisation is required to fully understand ink coatability e.g. extensional rheology is rarely quantified. As coating flows have considerable extensional components, its inclusion enables improved modelling of industrially relevant coating and mixing flows [13]. Additionally, there is room for in-line metrology, rheology can detect subtle but important variations within slurry batches during mixing and coating. For example, poor mixing may lead to inhomogeneous distributions of free carbon black within the ink, leading to variations in viscosity and viscoelasticity across the batch. [14][15]

The second is elucidating the interactions in electrode slurries, their dependence on formulation and mixing and how they dictate the flow properties, to allow optimisation of the rheology. For example, carbon black forms a network in N-methyl pyrrolidone (NMP) solvents which dictates the rheology of cathodes and binder only serves to shift to higher viscosity, whereas in water-based slurries the thickening agent determines the shear-thinning properties of the ink [5],[6],[16]. Therefore the deposition, drying and the resulting microstructures differ, requiring different control protocols. Further insights are required for existing and novel materials, to create empirical and multi-physics models and enable efficient optimisation of slurry rheology. This will be vital with the move to novel materials and more sustainable and lower cost water-based solvent/binder systems. [16]

The final challenge is to obtain a quantitative understanding of the optimum rheology for manufacturing and process control. Modelling will be key to understand the coating flow and potential problems; instability, accumulation of material in dead zones and defects such as pin holes, blisters, cracking, and delamination. Studies of slot-die coaters (most common industrially), exist for materials with similar bulk rheology to electrode slurries.[17] This needs expansion to include particulates, to assess the impact of flow on the coating structure and model the drying process. These models require accurate input parameters (e.g. wet coat structure) to capture movement of all components during deposition and drying, to ensure homogeneous and cohesive, adhesive coatings. [18] Correlating the cascading effect of rheology on later processing, electrode manufacturing can be rapidly optimised, which is vital to the rapid expansion of battery manufacturing, new cell chemistries and materials and greater sustainability.

Advances in Science and Technology to Meet Challenges

Advancing rheological characterisation methods to populate multi-scale models, requires a combined effort from academics, equipment manufacturers and industry professionals. Industrially relevant studies on similar mixers and coaters are required, as changes in dimensions and scale significantly affect the flow and transport of the composite fluids, and hence the influence of the rheological properties upon the final electrode structures may change. Novel technology is required, in-line rheometers, which exist for various manufacturing processes, need to be optimised for electrode slurries and integrated into manufacturing equipment to extract real time impact of rheology on processing. Extensional rheometers, for which commercial options are rare, also need to be developed for electrode slurries, as well as models for extensional behaviour of particulate slurries to extract the underlying microstructure from extension. [2]

For the second challenge of linking rheology to a thorough structural understanding of the slurry, current work needs to be coherently combined, and correlated to extract universal relationships that are material agnostic, enabling rapid adoption of the 'drop-in' technologies being developed (new chemistries, greener and safer solvents). For example, switching from NMP to water-based slurries, the driver for rheology is no longer the carbon black network but now the binder. [6],[16] Understanding this relationship quantitatively would give precise amount of binder required to match the rheology to the previous formulation and remove barriers to drop-in replacement. A model which encapsulates all the complex components and interactions to predict the bulk slurry rheology, would bring great advancements in manufacturing, but requires advancements in experimental parameterisation as well as understanding of the underlying physics in electrode slurries.

Finally, understanding the optimum rheology requires bringing together the most advanced research in rheology and manufacturing. Experimental studies must be combined with current bulk modelling approaches such as CFD (Computational Fluid Dynamics) to elucidate the conditions and behaviour of the slurry in the coating process. Additionally, a microscopic understanding must also be developed; how the complex flow in processing affects the particle distributions and creates the final coating microstructure. Control of the final microstructure will allow the manufacturing process to pushed to the limits of speed and final electrode performance, enabling high outputs and maximum performance from the materials used. The most advanced experimental research must be brought together with microscopic and bulk flow modelling to achieve this goal.

Concluding Remarks

In conclusion, control of rheological properties is essential in the electrode manufacturing process. A greater degree of characterisation of both shear and extension is required for off and in-line testing. This requires development of new methodologies and tools. The extracted rheological parameters will enable multi-physics models of the processes which will provide real time control and characterisation of these industrially relevant processes. This cannot be studied in isolation; realisation of its impact can only be achieved by combining the latest advances in measurement and modelling of the complete manufacturing process to elucidate the impact of the physics of the complex flows upon the final electrode.

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Coating current collectors with electrode slurries

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Status

Electrode coating encompasses all the steps that transform a pre-mixed electrode slurry into a layer with defined width and thickness that is supported on a metallic current collector foil which, after drying, becomes the core energy-storing component of a Li-ion battery. While differing in complexity and throughput, all the standard coating methods used in the manufacturing of liquid electrolyte-based Li-ion batteries rely on passing the electrode slurry through a gap of defined thickness onto the current collector foil. At the lab-scale, the gap is set by a doctor blade embedded in a frame that moves and spreads the slurry over a foil. In industrial, roll-to-roll processing, the slurry is applied continuously onto a moving foil. The gap was originally controlled by a comma bar but nowadays a slot-die arrangement is more common. In this process, the slurry is applied onto the foil through an internal die channel with a defined geometry at a set height and slurry flow rate. Slot-die coating has become the standard in the battery industry, currently allowing coatings of up to 4 m wide, up to a few hundred-microns thickness at 10 – 30 m/min rate, and with a coat-weight variation of only 1 – 2% [1]. Maintaining such small loading variation is crucial for minimising rejection rate and maximising output of the electrode fabrication line.

The uniformity of the coating is determined by five key factors: degree of dispersion of solid components within the slurry, rheology of the slurry, thickness uniformity of the current collector, rate of the slurry delivery, and the uniformity of the slot-die design (for a detailed review, see the work of Li *et al.*[1]). Although rarely controlled in a quantified manner, it is also known that the wetting of the slurry onto the metal foil surface (a function of e.g. surface pre-cleaning) influences coating quality, potentially leading to defects such as cracks after drying, a high scrap rate and potentially lower lifetime in the final cell [2].

There is a huge amount of capital spend planned for the next several years on manufacturing equipment based on the current coating process. Advances in coating technology must either be a drop-in replacement into the current coating lines or provide a significant improvement in battery performance to be attractive to industry. Thus, future advances in coating techniques are targeting either higher efficiency at speeds up to 90 m/min while maintaining current electrode performance i.e. lowering price per Wh while maintaining energy density, or improving electrode performance – e.g. increasing energy density or cycling stability by changing the electrode structure.

Current and Future Challenges

Many of the limitations in the current coating techniques are related to the use of liquid-based slurries. Typically in these slurries, 30-60% of the mass is solvent[3] – a temporary component that needs to be removed from the electrode and leaves excessive porosity in the dried layer so that it requires calendering to densify, making the process fundamentally inefficient. For the state-or-the-art cathode slurries, the preferred solvent, N-Methyl-2-pyrrolidone (NMP), is harmful, flammable and

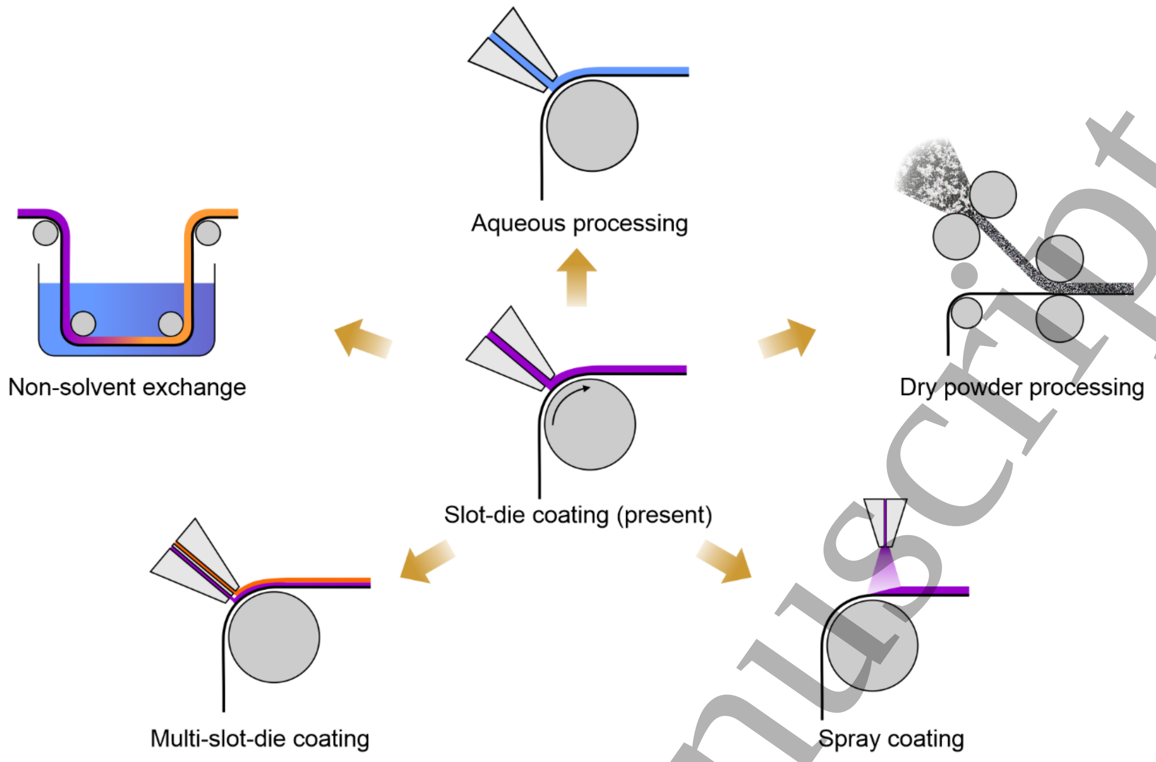

Figure 1. Upcoming advances in electrode coating techniques

requires complex recovery systems that significantly increase energy consumption [1], and manufacturing costs by 20% [4] equating to 3.4% to the cost of the pack [5][5]. If NMP is replaced by water, high energy density active materials such as lithium nickel manganese cobalt oxides (NMC) suffer from leaching of Li, lowering electrode capacity, alkalizing slurry and resulting in corrosion of Al current collector. Also, the higher surface tension of water results in higher capillary forces during drying and inferior wetting on current collectors, resulting in cracking and delamination of as-fabricated layers, particularly for thick (> 100 µm) electrodes [2]. The issues with mechanical stability of electrodes are not limited to water-based slurries – the migration of polymeric binders from the bottom of the wet electrode to the top during drying is known to result in layer delamination and cracking, which puts a technological limit to the thickness of both NMP- and water-derived electrodes to less than 100 µm [6]. Dry or low-solvent deposition can circumvent all of these challenges (described in Section 10) but comes with its own challenges; ensuring sufficient mixing of dry slurry components, temporally inducing flow behaviour to a mixture of dry powders for casting, shaping such mixture into a coherent layer of defined width and thickness and finally, ensuring its adhesion to the current collector.

On a macroscopic level, electrodes produced by slurry casting are intended to have a spatially homogenous composition and pore structure. The optimum composition, thickness and porosity of current battery electrodes are arrived at by trial and error, within the constraints of the slurry casting process. Relaxing these constraints and offering greater flexibility and control may enable the design of higher performance electrodes. For example, typical electrodes have a through-plane tortuosity factor of between 2 and 9, where 1 is ideal [7]. In sufficiently thick electrodes, rate performance is limited by ion transport in the electrolyte. If tortuosity were reduced, but total porosity kept constant, power density would be increased while maintaining the same energy density.

Advances in Science and Technology to Meet Challenges

Advances are being made in both industry and academia to meet the challenges discussed above, as schematically shown in Figure 1. To further increase the productivity of conventional slurry coating lines, coating speeds are increasing up to and above 100 m/min. The challenge is maintaining a stable coating flow as speed increases. New, more efficient drying methods are also being developed to reduce drying time, as discussed in Section 8. Currently, two passes of the coating line are necessary to coat both sides of the electrode foil. To increase productivity, industry is beginning to implement sequential and simultaneous double-sided coating methods that require only one pass – potentially doubling the throughput of the coating line.

Non-solvent exchange, a type of phase inversion, can potentially lower the costs associated with coating NMP-based slurries. If prior to drying, the freshly-coated electrode is passed through a tank containing an NMP-miscible liquid that is a non-solvent to the electrode binder (e.g. water), it will cause removal of the NMP from the electrode to the tank – where it can be collected in larger quantities and shipped for separation in dedicated facilities at much larger scale, and lower cost, than at the battery manufacturing line [8]. Also, non-solvent exchange results in rapid solidification of the binder within the wet electrode, leading to reduced migration of solid binder during drying and allowing for faster drying and thicker, mechanically stable electrodes [6]. In certain conditions, non-solvent exchange can also induce through-plane vertical pores that lower tortuosity of the electrode and are beneficial to electrode rate performance [9]. Like many pore engineering approaches, it is not yet clear whether benefits of vertical pores can be preserved sufficiently after calendering. Nonetheless, non-solvent exchange offers potential for scalability that is more restricted in alternative structuring methods, such as laser patterning, ice-templating or 3D printing [10]–[12].

To enable the aqueous processing of NMC cathodes, and overcome the associated Li-leaching challenges, strategies range from applying protective coatings on the NMC active material and aluminium current collector to control of slurry pH using amphoteric oxides or weak acids [13]. A particularly effective treatment is adding phosphoric acid to the slurry which simultaneously modulates the slurry pH and forms a thin protective lithium phosphate layer on active material particles. Recently, aqueous processed NMC811 cathodes maintained 70% capacity after 1000 cycles, comparable to electrodes produced by conventional NMP-based slurries [14]. Other issues are introduced by using aqueous based cathode slurries such as greater tendency for carbon black agglomeration, higher surface energy, and higher viscosity. These, in turn, are being managed by using slurry additives and the use of alternative or multiple binders.

