

Layer-by-layer manufacture of improved energy storage devices



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April 2020

A Thesis Submitted in Partial Fulfilment of the Requirements for the
Degree of Doctor of Philosophy in Materials Science

Declaration

I confirm that the work presented in this thesis is my own work and I have indicated all information which has been derived from other sources.

Acknowledgements

My PhD has been quite a journey and would not have been possible without the wide range of support that I received.

In terms of financial support, I would like to thank the Engineering and Physical Sciences Research Council for funding my research, St. Edmund Hall and the University of Oxford.

I would like to express my gratitude to my main supervisor Prof. Patrick Grant. Patrick allowed me the flexibility to pursue my research interests and helped me become a better and more independent researcher. His attention to detail has been invaluable while drafting this thesis, and has made me significantly happier with the finished product. I would also like to thank my co-supervisors: Prof. Mauro Pasta, specifically for his support at various times throughout my research, and Dr. Chun Huang for being a friendly point of contact in the laboratory.

I've appreciated all the colleagues from my research group who provided relaxation from work during lunches, of which there are too many to list. Special thanks to Alasdair, Sarah and Lukas, who have remained close friends outside of work and helped me get through the more tedious moments!

I'm indebted to all my friends and family who have helped me see the positives during hard times and made the good times even better. To my friends in Oxford: Ricky and Will, who were pillars (sometimes partly crumbling) from the first year to the last, and to Melissa, Evie and Violaine for providing laughter and brunch company. To the powerlifters, for excellent social events and provided a relaxing atmosphere in the evenings after long days of experiments.

Nick, Tom, Silvia and Chris, who kept in contact with me by video chat during my absence from the outside world while writing. I hope we can all reunite in the real world soon. To Jonny and James, who have always distracted me with video games and picnics. David and Pippa who always put a smile on my face with fun weekends and cute videos of Reuben and Ezra.

My family Penny, Ashley, Clare, Alice, Mollie (dog), Coco (cat) and Roo (cat). Leaving Oxford to visit the countryside was always lovely, with great company, amazing food, face licks (dog) and fewer scratches over time (specifically Coco). I really appreciate all your encouragement, advice, and for making me who I am today. Thanks to Lucy for getting in touch when I needed extra help.

I'm also thankful to Aivaras and Elvyra, who have made me feel welcome when visiting Lithuania and helped me take some time away from Oxford! A final thanks to Migle, who has supported me since we met in the powerlifting club near the start of her PhD studies. I'm grateful for your company and love every day, and you make my life much better. We've both (almost) made it to the other side, and I'm looking forward to the future!

Abstract

A scalable layer-by-layer (LbL) spray processing technique has been investigated for the fabrication of electrodes and separators for lithium ion batteries (LIBs) with novel arrangements of constituent materials. Spray deposited electrodes based on LiFePO_4 (LFP) had the same capacity ($\sim 148 \text{ mAh g}^{-1}$), rate performance (50 mAh g^{-1} at 10 C) and electrochemical impedance spectroscopy response as those manufactured by conventional slurry casting. Slurry cast LFP electrodes from water-based slurries cracked at a thickness of $\sim 10 \mu\text{m}$ and spontaneously delaminated from Al foil current collectors at a thickness of $70\text{--}80 \mu\text{m}$ ($\sim 10 \text{ mg cm}^{-2}$) due to capillary pressure generated during drying. Spray deposited electrodes were crack-free up to at least $115 \mu\text{m}$ because of sequential drying of each, much thinner suspension layer, approximately equal to the average particle diameter in the suspension. A $115 \mu\text{m}$ (17.2 mg cm^{-2}) thick spray deposited LFP-based electrode had a reduced capacity retention of 89 % after 100 cycles when compared with thinner 6 mg cm^{-2} spray deposited or slurry cast electrodes (both 92 %), but provided a significant improvement in volumetric capacity at charge/discharge rates between 0.1 and 2C .

LFP-based electrodes with a through-thickness variation in local particle size and local porosity were produced. Whereas conventional LFP electrodes had a single voltage plateau during discharge, those containing two different particle size distributions had two distinct voltage plateaux. Over 200 0.5 C charge/discharge cycles the electrode made from a mixture of the two distributions lost 0.056 % of its original 0.5 C capacity per cycle, while an electrode with higher porosity and smaller particle size next to the separator, and lower porosity and larger particle size next to the current collector, lost 0.046 % capacity per cycle, an 18 % improvement. An electrode with the "inverted" arrangement of identical

materials lost 0.065 % capacity per cycle, a 16 % decrease. The electrode with increased porosity and lower particle size at the separator reduced overvoltage compared with other arrangements of the same materials at 10 C. The reduction in overvoltage was suggested to be due to greater Li ion concentration near the current collector and a lower utilisation of MTI particles (which had a higher degradation rate and greater polarisation). This work provides some of the strongest experimental evidence to support prior modelling of the performance of electrodes with non-uniform distributions of porosity and particle diameters.

A porous, spray deposited Al_2O_3 -based separator was developed to enable the direct deposition of an electrode/separator/electrode full cell assembly in a single deposition operation. An optimised sprayed separator consisted of 50 nm Al_2O_3 particles, 1 wt. % polyacrylic acid (PAA) and 5 wt. % styrene butadiene rubber (SBR), deposited from an 80:20 suspension of water and isopropanol (IPA). Separators between 5 and 22 μm thick had consistent and similar porosity of ~58 %, excellent wettability, thermal stability to at least 180 °C, adequate electrochemical stability and high ionic conductivity of $\sim 1 \text{ mS cm}^{-1}$ at room temperature, double that of a commercial PP separator. A fully spray deposited LFP/LTO full-cell with a 10 μm Al_2O_3 separator, the first of its kind, showed similar rate performance to a cell with a conventional PP separator, with a capacity of $\sim 50 \text{ mAh g}^{-1}$ at 30 C. On long term cycling of 400 cycles at 2 C, the Al_2O_3 separator cell had excellent capacity retention of 96.2 % compared with 78.1 % for the PP separator cell.

The flexible spray deposition approach has been shown to facilitate ultra-thick electrodes, layered electrodes that open a large design space for electrode structural design and improved performance, and relatively thin, porous inorganic separators with enhanced stability.

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Chapter 1

Introduction

In the last decade, the need to reduce global dependence on fossil fuels has become increasingly apparent due to a combination of political, economic and environmental factors. It has been estimated that human activities have caused a 1 °C rise in global temperatures since pre-industrial levels [1]. Furthermore, the global temperature is expected to increase by 0.2 °C per decade, which may lead to permanent loss of eco-systems, habitable land and increased risk of extreme weather events [1]. In 2015, countries at the United Nations Climate Change Conference adopted The Paris Agreement, which established a goal of reducing the global average temperature rise to below 2 °C, and preferentially to 1.5 °C above pre-industrial levels [2]. To put the challenge into perspective, limiting warming to 1.5 °C requires that global CO₂ emissions reach net zero by 2055 [1].

A clean energy market is part of a solution to rising CO₂ levels and several countries have managed to transfer a considerable fraction of their energy generation to renewables [3]. However, there are still several issues that restrict wide-spread adoption of renewables, including for mobile and stationary energy storage [4, 5]. This has particular relevance to the implementation of zero and controlled emission vehicles (electric vehicles (EVs), full hybrid vehicles (HEV), plug-in hybrid vehicles (PHEVs)) and generation of energy based on intermittent sources, such as solar and wind. Electrochemical energy storage systems have been identified as being able to play a critical role in this space due to their relatively efficient storage and the capability for near on-demand release.

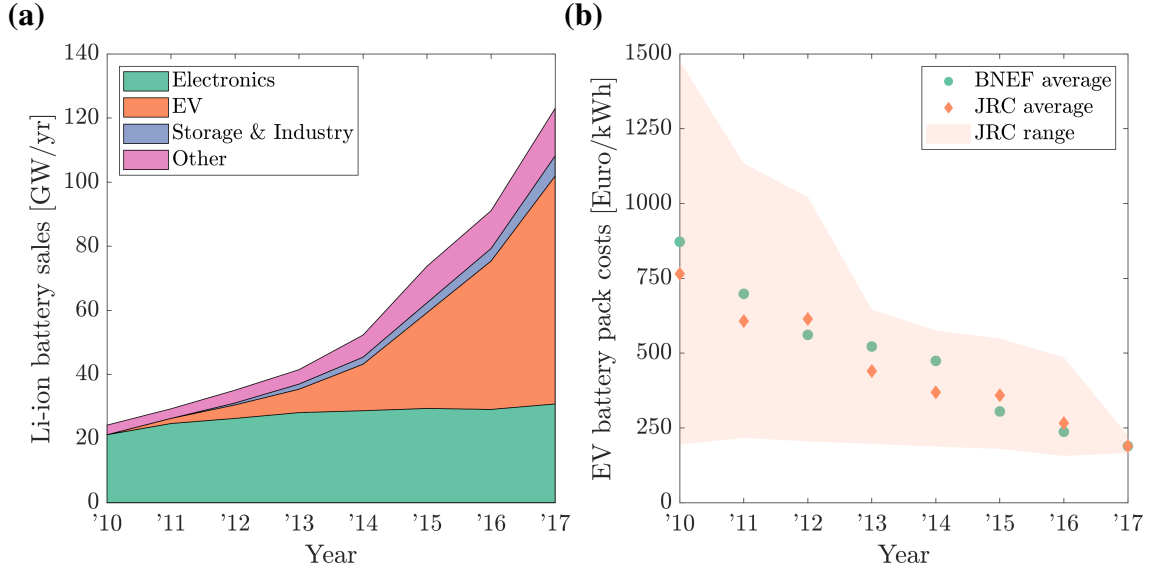


Figure 1.1: (a) Growth of lithium-ion batteries between 2010–2017 by sales in main market segments and (b) the average cost (€) and range of reported costs of EV battery packs between 2010–2017, as reported from Bloomberg New Energy Finance (BNEF) and the Joint Research Centre of the European Commission (JRC). Reproduced from [6].

After commercialisation by Sony in the 1990s, Li-ion batteries (LIBs) became the main enabler of the proliferation of consumer electronics, to the point where worldwide LIB cell production is now in the many billions [7]. In turn, the cost of LIBs has dropped due to economies of scale, and larger and larger formats have become commercially viable. Between 2010 and 2017, the commercialisation of EVs increased the sale of LIBs from 20 GWh yr⁻¹ to 120 GWh yr⁻¹ (Figure 1.1a), while the cost of EV battery packs has reduced from 1000 \$ kWh⁻¹ to <250 \$ kWh⁻¹ (Figure 1.1b) [6]. Significantly, the global market share of EVs is still low, e.g. 1.8 % in 2019 [8], and recent forecasts have predicted that with continued uptake, LIB pack cost may reduce to as low as ~100 \$ kWh⁻¹ by 2023 [9–11].

The dominance of LIBs in these emerging markets compared with other forms of electrochemical storage, as shown in Figure 1.2a, is due to a combination of favourable properties such as very high energy efficiency, high specific energy (~250 Wh kg⁻¹), high energy density (~700 Wh L⁻¹) and long cycle life (96 % capacity retention at 4000 cycles at 100 % depth of discharge) [5, 12, 13]. While other novel technologies are attractive in

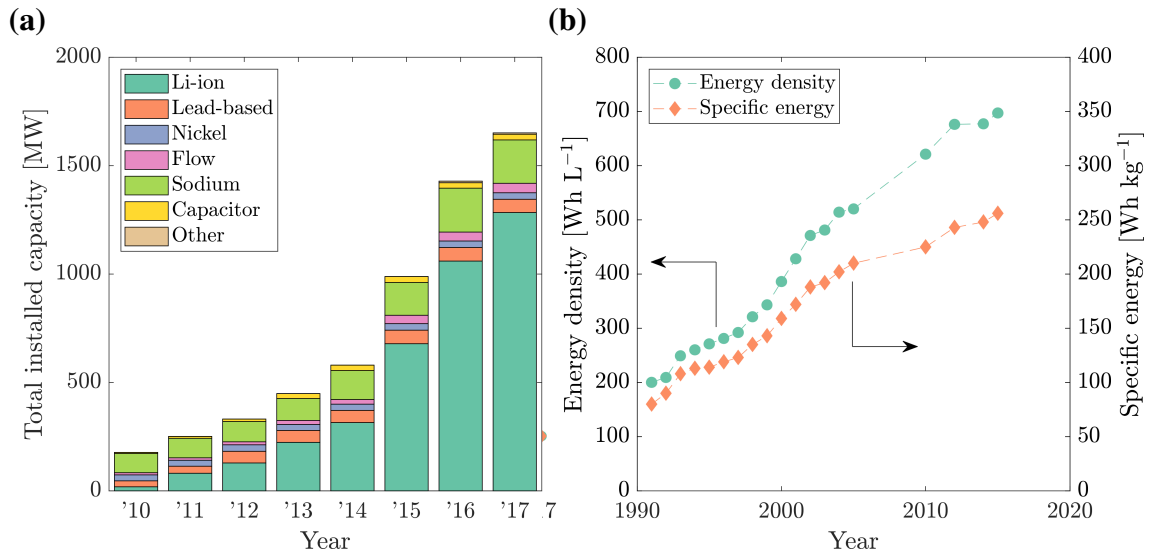


Figure 1.2: (a) Total installed stationary storage capacity of electrochemical storage technologies and (b) the energy density and specific energy of Li-ion 18650 cylindrical cells from 1991 to 2015. Reproduced from [6] and [12].

terms of abundance or energy density, e.g. Na-ion and post Li-ion (lithium-sulphur and lithium-air), they are unlikely to mature to compete with Li-ion technologies before 2030 [14–17].

Widespread adoption of LIBs in transport and stationary storage applications is not only dependent on battery pack price. Further improvements to performance (Figure 1.3) are necessary, along with the construction of compatible charging networks, second-life usage and end-of-life disposal or recycling. For instance, the three most economical EV models with a theoretical LIB cost of ~ 70 $\$/\text{kWh}$ (perhaps reached by 2030), would only be suitable for ~ 50 % of US consumers due to driving range limitations [18]. Between 1991 and 2015, the specific energy of Li-ion 18650 cells has increased from ~ 90 Wh kg^{-1} to ~ 250 Wh kg^{-1} (Figure 1.2b), mainly by increasing the proportion of active material in the cell from 47 % to 61 %, and by using active materials with greater specific energy, e.g. replacing LiCoO_2 cathodes with ternary transition metal alternatives [19]. Therefore, the improvements to cell performance so far have been derived from step-wise improvements in the manufacturing of cell components (e.g. thinner current collectors, separators, reduction in conductive

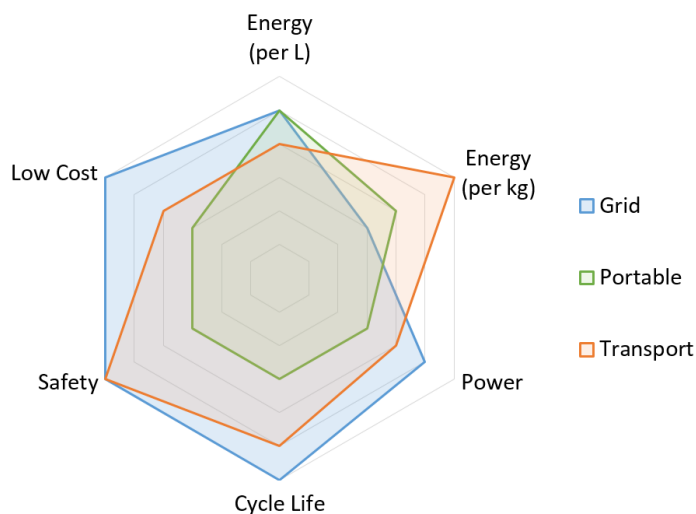


Figure 1.3: A qualitative comparison of the requirements of mobile, electric vehicle (EV) and grid applications.

additives and binder) and component chemistry (active material type, electrolyte additives etc...), while from a materials science perspective the electrode structure and method of manufacture has not changed. Recently, there has been a growing interest in whether alternative electrode and cell structures could benefit cell performance. While complex electrode structures can be difficult to achieve with conventional slurry deposition used across the industry, several novel manufacturing techniques have shown promise.

This thesis investigates whether the microstructural control provided by a pneumatic spray deposition technique can improve the performance of LIBs. The following objectives are pursued: (1) to examine whether spray deposition is a valid technique for deposition of high performance Li-ion cathodes and whether there are inherent performance advantages of the technique compared with conventional slurry processing, (2) to study how through-thickness variations in certain local properties in multi-layer cathodes might be used to alter their performance and to test theoretical models of microstructural effects on performance, and (3) to explore how layer-by-layer deposition of electrode and separator materials might enable novel manufacturing of high performance LIB cells.