Coating methods are being developed that enable through-thickness layering or grading of electrode composition. By using either a multi-slot die, or multiple passes of conventional slot die, it is possible to produce a layered electrode structures[15], such as the ones presented in Figure 2. Although there is the added complexity of handling multiple slurries and ensuring deposited layers are uniform and nonmixing, this approach is only a modification of the current process and so may be relatively easy

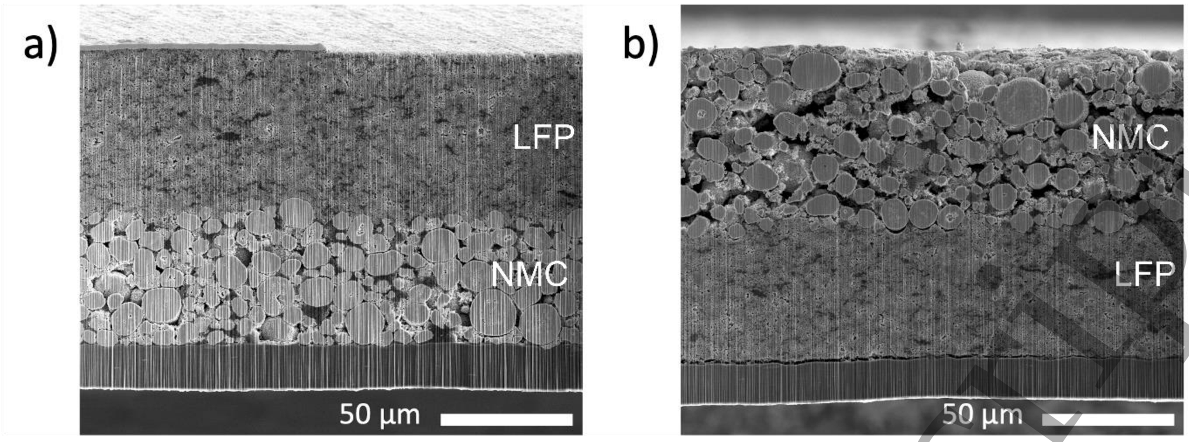

Figure 2. SEM-FIB cross section images of a) NMC/LFP and b) LFP/NMC bilayer electrodes produced by multi-pass doctor blade coating.

to implement. Spray deposition or spray printing approaches are also being explored that enable grading of electrode composition. Typically, a dilute suspension (around 3 wt.% solids) is pumped through a spray nozzle which is atomized by compressed air and deposited onto a heated current collector foil [16]. The composition of the electrode can be graded in a continuous manner by changing the composition of the suspension over time, although the method relies on significantly higher solvent use.

Concluding Remarks

The electrode coating process based on slurry casting has been highly optimised over the past three decades, driving huge gains in productivity and price reduction. Nonetheless, there remains a need to further reduce cost and increase safety and sustainability. In particular, there is a significant motivation to replace NMP-based slurry processes with water-based alternatives, as has already been implemented for graphite anodes and will likely be implemented for many cathodes formulations soon. Beyond this, greater control and flexibility in electrode microstructure design or the employment of next generation electrode materials may demand changes to the electrode coating process.

Once aqueous-based slurries are fully applied in slurry coating, the incentive for development of completely solvent-free processing, and its fundamentally dry extrusion approach, may be reduced. On the other hand, once developed, dry processing may also be adaptable for the fabrication of solid-state battery cathodes that are made from dry powders of active material and solid electrolyte. Therefore, it is likely that the upcoming future will see both the improvements of wet coating methods and the development of emerging dry processes.

Acknowledgements

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Electrode Structuring Through Slurry Cast Processing

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Status

Slurry casting is a prevailing manufacturing process that has been adopted to produce electrodes for lithium-ion batteries in both industry and academia due to its high productivity and cost-effectiveness. A typical slurry casting process includes four steps: mixing, coating, drying and calendering [1]. Active material particles, conductive additives, binder and solvent are first mixed to form electrode suspension. The electrode suspension is then coated on a metallic foil via a doctor blade in labs or a slot die in industry, followed by drying. The solvent is evaporated in the drying process and the dispersed particles are bound together by the binder. The dried electrode coating is subsequently densified by calendering to achieve the intended electrode densities. This slurry casting process produces electrodes, which have a tortuous porous structure with random porosity formed by solvent evaporation between adjacent particles [2]. Thick, or high coat-weight slurry-casted electrodes have kinetic limitations caused by sluggish lithium-ion transport through the film, resulting in limited battery performance [3]. In the pursuit of higher-performance lithium-ion batteries, particularly high energy density and fast charging/discharging rate, the electrode thickness, porosity, pore size, pore shape, tortuosity, active material mass loading, conductive additive and binder distributions are crucial factors to control and optimise. To this end, many new manufacturing technologies have been proposed to produce electrodes with tailored structures, like coextrusion [4], direct ink writing [5] and laser processing [6]. However, these techniques are still in a very early stage and cannot replace slurry casting in the short term. Furthermore, these manufacturing processes are not compatible with slurry casting and need extra equipment investment, which limits industrial acceptance. Therefore, technology modification and improvement in the existing slurry cast processing to enable controllability over the produced electrode structure is a promising approach for the development of high-performance next-generation lithium-ion battery electrodes.

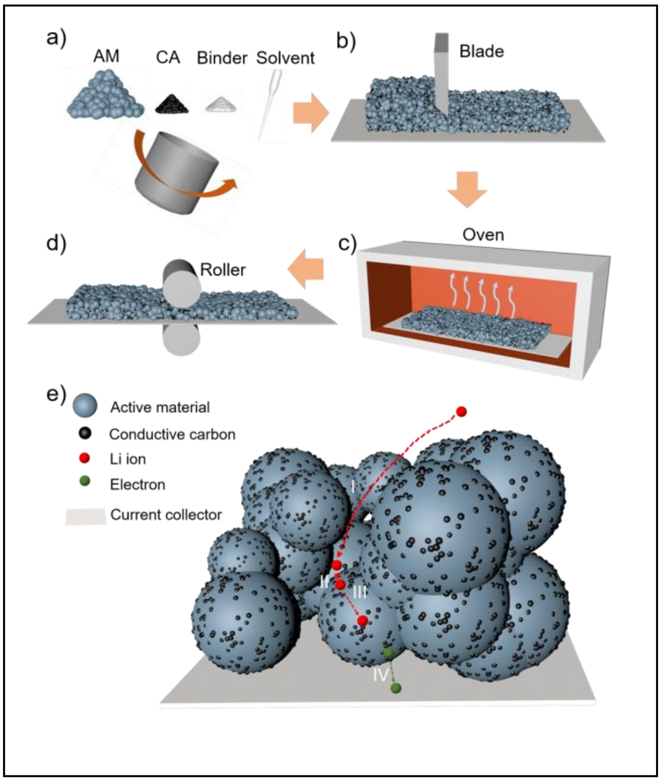

Figure 1. Slurry cast processing a-d; a) mixing of active material (AM), conductive additive (CA), binder and solvent; b) coating via a doctor blade on a metallic foil; c) drying; d) calendering; e) schematic illustration of the transport of lithium ions and electrons, I) lithium ions diffuse in the bulk electrolyte, II) charge transfer at the electrode/electrolyte interface, III) solid-state diffusion of lithium ions within active material particles, IV) electrons transfer from conductive carbon network to the current collector

Current and Future Challenges

The energy storage/extraction process of a lithium-ion battery mainly contains four steps: a) lithium-ion diffusion in the bulk electrolyte, b) charge transfer at the electrode/electrolyte interface, c) solid-state diffusion of Li ions within active material particles, d) electron transfer from conductive carbon network to the current collector, as shown in Figure 1. In order to obtain a high-performing battery electrode using a slurry casting process, a number of factors need to be considered with an aim to optimise the electronic and ionic transport properties; such as thickness, porosity, tortuosity, coat weight, electronic conductivity and adhesion.

Electrode thickness is one of the key structural parameters, which can affect the energy density of lithium-ion batteries. To reduce the inactive components, for example, current collector, separator and battery housing, and increase the energy density, higher loadings resulting in thicker electrodes are required [7]. The electrode thickness produced by slurry casting is normally limited to the range of 50-100 µm, since thicker slurry-casted electrodes suffer from sluggish lithium-ion transport due to long diffusion pathways [8]. Besides, thick electrodes are also vulnerable to cracking and delamination from current collectors. There are thus a number of challenges to overcome to allow increased electrode thickness.

Porosity is another critical parameter that has both positive and negative effects on lithium-ion battery performance. On the positive side, high electrode porosity facilitates electrolyte penetration and lithium-ion diffusion, which is advantageous for improving the rate capability of lithium-ion batteries [9]. On the negative side, increasing electrode porosity inevitably reduces the volumetric proportion of active materials, electrical conductivity and mechanical properties of the electrode, reducing the volumetric energy density. Therefore, most commercial electrodes have a porosity in the range of 0.3-

0.4 for a trade-off in diverse battery performance. In current lithium-ion batteries, the controllability of slurry casting over the electrode porosity predominantly relies on the calendering step [10]. Future advances to deliver thicker electrodes, however, require additional processes to deliver the necessary control of the porosity to ensure good performance.

Tortuosity, i.e. the ratio of actual lithium ions diffusion path length to the straight distance between start and end points, is a structural parameter that describes the difficulty of li-ions diffusion in an electrode. The correlation between electrode porosity, ε, and tortuosity, T, can be approximately estimated by the Bruggeman equation [11]

$$\mathrm{T} = \gamma\varepsilon\hat{}(-\alpha)$$

γ and α are two constants that depend on the manufacturing process and raw material used. Though the electrode tortuosity can be reduced by increasing electrode porosity, it is unwise to increase electrode porosity infinitely. For the next-generation lithium-ion battery electrode with higher mass loading, the challenge is a need to develop novel electrode structuring strategies to achieve low electrode tortuosity without sacrificing other electrode performance by controlling electrode pore shape, size and even distribution.

Advances in Science and Technology to Meet Challenges

A range of methodologies is being investigated to improve slurry processed electrode performance, notably to control the porosity and tortuosity so as to achieve the balance of energy density, power density, cost and weight. There are three aspects of coatings that can be utilised to meet these technology challenges, incorporation of templating agents in the mix, use of secondary solvents and control of the drying process, either in isolation or together.

Salt particles have been used as templates to produce electrodes with the desired porous structures [12]. The salt is added in the electrode ink mixing step, coated onto the current collector, and finally removed to leave pores/channels in the electrode. As an exemplar, Elango et al. used NaCl particles as the template to make 1mm thick $LiFePO_4$ and $Li_4Ti_5O_{12}$ electrodes with well-controlled porosity of 0.4 and pore size in the range of 6-10 μm [13]. The as-produced electrodes deliver 4 times higher areal capacity than conventional slurry-casted electrodes (20 against 5 mAh cm^{-2}), which can be ascribed to increased electrode thickness and reduced tortuosity of the resultant optimised porous structure. Nevertheless, there are limitations for NaCl templating, notably the fact that it requires water dissolution for the removal of the NaCl templates, which is challenging for some water-sensitive electrodes, like high-Ni content NMC cathodes. To overcome this issue, recent work has used NH_4HCO_3 particles as the template which can be removed by low-temperature heat treatment, providing a promising alternative solution in this area [14]. Other templating methodologies, like wood and magnetic-assisted templating, have also been proposed in the literature [15, 16].

The addition of an immiscible secondary solvent can drastically alter the rheological properties of the electrode slurry and further change the movement of active material and conductive additive particles, resulting in distinct porous structures [17]. Recently, Gastol et al. illustrated the beneficial effect of a small amount of 1-octanol (0.1-10 wt.%) as the secondary solvent in water-based graphite slurry with CMC and SBR [18]. In this example, 1-octanol preferentially wets the particles over water and forms pendular bridges between adjacent particles, resulting in electrodes with a sample-spanning network. Furthermore, the addition of 1-octanol also increases the viscosity of the electrode slurry, enhancing the dispersion of particles. The as-produced graphite electrodes were shown to have lower tortuosity and better cycling performance. On the contrary, the addition of a miscible secondary solvent can also help to control electrode structure by affecting the drying process, which will be discussed next.

Drying follows a three-stage process: solvent evaporation from the surface and film shrinkage, the removal of the solvent through the capillary network between the particles, gaseous removal of the final solvent. The electrode structure can be tuned by manipulating the solvent, temperature, drying speed. Recent work reported that $VOPO_4$ electrodes with vertical channels were fabricated by fast solvent evaporation which is achieved by using two miscible solvents of 2-propanol and water (1:1 v/v) at 60 ˚C under vacuum. The $VOPO_4$ nanosheets simultaneously experience an upward force induced by evaporation flow and downward gravitational force, resulting in a net torque on the nanosheets and thus aligning the nanosheets perpendicular to the current collector [19]. It also should be noted that severe binder migration may take place driven by capillary action during fast solvent evaporation, resulting in non-uniform binder distribution. A two-step drying process, consisting of an initial low-temperature drying at 25°C for 16 hours to stabilise the electrode structure and followed by a high-temperature drying at 70°C for about 3 hours to completely remove the solvent, has been successfully applied to produce NMC electrodes with uniform distribution of binder and conductive additive [20].

Concluding Remarks

Slurry casting is currently the prevailing manufacturing process for lithium-ion battery electrodes. However, the low controllability over electrode structures, e.g. thickness, porosity and associated high electrode tortuosity, restricts the future adoption of slurry casting for thicker higher-performance lithium-ion battery electrodes. To further explore the potential of slurry casting, electrode structuring strategies, like templating, the addition of a secondary solvent and drying control, have been proposed to produce electrodes with tailored structures. These electrode structuring strategies are compatible with the existing slurry cast processing and can be achieved with only minor modifications, providing promising approaches for the manufacture of the next-generation lithium-ion battery electrodes.

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Mechanistic Understanding of Electrode Drying by Modelling

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Status

Improved lithium-ion battery (LIB) performance and decreased failure rate are possible through a better understanding of the electrode drying process (EDP). Mastering the EDP will allow the synthesis of defect-free electrodes which leads to homogeneity in both current densities and lithium transport between the electrodes. Even though the slurry casting of electrodes is a well-developed method for manufacturing electrodes [3], the coating inconsistency and microstructure defects occurring in the EDP cannot be avoided [4]. The drying protocol and the wet slurry casting process play dominant roles to form the microstructural and morphological properties of the electrodes cast by wet processing [5]. The optimum slurry casting process is closely related to the electrode drying mechanisms. In order to manufacture the electrodes with controlled properties an in-depth understanding of the electrode drying mechanism is necessary [6]. It will guide the future electrode manufacturing process for casting made-to-order electrodes [5].

The EDP is a complex process which includes certain number of parameters/variables which would affect the manufactured electrodes in terms of microstructural, mechanical and electrochemical properties. Zhang et. al. [7]have reviewed the EDP and summarized the effect of the different variables as shown in Figure 1. There are three primary classes of methods that have been introduced in the EDP for understanding the drying mechanism [5]: electrochemical testing, physical characterization, and modelling . Although the first possibility makes the strongest link with battery performance, the multiple and interconnected variables that must be investigated (see Figure 1) make it difficult to attribute changes in the EDP to the measured results in a timely manner. To isolate effects more strongly and streamline investigations into the EDP, the second method is preferable, but the objective to observe the fine structure of the electrode usually necessitates *ex-site* techniques. *In-situ* measurements are preferable, but there is a long way to go on this front. The third class, modelling, offers advantages like the ability to observe normally hidden quantities, like binder movement [8] or colloidal stability and thermodynamic properties[9]. The most effective will be modelling supported by advanced *in-situ* metrology, both to design the model and for observations of the EDP. To achieve this, we need to develop a better mechanistic understanding of the EDP through/in addition to models. Here we will present the present state of the art for EDP modelling, what the important challenges are and explain what the road forward will be.