Chapter 2 describes conventional electrode manufacturing and reviews examples of

novel Li-ion electrode and cell structures enabled by alternative manufacturing techniques from the literature. Chapter 3 outlines the basic processing techniques and characterisation methods used subsequently in Chapters 4, 5 and 6. Chapter 4 explores the processing and mixing of aqueous LiFePO_4 -based (LFP) electrode suspensions, the deposition of suspensions onto current collectors using the layer-by-layer spray deposition technique, and compares conventional slurry processing of thick cathodes when using an aqueous route with spray deposition. Chapter 5 employs the spray deposition technique to create two layer LFP cathodes with through-thickness variation of local porosity and local particle size to study the effect of electrode structure on electrochemical properties. Chapter 6 compares the direct spray deposition of an optimised ceramic-based separator with a conventional industry standard polymer separator, and shows how this approach can enable the manufacture of high performance full cells using a single, continuous deposition technique. Lastly, Chapter 7 summarises the work and suggests potential future prospects and applications.

Chapter 2

Literature review

2.1 The Li-ion cell

There are a number of key parameters that have made LIBs the electrochemical storage technology of choice for many applications. Significantly, their attractive combination of high energy and power (Figure 2.1) arises from the use of relatively stable electrochemically active materials with high operating voltages and high Li storage capacity. The voltage (V) at which a Li-ion battery operates is defined by the difference in chemical potential between the cathode and anode, but may need to be limited based on the electrochemical stability window of each component, commonly determined by the stability of the electrolyte and cathode [20]. The capacity of a material is a measure of how many Li^+ ions can be intercalated into the structure and can be measured in terms of weight or volume (e.g. $>180 \text{ mAh g}^{-1}$ for high capacity cathodes). The energy stored is a combination of both the average operating voltage and the capacity (Wh kg^{-1} or Wh L^{-1}). The specific power, W kg^{-1} , is a measure of how much energy a cell can deliver within a time frame. C-rate is the current that will fully charge or discharge the cell within a time frame e.g. a 1 C rate is the current density at which the cell is charged in one hour, while a C/2 rate will take 2 hours. Therefore, a high capacity at high C-rates yields high power.

A conventional LIB consists of a graphite anode on a Cu current collector and a transition metal oxide cathode (LiMO_2) on an Al current collector separated from one another by a

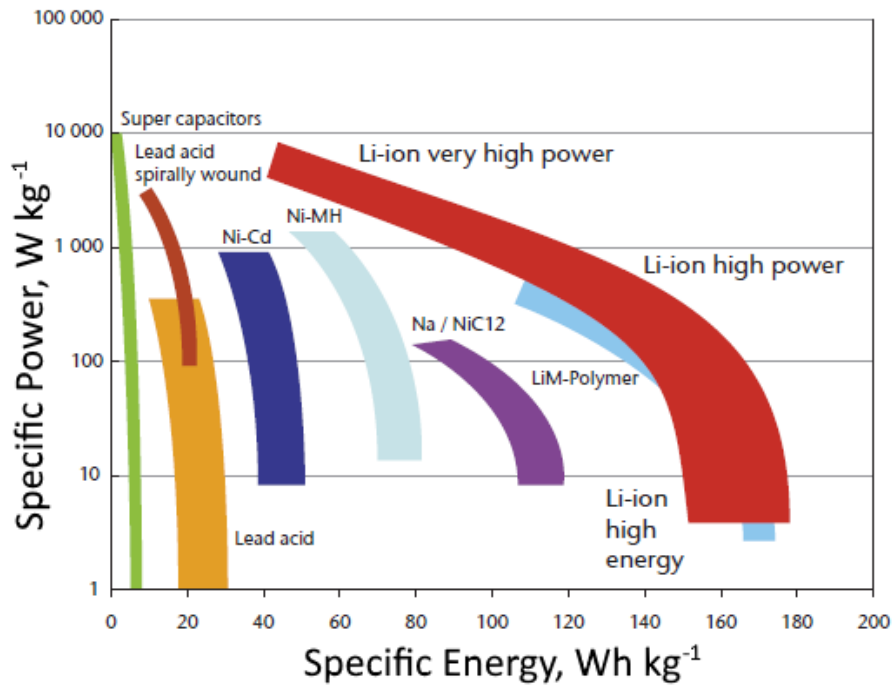


Figure 2.1: A comparison of the specific power and energy achievable with different electrochemical systems [21].

porous separator. The electrodes and separator are infiltrated with a Li salt electrolyte, e.g. LiPF_6 dissolved in a mixed organic solvent (e.g ethylene carbonate/dimethyl carbonate, EC/DMC). Li^+ ions are transferred from one electrode to the other by diffusion through the electrolyte, under the action of an applied electric field, and intercalate/de-intercalate between crystallographic planes of the electrochemically active material (Figure 2.2). The separator provides pathways for Li^+ diffusion, insulates against electronic conduction and blocks the electrodes from physically touching one another, reducing the chance of short circuits. Upon discharge, Li-ions within the negative electrode (graphite anode) are transferred to the positive electrode (LiCoO_2 cathode in Figure 2.2) according to the

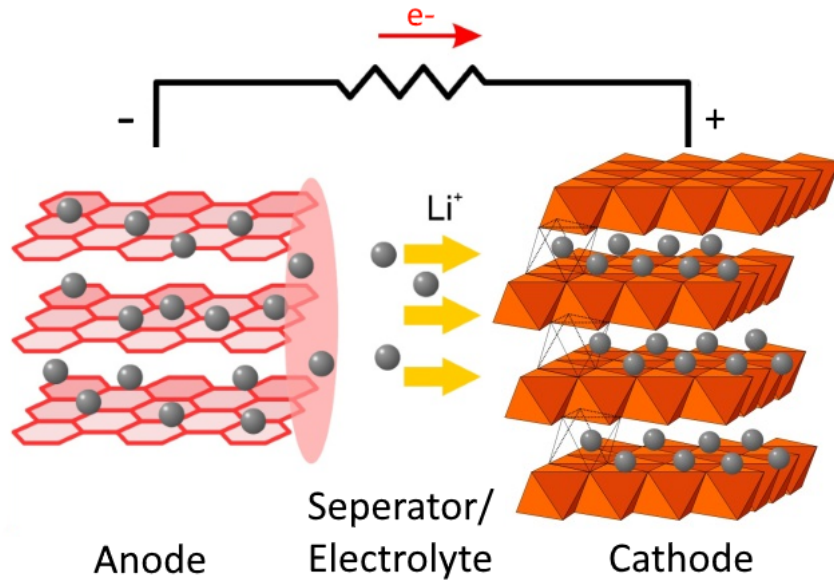
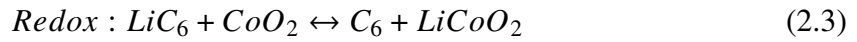
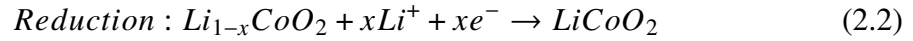
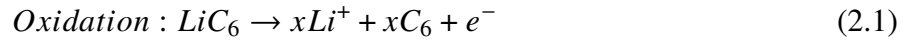


Figure 2.2: A scheme of the conventional Li-ion cell during discharge.

reactions;



Although the above reactions are relatively simple, matters are complicated by the redox process occurring at the graphite electrode at 0.05 V vs Li below the stability range of the electrolyte (0.8 V vs Li). Fortunately, the initial reaction of the electrolyte with the graphite partially forms a protective surface layer, called the solid electrolyte interphase (SEI), that prevents further side reaction in certain organic solvents. But, SEI formation leads to irreversible capacity loss in the first cycle due to consumption of Li from the electrolyte and slightly limits the rate at which Li can diffuse subsequently into the anode material.

Anodes - A Li metal anode has extremely high specific energy of 3860 mAh g⁻¹ and the lowest negative electrochemical potential of -3.040 V vs the standard hydrogen electrode [22]. However, the tendency to short circuit due to Li dendrite formation has limited

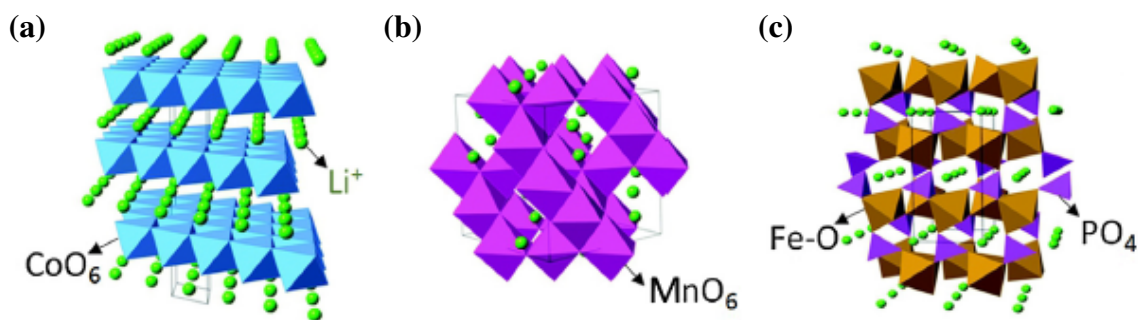


Figure 2.3: The crystal structure and Li intercalation of (A) LiCoO_2 , (B) LiMn_2O_4 and (C) LiFePO_4 [26].

commercial applications of Li anodes. Graphitic carbon materials have been the most commercially viable anode material since 1991 due to useful capacity (372 mAh g^{-1}), low cost, relatively low volume expansion during charge/discharge (10%), high availability, high electrochemical stability, high Li diffusivity (10^{-9} to $10^{-7} \text{ cm}^2 \text{ s}^{-1}$), high electrical conductivity and a low average voltage of 150 mV vs Li/Li^+ . However, the low theoretical density of most carbons results in electrodes with relatively low volumetric capacity of $330\text{--}500 \text{ mAh cm}^{-3}$, even when compressed to low porosity ($\sim 30\%$). Alternatives to graphite, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and Si, have had limited commercial implementation due to high cost and low specific capacity (LTO) or high volume expansion leading to pulverisation and low cycle life (Si) [23–25].

Cathodes - Common commercial cathode materials can be classified by their crystal structure, i.e. layered, spinel and olivine, as shown in Figure 2.3, with properties summarised in Table 2.1. Layered cathode materials are generally characterised by high specific energy and energy density. LiCoO_2 (LCO) historically has had the majority of the cathode market share (90% in 2005 [27]) since Li-ion commercialisation, but the high cost (due to Co), low thermal stability and high capacity fade at high current rates has limited its uptake in EV and stationary applications. Alternatives, such as $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA) and $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (NMC), have a lower cost due to their reduced proportion of Co and their improved specific capacity and calendar life has lead them to be the two most favoured

cathode materials for EVs [28–32].

Spinel LiMn_2O_4 (LMO) benefits from high operating voltage, low cost, low toxicity and abundance of Mn, while achieving high rate performance with nano-scale particles. However, side reactions, Mn dissolution, and low usable capacity of 120 mAh g^{-1} has limited commercial uptake compared to NCA and NMC [13, 33–36].

LiFePO_4 (LFP) was the first olivine material to be commercialised but a low operating potential of $\sim 3.4 \text{ V}$ and a low theoretical density of 3.6 g cm^{-3} limit the specific energy and energy density of cells compared to NCA and NMC. However, it has a unique combination of advantageous properties, such as high power capability, long cycle life, environmental compatibility, low metal content, low cost and high thermal stability, which has lead to significant commercial application in power tools and certain lower range EV applications [37]. Low electrical conductivity (10^{-10} to $10^{-7} \text{ S cm}^{-1}$) and a size-dependent ionic diffusivity have been overcome sufficiently by coatings and reductions in particle size (see Section 2.2.2).

Structural and conductive additives - For both anodes and cathodes, the particulate active materials are held together and adhered to the current collector with the addition of a binder, usually a polymer. Fine-scale carbon particulate is also added since along with Li diffusion throughout the porosity of the electrodes, electrons must be able to percolate through the electrode thickness to and from the current collectors to facilitate charge and discharge of the cell.

Electrolytes & separators - The versatility of the Li-ion chemistry allows for a wide variation in the configuration of cells. Different configurations can alter the performance and safety of the cell considerably. For electrolytes in particular, an ionic conductivity of $>10^{-3} \text{ S cm}^{-1}$ is seen as the commercially viable minimum. Physical properties, such as the wetting of the active material, also determine the efficacy of an electrolyte since poor wetting onto the active material will lead to increased interfacial impedance.

Since the commercialisation of Li-ion batteries by Sony in 1991, the majority of Li-ion

Table 2.1: Properties of commercial cathode materials used in Li-ion batteries [26, 38–40]

	LCO	NCA	NMC	LMO	LFP
Structure	Layered	Layered	Layered	Spinel	Olivine
Avg. voltage ¹ [V]	3.9	3.8	3.8	4.1	3.45
Spec. capacity [mAh g ⁻¹]	140	180-200	160-180	100-120	140-160
Spec. energy [Wh kg ⁻¹]	546	680-760	610-650	410-492	518-587
Crystal density [g cm ⁻³]	5.05	~4.8	~4.8	4.15	3.6
Safety	Fair	Fair	Fair	Good	Superb
Cycle life	Fair	Fair	Superb ²	Fair	Superb

¹ Average potential vs Li/Li⁺ ² Single crystal [13]

batteries have contained organic liquid electrolytes and a porous polymer separator. These electrolytes provide good wetting onto the active materials and conductive additives, but preventing leakage is critical as they are highly flammable. The porous polymer separators are often poorly wetted by the electrolyte and are unstable at temperatures >90 °C [41, 42]. Larger battery packs are required for electric vehicles, and the higher chance of catastrophic puncture and thermal runaway, means a greater emphasis must be placed on safety in these applications [43]. As a result, research into non-flammable solid, gel and ionic liquid electrolytes has grown in the past decade, however, they generally suffer from much lower ionic conductivities and poor wetting compared to conventional organic solvent-based liquid electrolytes. Replacing the liquid electrolyte component is one of the bigger paradigm shifts for future Li-ion cells, and also one of the most difficult to achieve [44].

2.2 Conventional electrode manufacturing

2.2.1 Slurry coating

Slurry coating, in its various forms, has dominated Li-ion electrode manufacture due to its relative simplicity, scalability and reproducibility. A viscous slurry consisting of the active material, conductive additives, binders and solvent is transferred onto a conductive

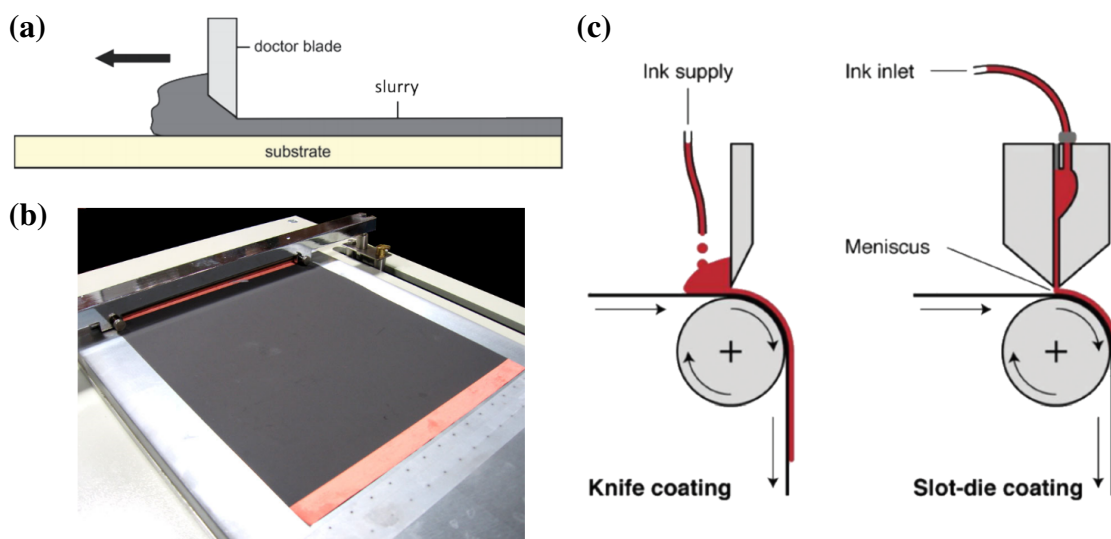


Figure 2.4: Slurry coating techniques: (a) doctor blade coating, (b) a bar coating apparatus with a dried electrode film and (c) knife coating and slot-die roll-to-roll coating processes. [45].

substrate (current collector) and spread over the surface at a controlled thickness of 5-200 μm . Laboratory scale casting is commonly achieved with doctor blade apparatus (Figure 2.4a) or bar or screen printing (Figure 2.4b). Industrial variants include roll-to-roll processing such as reverse roll, doctor blade coating, knife-over-roll and slot-die coating (Figure 2.4c), at coating speeds of up to 90 m/min.