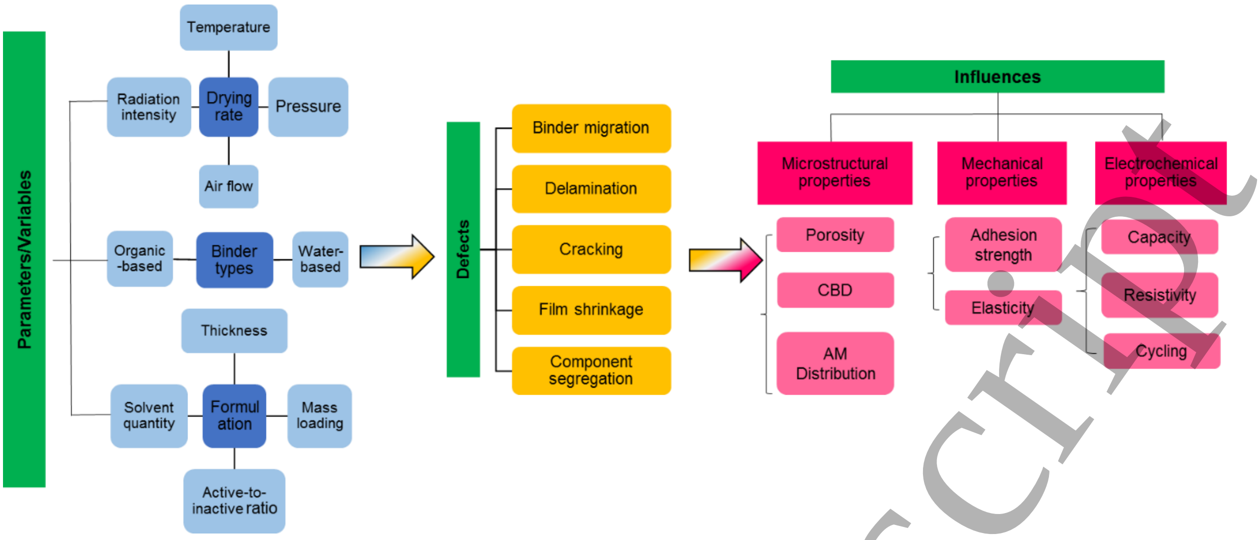

***Figure 1.** Summary of measurable parameters/variables which can affect the electrode formation during the DP and corresponding issues and consequences [1].*

Current and Future Challenges

The key expectation to create a feasible model is to correlate dynamic measurements of drying conditions with the final properties of the electrodes to achieve a more controllable EDP. There are several models of drying non-LIB slurries which can be applied to the LIB EDP. Tsotsas and Mujumdar [10] described different types of modelling: continuum-level models and computational fluid dynamics models. Defraeye *et al.* [11] presented a discussion of convective heat and mass transfer modelling at air-porous material interfaces. Tirumkudulu *et al.* [12] and Yow *et al.* [13, 14] studied the critical stress of cracking in drying latex films. Theoretical models for the drying of single-component and two-component colloidal suspensions have been studied [15]. Meanwhile, the drying of polymer solutions was investigated [16]. An 1D model of particulate coatings that includes Brownian diffusion, sedimentation, and evaporation was implemented [17]. Translating the predictions of these models to LIB EDP is a challenge.

Models designed to tackle the drying of LIB electrodes at industrially drying rates was first tackled in 2018 by Font *et al.* [18].. During the EDP, the active material (AM) forms the skeleton of the porous structure of the dried electrodes as a continuous process which can be affected by the individual variables. Importantly, this dynamic process does not include the binder movement during EDP, therefore the effect of binder migration on the dried electrode cannot be identified. A model of binder migration had previously been proposed by Li *et al.* [20] but, it is questionable whether this analysis holds for LIB EDP because of improperly specified volume phases as noted by Font et al[18]. Font *et al.* [18] presented a one-dimensional model to describe binder migration during the first stage of drying. Their model ceases to be valid when the film becomes consolidated at the end of film shrinkage, or when the pores begin to empty. Susarla et al. [8] also suggested a one-dimensional model for describing the solvent evaporation during the EDP. An established volume-averaging technique proposed by Whitaker et al. [19] has been applied to create the macroscopic model. Susarla et al. [8]proposed the model to take into account temperature, partial pressure of vapour and liquid saturation of the pore network. The model could predict convective transport of the liquid and gas-phase solvent, and air via Darcy's equation. Gaseous diffusion can be modelled based on the Fick's Law, and transport section of the model were coupled to an equation of energy conservation. The solvent removal was expressed as a function of saturation, temperature and porosity. It is also noticed that the capillary pressure depends on temperature via the surface tension A latest three-stage drying mechanism is illustrated in Figure 2. However, neither of these existing models [8, 18] can be relied upon to predict the whole optimal LIB EDP because neither covers the entire EDP as it is understood.

Advances in Science and Technology to Meet Challenges

Given the challenges presented by understanding and modelling the EDP, it is no surprise that advances are required to realize its potential. To start, developing a more accurate and reliable model, more advanced metrology is required, especially *in-situ* metrology. Previous investigations are mostly based on *ex-situ* characterizations (surface morphology, microstructure, element distributions, particle microstructure, pore size distribution and thickness) of the electrodes dried under different conditions. Although there are techniques that have been used in the EDP as *in-situ* methods to investigate the microstructure evolution, drying rate, binder migration, particles distribution and drying stress development, the dynamic profile of EDP acquired by these techniques can only provide limited details because of the limitations of each technique [1]. *In-situ* characterization is important because developing a model based on the entire EDP is advantageous over only having access to the initial and/or final conditions.

The models themselves also still require advances. Essentially there has yet to be a model which fully explains the whole EDP as presented in Figure 2. . With all the mentioned details from Susarla's model [8], it still did not predict binder migration which makes it difficult to predict properties of the electrode such as adhesion. Meanwhile, in the model developed by Font *et al.* [18] that does predict binder migration, with the assumption that the AM particles are uniformly distributed throughout the process of film shrinkage, as sedimentation and agglomeration are believed to have a negligible effect on the timescale of drying. It is also assumed that the temperature is spatially uniform due to the high thermal diffusivities of the components. This limits the applicability of the model. Very recently, Lombardo et al.[21] developed the first physics-based three-dimensional model to mimic additive migration during EDP, which is able to unlock the generation of three-dimensional heterogeneous electrode mesostructures. In the end what is needed for improvement in modelling is a model which can incorporate the dynamic aspects of drying on both the AM distribution and binder movement, so that the model predicts relevant properties for a range of drying conditions.

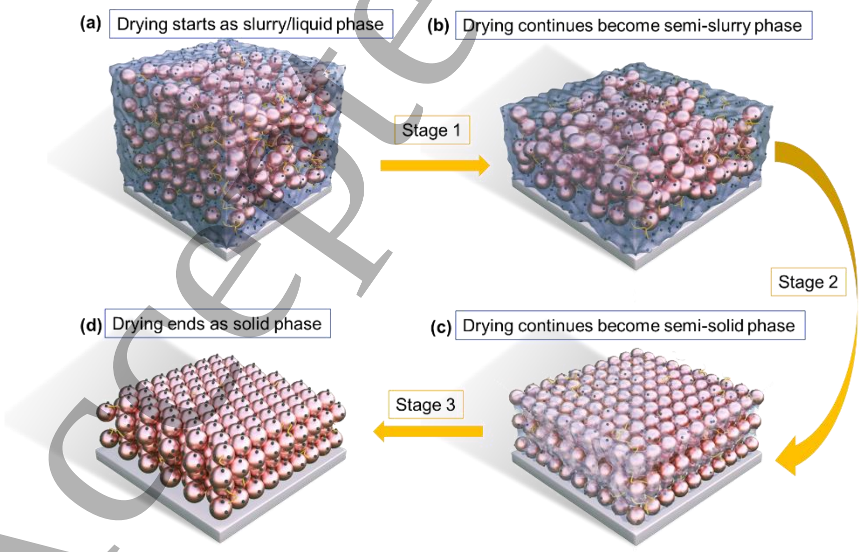

Figure 2. The three-stage drying mechanism. (a) Stage 1 is from slurry phase (e-I) to form a semi-slurry, (b) stage 2 is following with the further removal of solvent and (c) stage 2 ends up with a compacted solid film of coating (d) (yellow lines indicate the binder, pink particles indicate active material particles, black dots indicate the conductive carbon and light blue colour indicates the solvent). (Adapted with permission from [2]. Copyright (2021) American Chemical Society.)

Concluding Remarks

The electrode drying mechanism follows several stages and each stage can be modelled. The *in-situ* metrology that has been applied during EDP can provide the characteristic measurements to validate the models. However, the existing models are not reliable enough to predict the entire LIB EDP due to limitations of the existing metrology. A more comprehensive and reliable model is needed to further study the drying mechanism, and thereby to predicate the optimal drying protocol. It is necessary to further develop the *in-situ* metrology for better control and monitoring of the EDP. A developed model with more measured parameters is needed to provide electrode evolution information during EDP, in terms of microstructure, morphology and component distributions. The urgent need for developing a multi-functional *in-situ* metrology with integration of various measurements is important, including film thickness, coating weight, and morphological properties of the electrodes. Creating comprehensive model for the EDP will help tackle several problems in the complex process of LIB manufacturing in a time efficient manner, unlike experimental studies of LIBs must be. It has the opportunity to solve important problems like reproducibility, lead to high quality products, and improve waste management.

Acknowledgements

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Advanced Metrology for the Electrode Drying Process

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Status

Lithium-ion battery (LIB) is an ubiquitous energy storage technology in numerous important applications and their performance is directly determined by the manufacturing process. The LIB manufacturing process is complex with strongly coupled interdependencies, especially during the electrode drying process (EDP). The typical electrode manufacturing process consists of mixing, coating, drying, calendering, post-drying, cell assembly and formation steps [1]. The authors reviewed the entire LIB manufacturing process with brief coverage of the EDP and the metrology which can be used to characterise the electrode during EDP [1]. Very recently, Liu, *et al.*[2] reviewed the advanced electrode processing of LIBs, focusing on the powder technology in battery fabrication. Other reviews have been published to discuss specific elements of the LIB manufacturing process such as the raw materials [3], separators [4] and laser electrode processing [5], without covering the EDP.

During the EDP, a set of parameters would affect electrode properties, including drying rate, binder types and formulation as reported [1]. The drying rate is mainly controlled by the temperature, pressure, radiation intensity and airflow. The binder and solvent system directly correlate with the drying time, as slurries with water-based binders dry more rapidly than slurries made from an N-Methyl-2-pyrrolidone (NMP)-soluble binder. The types of defects for the as dried electrodes are depending on the drying conditions, including binder migration, coating delamination, film shrinkage and the component segregation. The types of defect will subsequently determine the microstructure of the dried electrode, adhesion strength, cell capacity, resistivity and cycling performance [1].

Efforts to study the EDP have been limited, particularly in terms of *in-situ* metrology. A wide variety of methods are available to study the effect of drying parameters, these being the methods which are typically used to study electrode morphology, such as scanning electron microscopy (SEM), X-ray computed tomography (X-ray CT), energy dispersive X-ray spectroscopy (EDX). A method which has been developed in order to study electrode-drying *in-situ* is the use of ultrasound acoustic measurement [6]. By studying the changing attenuation of ultrasonic waves during EDP, different stages of drying can be identified, and the impact of drying conditions on the dynamics of the EDP can be analysed. This approach may therefore be used to identify in time the points where coating faults occur, and to probe their causes. Further *in-situ* metrological development is necessary in order to more thoroughly understand the EDP.

Current and Future Challenges

The physics and chemistry of LIB EDP are often overlooked, and optimisation is performed by empirical design, rather than with understanding of the underlying physical behaviour, due to the complexity of

LIB manufacturing systems. The drying dynamics of wet electrode films are particularly complex, and the physical processes are poorly understood. To better manipulate electrode structure and their corresponding electronic and ionic transport properties, we need to understand the process by which electrode structures form. The EDP is fundamental to the formation of electrode structure, and it is therefore necessary to develop metrology tools to understand the physical processes which occur during drying. In particular, metrology design and analysis is required to understand the effects of solvent evaporation on defects, such as crack formation or the promotion of self-assembly processes [7]. In order to better control the electrode properties during EDP, drying dynamic is imperative to be further investigated therefore to unlock the potential of LIBs [8] [9].

An effective LIBs manufacturing process will need a suite of advanced analytical techniques including *in-situ* and *ex-situ* characterizations [10-13]. As a complex process for drying electrode which involves numerous parameters, the effects of each parameter on the properties of the dried electrode need to be identified. The current metrology which have been used in the EDP to measure the properties of the electrode are illustrated in Figure 1 [1], which are grouped based on observable features in the early stage of the EDP. Binder distribution can be characterised by energy dispersive EDX, Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and multi-speckle diffusion wave spectroscopy (MSDWS). Solvent evaporation can be measured with thermal gravimetric analysis (TGA) and quartz crystal microbalance (QCM). Surface temperature and drying stress during the solvent evaporation can be measured by Infrared (IR) thermal camera and cantilever deflection method. In dried electrodes, the active materials can be characterized by SEM, X-ray CT and fluorescence-based imaging/microscopy. The structural evolution has been evaluated by a contrast-variation small-angle neutron scattering (CV-SANS) technique [1]. Cantilever deflection method with mercury intrusion porosimetry, as well as X-ray CT enable the evaluation of the particle size distribution in the as dried electrode. The surface morphology or thickness of the dried electrode can be characterized by SEM, optical interferometric profilometry, atomic force microscopy (AFM) and ultrasound acoustic measurement. Characterisation of electrode composition can be achieved using X-ray photoelectron spectroscopy (XPS) [1].

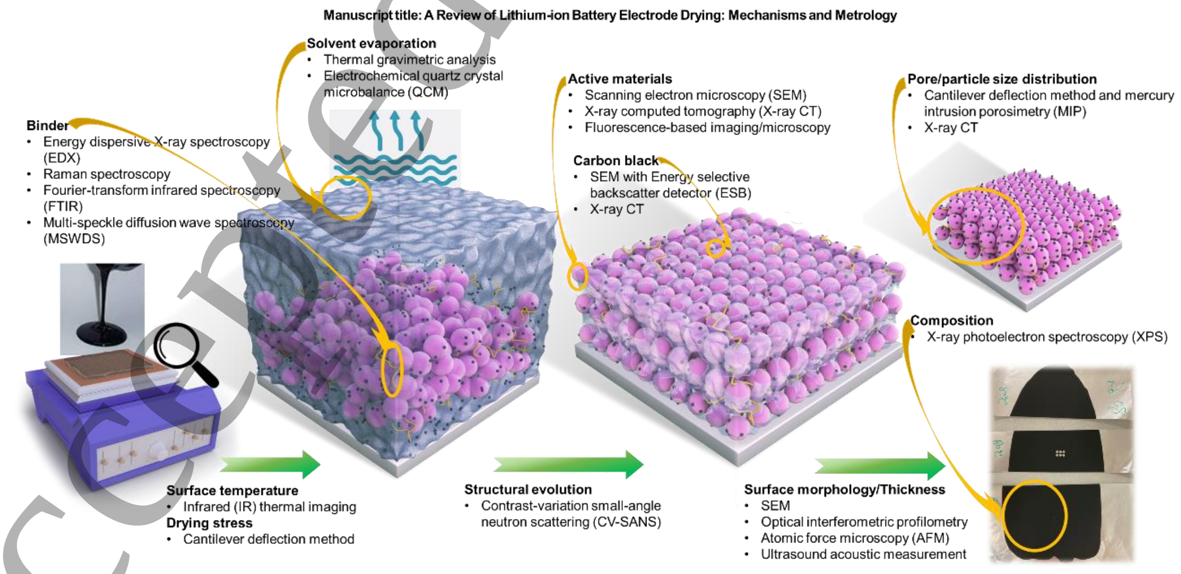

Figure 3 Reviewed metrology for characterizing the various properties of Lithium-ion battery electrode at different stage of drying process.