A vacuum plate, flat surface or roller holds the current collector while a blade/bar passes over the applied slurry at a constant rate and a pre-adjusted height. Once coated onto the current collector, the electrode is dried to remove either organic (non-aqueous processing) or water-based (aqueous processing) solvents and calendered (rolled) to reduce porosity, while avoiding cracking or delamination. Roll-to-roll drying is usually achieved by passing the coated electrode through a "tunnel" of heaters set at different temperatures, while laboratory scale methods usually consist of a combination of air and vacuum oven drying. The final thickness of the dried electrode coating is determined by the combination of the blade/bar gap, particle size distribution, rheological properties of the slurry and the calendering force and temperature.

Solvents are used to obtain a stable dispersion of particulate components and provide

intimate mixing of binders. Polyvinylidene fluoride (PVDF) was the only satisfactory binder for 15 years after Li-ion commercialisation and requires an organic solvent, usually *N*-Methyl-2-pyrrolidone (NMP). There has been a drive towards aqueous systems due to their better environmental compatibility and lower costs. However, adoption of aqueous systems has posed a challenge as many active materials and conductive additives are hydrophobic, resulting in strong agglomeration upon mixing, while others are not chemically stable in water. The combination of a thickener e.g. carboxymethyl cellulose salt (CMC), and a strong particulate binder e.g. styrene butadiene rubber (SBR), has provided excellent performance at lower concentrations for graphite-based electrodes compared with PVDF/NMP, which is leading to progressive commercial adoption [46, 47].

Figure 2.5 shows the cross section of a battery cell consisting of a cathode and anode made by slurry coating; a randomly mixed structure of electrode constituents (active, carbon, binder, porosity) with no intended spatial control and is considered typical of a commercial Li-ion electrode structure. The slurry process is limited in terms of its ability to alter electrode shape and structure [44, 48]. Lateral variation in material or structure (patterning) generally cannot be achieved in any feasible or performance altering manner [49]. Even at low coating thickness (10–20 μm), a long drying step is required after application. Poor mechanical integrity (i.e. delamination) due to binder migration or cracking limits realistic coating thicknesses to below $\sim 200\text{ }\mu\text{m}$ [44]. In spite of the lack of finesse in the slurry coating process, the performance of these monolithic electrodes has been improved by new electrode compositions (i.e. Sony's Nexelion, single crystal NMC and optimisation of conductive additives, binders, mixing and porosity [13, 50]) and other approaches, which are now discussed.

2.2.2 Conventional modifications to improve cell performance

Many critical properties of batteries can be controlled by their physical and compositional modification, such as their ability to deliver and store large amounts of energy (specific

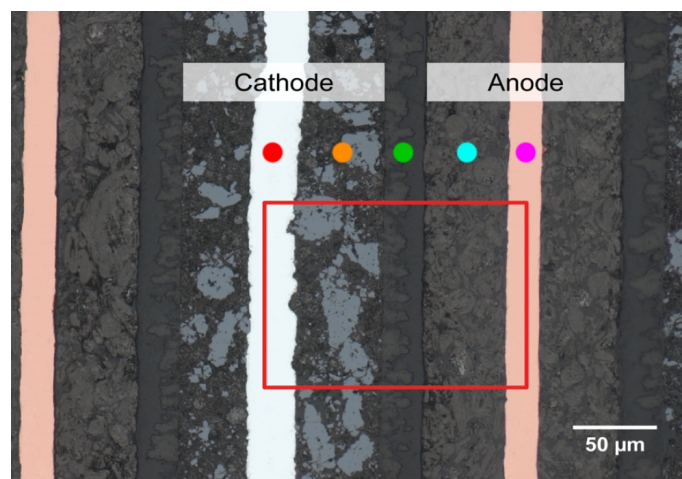


Figure 2.5: An optical microscopy cross section of a 18650 cell produced by slurry casting [51].

energy and energy density), the dynamic response of this energy (specific power) and the number of times they can perform this action (cycle life). Internal resistance is a major factor in the ability to realise the theoretical performance of a battery in practice. Table 2.2 summarises the main types of resistance how they may be modified. For example, thinner electrodes and separators reduce the distance that Li^+ ions are required to travel upon charge or discharge, reducing ionic resistance. While this approach works for any system, the proportion of inactive material in the cell is increased for a fixed volume, reducing volumetric and gravimetric energy density at the cell level. Therefore, there is usually a compromise between energy and power, exemplified by the commonly used Ragone plot shown previously in Figure 2.1. Some of the approaches to improve LIB performance will be described in the following sections, while others are out of the scope. For example, the interfacial resistance between active materials and the electrolyte is generally not significant in liquid electrolyte-based batteries but is a serious problem in solid-state batteries, and is yet to be resolved.

In the past decade there has been growing interest in improving the performance of electrodes of all length scales: for thin film batteries ($<10\text{ }\mu\text{m}$), conventional LIBs (commonly $70\text{--}100\text{ }\mu\text{m}$) and for new thick electrodes ($>200\text{ }\mu\text{m}$). Thin film batteries (usually solid-state) are not usually manufactured by slurry casting but using variants of

Table 2.2: A table describing the sources of internal resistance in a battery cell [52, 53].

Resistance	Internal resistance of cell	Modifications
Ionic	Electrode to electrode	Increase calendering force
	Electrode particle	Improve ion diffusivity in active material
	Electrolyte	Change type of solvents & additives Reduce electrode thickness Reduce pore tortuosity
Electrical	Electrode particle	Improve electrical conductivity in active material, coat active material with conductive additives
	Percolation network of additives	Homogeneous mixing & composition; high aspect ratio particles
	Current collectors	Material & surface treatment
	Electrical tabs	
Interfacial (ionic)	Electrolyte and electrodes	Reduce binder quantity
Interfacial (electrical)	Electrode particles and conductive additives	Homogeneous mixing & calendering
	Electrode and current collector	Increase calendering force
	Conductive additives and current collector	Increase calendering force

physical and/or chemical deposition, but their structuring is discussed briefly when relevant to some novel manufacturing techniques in Section 2.3.1.

2.2.3 Calendering

The calendering technique involves compressing the electrode after the drying step. This step enables: (1) decreased porosity, (2) reduced surface roughness, (3) adjustments to pore structure and (4) homogenisation and improvement of mechanical properties and conductivity. Many of the resulting performance improvements (reduced impedance) are due to improved contact between particles, binder, conductivity enhancers and the current collector. Calendering not only leads to various improvements in the electrochemical properties of cells, but also boosts volumetric capacity. However, the reduction in porosity also limits the amount of electrolyte within the electrode, which will reduce overall capacity

at a limiting current density.

Most studies agree that a reduction to 25-40% porosity by calendering is optimum for both cathode and anode materials, however, the reasons why this produces improvements maybe different [54–57]. For instance, the extent of reduction in graphite electrodes has minimal effect on rate performance, but a noticeable effect on cycle stability [57]. Rate performance was suggested to be dependent on the pore fraction where the pore size was in the range of 0.2 μm to 50 nm, with a 15% reduction of the as-cast thickness providing the optimum performance. Many have found that the rate performance for cathodes based on NMC was a strong function of porosity [58, 59]. For example, rate performance worsened significantly as porosity was reduced from 37 % to 18 %. Conversely, Bommel and Divigalpitiya identified that calendering, among other techniques, decreased contact resistance between LiFePO_4 and Al current collectors which lead to substantially improved rate capability [60].

Calendering is an important step for increasing volumetric capacity, but excessive calendering (reduction in thickness and pore fraction) should be avoided as there is a trade-off between increased electrode density and decreased electrolyte infiltration which limits Li^+ diffusivity, i.e. rate performance.

2.2.4 Particle size

When the rate determining step for charge/discharge is diffusion of Li^+ within the active material itself (rather than diffusion through the pore structure), the most direct route to improving dynamic performance is to reduce the diffusion length. This is achieved by reducing at least one particle dimension possibly down to the nanoscale (nano sized 0D particles, 1D fibres [61–65], wires [66, 67] and tubes [68, 69], 2D sheets [70], 3D porous particles), and is one of the driving forces for nanomaterial research in the Li battery field [71]. The characteristic time constant for diffusion, t , is given by $t = L^2/D$, where L is the diffusion length and D is the diffusion constant. Therefore, the time for diffusion or

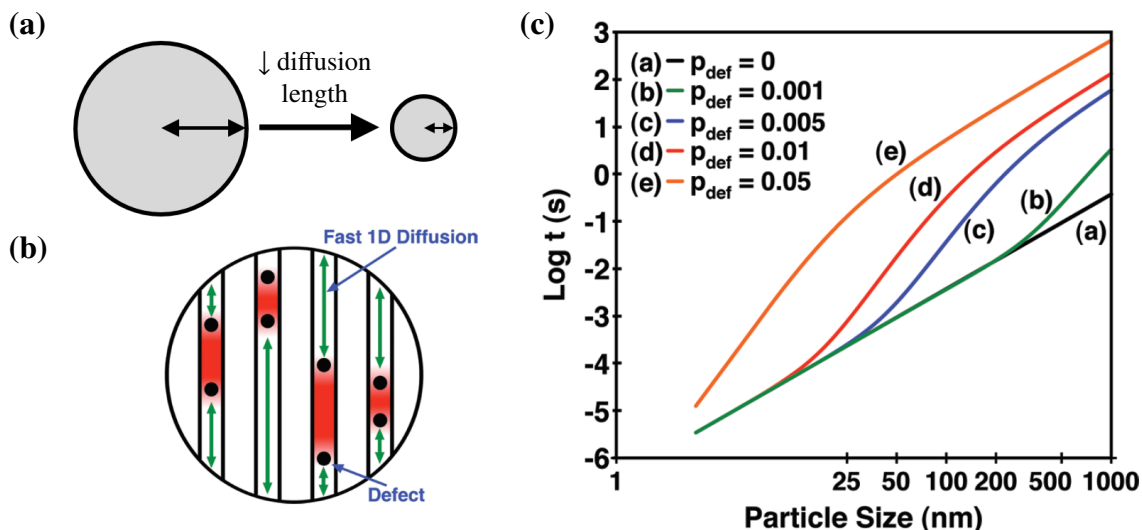


Figure 2.6: Diffusion in different particle sizes. (a) Reduction in diffusion distance with particle radius, (b) 1D diffusion channels blocked by defects and (c) the relationship between defect concentration and particle size in LFP particles [77].

intercalation decreases with the square of the particle size [72].

In practice, implementation of this concept has been met with varying levels of success. For example, Li diffusion in LFP is limited by point defects in 1D diffusion channels [73]; the ion diffusivity, and in some cases the capacity, is effectively particle size dependent, as the probability of two defects blocking part of a channel increases with increasing particle radius, as shown in Figure 2.6 [74]. Therefore, a reduction in particle size not only reduces diffusion distance but also improves Li diffusivity. LFP with particle diameters of 40-200 nm have exceptional rate capability when suitable conductive additives are also employed [75, 76]. It is interesting to note that materials generally known for high rate capability often derive it from particle size reduction rather than high intrinsic Li diffusivity or electronic conductivity, i.e. LFP and LTO.

Particle size reduction results in low tap density, an important factor in determining the commercial viability of a material. Commonly, nano-LFPs have tap densities of 0.6-1.0 g cm⁻³, a considerable disadvantage in terms of volumetric and gravimetric energy density compared with, for example, commercial LCO (2.6 g cm⁻³) [78–80]. Additionally, it is common for nanomaterials to experience capacity fading and difficulty maintaining

intimate contact between particles, leading to a compromise on the practical size reduction that is desirable [71]. High specific surface area also leads to increased reactivity with the electrolyte, Li consumption, and excessive formation of solid electrolyte interphase (SEI), blocking further Li intercalation. Therefore, graphite, NMC and NCA, to name a few examples, are typically manufactured with a compromise in particle diameter of $\gtrsim 5\ \mu\text{m}$.

2.2.5 Surface coating and conductive additives

Surface coatings may offer a route to improve rate performance and cycle life of cathode materials. Coatings aid charge transfer across the particle surface interface, between individual particles, and from particles to the current collector [81]. Most electrode materials have been shown to benefit from carbon coatings of 1–6 nm thickness (Figure 2.7) and intermixing of carbon black particles ($\sim 50\ \text{nm}$) and graphite particles (micro-scale) [82–91]. Carbon is an attractive additive material due to its low cost, low concentration requirement (0.5 - 2.0 wt. % coatings and/or additives) and electrochemical stability [92]. Carbon coatings aid the charge transfer process at the active material surface; carbon black additives generate short range conductive bridges between particles, while conductive graphite fills the voids between larger particles of active material, i.e. long range conductive bridging [93–95]. Therefore, carbon coatings are more necessary for materials with poor intrinsic electronic conductivity [96–98]. Conductive or inert material additions may improve rate performance but reduce the fraction of active material.

2.3 Novel structuring & manufacturing

The overall structure of an electrode, i.e. the way the different materials and pores are arranged on a microstructural scale, determines the kinetic properties of the battery. In typical slurry cast 'monolithic' electrodes, the principle structural control is only the final porosity. However control of pore tortuosity is also an important factor and has not been

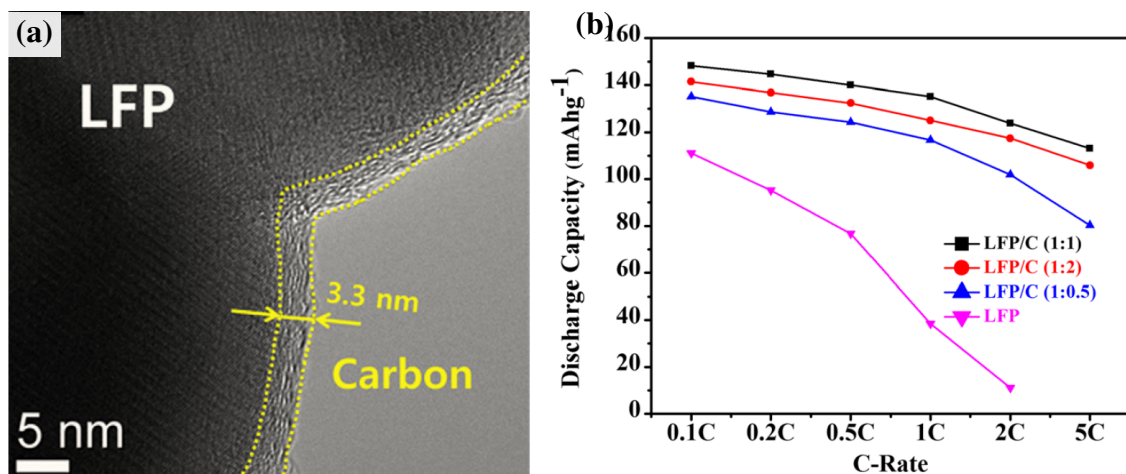


Figure 2.7: (a) Transmission electron micrograph of a carbon coating layer on an LFP particle and (b) improvement in capacity between 0.1 and 2 C for LFPs coated in different quantities of carbon ('LFP/C 1:1' does not mean 50% carbon, rather the coating was ~4 nm thick) [99, 100].

exploited as a free variable until relatively recently (Section 2.3.2.2). A high pore fraction reduces the active to inactive material ratio, and therefore capacity, but carefully controlled pore tortuosity can bring significant benefits for a constant overall pore fraction.