Advances in Science and Technology to Meet Challenges

Figure 3 illustrated the reviewed metrological methods which have been used or have potential to be introduced in EDP. These methods have been grouped based on the characterization is either qualitative or quantitative, which are powerful techniques which could be used in EDP to assist the understanding of drying mechanism. Some of these techniques have been used in the LIB EDP either as *ex-situ* or *in-situ* methods to study the electrode microstructure evolution or component distributions [1].

Although some methods, such as XPS and Raman spectroscopy [14], have been applied in morphological characterisation of LIB electrodes after drying, development of these techniques for studying the EDP has been limited. For instance, *in-situ* investigations of electrode drying have not been attempted. Shown in Figure 4 illustrates both of the existing metrology which has been applied to study EDP and the emerging metrology that has potential to be developed for understanding electrode drying dynamics [1]. These techniques are grouped according to the length scales on which they operate and a classification of the data they produce. For example, cryo-scanning electron microscopy (Cryo-SEM) and fluorescence microscopy are qualitative methods which can be applied as *in-situ* techniques to study microstructure evolution [15]. SEM with energy selective backscatter (ESB) detector can distinguish carbon black, binder and graphite for anode characterization [16], which are useful for understanding the binder migration behaviour. *In-situ/operando* characterization methods have been developed and applied to characterize LIBs in terms of electrochemical reactions and degradation mechanisms. Chemical and physical properties of battery materials have been characterized during electrochemical processes by a variety of spectroscopy and microscopy techniques [17] as listed in Figure 4. According to the published drying mechanism [18-20], the LIB electrode drying mechanism mainly consists of physical changes including phase change of solvent and movements of the components. Given the ability of the these techniques to variously probe physical parameters of the coatings as well as the spatial arrangement of their constituent parts, there is potential to introduce some of these techniques in the analysis of the LIB EDP. Further development of metrology as described is necessary in order to develop and in-depth understanding about the electrode drying mechanism, and therefore to better control the manufacturing process.

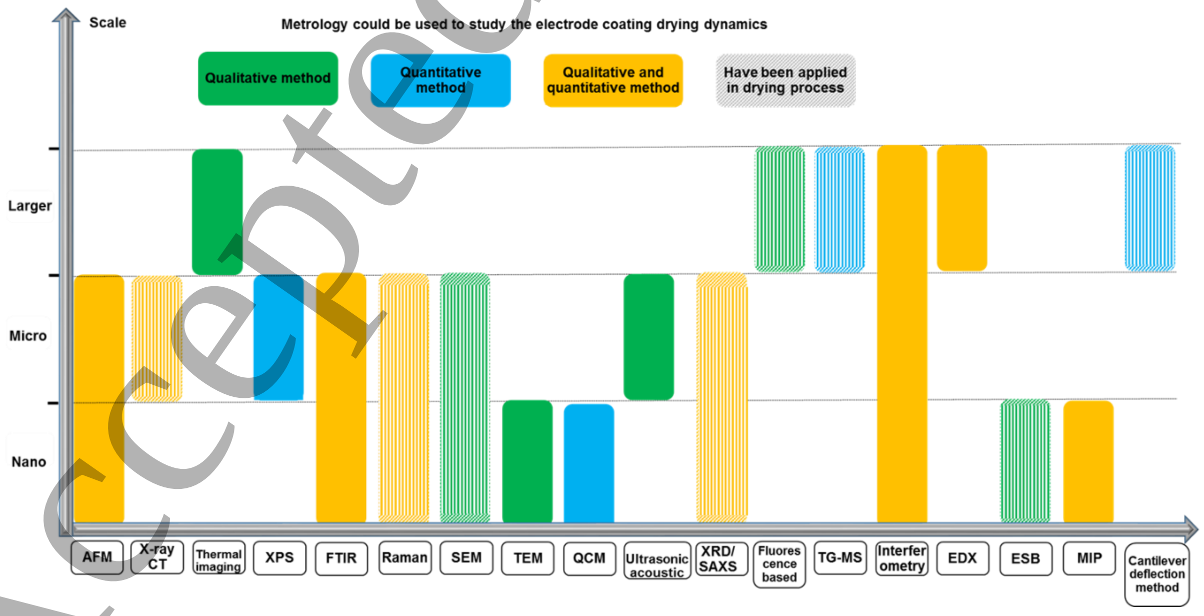

Figure 4 A summary of techniques have been used to study the electrode DP and the potential techniques that could be introduced to study the process [1].

Concluding Remarks

There are limited number of techniques have been used as *in-situ* techniques to investigate the binder movement, particle distributions, microstructure evolution, drying rate and drying stress development. There are many advanced characterization methods that have not been used to analyse LIB electrodes, which nonetheless show the potential to be used to study the EDP. For example, QCM could be an effective tool to study solvent evaporation rate in a nano-resolution. IR thermal imaging could map the surface temperature profile to help optimise heat pulsing effects and effectiveness of EDP. MSDWS could be an effective technique to trace particle movement during EDP. X-ray CT is a powerful method to characterize the electrodes in terms of 3D microstructure evolution. Raman spectroscopy could be an *in-situ* tool to identify binder distribution throughout the electrode film. Ultrasound acoustic technique is capable to obtain physical dynamics of the electrode for a long period due to its fast signal responses. There is indeed a need to develop the existing metrology and also identify new *in-situ* metrology to study LIB electrode DP for process optimization to manufacture high quality of electrodes.

Acknowledgements

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Solvent-free electrode processing: opportunities and challenges

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Status

Commercial energy storage is driven primarily by large and influential corporations in the Li-ion battery (LIB) and electric vehicle (EV) markets with an emphasis on cost and performance. In research, the focus has tended to be on new chemistries or cell designs such as all-solid-state batteries (ASSB). But for both commercial and research activity, new and sustainable battery manufacturing processes are increasingly recognized as essential for a comprehensive green energy transition [1] [2]. In 2022, commercial LIBs are made with a relatively energy intensive process based on slurry casting that offers high and scalable production rates matched to the ever-growing demand for LIBs. However, the electrode fabrication process relies on the use of highly toxic and costly solvents (especially for the cathode) such as N-Methyl-2-Pyrrolidone (NMP) and continuous operation of long drying oven lines. Evaporated solvent requires expensive recovery steps for safe disposal or recycling [1] [2] [3]. Dry, or solvent-free, electrode processing would make a major contribution to a more sustainable battery industry by avoiding the use of solvents altogether and consequently reducing significantly the embodied energy of the electrode which largely (approximately 50%) comes from the solvent removal step [2].

Solvent-free electrode processing has been gaining traction in recent years, with interest from large corporations including Tesla, LG Energy and Samsung. Academic research groups have also successfully manufactured electrodes and also solid-state electrolyte films for ASSBs using different dry processing methods [4] [5] [6] [7] [8] [9] [10]. A dry electrode fabrication process developed by Maxwell Technologies received attention following its purchase by Tesla in 2019. Their method is based on the formation of a 3D network of polytetrafluoroethylene (PTFE) fibrils that effectively bind the active material (AM) and carbon additive (CA) together in a flexible, 3D fibril web, creating a free-standing electrode film. Another technique involves electrostatic coating or dry painting of the AM, binder and CA powders directly onto a current collector, followed by a thermal treatment (hot rolling or pressing) that activates the polymeric binder to interact physically and bind with the particulates [5] [6]. A third process, based on powder extrusion moulding (PEM), combines composite extrusion, de-binding and then sintering [9] [10].

While the feasibility of solvent-free electrode manufacturing has been demonstrated, further research is needed to understand the science behind the dynamics of structural formation, the key parameters influencing the performance of electrodes (lifetime, degradation, energy and power density, and cost), and how such approaches might be scaled up to provide a compelling performance-cost balance that may compete with slurry casting.

Current and Future Challenges

In slurry casting, the solvent is introduced necessarily into the process to dissolve and suspend electrode constituents during casting but has no function in the final product. In fact, if not completely removed, the solvent may harm battery performance. In contrast, manufacturing electrodes without solvents conceptually offers the opportunity to make LIBs more environmentally sustainable, to decrease production cost, and to control better the binder distribution.

For any dry process to replace slurry casting, three conditions need to be met: (i) the performance of the dry electrodes should be as good as slurry cast, (ii) the process should reduce the production cost and impact on the environment, and (iii) this therefore implies that the process should also be easily scalable. One further intriguing possibility is that solvent-free fabrication routes have the potential to create carbon binder domains (CBD) different from their solvent-based equivalents: in solvent-based slurries, the small fraction of polymeric binder is distributed within the electrode by a difficult to control dissolution and re-precipitation process that tends to coat binder onto most of the active surface; in dry processing, the binder is instead distributed by thermo-mechanical means, potentially offering greater control and different, possibly advantageous, CBD morphologies. In addition, by avoiding the drying step altogether, solvent-free processing suppresses binder migration, which is known to produce heterogeneous microstructures and lead to decreased rate performance and capacity in slurry cast electrodes [11]. Practically, better control and minimisation of binder may provide electrodes that are intrinsically higher performing (especially at high charge/discharge rates) than slurry cast equivalents. Alternatively, thicker electrodes in the 100 - 200 µm range with high volumetric capacity may be facilitated. So far however, there are relatively few like-for-like or ("back-to-back") quantified performance comparisons of slurry cast versus equivalent solvent-free electrodes.

The main challenge of the dry painting process is to reduce the content of non-active material to fractions comparable with state-of-the-art cast electrodes (e.g. <5 wt.% for $LiNiMnCoO_2$ (NMC) cathodes and graphite anodes). While Ludwig [5] and Schälicke [6] showed attractive solvent-free electrode formation, fractions of 10 and 14 wt.% of non-active material respectively should be reduced further to boost performance. In terms of scalability, dry painting seems to be the most promising solvent-free process due to its simplicity and the fact that both electrostatic coating and hot rolling are easily scalable. However, electrostatic coating is inherently slower than slurry casting and might not be suitable for the high production rates required in modern gigafactories. In the case of PEM, de la Torre-Gamarra *et al.* manufactured binder-free $LiFePO_4$ (LFP) cathodes. Starting with 50 vol.% polymeric binder in a first extrusion step, de-binding was then achieved by both solvent and thermal treatment. A final step sintered the green body above 500 °C to obtain successfully a binder-free electrode, which might offer an attractive electrochemical response. However, while providing a proof-of-concept route, the de-binding step involving solvents undermines a fully solvent-free process. In addition, the complexity of PEM and the presence of several de-binding steps and high temperature sintering makes this process costlier and likely difficult to scale-up. [12]

Advances in Science and Technology to Meet Challenges

The thermo-mechanical dry processing of electrode components to form polymer binder fibrils is conceptually attractive for the large-scale production of electrodes due to its apparent simplicity and use of existing technologies such as dry mixing, and extrusion or rolling. There are also potentially relatively few steps: mixing of AM, binder and CA, then electrode formation and finally calendering. However, the significant challenge is in understanding and exploiting the crucial fibrillation step as a flexible, platform technology for electrodes of different types. Hippauf *et al.* [4] used a pestle and mortar to achieve fibrillation of PTFE but had difficulty resolving the fibrils by electron microscopy. Our recent work resolves successfully the fibrils in more detail than previously reported [4] , [7]. For example, Figure 1 shows a complex 3D network or web of PTFE fibrils binding the active material particles (in this case a NMC variant) together. There are larger primary fibrils of up to a few 100 nm diameter that extend across several powder particles, from which thinner (a few nm diameter) secondary fibrils branch. We have shown recently that these fibril webs are robust to cold compaction and flexible, foldable and integral electrodes can be achieved with a thickness ranging from 70 to 500 µm. The self-standing electrodes can be laminated on conventional metallic current collectors by a final calendering step. However, a comprehensive exploration and understanding of the structure-property relationships of these types of electrodes has yet to emerge.

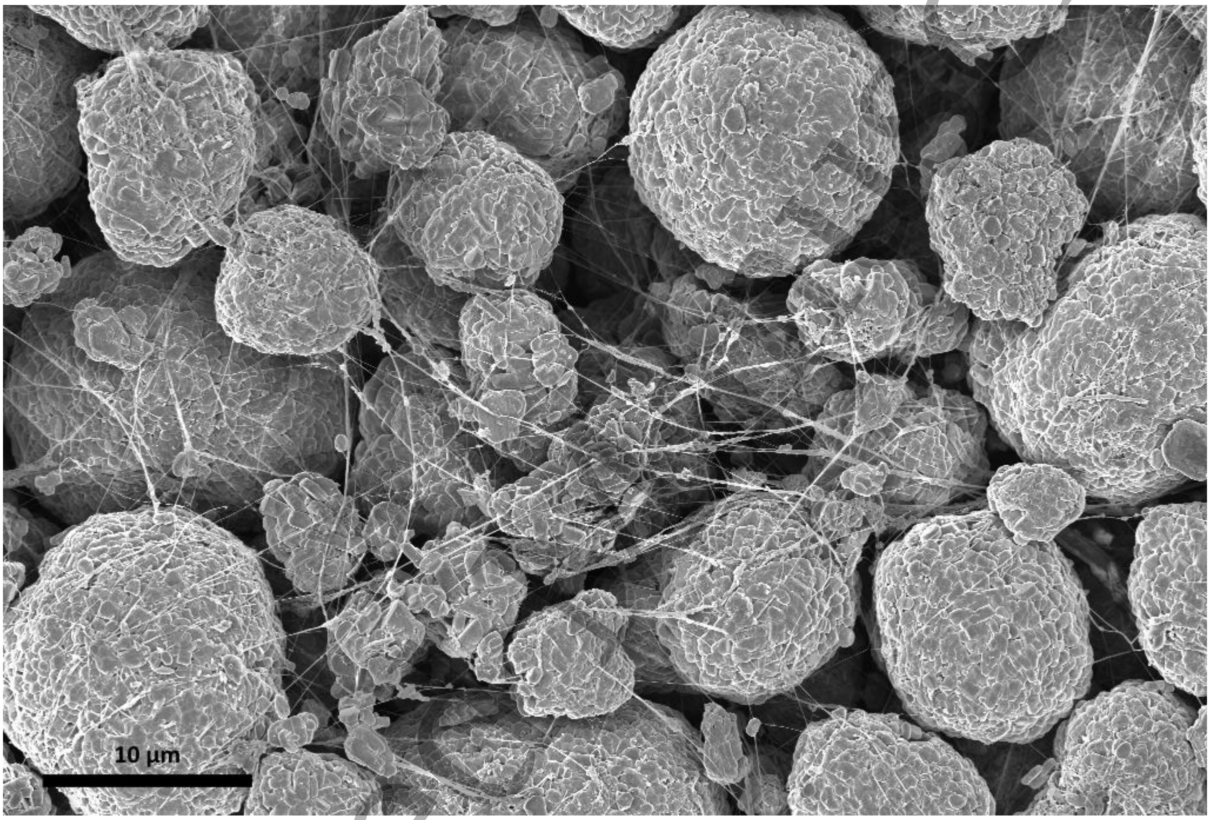

Figure 1. The typical microstructure of a dry processed NMC electrode showing the complex nature of the 3D fibrils network, acting like a spider web that holds the active material powder together, leaving most of the active surface unobscured.

The most comprehensive electrochemical characterisation of solvent-free electrodes relates to those manufactured by dry painting technique. Several investigations [5] [6] [12] [13] have compared the rate and cycling performance of their dry-processed electrodes to slurry cast of similar composition, which are summarised in Table 1. For both typical LIB anodes and cathodes, preliminary energy storage performance was typically as good or slightly better than conventional equivalents. However, more detailed work is required to account fairly for any differences in electrode mass loadings per unit area, porosity fraction, thickness, etc. Compelling demonstrations of the scalability of solvent-free processing are also yet to emerge, and therefore it is difficult to forecast if any solvent-free process will be able to address electrode mass markets. Nonetheless, scientific and technological progress provides significant encouragement for the further exploration of solvent-free LIB and other electrodes.

Active material	Binder	Rate performance	Cycling performance	Ref.
$LiCoO_2$ (LCO)	Polyvinylidene fluoride (PVDF)	Up to 5-10% better at higher C rates (>1C)	70% capacity retention @ 0.5C after 50 cycles, compared to 58% for slurry cast	[5]
NMC	PVDF		87% capacity retention @ 0.5C after 50 cycles, compared to 84% for slurry cast	[5]
Graphite	FEP	Similar to slurry cast	97% capacity retention @ 0.5C after 50 cycles	[6]
NMC	PVDF	Up to 10-20% better at higher C rates (>1C)	69% capacity retention @ 1C after 300 cycles, compared to 52% for slurry cast	[12]
NMC	PVDF	Lower than slurry cast	80% capacity retention @ 0.2C after 300 cycles, compared to 65% for slurry cast	[13]
NMC	PVDF	Similar to slurry cast	80% capacity retention @ 0.5C after 500 cycles, slightly better than slurry cast	[14]

Table 1. Electrochemical performance comparison of dry painted electrodes and conventional slurry cast of similar composition.

Concluding Remarks

Solvent-free processing may help to reduce the operational and capital costs associated with conventional LIB electrode manufacture. Removing the solvent can reduce the number of production steps, floor space requirements and energy demand associated with electrode drying and the associated solvent recovery. For example, cost analysis has shown that, with some assumptions, dry painting of electrodes might be cost-competitive with conventional LIB manufacturing [5]. Most significantly, solvent-free processes can reduce health and environmental hazards and make a significant contribution to the sustainability of the battery manufacturing sector. Early results have also suggested that a solvent-free process may facilitate improved rate and cycling performance due to a better control of the binder morphology and its distribution. From an electrode perspective, the key challenge following the elimination of the solvent is how to distribute a minimum fraction of binder while ensuring all particulates are bound together into an integral coating, that this coating is adhered to the current collector and, and that integrity is maintained even under the stresses and strains induced by cycling. Active particulates have been shown to be robust to thermo-mechanical approaches to distribute binder at elevated temperature under shear forces, and along with dry painting, demonstrate practical routes to functioning LIB and ASSB electrodes. Given the self-evident benefits of solvent-free processing, it is likely modified or entirely new approaches will also rapidly develop, with prospects for new intellectual property and a family of new electrode manufacturing technologies.

Acknowledgements

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Deformation mechanism of lithium-ion battery electrodes during manufacture

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Status

The mechanical properties of lithium-ion battery electrodes including deformation and particle breakage are known to be strongly affected by the manufacturing process, especially electrode calendering. Figure 1 illustrates cross sections of electrode structures before and after calendering. During calendering, the active material (AM) particle structures and carbon binder domain (CBD) phase are compressed and rearranged, and the inter-particle porosity is reduced. The compaction of the electrode particle-pore structures can in turn affect the transport properties and battery performance.

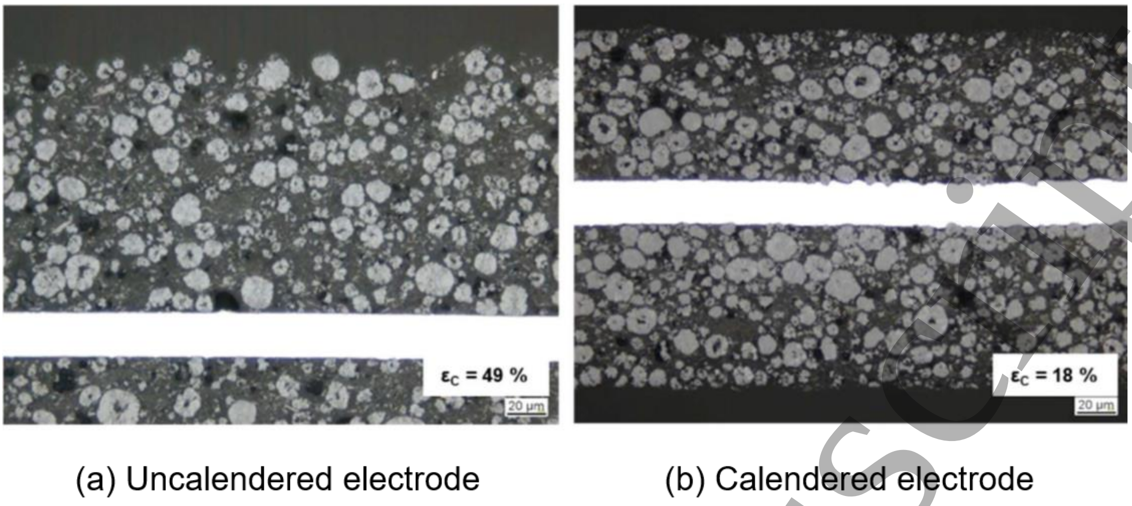
Previously, researchers have attempted to relate the manufacturing process parameters to the deformation of electrodes [1, 2] , and have also started to use numerical methods to understand the relationships between manufacturing process, mechanical properties and microstructure [3]. However, these relationships still require further investigation. This is especially true in the face of rapid developments of lithium-ion batteries, with increasing need for high-performance electrodes with controlled microstructures, e.g. thick/graded electrodes [4]. Understanding and predicting the deformation mechanisms of these electrode structures during manufacture is clearly important for next generation electrode design. Recently dry electrode coating process has been applied to thick electrode manufacturing by Tesla. However, the calender rolls are dented during the calendering process, indicating the need to understanding and improve electrode calendering process [5]. By using advanced experimental characterisation techniques and high-fidelity numerical methods, the evolution of the electrode microstructure including essential information such as AM particle positions and porous CBD phase (e.g. pore size distribution and detailed structures) can be resolved under varying calendering conditions. It is also expected that complex mechanical properties (e.g. elastic-plastic behaviour, inter-particle friction and strain rate sensitivity) can be captured by numerical models.

Current and Future Challenges

Experimental investigations

During manufacturing, the mechanical properties of electrodes are affected by material compositions, operating parameters (e.g. roller temperature, circumferential speed) and electrode thickness [1]. As the effect of these properties and parameters on electrode deformation is very complex, it would be useful to characterise mechanical properties of electrodes. Micro and Nano indentation techniques have been widely used to assess electrode mechanical properties including hardness and elastic deformability [6, 7]. A new grid indentation approach has recently been developed [8, 9], in which the Young's modulus and hardness of both the AM particles and CBD phase within electrodes are measured in a single test. Apart from this, the adhesion property between electrodes and current collectors is also very important as it can affect the battery performance. The adhesion property is a function of polymeric binder material and electrode microstructures. Previous results have shown that the adhesive strength could be affected by the carbon black dispersing and calendering process [10].

Experimental techniques have been developed to characterise the coating adhesion strength (e.g., conventional peel test, pull-off test and surface and interfacial cutting analysis [11, 12]). These developments are certainly encouraging, however to date experimental studies are limited in materials and test conditions. To gain further mechanistic understanding, systematic studies spanning large parametric and material property spaces are required. Of particular importance for further numerical study is experimentally gained understanding of the dynamic mechanical response of the porous CBD phase, which often consists of Polyvinylidene fluoride (PVDF) and carbon black aggregates but can vary in composition and structure.



(a) Uncalendered electrode (b) Calendered electrode

Figure 1. SEM images of electrode deformation before/after calendering, showing the active material (AM) particle phase and carbon binder domain (CBD) phase [1]

Computational modelling

The compressibility of particle assemblies can be described by an exponential compaction equation first proposed by Heckel [13]:

$$\varepsilon = \varepsilon_{\min} + (\varepsilon_{\text{ini}} - \varepsilon_{\min})\, e^{(-P/\gamma_C)} \tag{1}$$

Where ε is the electrode porosity, ε_{ini} and $\varepsilon_{\min}$ are the initial and minimum structure porosities, P (MPa) is the compression pressure and γ_C (MPa) is the compaction resistance. This relationship has recently been applied to analyse the calendering of electrodes [1, 7].

While Equation (1) provides an estimate of the porosity achieved, the effects of the CBD phase and particle arrangements cannot be considered. To incorporate these factors, high fidelity simulation is necessary to investigate the microstructural evolution within electrodes. Discrete Element Method (DEM) is a promising technique which has been recently applied to model the manufacture of electrodes, and in particular the electrode calendering process [3, 14]. At its essence, DEM is used to model motions and forces of particles at an individual particle scale. An example of a DEM study of electrode manufacturing process across the length scales is illustrated in Figure 2. The manufacturing process from slurry drying to calendering is simulated. In this figure, the AM particles are coloured in red, and the CBD phase represented by nano-sized adhesive particles is coloured in blue. DEM simulations are currently limited in using virtually generated structures and spherical particle approximations. Recent work demonstrates the capability to twin DEM with microstructures from X-ray computed tomography [15]. However, there are challenges in capturing particle plastic deformation and breakage under high calendering levels. In addition, more complex understanding of the inter-particle bonds is still necessary to establish the non-linear constitutive behaviour [16].

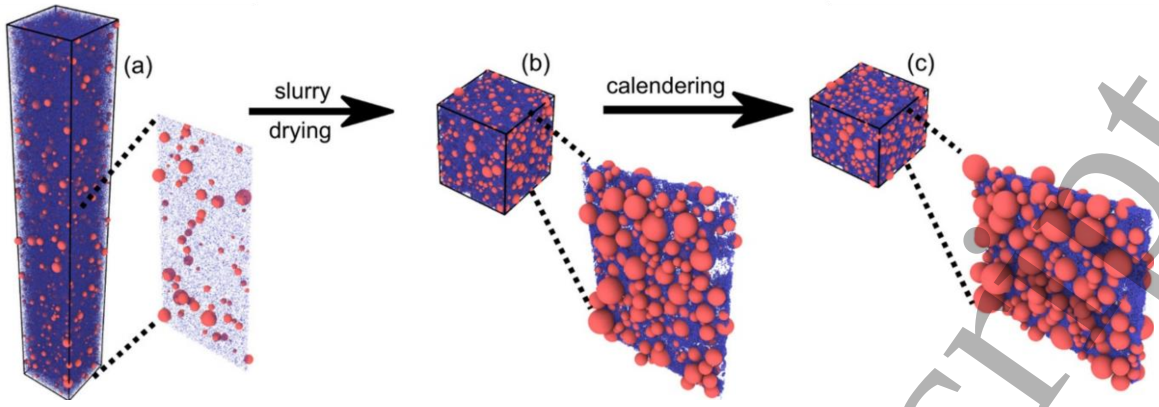


Figure 2. DEM simulation of the electrode manufacturing process, the AM particles are colored in red, and the CBD phase is colored in blue. [17]

Advances in Science and Technology to Meet Challenges

To further understand electrode deformation mechanisms and advance model development in this field, systematic dynamic experimental characterisation of the electrodes is necessary. Some recently developed experimental techniques present promising characterisation options. In situ compression tests present a possible method to track evolving particle structure [18]. By using indentation testers and X-ray nano-computed tomography, Daemi and co-authors investigated the particle movement and strain evolution of an electrode during compression [18]. To further understand the visco-elastic and plastic deformation of binder materials, other techniques such as dynamic mechanical analysis can be considered to characterise the materials under varying strain rates.

DEM simulation, with the use of suitable contact models, is a promising tool to investigate electrode structure deformation. The commonly used particle contact models in this field are the Hertz model, the Johnson-Kendall-Roberts (JKR) model, and also the parallel bond model to describe the inter-particle binder phase [19, 20]. In general, with carefully chosen/calibrated parameters, these contacts may fit the purpose under certain conditions to predict the particle assembly structure evolution during compression [17, 21]. However, it is likely new constitutive models need to be developed and implemented in DEM to capture the complex mechanics of non-linear materials [16]. The application and coupling other numerical approaches, e.g. Finite Element Method (FEM) may be a new route to tackling this issue. In addition to this, advances in generating realistic synthetic electrode structures is also important. This includes the generation of irregular shaped particulate assemblies, and also CBD phase generation considering nano-sized pores [4, 22]. The combination of DEM with realistic structural generation algorithms would provide a powerful tool to numerically understand dynamic electrode deformation.

Concluding Remarks

Further experimental understanding and computational simulation of the deformation mechanisms of electrodes are important for electrode microstructure design, and manufacturing process optimisation. Recent developments have shown the mechanical behaviours during electrode calendering are very complex. Systematic dynamic experimental characterisation under controlled conditions is necessary to track the particle structure evolution, and measure the mechanical response of non-linear materials. The numerical modelling approach DEM has been demonstrated to be a useful tool to understand the deformation mechanisms at the individual particle scale. More effort is required to establish constitutive mechanical models of the porous CBD phase, and also in the consideration of irregular shaped AM particles and porous CBD phase. By combining mechanical tests and advanced numerical modelling approaches, substantial improvements in the understanding of electrode mechanics during calendering is expected in the coming years.

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Model-driven design of structured electrodes for lithium-ion batteries

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Status

Significant improvements in battery energy density, power density, lifespan, cost and safety are needed to deliver the next generation of mobile technologies, including electric vehicles and aircraft. This will require new innovations in lithium ion battery (LIB) technology either by making improved batteries or by advancing our current battery technology. It can be argued that the former approach has received the most attention, with significant capital invested in accelerating the discovery of new chemistries and materials. However, while the invention of new electrode materials promises a step-change in performance, material discovery is a difficult process [1]. To hedge against these risks and deliver improved batteries at the scale and within the time-frame needed for the green energy transition, there has been a shift in focus towards making our current batteries more efficient [2] by advancing battery analytics, control and, notably, by improving manufacturing. Battery modelling is key to delivering these objectives.