Attempts to increase the areal energy capacity of electrodes, i.e by reducing the proportion of conductive additives and increasing the thickness, results in batteries with limited power and rate performance due to limited Li^+ ion diffusion in the thicker electrodes - unless the pore tortuosity is controlled in a way to promote through-thickness ion mobility. In combination with research into how to accommodate the strain of high volume expansion materials, new avenues such as altering the structure, particularly the porosity, of electrodes have become increasingly popular, exemplified by the extensive research into 3D microbattery architecture [101–103]. Novel manufacturing techniques have been investigated in order to provide more control over diffusion distances and mobility in the electrodes, either by generating internal macro/meso/nano pores, patterning through thickness pores/channels, or by using spatial variation (layering or gradients). Many of these techniques have additional advantages, such as better compatibility with solid-state electrolytes and the ability to manufacture arbitrary, conformal and flexible form-factor electrodes. However they are generally commercially immature and suffer from poor

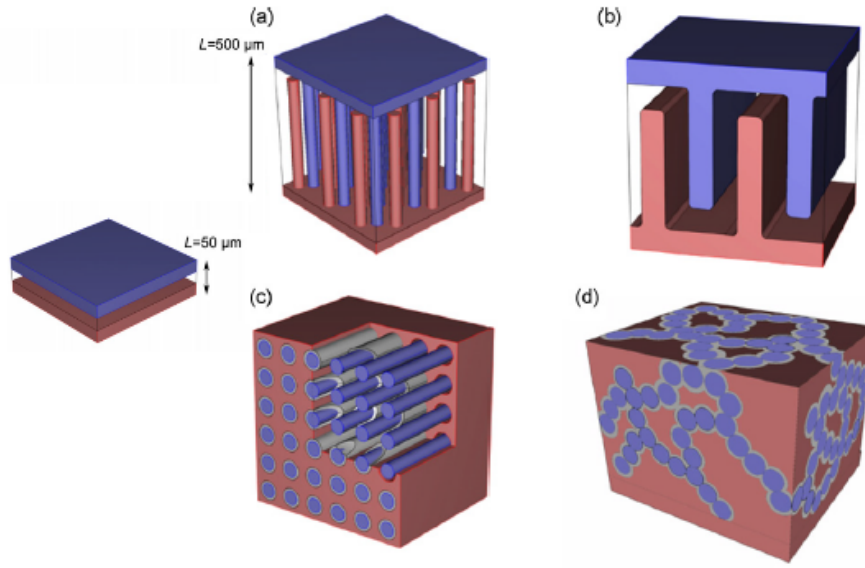


Figure 2.8: A comparison of a 2D thin-film micro lithium-ion battery (MLIB) and 3D-architecture MLIBs: (a) 3D interdigitated rods/pillars/tubes, (b) 3D trench, (c) 3D concentric, (d) 3D aperiodic [105].

scalability and higher cost.

2.3.1 Microbatteries

Microbatteries are usually $1\text{-}10\ \text{mm}^3$, and require energy and power densities in the range of $0.1\text{-}100\ \text{J cm}^{-2}$ and $0.0001\text{-}10\ \text{mW cm}^{-2}\ \mu\text{m}^{-1}$ [103, 104]. As new applications for microbatteries become apparent, areal capacity and power density have been identified as limiting factors to full commercialisation, and 3D and 2D designs have been compared [104].

For instance, in Figure Figure 2.8 for a 2D design to match the same average diffusion distance and volumetric capacity of the 3D design in Figure 2.8a, the areal footprint of the 2D design would have to be 330% greater [104]. Additionally, the thickness of the 3D structure (L) could be readily increased to improve areal capacity while maintaining constant diffusion distance between electrodes (Figure 2.8). The limiting factor for power upon increasing L was ohmic losses, determined by the electronic pathway to the current collector and the ionic conductivities of the electrodes and electrolyte (i.e only a small

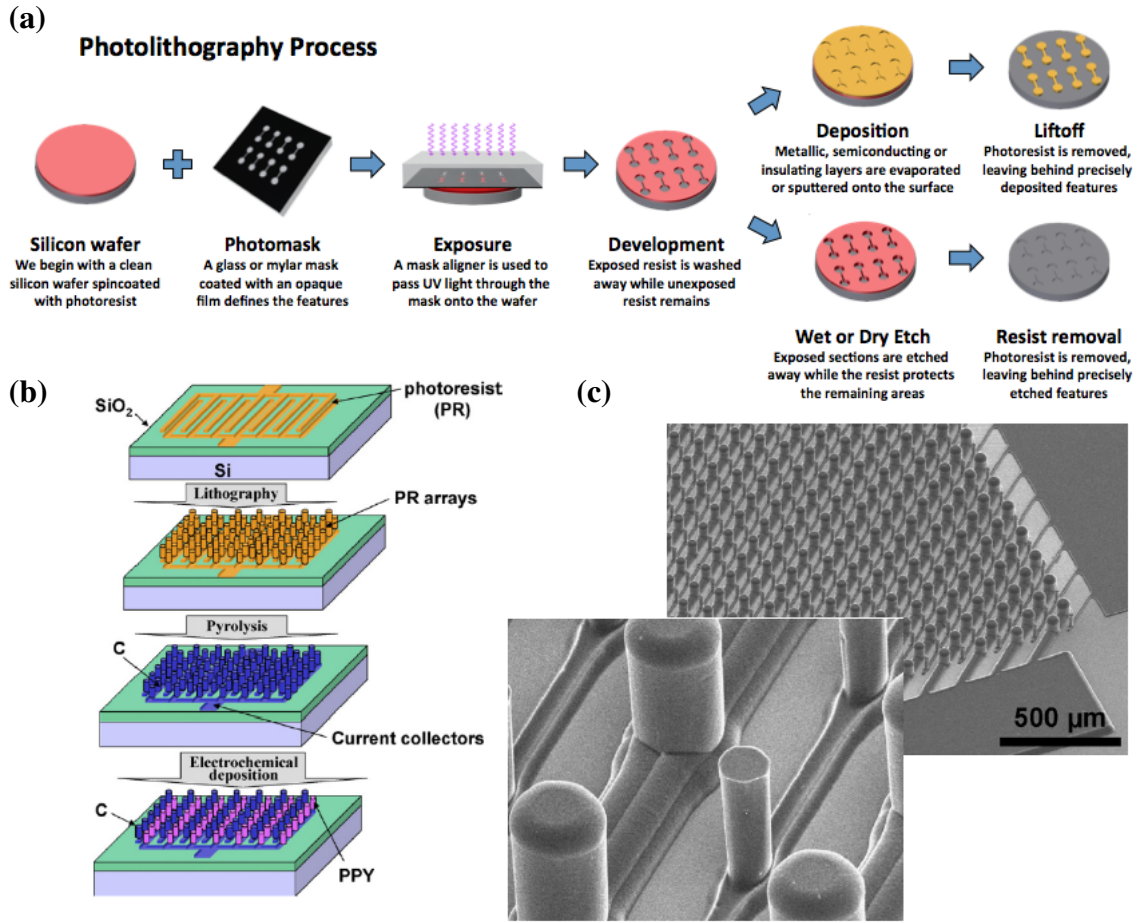


Figure 2.9: Photolithography as a process for structuring electrodes. (a) The photolithographic process with an etching or deposition end step [107], (b) Creating carbon pillar arrays using lithography and pyrolysis and (c) SEM micrographs of carbon pillar arrays with tailored pillar dimensions [108].

proportion of ions will diffuse distance L). These insights were later further supported by simulations [106].

2.3.2 Templating

Lithographic and etching techniques have been used to create 3D structured current collectors and porosity templates for thin and conventional electrode scales (Figure 2.9). Although lithography provides very high spatial definition, it is over-specified for pore formation/templating and too expensive for commercial scaling.

For example, there are many examples of pillared structures generated by photolithography [108–113]. A full 3D battery was produced with pyrolyzed photo-resist derived carbon rods. Calculations of areal capacities based on pillar dimensions, mass loading, theoretical capacity and cathode and anode pitch were used to optimise the structures [114]. Even with a relatively large pillar diameter (50-100 μm), rate performance was shown to be better than comparable 2D batteries.

Nanosphere lithography and inductively coupled plasma etching have also been explored, for example, to create a Si bottle-shaped nanorod array on a Si substrate [115]. Radio frequency (RF) sputtering of SnO_2 was then used to form core-shell Si/ SnO_2 arrays. A capacity of $0.25 \text{ mA h cm}^{-2}$ was achieved at a high current density of $500 \mu\text{A cm}^{-2}$; favourable when compared with commercial 2D microbatteries which provided only $0.08 \text{ mA h cm}^{-2}$.

Alternative routes to generating nanorod templates include electrodeposition. Patterned anodic alumina (AAO) or polycarbonate membranes are used as a template to control rod spacing. The template is dissolved after deposition to obtain free-standing structures [116]. The rod height is simply controlled by deposition time. The result is a highly ordered and controllable structure that can be used as a substrate for active material deposition (Figure 2.10a and b). Electrodes formed using this technique have been suggested to achieve high rate performance at a lower cost than those manufactured using photo-lithography.

Taberna et al. formed Cu nanorods and coated them in Fe_3O_4 , providing a low-cost electrode [117]. Very high rate capability at 8 C of >80% capacity was displayed compared to 25% capacity retention of a similar planar electrode. The planar electrode had a mass loading 5 times lower than the highest performing 3D electrode. Porous anodic alumina (PAA) templates and co-electrodeposition were also used to generate Ni-Sn nanowire arrays, as shown in Figure 2.10c-e [118]. Straight wire arrays showed agglomeration upon increasing the wire length, which caused a degradation of cycle stability and rate performance. A solution was proposed: PAA templates were synthesised using low

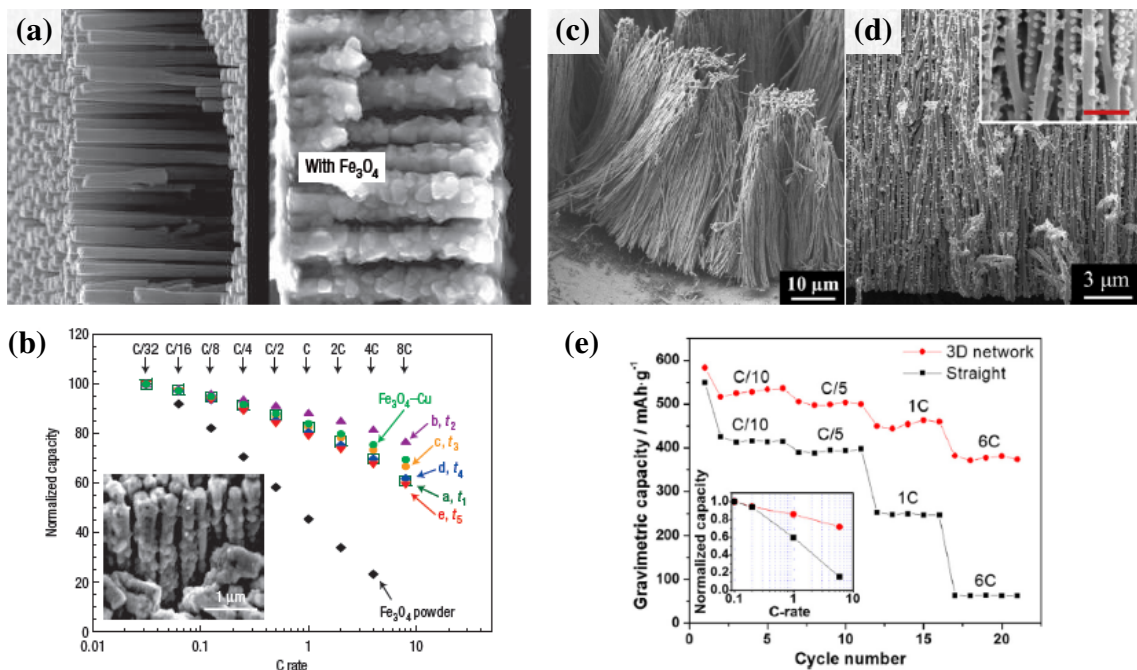


Figure 2.10: Nanorod/wire arrays. (a) A nanostructured Cu current collector formed by electrodeposition (left) with subsequent deposition of Fe_3O_4 (right), and (b) rate performance of nanostructured electrodes with increasing mass loading from 'a, t_1 ' to 'e, t_5 ' compared to that of a planar electrode (Fe_3O_4 powder) [117]. (c) Agglomeration of Ni-Sn wire arrays at a length of 40 μm , (d) modified wire arrays with bridging material generated from defective templates and (e) a comparison of the rate performance [118].

cost Al. The resulting structure consisted of wires joined by bridges, creating structural rigidity while leaving space for volume expansion and electrolyte infiltration. The modified wire array achieved 72% capacity retention between 0.5 C and 6 C and much improved performance compared with straight wire arrays (15% retention).

These two examples benefited in two ways from a 3D current collector: (1) greater surface area and (2) shorter electronic pathways to the current collector. This may address the increase in ohmic losses as electrodes become thicker, as discussed in Section 2.3.1. However, 3D current collectors increase the inactive material fraction in the cell and complicate manufacture, therefore the benefit to the rate performance and areal capacity must be weighed against the loss of volumetric capacity, potential extra weight and loss of productivity. Essentially, patterned current collectors are likely to find use when pulse power/rate capability cannot be compromised, and low areal footprint is required (therefore

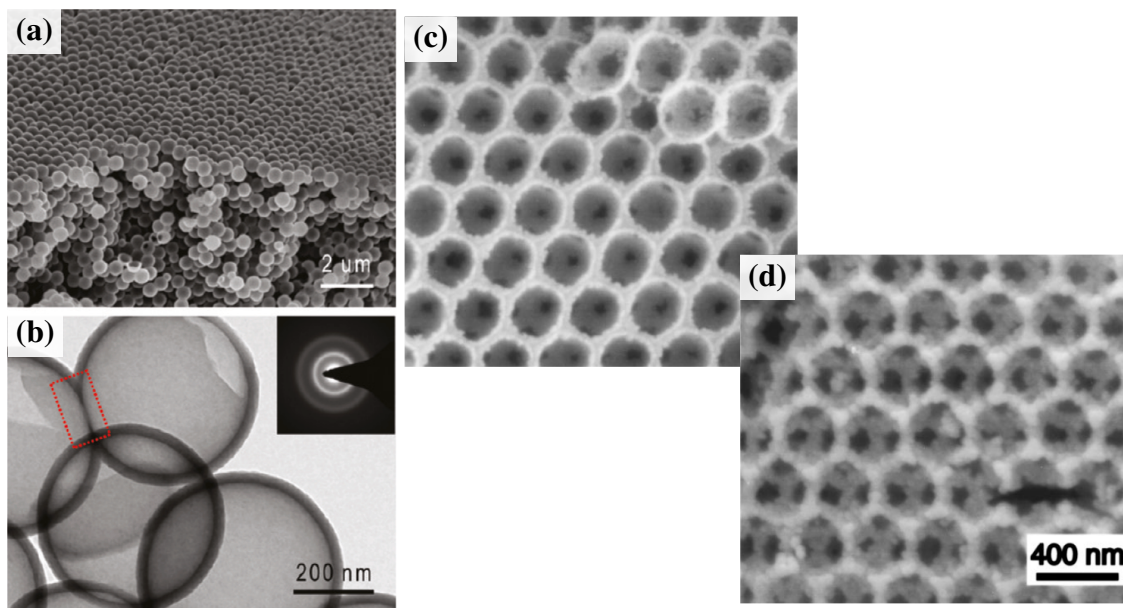


Figure 2.11: Structures generated by colloidal self-assembly lithography. (a) Si hollow nanospheres [120] and (b) SnO₂ calcined at 500 °C (left) and 800 °C (right) [121].

greater thickness, L , is needed).

Nanosphere templating has become popular for its ability generate 3D ordered macroporous (3DOM) or mesoporous monolithic materials (aka. inverse opal). One such technique is colloidal self-assembly lithography or colloidal crystal templating. The process involves producing a 3D periodic array of polystyrene, poly(methylmethacrylate) or silica spheres. The structure is infiltrated with the electrode precursor, and calcination at 350 °C or etching with HF removes polymer and silica spheres, respectively. Additionally, pyrolysis can convert polymer templates and organic precursors into a carbon coating. The resulting structure is bicontinuous with good control over active material and void phase structure (Figure 2.11a-b) [119].

A hollow sphere 3DOM structure of Si retained 57% of its 0.2 C capacity at 10 C [120]. The capacity decreased 8% per 100 cycles, which was relatively good for an Si-based electrode without a carbon additive or coating. Electrodeposition of Ni onto polystyrene spheres was used to form a 3DOM current collector, on which LiMnO₂ was deposited, and the resulting cathode reached rates of 400 C [122]. Additional structures and similar

techniques have been used to form anodes [121, 123–125], cathodes [121, 126, 127] and separators [128]. For more information on similar techniques, one can refer to an in-depth review of templating for structuring porous materials by Vu et al. [129].

2.3.2.1 Particle structuring

Although it is not within the scope of this review, it should be mentioned that techniques used for particle structuring are another avenue to enable high performance electrodes. Particularly, etching is a processing technique under the umbrella of templating/lithography that can be used to create 3D structures. The structures are achieved by the combined use of sacrificial templates (polystyrene, alumina, metals etc.) and etching processes, which remove the templates and/or etch material around them anisotropically. Common etching processes include deep reactive ion etching (DRIE), electrochemical etching, photo-assisted anodic etching and metal-assisted chemical etching [130]. Etching is controllable to some extent and can produce electrodes with well organised or random nanoarchitecture [131].