Battery electrode manufacturing is an area ripe for innovation. The standard manufacturing approach [3], known as “slurry casting” or “slot-die-coating”, involves mixing the electrode’s constituent materials (the active material, conducting carbon additive and binder) and a solvent into a highly-viscous slurry, which is cast onto metal foil current collectors before the newly formed electrode is dried and calendered. The origins of this manufacturing process can be traced back to the first commercialised LIBs from 1991, and it is remarkable how similar those early manufacturing processes are to those of today, especially in light of the massive scale-up in gigafactory production of recent years.

The main limitation with slurry casting is that it gives battery designers only limited control of the electrode microstructure. As a result the electrode’s microstructure is not able to compensate for the non-uniform electrochemical response through its thickness when used aggressively, for example during fast charging. Non-uniform electrochemical responses can lead to a uneven utilisation of the electrodes’ active material and consequently less efficient charge storage [4]. Sources of electrochemical inhomogeneity include: i) the overpotential gradients that build up through the electrode thickness, ii) local concentrations of ions within the bulk electrolyte, and iii) thermal hotspots, with these issues growing as the battery ages. Removing these sources of inefficiency will be key to delivering cells whose capacity does not drop off at high C-rates.

Advances in Science and Technology to Meet Challenges

Structured electrodes that are designed to have non-uniform spatial distributions in electrode microstruc- ture have been proposed to overcome the limitations of slurry-cast electrodes, especially when operated at high C-rates. In contrast to slurry-cast electrodes, structured electrode microstructures are not uniform throughout the electrode. Instead, the microstructure can vary, with different regions of the electrode having different compositions [4, 5] or particle sizes [6, 7, 8, 9, 10, 11]. These spatial distributions can either be discrete, in the form of differing layers of slurry-cast electrodes [5, 12], or continuous, achieved using ice templating [13, 14], vertically aggregated bubbles [15], magnetic templating [16] and additive manufacturing processes such as spray forming [4]. The idea behind structured electrodes is to tailor the non-homogeneous microstructures to account for the non-homogeneous electrochemical responses, and it has been shown that structured electrodes could deliver a significant increase in high C-rate capacity and reduction in long-term degradation rate[4].

The concept of structured electrodes raises several questions. How should the spatial distributions of the structured electrode microstructure be designed? What performance gains can theoretically be achieved? Can the scalability of additive manufacturing methods for structured electrodes be improved? Efficiently answering electrode design questions such as these is a non-trivial problem requiring the use of mathematical models. Several models have been proposed for structured electrodes, including [17, 18] and [19] which replicated impedance data [4] from both uniform and graded electrode structures, with the model helping to explain the reduced impedance of the structured electrodes. Figure 1 compares the imaged microstructure of the structured electrode from [19, 4] with its interpretation from the modelling approach. In [17], it was found that grading through the thickness in both the anode and cathode had the largest effect on gained energy and power, though only limited porosity distributions were studied. By considering multiple performance objectives together, [20] found that multilayer designs were able to meet many design requirements simultaneously, emphasising the increased flexibility of structured electrodes.

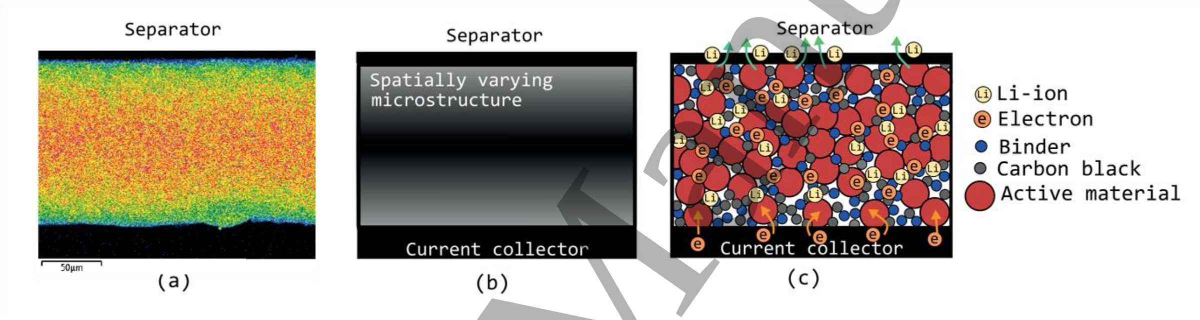

Figure 1: A structured $Li_4Ti_5O_{12}$ based anode. (a) shows the distribution of the active material at the electrode cross-section [4] (reproduced with permission), with $Li_4Ti_5O_{12}$ particles enriched in the centre of the electrode. (b) approximates this structured electrode as a spatially varying continuum. (c) shows the charge transfer mechanism of the structured electrode as considered in the mathematical models.

Current and Future Challenges

The new design space opened up by structured electrodes (e.g. encompassing layer widths and local com- positions) is so vast that searching through it using a purely experimental trial-and-error based approach quickly leads to problems of scale and result in only a few candidate electrode designs being considered, as experimental trials are both expensive and time consuming. Overcoming these issues motivates the use of mathematical models for electrode design to allow candidate electrode designs to be quickly screened and their performance quantified.

A quick and effective method to accelerate the design process of Li-ion electrodes is a critically needed feature of battery electrode manufacturing, both for slurry-cast and structured electrodes. As LIB technology matures, there is increasing pressure to optimise existing battery technology and make it more efficient. Electrode design optimisation of the future will be a hybrid process, combining electrochemical modelling, manufacturing methods, numerical optimisation, and experimental data, with each of these components interlinking and influencing each other. Delivering this process requires new advances in each of these three fields, and an inter-disciplinary approach becomes critical.

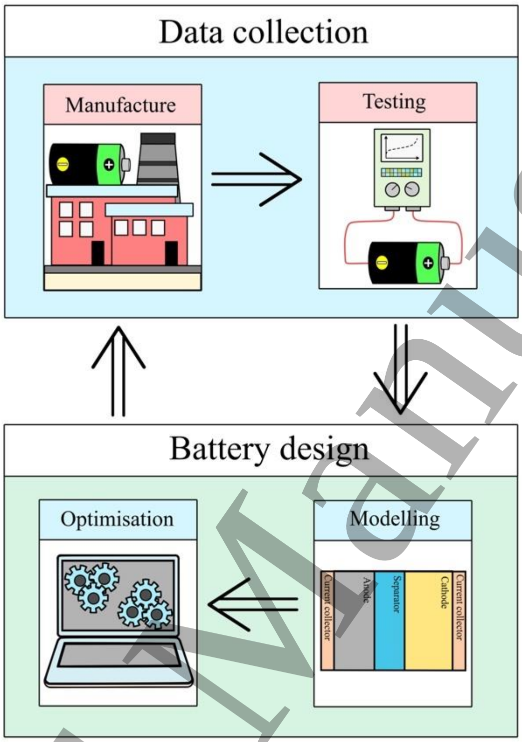

Figure 2: Model-driven Li-ion battery design cycle composed of four parts. Data is first generated of a candidate electrode design, with this data used to train an electrochemical model. The model is then optimised to generate a new candidate electrode design which is then built and tested. The data from these new tests are then used to re-train the model, and the process then repeats.

Figure 2 illustrates a design cycle for structured electrodes using this hybrid approach. The first step generates experimental data for the structured electrodes. A suitable battery model (capable of providing useful physical information about the battery's internal behaviour whilst being simple enough for optimisation) is then created. With the model generating accurate predictions, an optimisation problem is then solved to generate a candidate design. This candidate design is then prototyped and tested, with the process then being repeated with the new data, until converging towards an optimum design.

Concluding Remarks

New advances in electrode manufacturing are extending the possibilities of battery design, which is increasing the demand for new methods to efficiently optimise cell designs. Satisfying this demand has led to a shift from a purely experimental based design process to one which combines electrochemical modelling, numerical optimisation, manufacturing methods and experimental data together. By fusing these elements together, the design process becomes accelerated and refined, improving the efficiency of our existing battery technology especially when operated close to its performance limits.

Several questions remain:

1. What performance metric should be used to optimise battery performance for real-life applications?
2. What key features should be included within the model?
3. How should the design optimisation be solved; via multiple simulations or by direct optimisation with the model parameters as decision variables?
4. Can additive manufacturing methods for structured electrodes be made more scalable?
5. Do structured electrode designs that perform well for one active material composition translate to other chemistries?

Providing a framework to answer these questions effectively and efficiently will be key to realising the potential of novel LIB designs.

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Image-based modelling for rational design and optimisation of electrode microstructures

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Status

Modelling is a cornerstone of lithium-ion battery (LIB) research, design, and optimisation in both academic and industrial settings. It provides cheaper and faster development of new battery technologies, through access to data, which are costly or otherwise unobtainable using experimental techniques. From molecular dynamics simulations, to the cell or pack level equivalent circuit models, battery models take many forms and consider numerous length scales. Continuum physics-based models fall within this category and operate at multiple length scales: the single particle, micro-scale electrode level, and cell levels. These models are typically based on a Newman-type description [1] which is robust and computationally efficient, although they are limited in their ability to capture heterogeneity and prediction of degradation due to homogenisation of the electrochemical and transport equations. In contrast, image-based modelling, which typically combines X-ray computed tomography (CT) and multiphysics frameworks, has emerged as a powerful tool for resolving the electrode microstructure and predicting battery performance.

Image-based models provide high-fidelity insights into the complex geometry and the subsequent heterogeneity associated with the composite microstructure of LIBs [2]–[5]. They permit the prediction of complex interactions between the constituent phases: for example, pore geometry and its distribution within an electrode holds significant influence over electrode performance due to tortuous pathways [6], which limit lithium ion diffusion; this can now be resolved through the ever-improving resolution of X-ray CT. See Figure 1, for example, where gradients in state-of-lithiation and bulk electrolyte distributions are illustrated for a thick and thin electrode. Aside from electrochemical simulations, image-based models can be used to predict an array of mechanical and transport properties, and can also be used within discrete element method simulations, where the calendering performance for a given electrode is evaluated [7].

Image-based models have the potential to participate in the design of next generation electrode microstructures. Once an electrode image is acquired, it is segmented such that each phase is labelled, and this forms the basis of the model. However, techniques such as morphological operations allow rational alteration of the electrode microstructure, presenting the opportunity to expand or contract any given phase, at any given location within an electrode, while maintaining the realistic nature of the image/model [2]. This technique alone may facilitate the grading of the electrode microstructure and facilitate the rational design and optimisation of thicker, pore engineered electrodes with improved power density; a core goal of the Nextrode project.

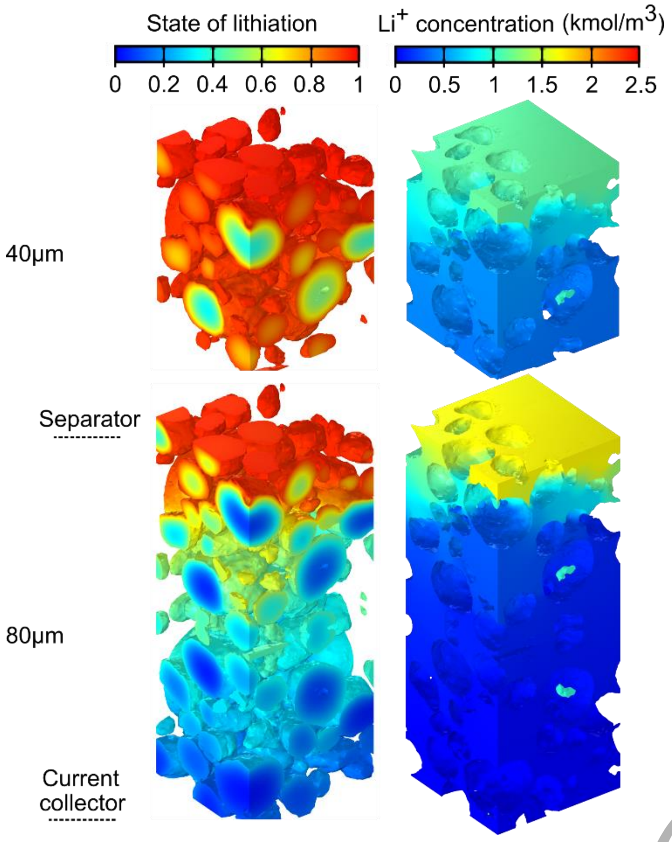

Figure 1. State of lithiation in active particles, and bulk electrolyte lithium ion concentration profiles for an image based, fully coupled, electrochemical and transport model with electrodes of 40 μm and 80 μm thickness. The NMC622 electrodes were discharged at a rate of 5C within a voltage window of 3 V-4.2 V. The profiles shown are at 100% degree of discharge (3 V). See Boyce et al. [8] for details on the associated equations and methodology.

Current and Future Challenges

Current image-based models place little emphasis on the wide variety of degradation mechanisms that occur in LIBs. Heterogeneity plays a significant role in degradation; localised heating or lithiation-induced cracking, for example, are known to lead to rapid deterioration of the microstructure and long-term performance of the LIB, perhaps even leading to thermal instability and runaway. Image-based models appear to be well placed given their suitability to prediction of heterogeneous mechanisms. Hence, it is necessary to consider the addition of further physical considerations such as thermal and mechanical based degradation mechanisms to the present models.

Image-based models are limited by both computational resources, and imaging technology. At present, such models resolve the particles as a homogenised agglomerate without due consideration for the underlying primary particulate or polycrystalline microstructure. If primary particles could be resolved throughout the entire electrode microstructure, then further heterogeneity could be captured in the models, for example, anisotropic diffusion coefficients, lattice parameters and Young's moduli of individual crystals may lead to improved prediction of performance and degradation. The carbon binder domain (CBD) is another example of the need for improved resolution. The nanoporous CBD has been imaged and modelled by Lu et al. [2]. However, acquiring this data is non-trivial, therefore imaging techniques and computational resources need to be improved for this phase to be routinely considered in image-based models.

Parametrisation is a key step in the accurate use of image-based models. It becomes difficult to determine experimental parameters at the micro-scale, for example, there is limited mechanical characterisation of the nanoporous CBD. Although some progress has been made by Grillet et al. [9], we need to understand the full mechanical and fracture response in order to fully capture the loads on particles during the calendering process, the role of the support it plays during lithiation induced swelling, or to model binder detachment from particles. In addition, image-based models are yet to be rigorously validated by experiment; it remains difficult to compare state-of-lithiation distributions, surface overpotentials, or bulk electrolyte concentrations throughout the electrode and its constituent components.

These issues are pertinent when we intend to use image-based models for the design and optimisation of electrode microstructures, particularly in the case of thicker and pore engineered electrodes. We need to improve the predictive capabilities of these models in order to understand how an optimised electrode degrades which allows us to use such structures in a realistic LIB.

Advances in Science and Technology to Meet Challenges

If we are to accelerate the development of these models, capture more complex degradation processes, and achieve greater resolution of performance-related mechanisms, then improvements in computational performance are required. This may be achieved via hardware advances, and perhaps, via enhanced computational methods for solving the underlying theoretical frameworks. The ever-expanding area of machine learning may play a role here [10].