Aside from monolithic/array structuring, an application of the technique is the ability to create microparticles with meso/nano-porosity. These structures not only provide greater surface area for charge transfer and reduce diffusion distance within active materials but can effectively reduce the large volume expansion of materials like Si by internalising it, limiting SEI delamination and material pulverisation and thereby improving rate performance and cycle life (Figure 2.12) [133–135]. These structured particles may enable electrodes with a greater proportion of Si to be manufactured with standard deposition techniques (i.e slurry coating). A relatively complete summary of progress in group IV anodes has been provided by Tian et al. [136] and several interesting examples of particle structuring have been published or commercialised [24, 133, 137–142].

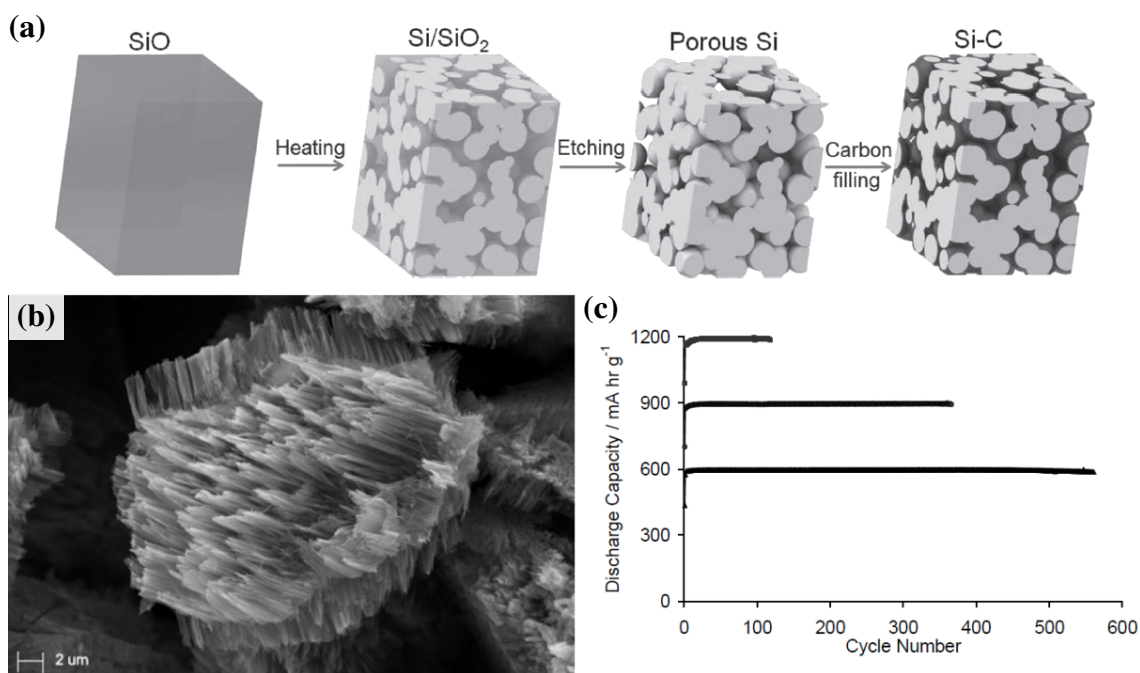


Figure 2.12: Examples of structures generated by etching: (a) porosity introduced into Si by etching an SiO precursor [132] (b) commercial pillared particles of silicon produced by Nexeon. (c) Cycle life of composite anodes using Nexeon pillared Si particles [133].

2.3.2.2 Ice templating

Ice templating (also known as freeze casting) is a technique that has mainly received attention with regard to biomaterial and biomedical applications [143]. Structures with directional and continuous porosity can be templated using this relatively simple technique (Figure 2.13a) and it has now been investigated for the manufacture of ultra-thick electrodes with low-tortuosity pathways for Li⁺ diffusion through the electrode thickness (Figure 2.13b). Biotemplating with wood has also been performed to create similar low tortuosity structures for electrode materials such as TiO₂, NiO and Mn₂O₃ [144–146] and carbon [147]. However, reports of detailed electrochemical characterisation are rare. This section briefly describes structuring enabled by ice templating and reflects on the possible relevance to high energy electrodes.

To create an ice templated structure, an aqueous based stable suspension is directionally frozen and then sublimated (Figure 2.13). In some circumstances, the resulting "green",

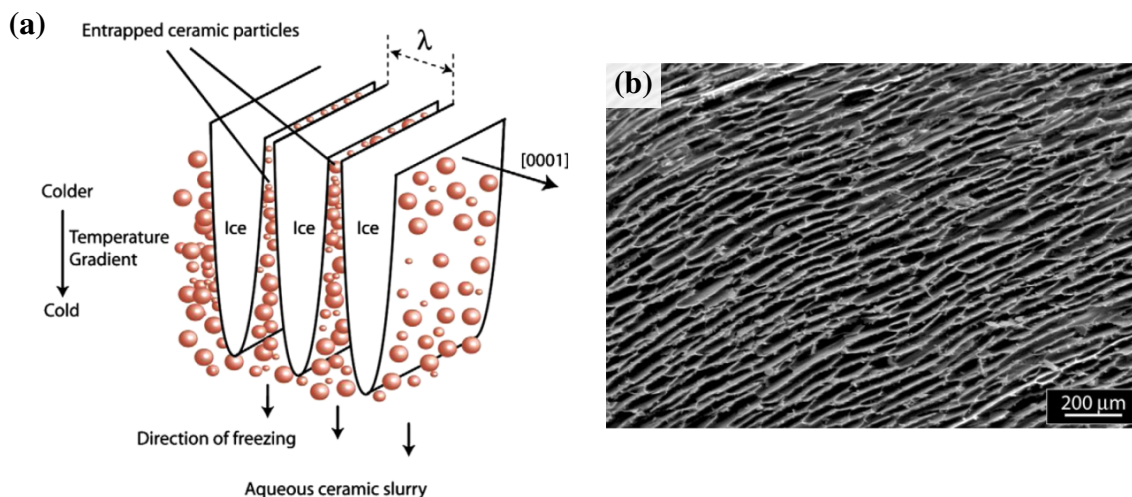


Figure 2.13: (a) A schematic of the ice templating process and (b) a typical ice templated microstructure [155].

powder based structure is sintered or heat treated to consolidate the material. Three ingredients are required: powders, water (or other freezable liquid) and processing additives (i.e. powder dispersant, binder, defoaming agent, freezing additives). A wide range of suspensions have been used to create ice templated structures, including those containing polymers, ceramics, metals or composites. Organic/inorganic systems, similar to those required for electrodes, have been studied for biomedical applications [148–154].

Extended pore channels can be a few to hundreds of microns in diameter and are commonly controlled by the freezing rate (a high rate reduces pore diameter), liquid-type and liquid fraction [155, 156]. When used as an electrode, the channels allow through-thickness electrolyte infiltration, effectively acting as fast ion diffusion pathways. Total porosity may be controlled by solid loading, particle size, particle morphology and additives. Additionally, although not always intentionally, a through thickness porosity gradient is observed in the frozen material (Figure 2.14), which could be beneficial for attempting to balance high rate and volumetric capacity (see Section 2.3.3.3) [155, 157–160]. The onset of this gradient can be controlled via an electric field [161].

A minimum of 40 % porosity is suggested to maintain a continuous pore structure, which is much higher than the percolation threshold which typically lies in the 12-18 % range for

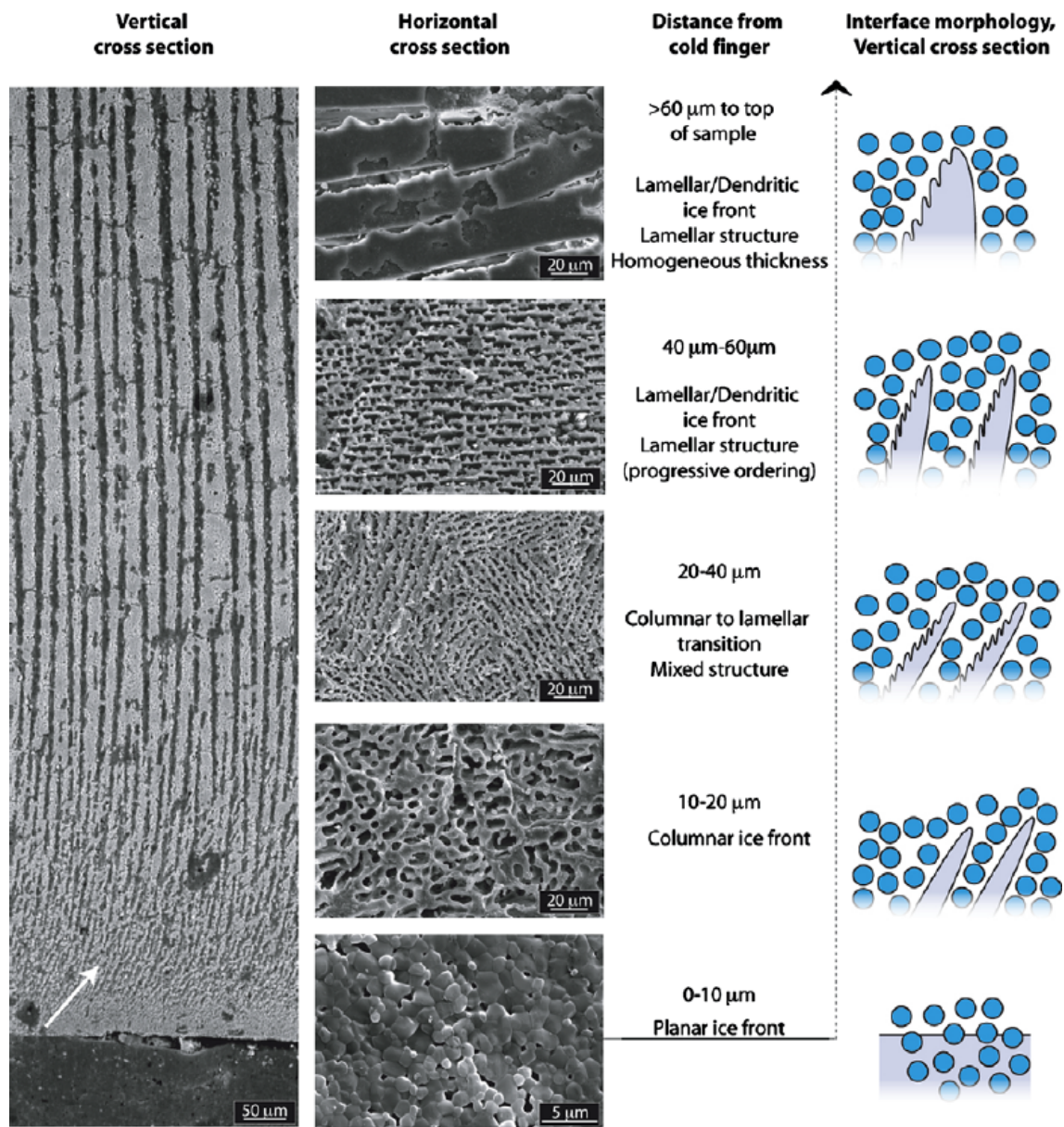


Figure 2.14: The hierarchical porosity and structuring which can be generated through ice templating [155].

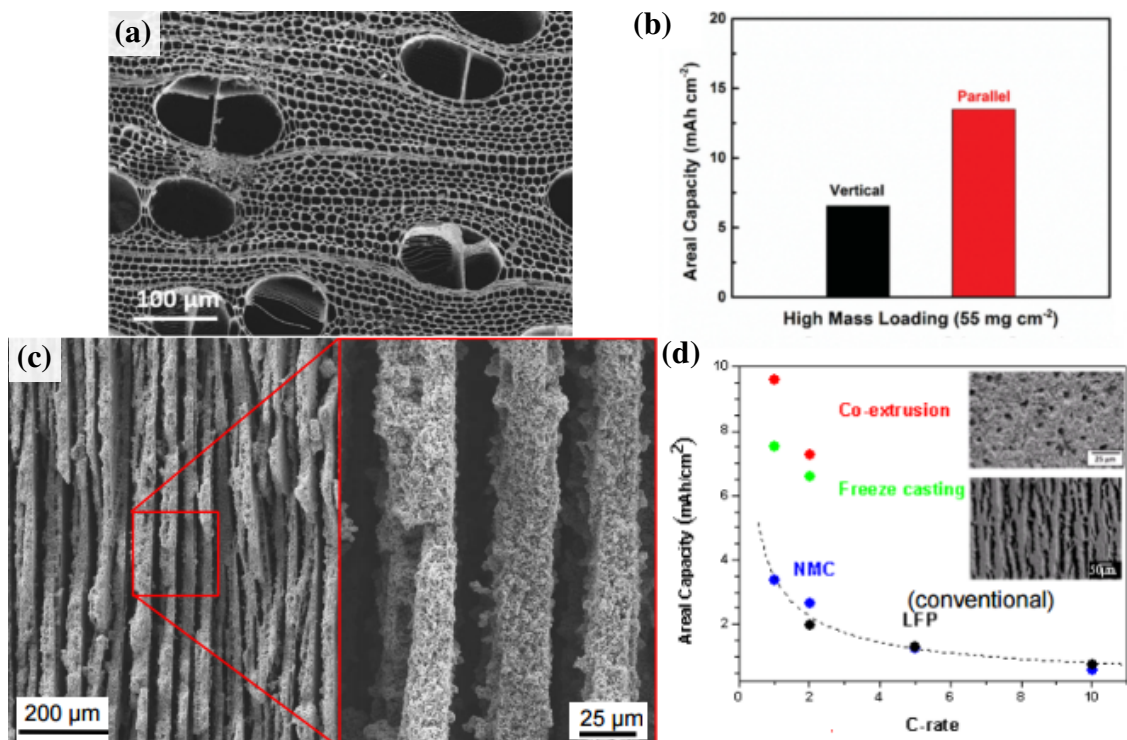


Figure 2.15: Low tortuosity porous structures. (a) Carbonised wood showing aligned porosity and thin walls of active material, and (b) the areal energy density with respect to the alignment of the pores and the ion diffusion pathway [147]. (c) Ice templated structure of $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{Fe}_{0.08}\text{O}_4$ and (d) areal energy density of high density low tortuosity electrodes fabricated by co-extrusion and freeze-casting techniques [163, 164]

randomly sized spheres [143]. Surface roughness within the channels can be generated from the dendritic morphology of freezing solvent crystals, possibly improving lateral diffusion of ions. Alternatively, sub-micron porosity can be obtained by altering certain sintering conditions, which might be useful for electrolyte infiltration and volume expansion accommodation [151]. If a sintering or heat treatment step were employed, organic additives could be included to decompose to carbon, potentially acting as a conductive coating method. Additional control can be provided by using substrate patterning for ordered structures and sequential freezing for graded porosity [156, 162].

Zheng et al. investigated increasing the areal energy density of conventional electrodes and the relationship with the rate capability [165]. Electrodes of NMC and LFP were fabricated at various thicknesses between 10 and 100 µm and electrochemically tested.

A power-law relationship between the electrode thickness (i.e. areal capacity) and the maximum working C-rate was established. This was attributed to Li-ion diffusion within the electrode influenced by internal resistance. Essentially, the energy density was increased at the expense of power density, and a thickness of 100 μm was the upper limit for commercially viable performance (2C rate).

In response, evidence of the efficacy of an anisotropic, low-tortuosity structure was also presented [163]. Modelling revealed that the optimised structure with regards to maintaining C-rate performance had 50% overall porosity and through-thickness pore channels. At a rate of 2 C, a 220 μm thick co-extruded structure with 6 μm diameter channels achieved an areal capacity almost 3 times that of the optimised conventional cathodes at a thickness of 100 μm (7.2 mAh cm^{-2} vs 2.7 mAh cm^{-2} , Figure 2.15d). Although effective, co-extrusion is not scalable, so work on ice templated monoliths was performed and attained similar areal energy density in initial experiments (Figures 2.15c and d) [164].