Simultaneously, improving imaging techniques while also coordinating with other experimental methods is required. For example, using imaging techniques from synchrotron beamlines will allow temporal resolution of the crack development in an electrode microstructure. Utilisation of advanced characterisation techniques such as, X-ray diffraction [11], and X-ray absorption near-edge structure (XANES) analysis [12], amongst others, may be used to assist in validating the state-of-lithiation predictions in image-based models for example.

While it is necessary and advantageous to improve the model resolution for each constituent microstructural component within an image-based model, it is still necessary for communication between cell and particle level simulations. For instance, a microstructure may be tailored to suit different locations within an electrode, and thus, results of an image-based model can act as inputs to the cell level model. Otherwise, degradation mechanisms (such as particle cracking) might be explored in detail within a single particle model and then implemented directly or on a homogenised basis in a micro-scale image-based model. In essence, improved linking of the length scales is required if significant advances in predictive understanding and design are to be achieved.

Concluding Remarks

Image-based models facilitate fundamental insights into battery performance and permit new ways to design and optimise a LIB electrode. They provide a wealth of knowledge on the local heterogeneities that occur within a LIB, which in turn allows us to carry out pore engineering of thick electrodes in a more efficient manner. With further improvements in imaging and computational technologies, this method of modelling has remarkable potential, where the rational design of LIB electrodes is concerned. Significant opportunities exist to expand its scope to consider degradation mechanisms, which is a crucial factor when considering the lifetime of a LIB, and even more crucial where new, thicker electrodes are being considered.

Acknowledgements

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The Application of Machine Learning Methods for Improved Battery Manufacturing

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Status

With the increasing demand for lithium-ion batteries (LIBs) to underpin decarbonisation of the transport and energy sectors, [1], it is critical to expand LIB manufacturing capacity and efficiency while concurrently reducing production costs and environmental impact [2]. LIB manufacturing cost and Co_2 emissions correlate strongly with the "quality" of products and the predictability at the different production stages and handling the material waste, the employed energy, and the accumulation of failed cells [3, 4]. Recent studies indicate that up to 40% of produced LIB cells could be either defective or in need of adjustments after production [5]. LIB production consists of various continuous and discrete process stages with different chemical, physical, electrochemical and thermal characteristics; an optimised "material-to-cell" production process is therefore not realisable without handling the numerous process interdependencies, control parameters and uncertainities being well understood and ideally quantified.

Artificial intelligene (AI) and its high-yielding subset machine learning (ML) offer powerful tools to address the complex and interconnected processes associated with LIB manufacturing [6]. Conventional LIB manufacturing data generation, analysis and control methods are historically based on a deep qualitative understanding, where considerable time and effort is required to commission and efficiently run the production process. AI and ML has the potential to enable researchers to conduct systematic analysis and in-situ evaluation, contributing significant benefits:

- Efficiently handle large amount of data
  The volume of data from large volume LIB manufacturing is growing exponentially. For example, BASF [7] generates approximately 100 million data points per day during battery testing. AI and ML methods help to efficiently curate this data, thereby underpinning new insights into production capability, quality, and LIB performance. They help in the extracting and interpretation of information that might remain hidden with traditional data processing techniques.

- Creation of predictive models, virtual quality gates and digital twins [8, 5, 6]
  AI and specially ML algorithms when practiced on representative and rich datasets, enable the creation of models to predict LIB cell characteristics and the properties of associated intermediate products (e.g. electrode thickness, porosity etc). The models can be employed to augment experimental analyses and reduce production set-up time. The models allow both researchers and manufacturer in research and development phase, to predict LIB performance directly from production parameters and conversely, to define a production process to meet a particular LIB specification.

Current and Future Challenges

Improvement of LIB production processes via ML techniques requires a closed-loop framework, Figure 1. However, several challenges exist that must be addressed for this to be realised.

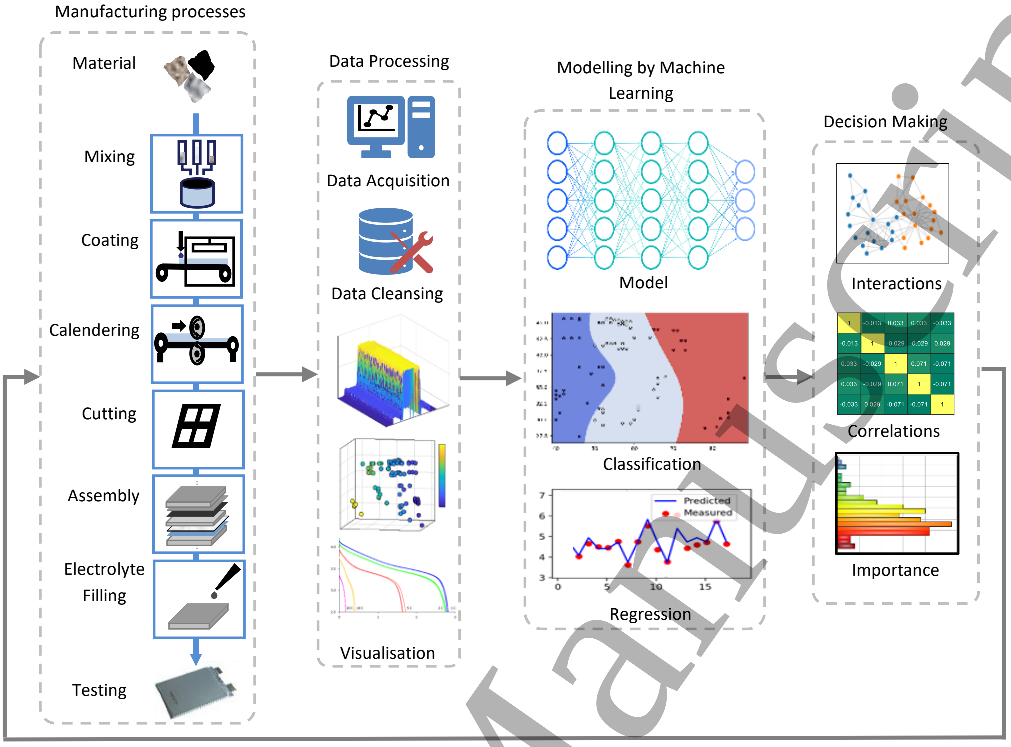


Figure 1. The procedure for battery Manufacturing optimisation via Machine Learning

Data acquisition and preparation

The reliability of ML models depends significantly on the underpinning data employed in model training. AI and ML techniques aimed at in-situ control of manufacturing processes face different challenges compared to those typically used for system/product design during research and development. The former is subject to the large volume of data with similar responses, high volumes of outliers, noise, missing values, and difficulty in facilitating a real-time implementation [9]. The latter faces challenges regarding the variability in the data. A data set suitable for ML modelling should be spread over the full range of the response variables and has sufficient breakpoints to capture the process dynamicity. Therefore, methods for sample preparation and reproducibility investigations are at high levels of importance [10, 11].

Model-based decision making and prediction

Decision making algorithms are focused on categorizing the intermediate products obtained during the manufacturing stages as well as the final LIBs. Conversely, regression models are aimed at predicting the product characteristics given the control variables. Examples of such models can be found in NEXTRODE [12, 13] and ARTISTIC [14, 8] project records. As the performance of models is unique to the data set used during training, model selection is a challenging task. Furthermore, the model's performance is highly affected by its hyperparameters, and its systematic optimisation is crucial. The other challenge is the unbiased validation of the models for generalisable results. Validation by traditional train-validation-test split is known to add unrealistic optimism for predictably and causes models to underperform for new, albeit similar data [15].

Explainability of Models

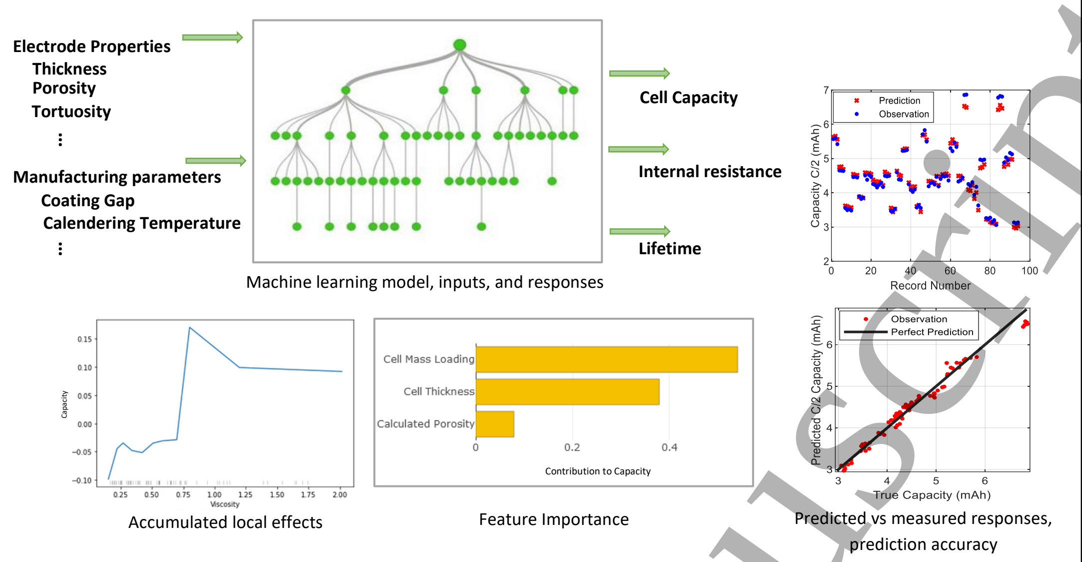
While the concepts of training and validation of ML models has been well understood and transferred to the LIB manufacturing context, the explanation and interpretation of models have only recently been explored when the reliability and transparency of ML models became critical in practice [16]. In fact, single metrics such as prediction accuracy are not enough to describe the predictability of highly interconnected LIB manufacturing processes. The explainability of ML models is the capability of providing insights into the model's behaviour, ensuring that the decisions are matched with the expectations. The explainable ML models should be able to answer "Why" questions and ultimately help to build confidence within the manufacturing community.

Advances in Science and Technology to Meet Challenges

Recent advances have contributed to the improvement of the design and implementation of ML models for battery manufacturing processes. The challenge of data quantity and quality in building models can be addressed via data-mining-assisted design of experiments (DoEs) [17], Section 15. The role of ML when equipped with DoEs is considerable when exploring the new materials. Unlike the traditional experimental procedures that change one control variable at a time, ML techniques can handle multiple variables that are changing at the same time [12]. In fact, they help to identify important control variables and refine the range/breakpoint of the key factors for more elaborated experiments.

Optimising an ML model is another challenge to overcome. While grid search optimisation is the first solution, a systematic method of model selection and optimisation is achievable via cost functions as addressed in online modelling tools such as [18]. This approach, although computationally demanding, guarantees generalisability of models. Beside model optimisation, validation methodology affects the model's ability for prediction/decision making. Compared with the train-test-split method, the single or double cross validation is a more reliable solution. In this approach, the data are separated into *k* non-overlapping groups, and while *k*-1 groups are used for training, one group is left for validation. Repeating the task for *k* times by shuffling the data ensures that each data point has been used for both validation and test at least once and evaluates the model's performance for the whole data range. The approach is particularly appropriate for small datasets and maximises the information taken out of the data [19].

Even the most accurate ML models are deemed to be "black boxes" and could be difficult to interpret. To clarify the impact of control factors on the LIB characteristics, explainable ML frameworks are one feasible solution [20]. Feature importance and ranking is an example that distinguishes the most influential factors and quantifies the strength of the interconnections between predictors and responses. Accumulated local effects and Shapley values [20] are among those items that help to increase model transparency. Both cases, quantify the contribution of the control variables in predicting the response variables and answer the question of how the response would change if one, or more of the variables are changing within a range. An example decision tree model and its prediction accuracy is shown in Figure 2. Further information about the results can be reviewed in [12, 17].



Machine learning model, inputs, and responses

Accumulated local effects

Feature Importance

Predicted vs measured responses, prediction accuracy

Figure 2. ML, show casing the model, prediction accuracy, and explanations

Concluding Remarks

AI and ML have started to show promising contributions for improving and optimising the LIB manufacturing processes. ML methods help to navigate through various options within the chemical, electrical, material, and operational spaces and reduce the number of experiments for building models that can accurately represent the manufacturing chain. They also offer model-based solutions for predicting the product characteristics at every and especially the early stages of manufacturing and suggest quality assessments where experimental tests may be technically unfeasible or uneconomical to run. They create new opportunities regarding the large amounts of data available through volume manufacturing, interpret the analysis and feedback them for corrective decisions.

Although the subject has been addressed within academic reports, the implementation of methods for volume manufacturing is still a challenge. It is necessary to up-scale methods validated within a laboratory to a volume scale production environment. In fact, to gain the trust of manufacturers and replace the traditional methods with the ML techniques further investigations are required. Increasing the robustness of models to the noise and uncertainties, and generalisation of methods from one specific process or formulation to another are the most urgent items to be addressed.

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The Role of Design of Experiments (DoE) Methods for Optimised Battery Manufacturing

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Status

More than 80 years have passed since the pioneering work of Ronald A. Fisher on the statistical design of experiments (DoE) [1]. DoE was created as a methodology (Figure 1) to determine based on statistical principles and minimum experimental effort, the relationship between the independent variables (or factors) and the dependent variables (responses). The first application of DoE was in the field of agriculture, were the concepts of randomisation, replication, factorial design, blocking and the analysis of variance were introduced. The methodology later spread to other industries, most notably to the chemical and the pharmaceutical industries. In the former it has been mainly applied for process optimisation, whereas in the latter it has become a tool in the quality by design concept (QbD) [2].

In DoE, experimental efficiency is maximised by studying all factors simultaneously according to the design matrix (the set of experiments) defined by the chosen experimental design. Although there are different types of experimental designs, these can be classified in three general categories: screening designs (to distinguish important from non-important factors), characterisation designs (to determine the effect of factor interactions and to establish the design space), and optimisation designs (to determine factor settings that optimise the response). Classical designs include the factorial, the fractional factorial, the Central Composite and the Box-Behenken [3].

In DoE, polynomials normally up to the quadratic term are used to represent mathematically the relationship between the factors and the responses. The values of the polynomial coefficients and the statistical significance of the polynomial terms are obtained by multiple linear regression (MLR) and the analysis of variance (ANOVA). From the model, the design space is established which allows for a visual determination of the region of applicability of the model, its accuracy and the identification of the optimum region of operability.

Although the contribution of DoE to several industries has already been demonstrated [4, 5], there is still not widespread dissemination of its use in the LIBs field [5]. A few examples of DoE applied to LIBs include the study of cycling and calender ageing as function of temperature, state of charge (SoC) and discharge current [6]; discharge capacity as a function of porosity and cathode/anode mass loading ratio [7]; optimisation of active material synthesis conditions [8]; design of LIBs' safety features [9]; development of charging algorithms [10], and model parameterisation for battery management systems (BMS) [11]. Nevertheless, reports on the application of DoE to aspects of the LIBs' manufacturing processes are scarce [12].