Similar work has been performed by Shen et al. by bio-templating from wood for sodium-ion electrodes [147]. Carbon electrodes with a thickness of 850 μm and a high mass loading of 55 mg cm^{-2} were prepared with a carbonisation process of wood at 1000 $^{\circ}\text{C}$ for 2 hours (Figure 2.15a). Half-cells with pore channels perpendicular and parallel to the principal Na-ion diffusion direction were compared, with electrodes showing areal capacities of 13.5 mAh cm^{-2} and 6.5 mAh cm^{-2} respectively (Figure 2.15b). Huang et al. compared ice templated and conventional slurry cast LFP cathodes with a mass loadings of $\sim 85 \text{ mg cm}^{-1}$ and $\sim 7 \text{ mg cm}^{-1}$, and thicknesses of 900 μm and 55 μm , respectively [166]. The specific energy between 5 mA cm^{-2} and 15 mA cm^{-2} was 408–276 Wh kg^{-1} and 245–117 Wh kg^{-1} for the ice templated and conventional electrodes, respectively, showing how the directional porosity provided a substantial advantage in terms of kinetics at high thickness. These works suggest some attractive potential for ice templating if it can be realised for larger areas.

Table 2.3: Examples of thin-film deposition rates [171, 172].

Technique	Material	Rate
DC reactive sputtering	TiO _y S _z	3 nm min ⁻¹
Radio-frequency (rf) reactive sputtering	LiPONB	5 nm min ⁻¹
Thermal Evaporation	Metallic Li	150 nm min ⁻¹
Electrodeposition	nc-Ni	3 μ m min ⁻¹

2.3.3 Deposition techniques

2.3.3.1 Thin-film

Thin-film electrodes are defined as <10 μ m thick, to separate them from conventional slurry cast electrodes. Established thin-film techniques include sputtering, pulsed laser deposition (PLD), chemical vapour deposition (CVD), sol gel methods and electrodeposition [108, 112, 113, 135, 167–170]. Thin-film deposition techniques are often combined with etching and templating to produce high performance structured electrodes. However, the main obstacle for these techniques, in a commercial sense, is slow deposition rate, associated cost and scalability (Table 2.3). A review by Ferrari et al. gives an extensive overview of progress towards 3D microbatteries encompassing these deposition techniques [103].

2.3.3.2 Direct writing

Direct-writing techniques are promoted as cost-effective, simple and scalable [44, 173]. They include direct deposition, laser direct writing (LDW), ink-jet printing and flexographic printing. There is no need for separate photolithographic processing steps and the processes generally have the ability to produce multi- μ m electrodes by layering. For instance, the LDW technique uses pulsed UV laser irradiation to transfer ink onto a substrate via computer control, without affecting its physical or chemical properties [174]. Volumes as small as 10 pL can be transferred giving advantages over conventional thin-film techniques,

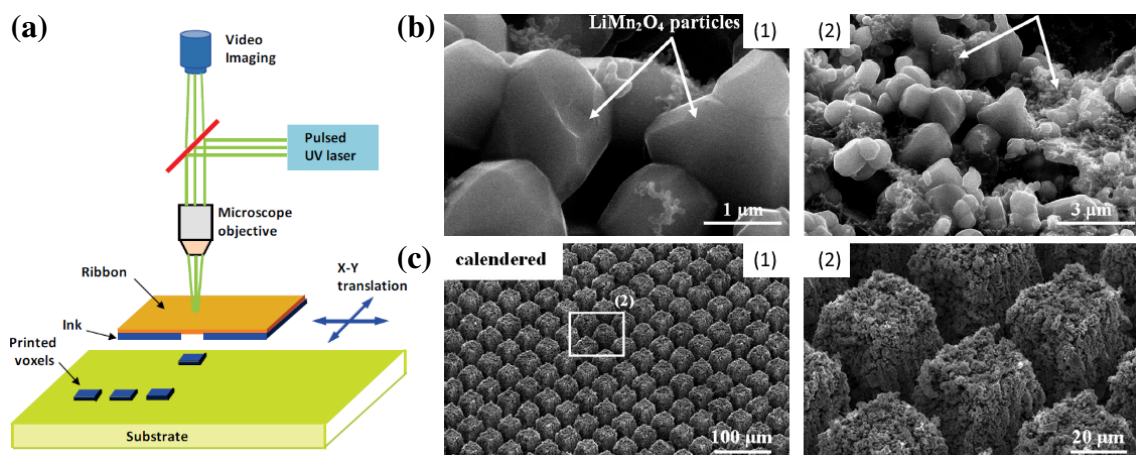


Figure 2.16: (a) Deposition of ink using a laser direct write (LDW) system [176], (b) the microstructure of LDW deposited LiMn_2O_4 with (1) active particle contact and (2) carbon/binder coating and (c) the structure of a calendered LiMn_2O_4 cathode deposited by LDW and patterned with fs-laser radiation [177]

which are limited by slow deposition times, diffusion limited rate performance obstacles (95 % and 70 % of maximum capacity at 1 and 4 μm respectively) and multiple processing steps [175]. Printed batteries cannot compete with the low cost and high throughput of slurry casting for conventional applications but there may be opportunity for low-cost processing of thin, flexible and eco-friendly electrodes. For example, successful application of solid state electrolyte inks may allow for the battery to be entirely printed, reducing both time and cost.

Non-patterned thick-film electrodes for microbatteries have been fabricated by Kim et al. using laser direct writing with attractive areal capacity and power when compared with 2D thin film sputter deposited analogues [176, 178]. Volumetric energy density was traded for improved areal capacity ($1600 \mu\text{Ah cm}^{-2}$ vs $160 \mu\text{Ah cm}^{-2}$) and high power (38 mW cm^{-2}) by creating a highly porous, thick electrode ($68 \mu\text{m}$ vs $2.5 \mu\text{m}$). Proll et al. deposited thick-film LMO using a laser-structuring process to create a grid-like structure (Figure 2.16b & c) [177]. A combination of calendering and structuring yielded the best rate performance (70% capacity at 1 C). An unstructured calendered electrode had slightly more capacity at 0.1 C, but poor rate performance. Essentially, in the structured electrode,

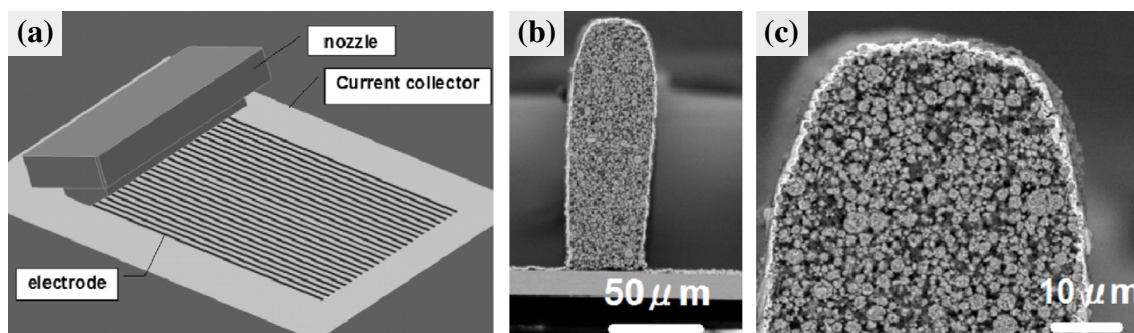


Figure 2.17: (a) Micropatterning apparatus for deposition of active material channels, and scanning electronic microscope (SEM) images of the cross section of a 3D LTO electrode at (b) x400 and (c) x1500 magnification [179].

the channels acted as low-tortuosity pores that were unaffected by calendaring.

Izumi et al. used a micro patterning apparatus consisting of direct deposition channels in parallel [179]. 3D LTO electrodes with the same capacity as conventional electrodes (1 mAh cm^{-2} and $70 \text{ }\mu\text{m}$ thick) had 2.5 times the surface area (Figure 2.17). The 3D patterned electrodes showed remarkable rate capability, with a capacity retention of 97 % and 90 % at 1 and 5 C, respectively, compared with only 38 % at 5 C for a conventional equivalent. The internal resistance of the 3D electrodes was suggested to be lower than that of the flat electrode.

One of the highest performing high aspect ratio interdigitated 3D microbatteries was produced using 3D filament printing [180]. 50 nm LTO (0 % volume expansion [181]) and 180 nm LFP (2.2 % volume expansion [182]) served as the anode and cathode materials, respectively, and were suspended in liquids suitable for filament printing. In order to facilitate printing, any particle agglomerates were removed by centrifuging to prevent clogging of the $30 \text{ }\mu\text{m}$ diameter filament nozzles. Inks with solid loadings comparable with slurries (60 %) were used [183, 184]. Rate performance was good (80% and 60% at 2 and 5 C, respectively) considering the distance between the relatively thick printed electrodes ($50 \text{ }\mu\text{m}$). This was likely due to the combination of the absence of a separator, which was enabled by the self-supporting interdigitated structure, and the application of high rate materials, as shown in Figure 2.18.

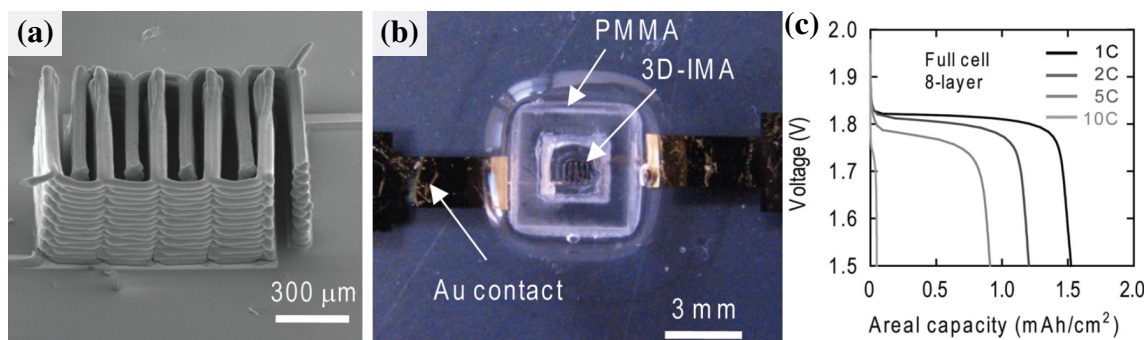


Figure 2.18: (a) Interdigitated LTO-LFP electrode printed via 3D filament printing, (b) packaged interdigitated cell and (c) rate performance of the full cell between 1-10 C [180].

One of the potential advantages of layer-by-layer techniques, is that the sequential deposition of the anode, electrolyte and cathode into a solid state battery might be achieved in a continuous production step. The main hurdle here is the reliable processing of the three suspensions into discrete (or mixed) layers of controlled and reliable thickness. In addition, to achieve the required ion mobilities in the electrolyte a sintering step is generally needed that requires high temperatures unsuitable for some active materials, additives (especially organic and carbon) and substrates. Alternatively to a ceramic electrolyte, if a polymer or a gel-polymer ion-conducting membrane/separator is to be printed, other challenges must be overcome, such as the balance between low viscosity for printing but poor mechanical rigidity once printed [185]. Surprisingly, despite the attractions of printed solid-state batteries (safety, appropriate thickness and area for printing techniques) examples of tackling this in Li-ion literature are few and far between.

Sutto et al. created a 3D microbattery by sequential printing of the cathode, a ceramic-solid polymer ionic liquid nanocomposite (c-SPIL) gel-polymer electrolyte and then an anode onto a 3 x 3 mm pocket on a polyimide/aluminium flexible substrate [186]. The gel-polymer electrolyte consisted of 60 wt.% 1.0 M Li/1-n-butyl-2, 3-dimethylimidazolium bis-trifluoromethanesulfonylimide (BMMITFSI) ionic liquid, 30 wt.% poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 10 wt.% TiO₂ nanopowder, yielding an ionic conductivity of 2.85 mS cm⁻¹ at 22 °C. Essentially the TiO₂ served to stiffen

the electrolyte, while allowing precise deposition via LDW. Each layer required thermal treatment in air at 75 °C for 10-15 minutes to remove dibasic ester solution (DBE). The areal capacity was similar to thin-film batteries with similar chemistries at low C-rates (110 $\mu\text{Ah cm}^{-2}$ at C/3 rate).

Delannoy et al. produced half-cells using inkjet printing of a ionogel precursor, which required a polycondensation step to form an electrolyte [187]. However, in the creation of a full-cell, high polarisation was observed and so a fibreglass separator was used instead. Difficulty in overcoming issues during fabrication may explain the relative lack of examples in literature, as the deposited separators need to be porous enough to allow ion transport once dried but also robust enough to avoid short circuits. Hence, UV curable gel-polymers present an interesting avenue to explore; they can have viscosity low enough for accurate and reliable printing, but may provide relatively good mechanical properties once cured, and high ionic conductivities ($10^{-3} \text{ S cm}^{-1}$) required for high rate performance [188, 189].

2.3.3.3 Spray deposition

Spray deposition is often included within the umbrella term of printing techniques due to similarities in pre-deposition material preparation. Suspensions (or inks) are prepared in similar ways to standard slurries or inks for printing. In pneumatic systems, the suspension is atomised into droplets at a spray nozzle by pressurised air or gas and propelled towards a heated substrate, as shown in Figure 2.19. The physics of the atomisation and deposition steps are complex and the suspension is also a complex mixture of different sized/shaped particles, organic binders, solvents and, in some cases, surfactants. The atomisation process is known to be affected by gas flow properties (pressure, viscosity, etc.), nozzle design and liquid properties such as surface tension, density and viscosity. The quality of the coating will depend on several factors, for example: nozzle-substrate distance, droplet diameter distribution and velocity, substrate temperature, substrate wetting angle and suspension solvent combination. Alternative processes will have similar or possibly more

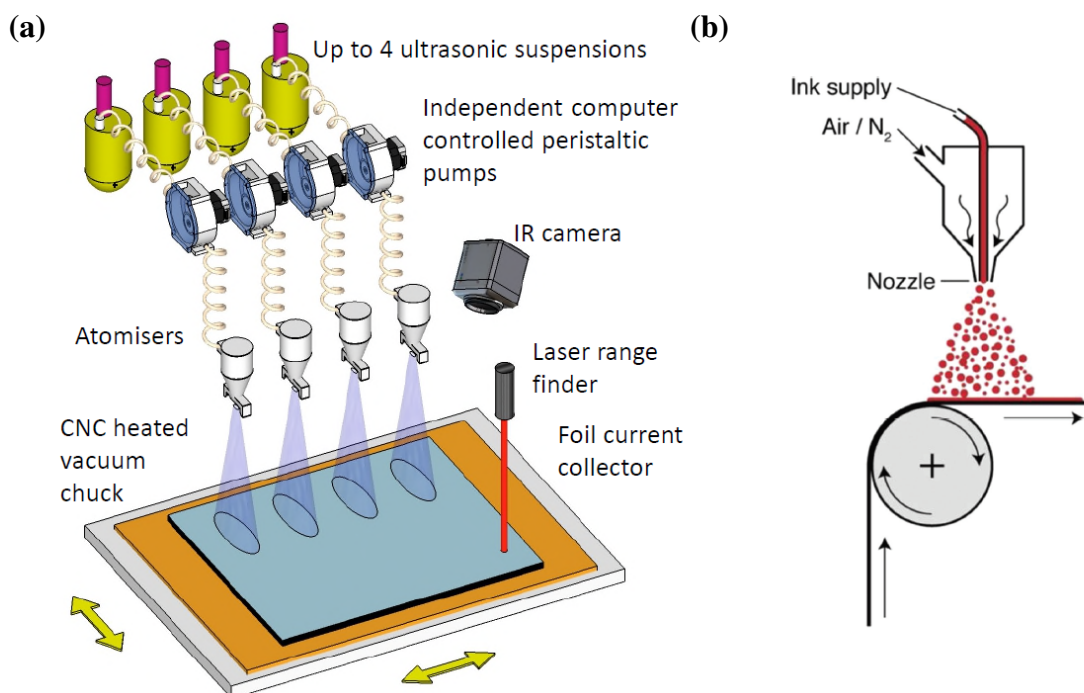


Figure 2.19: Spray deposition method at (a) the lab scale and (b) roll-to-roll for high throughput [45, 194].

complex considerations (ultrasonic nozzles and electrospray deposition (ESD)). Even so, high performance electrodes have been fabricated using spraying techniques for both supercapacitors and Li-ion batteries [190–193].

Koike and Tatsumi used ESD to deposit LCO films without binder or conductive additive, retaining maximum capacity at 1 C, with minimal fading after 90 cycles and 78 % of the capacity retained at 10 C [195]. Interestingly, the active material was synthesised by heat treatment after deposition of the fine-scale precursors, which can be speculated to have promoted intimate contact between particles.

Unlike printing, patterning during spray deposition is usually only possible with the use of masks, although for most configurations in-plane patterning is not as important as covering a large area cost-effectively. A unique advantage of spray deposition is the ability to coat conformally arbitrary shapes and surfaces, and being suitable for flexible coatings and environmentally friendly processing (e.g. aqueous suspensions). For conformal electrodes to be realised, each component of the battery needs to be sprayed. Singh et al. produced

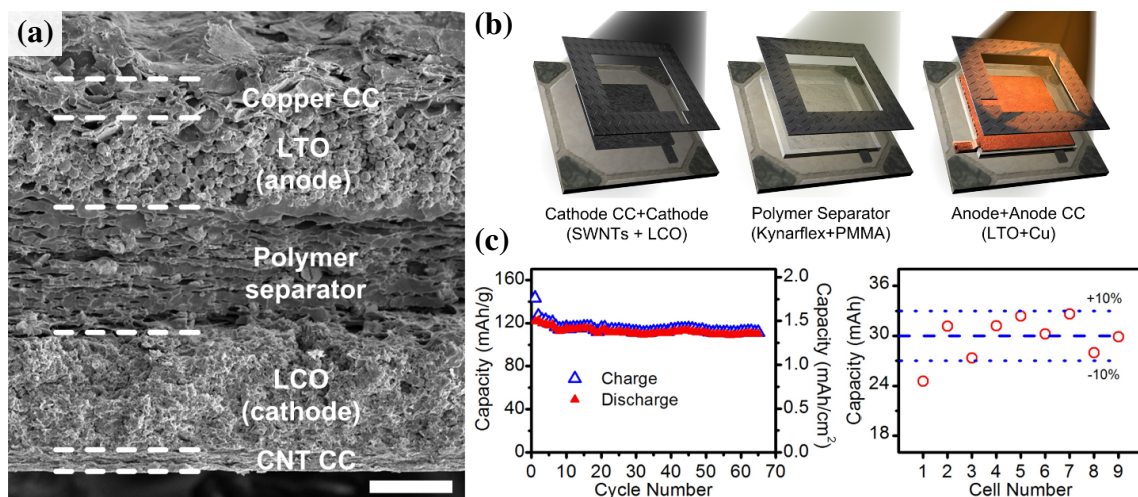


Figure 2.20: (a) A cross-section of a complete Li-ion cell fabricated using (b) sequential spray deposition of each component [196].

one of the first batteries fabricated using a single manufacturing technique, including current collectors, electrodes and separator [196]. Sequential spray deposition of carbon nanotubes (current collector, CC), LCO (cathode), Kynarflex-poly(methyl methacrylate) (separator), LTO (anode) and copper (CC) resulted in a cell with a discharge capacity of 120 mAh g^{-1} and a 90% capacity retention after 60 cycles at $C/8$ rate. The separator displayed high porosity and excessive electrolyte uptake, which was corrected with the addition of N,N-Dimethylformamide (DMF) to reduce microporosity and fumed SiO_2 to counteract the loss of ionic conductivity from the addition of DMF. The separator thickness was $200 \mu\text{m}$ to prevent internal shortage due to solvent penetration while depositing the top electrode. The relatively thick electrolyte restricted rate performance, although this system was obviously unoptimised and for proof-of-principle only. A spray painted cell was fabricated on the curved side of a ceramic mug using the same approach to display the flexibility of the process, termed a "painted battery".

In terms of microstructuring for improved performance, spray deposition has the potential advantage of being a layer-by-layer technique with each subsequent layer having some composition or property different to the prior layer. It is important that each sprayed electrode layer dries before the next arrives and that the temperature of the substrate on

which the current collector foil is placed is tailored for the rate of deposition (i.e. quantity of solvent) and the type of solvent being used (Figure 2.19a). Multiple spray heads or material inlets can be employed, creating a very flexible fabrication process, in which co-spraying of suspensions, graded electrodes or multilayer electrodes can be achieved.

Recently, Grant et al. have produced a number of examples of through-thickness and patterned structures using spray deposition [197–205]. Cheng et al. produced electrodes with through-thickness composition gradients of active material, carbon black and PVDF binder [200, 201], as shown in Figure 2.21b and c. The optimised electrodes showed improved C-rate performance and reduced capacity degradation during long term cycling compared with a uniform electrode with the same overall ratio of components. The improvement was suggested to be due to the reduction in interfacial resistance at the current collector due to the C-rich region, and a reduction and improved spatial homogenisation of overpotential [201]. When graded LFP and LTO electrodes were combined into a full cell, C-rate performance improved by 126 % at 1 C compared to cells consisting of uniform electrodes, showing that the individual improvements observed in half cells contributed in combination to full cell performance [200].

Similar improvements have also been obtained for spray deposited supercapacitor electrodes involving thinner, discrete interfacial layers at the current collector (200 nm graphene layer to promote electron transfer in and out of the electrode) and at the separator membrane (650 nm meso-porous TiO₂ layer to promote ion transfer in and out of the electrode) [191, 194, 206, 207].

2.4 Conclusions

This review has shown that while electrochemical energy storage improvements have traditionally been accomplished by the electrochemist, structuring of materials and electrodes can also play an important role in reaching higher performance. In particular, the

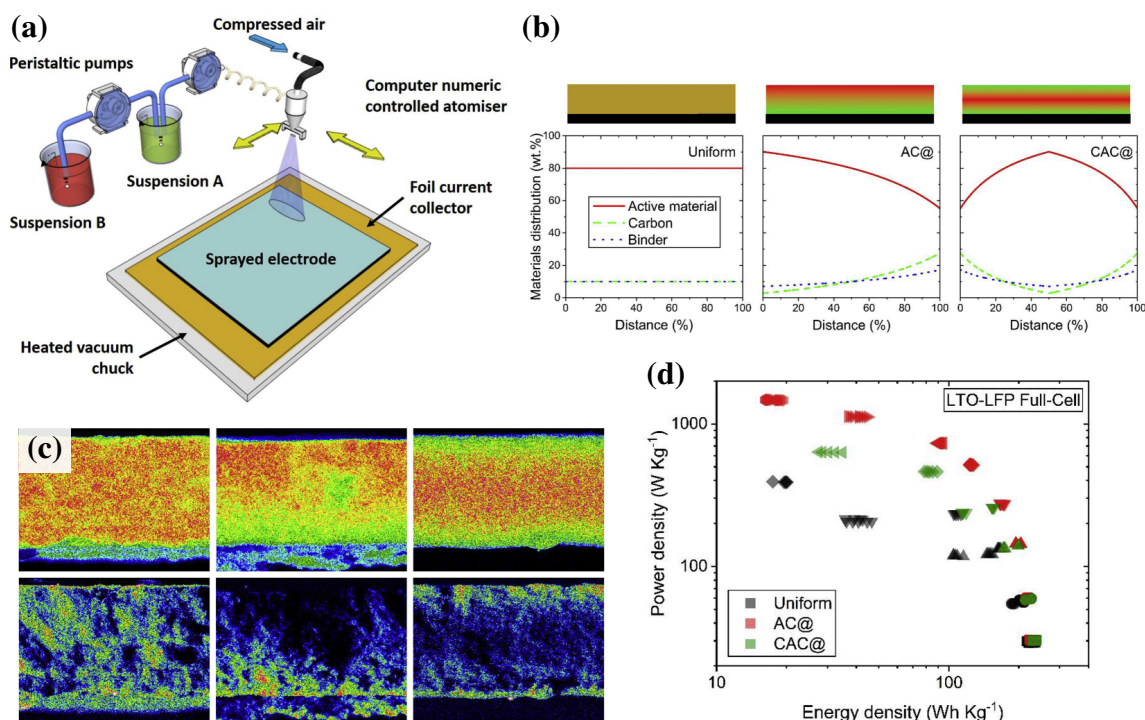


Figure 2.21: Composition graded LTO and LFP electrodes and full cells: (a) spray deposition of graded electrodes by pumping two suspensions in series, (b) target distribution of materials in uniform and graded electrodes, (c) EDX maps of Ti (top row) and C (bottom row) corresponding to the target composition distributions in (b) and, (d) a ragone plot of uniform and graded LTO-LFP full cells. [200].

performance of batteries is a complex mixture of electrochemistry, microstructure and ion kinetics. Conventional approaches to optimisation have steadily improved battery performance but have reached a point where there are diminishing returns and unavoidable compromises. Electrode structuring can achieve (i) improved Li^+ ion macro-diffusion pathways through lowered pore tortuosity within electrodes, (ii) improved Li^+ ion electrolyte/electrode interfacial diffusion through increasing active material surface area, and (iii) increased active material utilisation within a short period of charge/discharge time through reducing Li^+ ion micro-diffusion distances within the active material particles.

The electrode structuring techniques detailed in this review have not only shown how ion kinetics can be improved, they also point to the ability to manufacture new and unique form factors and have the potential to enable high performance battery materials by accommodating volume expansion (Table 2.4). If scalable and cost-effective manufacturing

techniques for structured electrodes can be realised, it is not far-fetched to believe that structured electrodes and materials will enlarge the design and application space of batteries considerably.

Table 2.4: A table to compare advantages and disadvantages estimated future directions and realistic application spaces of manufacturing techniques used for structuring electrodes [208, 209].

Negative (Structuring)		Advantages	Disadvantages	Directions	Applications
Photolithography (i-line, DUV, EUV)		Easy integration with electronics	High cost (1M - 100M, \$)	Combination with novel techniques	MEMS
		High resolution (10^5 - 10^1 nm)	Requires masks		
		Mid to high throughput (10^{-4} - $>10^{-1}$ m ² h ⁻¹)	Low throughput deposition techniques		
Etching		Can generate intra-particle porosity	Waste (Template removal)	Group IV materials	High energy & rate batteries
		High resolution (40 nm wall thickness)	Hazardous chemicals		
		Unique structures (3DOM, mesopores)			
Negative-Positive					
Direct Laser Writing	Maskless 3D Patterning		Low throughput (10^{-10} - 10^{-6} m ² h ⁻¹)	R&D	Prototyping
	All-in-one technique				
	Mid resolution (10^3 - 10^2 nm)				
	Low cost negative technique (200K to <1M, \$)				
Positive (Additive)					
Printing		Environmentally friendly (Water-based)		Flexible, low cost electronics	2D/3D microbatteries
		Layer-by-layer process - thin film			Wearable/disposable electronics
Ink-jet printing		Very low cost (1K - 20K, \$)	Low resolution (10^4 - 10^5 nm)		Low cost prototyping
		High throughput (10^{-2} - 10^{-1} m ² h ⁻¹)			

Positive (Additive)	Advantages	Disadvantages	Directions	Applications
<i>EHD jet printing</i>	Low to mid cost (100K+, \$) High resolution ($>10^1 - 10^3$ nm)	Low to mid throughput ($10^{-8} - 10^{-4}$ m ² h ⁻¹)		Prototyping
<i>Flexographic printing</i>	High cost High throughput ($10^0 - >10^2$ m ⁻¹ h ⁻¹)	Low resolution ($10^4 - 10^5$ nm) Maximum thickness (20 μ m) [210]		Large scale processing
Chemical Vapour Deposition	High cost Ultra-thin film	Very low deposition rate (1 - 10s nm min ⁻¹)	Mechanism studies Thin-film microbatteries	MEMS
Spray Coating	Relatively high throughput ($10^0 - >10^1$ m ² h ⁻¹) Conformal coatings Layer-by-layer process - thin film Environmentally friendly (Water-based)	Usually requires masks for patterning Poor edge definition Waste (material blowback & mask)	Arbitrary substrates Layered & graded electrodes Conformal electrodes	Wearable/conformal electronics High power Prototyping
Slurry Coating	High throughput Well studied Reproducible	No structuring Minimum thickness (10 μ m) Maximum thickness (200 μ m)	New materials Structured particles	Portable electronics Transport Grid
Ice Templating	Scalability and control of unique structures Low tortuosity High through-thickness anisotropy Hierarchical porosity	Multi-step processing	Ultra-thick electrodes	Grid

Chapter 3

Experimental techniques

This chapter outlines techniques used in the fabrication and characterisation of the various electrodes and separators. Subsequent chapters elaborate on specific materials and techniques used therein.

3.1 Electrode and solid-state cell fabrication

3.1.1 Materials

Active materials used were LiFePO_4 (LFP; d_{50} 3.5 μm , MTI Corp.), LiFePO_4 (LFP; ~ 100 nm primary particle size, Hydro-Quebec) and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO; < 200 nm, Sigma Aldrich). Carbon black (CB; C-ENERGY Super C65, Timcal Ltd.) was used as conductive additive. Binders included sodium carboxymethyl cellulose salt (CMC; M_w 250,000, degree of substitution 1.2, Sigma-Aldrich), a commercial water-based aqueous binder (WSB; Polyolefin grafted acrylic acid copolymer, MTI Corp.), Polyvinylidene fluoride (PVDF; $M_w \sim 543,000$, Sigma-Aldrich), polyacrylic acid (PAA, M_v 1,250,000, Sigma Aldrich) and styrene butadiene rubber (SBR; MTI Corp.). Deionised water (DI water), 2-Propanol (IPA; anhydrous, 99.5%, Sigma-Aldrich) and 1-Methyl-2-pyrrolidinone (NMP; $\geq 99.0\%$, Sigma Aldrich) or mixtures thereof were employed as solvents. Oxide powders used for spray deposited separators included Al_2O_3 in sizes of < 50 nm (AP50; Sigma Aldrich) and 250–450 nm (AP300; Alfa Aesar), and Y_2O_3 powder (Y_2O_3 ; 99.99% purity,

PI-KEM UK).

3.1.2 Suspension preparation

Suspensions for fabrication of electrodes consisting of active material, binder and conductive additives were created using two main processing routes: dilution of a relatively viscous slurry, i.e. 30-45 wt.% solid, to lower viscosity and lower mass loading, ≤ 1 wt.%. For each, the mass of powder components and solvents were measured using an analytical balance (Nimbus, readability ~ 0.0001 g, Adam Equipment) and a standard balance (Navigator Balance, readability 0.1 g, OHAUS) respectively. Dilute electrode mixtures were dispersed using an ultrasonic processor at 70 % amplitude (Vibracell VCX 750, 750 watt, 20 kHz, Sonics & Materials). Alternatively, more viscous electrode slurries with higher solid to liquid ratio were dispersed using a ball mill (Fritsch Pulverisette 6) or pestle & mortar as specified. Dilute suspensions could then also be formed from slurries by dilution with, additional solvent added while stirred by magnetic stirrer (RCT Basic, IKA). Dispersed suspensions were agitated by magnetic stirring until use.

3.1.3 Spray deposition

Unlike slurry coating of electrodes, which is fully industrialised, spray deposition is a much more immature process operated within the group for a number of years, and gradually explored by others. The spray deposition configuration consists of (a) a magnetic stirring plate, (b) a pumping system (Watson Marlow CM300 peristaltic pump or a simply by venturi suction), (c) a commercial pneumatic atomising nozzle attached to a commercial X-Y stage and (d) a heated vacuum plate. A bottle containing the suspension and a magnetic stir bar of 25 mm diameter was placed onto a magnetic stirring plate and stirred at 200 rpm. The substrate, typically a standard Li ion battery current collector Al (16 μm) or Cu (10 μm) foil, was placed onto the vacuum plate, secured by high temperature tape

(Kapton) and heated to a temperature determined by the solvent evaporation temperature and pump flow rate. Alternatively, the foil substrates were sometimes replaced by thick, inflexible stainless steel spacer discs ($\sim 500\ \mu\text{m}$, 15.5 mm diameter, MTI Corp.) which were then coated. The suspension was pumped through nylon tubing and atomised with compressed air into a myriad of droplets that were propelled from the nozzle towards the substrate. Upon deposition, the solvent component of the suspension evaporated and the suspended materials adhered to the substrate and become integrated into the progressively forming electrode. The nozzle was rastered by the X-Y stage at constant Z at a speed of $40\ \text{mm s}^{-1}$, with a resolution of 2 mm and covering an X-Y area typically between $1600\text{--}10\,000\ \text{mm}^2$. The final thickness of the spray deposited electrode for a specific suspension was determined by the experiment duration and the concentration of solid in the suspension. After deposition, the substrate was removed from the heated plate and placed into an oven to dry overnight at $60\ ^\circ\text{C}$. This initial drying was then followed by vacuum drying.