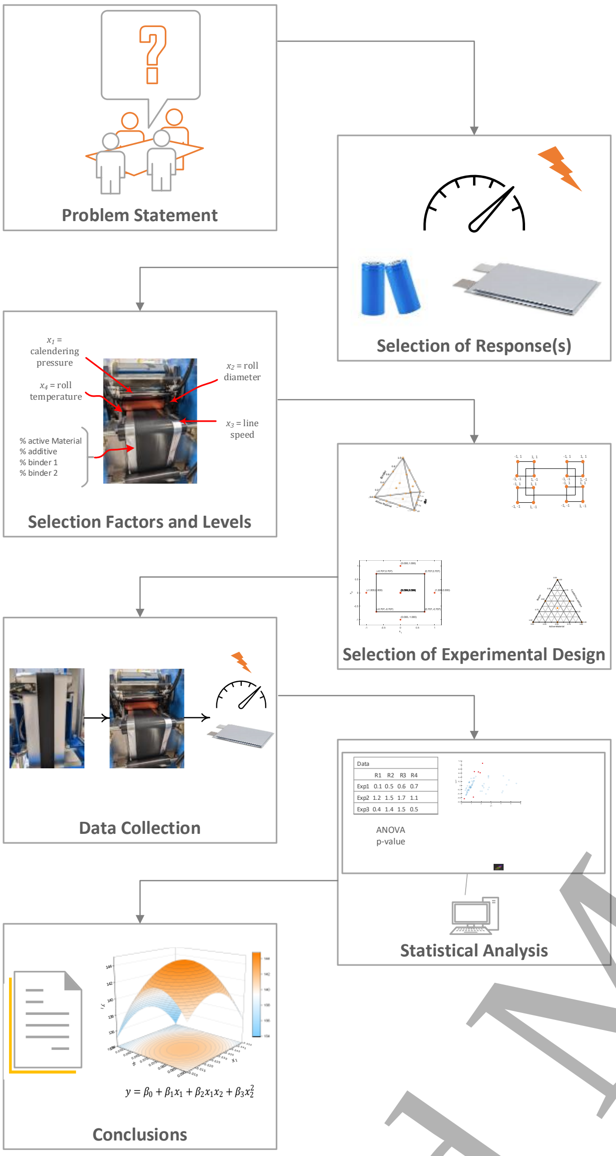

Figure 1. Steps in the statistical Design of Experiments (DoE) methodology.

Current and Future Challenges

While the basic theory around DoE is well stablished [3], DoE is still an active area of research and new developments are reported in specialised statistical journals. Nevertheless, most of the challenges around the application of DoE to the manufacturing of LIBs, and to the LIB field in general, are related to a lack of awareness of the methodology or of its principles by a wider community, resulting in a barrier to its regular application. Additionally, some of the mathematics involved in DoE can be complicated, especially for users with no statistical and programming background. This aspect is particularly true for modern experimental designs known as *optimum designs*, where optimisation algorithms are required to define the design matrix. An example of the implementation of optimum designs is presented by Mathieu, et al. [6] in their study of battery ageing for model calibration.

In the particular case of LIBs manufacturing, it is possible to mention the following challenges in terms of experimental design: *Formulation*: The role of the formulation takes centre stage since many of the slurry properties, coating conditions and final electrochemical performance are dictated by the nature and concentration of the compounds. A special type of experimental design, the mixture design, is required in this case as demonstrated by Rynne, et al. [13]. However, to date, there are no studies on LIBs addressing the formulation problem coupled with the simultaneous study of operating parameters. Such studies could reveal, for instance, the settings of the mixing operating parameters needed to obtain a slurry with desired rheological properties depending on the formulation used; or to determine the optimum coating and drying parameters as a function of slurry formulation that maximise cell electrochemical performance. *Hard-to-change (HTC) factors*: These are factors whose settings are not easy to vary during the experimentation, e.g. temperature. In a formulation study, if large batches of slurry need to be prepared, changing the formulation between experiments would be extremely time consuming, costly and unpractical. In this case, the formulations can be considered HTC factors. *Blocking*: A technique used to minimise the variability associated to known and controllable nuisance factors, it is also likely to be required in a volume manufacturing experimental design. Common nuisance factors are the different operators and the batches of the raw materials. Furthermore, different *types of variables* (continuous, discrete, categoric: nominal, dichotomous or ordinal) will likely be involved in the study of manufacturing conditions. All of these considerations add layers of complexity to the definition of the design matrix and to the statistical analysis of the collected data.

Advances in Science and Technology to Meet Challenges

The DoE methodology could be applied to almost any stage of the manufacturing process chain. It can be applied to the already existing processes and technologies, or it could be used in the development of emerging ones such as those of thin-film solid-state batteries [14] or sodium-ion batteries [15]. Regardless of the Manufacturing Readiness Level (MRL) of the battery technologies, the ultimate goal of the application of DoE to the LIBs manufacturing is to understand the process-structure-performance relationship to make a commercially viable process as the technology transitions from the laboratory scale to the industrial manufacturing scale. Following the QbD concept, DoE can be applied to first identify the critical material attributes (CMA) (e.g. slurry density, weight fraction, electrode porosity), and the critical process parameters (CPP) (e.g. coating speed, drying temperature, calendering pressure), of the different sub-processes in the LIB manufacturing, to then stablish the design space and optimum regions of operation.

While advances in DoE theory must come from the field of statistics were new designs or forms of statistical analysis are proposed, it is the role of DoE practitioners to act as a bridge between the theory and its application to the field of LIB manufacturing. Perhaps the major advance in the application of DoE towards this end has been the development of specialised DoE commercial software. This has allowed users, irrespective of their mathematical background, to create advanced experimental designs and to perform the statistical analysis in a straightforward manner.

Concluding Remarks

The DoE method is increasing in importance in several aspects of the LIBs field. Its application to the study of the manufacturing process and sub-processes is, however, still rare. Nevertheless, DoE is a powerful statistical tool for high experimental efficiency that guarantees that the models and the conclusions obtained are objective and supported statistically. While classical designs can be implemented relatively simple, optimal designs require the use of computer algorithms for their implementation. The current existing gap between the DoE theory and its application is being shortened by specialised software. Still, a proper understanding of the method and its principles is needed to guarantee its correct application to the study of the LIBs manufacturing process.

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An Industrialisation Perspective from UKBIC – Towards Sustainable Manufacturing of Lithium-Ion Battery Cells

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Status

As the effects of climate change impact our environments, economies, and social balance, the need for sustainable energy sources is key to achieving net zero emissions [1]. The demand for batteries across the globe has risen dramatically through enabling technology developments and consumer behaviour, from mobile phones, laptops, to electrification of transportation. Evolution and scale-up of battery manufacturing processes are required to industrialise this transition further. Current manufacturing techniques haven't fundamentally changed since they were developed in Japan during the 1980s and adopted later in Korea and China. Planetary mixing machines produce electrode slurries which are subsequently coated onto foil current collectors. Roll-to-roll drying machines evaporate the solvents producing a 'parent' roll of electrode which is then calendered between large steel rolls to densify the coatings. Slitting machines divide the 'parent' roll into 'daughter' rolls for subsequent conversion into battery cells.

The three cornerstones of sustainable development; environmental protection, economic growth, and social inclusion (Figure 5) must be respected with equal importance. Current industry focus is on achieving an economic target of $50/kWh [2], but this cannot be accomplished at the expense of failing to meet or even set environmental and social targets.

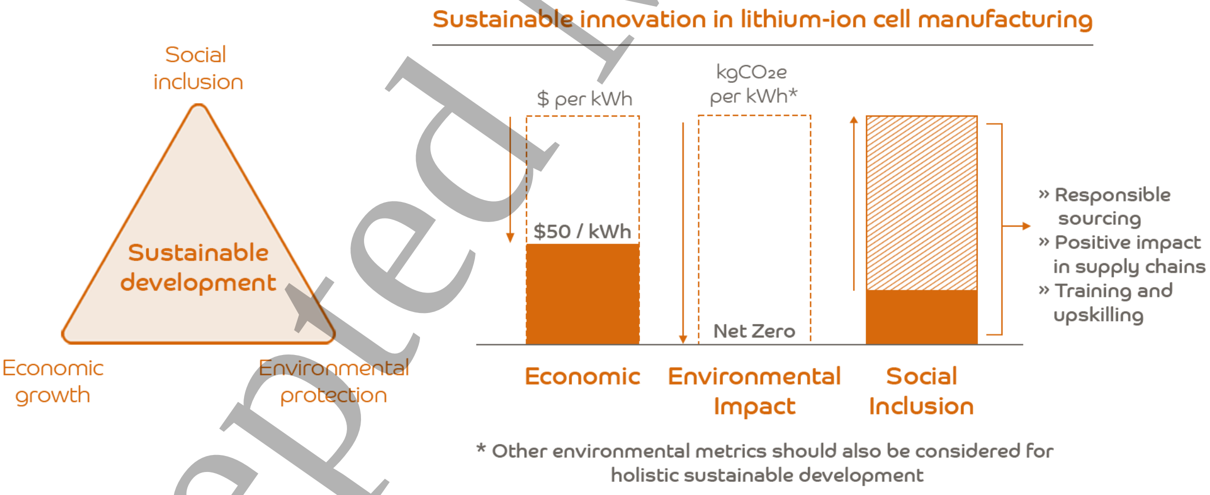

Figure 5: Sustainable innovation targets for lithium-ion cell manufacturing

Figure 5 shows the direction of travel required for the battery industry, with respect to each of the three cornerstones, from the current situation to the realisation of sustainable manufacturing practices. Alongside the economic target of \$50/kWh [2], the environmental impact[1] of producing batteries must be aligned to Net Zero targets before 2050 [3], and social inclusion parameters must improve. It is not straightforward to assign one key indicator to social inclusion; responsible sourcing of battery materials, removal of hazardous materials, and providing new employment opportunities should be the norm.

To achieve sustainable cell manufacturing, newer, more efficient process methods must be developed by both continuous improvement and disruptive innovation. The former is important to remain competitive, through yield optimisation and energy efficiency to reduce cost and kgCO_2e, but sustainability can only be achieved by parallel development of innovative and disruptive technology.

Current and Future Challenges

UKBIC is an industrialisation facility which is well positioned to understand current and future manufacturing challenges, as it sits between research centred laboratories and high-volume production. In an industrialisation facility the products and processes are in development, meaning both energy use and waste are higher than for a stable full-scale facility producing a fixed product, emphasising the need for efficient industrialisation.

Production Yield

Waste can occur at all manufacturing stages but to minimise material, component and assembly scrap, faults should be detected as early as possible. Traditionally, electrode defects are detected in the latter stages of cell assembly, where optical and other sensors identify defects before assembly into the final cell. Although relatively effective at identifying and removing faulty electrodes, often other components are disposed of at the same time. Defect identification equipment can be installed at electrode coating for earlier detection. However, electrodes are often coated with intentional gaps to enable tabs to be welded to the foil, requiring the detection system to understand the difference between intended and unintended coating gaps and flaws. Faults must be continuously characterised and fed back into the system to create robustness, but large trials and huge amounts of data are needed.

Energy Consumption

The largest energy users within manufacturing are electrode solvent drying, dry rooms for assembly, and formation. In electrode manufacturing, n-methyl-pyrrolidone (NMP) is an essential solvent in cathode slurries, and water for anode. Each electrode must spend at least a minute in a dryer to evaporate these solvents. To achieve an industry target of 100m/min coating speed, a 100m long dryer is required, which consumes a large amount of energy and factory footprint to evaporate, collect, recycle, and reuse costly and hazardous solvent [4]. Once dried, moisture absorption must be avoided by maintaining less than 1% relative humidity in dry rooms for cell assembly which is another huge energy consumer.

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[1] The whole value chain must achieve net zero for global greenhouse gas emissions targets to be met, and each stage within the chain has its own part to play as part of the overall picture. However, for the purposes of this paper, the focus is on the part of the value chain where UKBIC has most influence: manufacturing techniques.

The formation process electrochemically forms the cell which is energy intensive and time consuming [4]. Accelerated ageing tests at aggressive cycle rates can only second-guess the true performance in real world conditions, so optimisation of the formation protocol is difficult.
Significant amounts of real user cycling data over the long-term is necessary to prove out new protocols. This long-term cycle data is only recently becoming available due to the relative infancy of batteries used in products with 10-year duty-cycles, such as vehicles.

Advances in Science and Technology to Meet Challenges

Any technology that is developed towards the goal of sustainable manufacturing should as a minimum have no adverse economic, environmental, or social impact. But to be industry leading and truly innovative, solutions should overcome multiple challenges at once.

For electrode production, efforts are underway to replace NMP with more environmentally friendly and safer alternatives. Solvent-free coating removes the solvent entirely and overcomes several sustainability challenges at once. The removal of solvents mitigates the environmental and safety implications of NMP as well as the high energy use for evaporation and collection. The space requirements for long dryers are also mitigated, liberating factory footprint.

In cell assembly (and electrode production where the material requires dry conditions), the large energy-use for dry environments can be reduced through use of micro-environments. Micro-environments envelope the processing equipment, meaning that the smallest space possible is kept at the required dryness, reducing the energy demand. However, micro-environments are less accessible to interaction by operators, so increased digitalisation and automation is required.

Higher capacity equipment reduces the kWh of energy required to produce kWh of cells, assuming the energy demand of the equipment does not increase at the same rate as material throughput. For example, a faster throughput through a smaller dry room will have a beneficial impact on environmental and economic sustainability.

To advance formation protocols, detailed manufacturing traceability from cell materials through each stage of the process is vital. When coupled and compared with real-world performance data from electric vehicle telemetry data, this provides a lucrative source of information from which to innovate and unlock sustainability benefits. As cell manufacturing scales, the use of regenerative formation channels, where discharging cell energy can be used to charge new cells, becomes efficient, as does the use of renewable energy sources such as solar and wind, stored in banks of cycling cells from the factory.

In the near-term, as digital technologies develop and rich data sets from supply chains and manufacturing are collected, integrated, and analysed it will aid the creation of advanced cell digital models [5]. This will enable faster feedback on how changes in all aspects of production impact performance, further advancing the ability to innovate. This will also facilitate the increased application of Industry 4.0 principles.

Concluding Remarks

Batteries are a critical contributor to achieving global decarbonisation targets, but current production methods inherited from 1980s are unsustainable for the future as demand grows. The challenges need to be addressed in two ways; incremental improvements to drive process efficiency together with transformational innovation to achieve large gains towards sustainable cell manufacturing.

Building a body of knowledge of the intimate structures of electrodes, learning how this is affected by industrialisation will contribute to the mastering new ways to manufacture electrodes in a cleaner, more productive and energy efficient way, and realise the three cornerstones of sustainable development.

UKBIC has most direct influence and knowledge of cell manufacturing, but this is only part of the bigger picture. Further advancement towards sustainability can and should be made over the whole life cycle of the battery, for example through new materials innovation, innovative module and pack designs facilitating easier strip-down for module replacement, repurposing and recycling, and elongating the useful life of each battery to retain most economic, environmental, and social value. The whole industry needs systems-thinkers working together across the entire value chain from raw material extraction through to end-of-life recycling to ensure batteries are truly a sustainable solution.

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