3.1.4 Slurry deposition

Slurry deposition was performed using a doctor blade coater (MTI). Current collector foils were placed onto the doctor blade coating platter after it was brushed with ethanol, and any air bubbles under the foil were removed using a lens cleaning tissue. A controlled volume of slurry was then dispensed onto one end of the foil and the blade was translated over the slurry using a motor drive at a pre-determined speed ($\sim 10\ \text{mm s}^{-1}$). Cast slurries were then dried at room temperature overnight and then placed in an oven at $60\ ^\circ\text{C}$. Initial drying was then again followed by vacuum drying.

3.2 Physical characterisation of slurries and suspensions

Slurry viscosity was measured by taking ~0.5 ml of slurry and placing it in a cone & plate viscometer (Brookfield DV2T, AMETEK), which was operated between the shear rates of 1–400 Pa s. Particle diameter distributions and zeta-potentials of active, conductive and oxide materials in aqueous-based suspensions were measured using a laser diffraction particle size analyzer (Mastersizer 2000, Malvern Instruments) and dynamic and electrophoretic light scattering (Nano ZS, Zetasizer), respectively. For particle diameter measurement, suspensions were added to 800 ml of solvent drop-wise until a 7.5 wt.% obscuration was reached, then 7 distributions were measured over 30 minutes, and the data averaged. Suspensions for zeta potential were diluted using an aqueous solution of NaCl for a final concentration of oxide particles and NaCl of 0.1 g/dL and 10 mM.

3.3 Physical characterisation of electrodes

Discs of 12 mm diameter were punched from dried electrodes on foil substrates using a disc cutter (Precision Disc Cutter, Gelon). Electrode coatings on spacers were left as-sprayed. The total mass of the electrode disc and substrate was measured using an analytical balance with a readability of 0.1 mg (Entris, Sartorius). Electrode thickness was measured using a micrometer with an accuracy of $\pm 1 \mu\text{m}$ and a resolution of $1 \mu\text{m}$ (293 Series, Mitutoyo). The mass and thickness of foil substrates was established from an average of 10 measurements from the as-supplied foils. Mass and thickness of spacer substrates were measured on a per sample basis due to greater variation between individual spacers than punched foils. Mass and thickness of electrode films were calculated by subtracting the substrate from the combined measured values. Surface roughness measurements were performed using a stylus profiler (DekTak 6M, Veeco) on as-sprayed electrodes. Profiles of 2 mm length were performed five times to assess the surface roughness of substrates (Al and stainless steel) and deposited electrodes. The high pass and low pass filters between the Ra, the arithmetic

average deviation from the mean line of the profile, and W_a , the arithmetic average deviation of waviness from the mean line, were set to 20 μm and 100 μm respectively, based on manufacturer recommendations. Electrodes on foil substrates were calendered using a polished steel electric roller (MSK-2150 Electric Precision Rolling Press, MTI Corp.).

3.3.1 Electrode cross-sectioning

Cross-sections of electrodes were polished using a Precision Etching Coating System (PECS; Gatan) or a plasma focused ion beam system (PFIB; FEI HELIOS). PECS cross-sections were mounted on PECS blades with Electrodag 1415 and were loaded into a secondary electron microscope (SEM; JSM-6500F, JEOL) for imaging using a cylinder 'gripping' or 'vice' stub. Simply snapped cross-sections were mounted using carbon adhesive tabs on a 90° angled cylinder stub. For PFIB cross-sectioning, multi-layer assemblies of electrodes and separators deposited onto stainless steel spacers were mounted onto pin stubs using Electrodag 1415M. Once loaded into the PFIB, the process proceeded as follows: (1) a 50 by 20 μm area of Pt was deposited to define the area to be polished, (2) a large 120 μm by 70 μm area was milled at 60 nA beam current below the Pt coated area to expose a rough cross-section to a depth of 60 μm , (3) small 35 μm by 20 μm areas either side of the Pt coated area were milled at 15 nA beam current, and (4) the bottom edge of the Pt coated area was polished in three separate steps with a decreasing beam current of 15, 4 and 1 nA.

3.3.2 Secondary electron microscopy

Secondary electron microscopy (SEM) was performed on a JEOL JSM-6500F at an accelerating voltage of 5 keV or in the in-built SEM column in the PFIB system. Electrodes were mounted onto 12 mm cylinder pin stubs with carbon adhesive tabs. For powder characterisation, powder was dropped onto the carbon adhesive tab and any excess was removed by blowing compressed air across the surface.

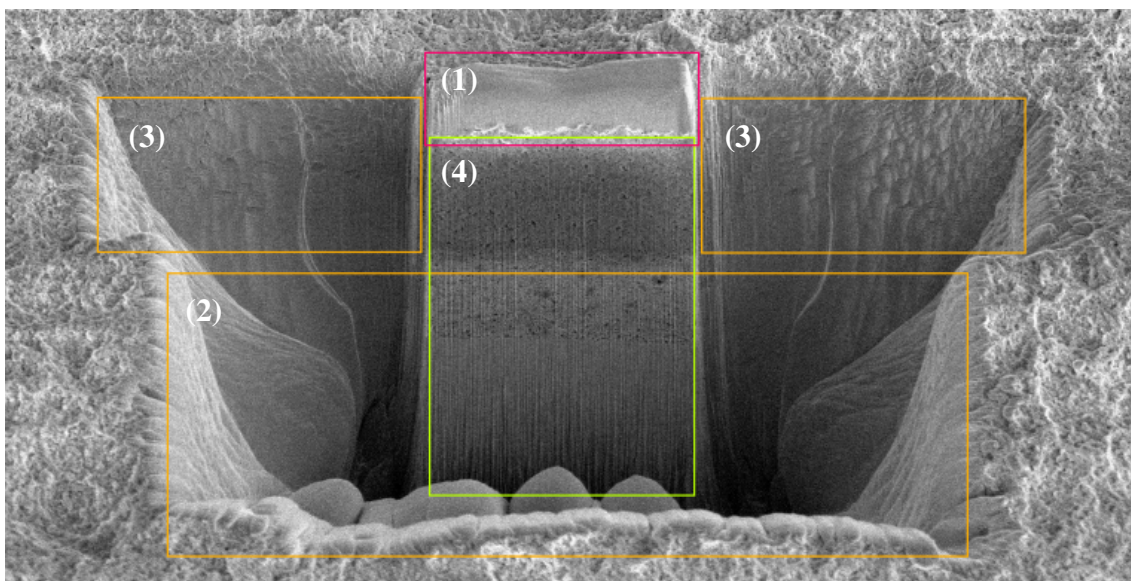


Figure 3.1: Plasma focused ion beam (PFIB) cross-sectioning method. The pink box shows Pt deposition (Step 1), the orange box defines the large roughly milled areas (Step 2 and 3) and the green box shows the polished cross section of the sample (Step 4).

3.3.3 Nitrogen gas surface adsorption

Oxide separators deposited onto foil of approximately 25 cm^2 were evacuated and held under vacuum for 10 h in a surface area analyser (SAA; Micrometrics Gemini V). The sample was then immersed in liquid nitrogen and dosed aliquots of nitrogen for 37 steps of increasing pressure and then 30 steps of decreasing pressure. After each aliquot, pressure was equalised and the measurement performed. Manufacturer supplied software was used to model the resulting data with a non-local density functional theory model.

3.3.4 Thermogravimetric analysis

Thermogravimetric analysis was performed in nitrogen gas from $25\text{--}900^\circ\text{C}$ at a 10°Cmin^{-1} heating rate (TGA; PerkinElmer Pyris). For each sample, the TGA dish was coated with a bed of inert oxide powder to protect the Pt crucible from contamination. The Celgard 2500 separator was cut to the size of the dish, spray deposited separators were scraped off the substrate and powder samples were tested as-supplied. The mass loading of samples,

dependant on the sample volume, was an average of ~4 mg.

3.3.5 Cell assembly

Unless otherwise stated, electrodes were dried in vacuum for 12 hours at 130 °C in a vacuum oven (MTI Corp.) and then transferred to a glove box with an Ar atmosphere of <0.1 ppm H₂O and < 0.1 ppm O₂.

Foil electrodes were assembled with the following components placed one after another in the centre of a CR2032 coin cell cup (MTI Corp.): (1) the working electrode, (2) 75 µl of LiPF₆ EC/DMC=50/50 (v/v) electrolyte (Sigma Aldrich), (3) a glass fibre separator (0.5 mm thick, 18 mm diameter, Watson Marlow), (4) 75 µl of LiPF₆ EC/DMC=50/50 (v/v) electrolyte, (5) a pre-cut Li chip (0.6 mm thick, 15 mm diameter, MTI Corp.), (6) a stainless steel spacer (1 mm thick, 15.5 mm diameter), (7) a stainless steel wave spring (0.3 mm thick, MTI Corp.) and (8) a CR2032 coin cell cap (MTI Corp.). The assembled cells were crimped at 0.08 T (arbitrary units) using an MTI MSK-160E Electric Crimper and cleaned with ethanol after removal from the glove box. Cells were allowed to rest for at least 20 hours before initial cycling was performed.

Cells for linear sweep voltammetry (LSV) and impedance measurements (EIS) for investigation of separators had alternative assemblies. For LSV, the working electrode, (1), and the glass fibre separator, (3), were replaced with a stainless steel spacer and the separators under investigation, respectively. Separator cells for impedance measurements used stainless steel spacers instead of working and counter electrodes, (1) and (5), and replaced the glass fibre separator, (3), with the separators under investigation.

3.4 Electrochemical characterisation of electrodes

The mass of active material in the electrode was determined in order to calculate accurate current densities per unit mass of active material, according to:

$$M_{AM} = M_{EM} \times \%_{AM} \quad (3.1)$$

where M_{AM} (g) is the mass of active material, M_{EM} (g) is the mass of the electrode and $\%_{AM}$ (%) is the percentage of active material in the electrode.

Current density, or C-rate current was calculated from the theoretical capacity of materials according to:

$$I_{CR} = M_{AM} \times Cap_{TH} \times t^{-1} \quad (3.2)$$

where I_{CR} (A) is the C-rate current, M_{AM} (g) is the mass of active material, Cap_{TH} (Ah/g) is the theoretical capacity of the material and t (h) is the time in hours to discharge. A 1 C current discharges an ideal cell in one hour, while 0.1 C and 2 C currents discharge an ideal cell in 10 hours and 30 minutes respectively.

Galvanostatic charge and discharge cycling was performed on a commercial battery testing system (Models: BT-G-25 and IBT21084LC, Arbin Instruments). Voltage limits were 2.5–4.0 V and 1.0–2.5 V vs. Li/Li⁺ for LFP and LTO respectively. C-rates were varied from 0.1 C to 30 C depending on the material and the test length. Coulombic efficiency was calculated by the ratio of discharge capacity to charge capacity per cycle.

Electrochemical impedance spectroscopy was performed using a potentiostat/galvanostat/ZRA system (Gamry Instruments Reference 600). Half cell impedance between 1 MHz and 0.01 Hz was recorded at open circuit voltage, with a 10 mV sinusoidal perturbation at room temperature after discharging cells to their lower voltage cut-off and resting for 6 hours. Separator cell impedance was measured between 200 kHz and 1 Hz at open circuit voltage, 20 hours after construction. EIS data was fitted with an equivalent circuit to study

impedances of electrodes and effective resistance of electrolyte within the separators.

Linear sweep voltammetry measurements were collected on a potentiostat/galvanostat/ZRA system (Gamry Instruments Reference 600). After resting for 20 hours, cells were subject to a linear voltage sweep between 2 and 6 V vs Li/Li⁺ at a rate of 1 mVs⁻¹.

Chapter 4

Spray deposition for aqueous processing of thick LFP cathodes

4.1 Introduction

A low-carbon economy requires energy storage technologies with ever increasing energy density, safety, cycle life, charging rate and economic efficiency. Although Li-ion batteries (LIBs) have emerged as a dominant technology for EVs, due to their relatively high energy density in comparison to competing battery chemistries, the range per charge and high cost cannot currently compete with internal combustion engine or hybrid vehicles [211]. In response, current research and development has focused on reaching energy targets of 500 Wh kg^{-1} and 700 Wh L^{-1} , while at the same time substantially lowering manufacturing costs [211, 212].

Aside from changes in cell chemistry, energy density can be improved by reducing inactive components, i.e. thicker and denser electrodes, while manufacturing costs can be reduced by switching to aqueous processing [213, 214]. However, where these manufacturing goals have been pursued, it has become apparent that thick cathodes prepared using an aqueous process often crack during drying. This was first observed in NMC cathodes prepared with aqueous processing at a mass loading of 7.5 mg cm^{-2} , although the cracking was suggested to be due to CMC binder shrinkage and the limited capability

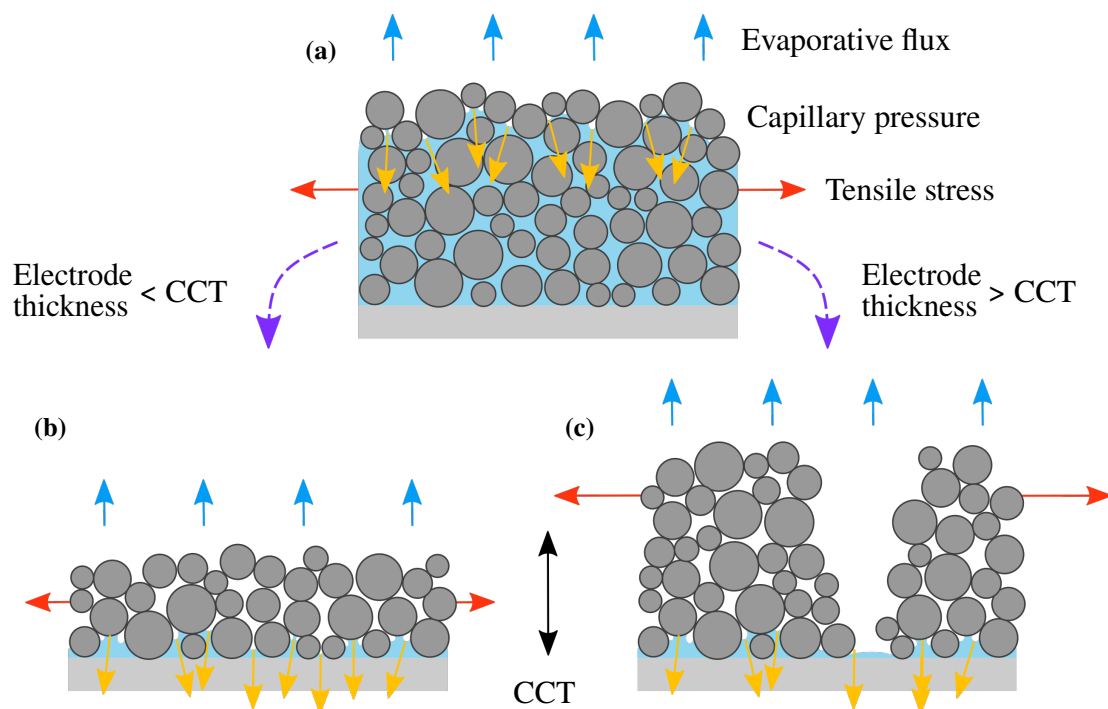


Figure 4.1: Schematics of crack formation in drying slurry cast electrodes: (a) a close packed structure forms as solvent evaporates (b) thickness $< CCT$, and (c) cracked if electrode thickness $> CCT$.

of lab scale equipment [215]. Later, Du et al. suggested that the cracking phenomenon was the same as that observed and studied in previous literature [216], such as in soils [217, 218] and colloidal films of ceramic or polymer particles [219–222].

It is generally accepted that cracking in drying particulate films is due to capillary pressure. When a particle suspension is coated onto a rigid substrate, evaporation of the solvent causes the suspended particles to pack towards the substrate. When the liquid-air interface reaches the subsequent close-packed particles, menisci form in the capillaries, giving rise to a negative capillary pressure in the solvent. The curvature of the menisci increase with further evaporation, leading to film shrinkage in response to increasingly negative pressure in the remaining solvent. The film, being constrained by a rigid substrate, is placed under tensile stress and if a critical value is reached the film will crack, as shown in Figure 4.1.

Chiu et al. studied aqueous dispersions of alumina, polystyrene and zirconia cast onto

glass substrates [219]. The measured critical tensile stress at cracking scaled with capillary pressure, which allowed the prediction of a critical cracking thickness (CCT) using the film fracture toughness and capillary pressure generated stress [219]. Lee and Routh found that the relaxation of capillary pressure upon the yielding of the film produced a pressure gradient, with the distance of the subsequent flow of solvent determining the crack spacing [223].

Tirumkudulu and Russel used the Griffiths criterion for crack propagation with a non-linear stress strain relationship for drying films of homogenous deformable particles, developed by Routh and Russel [224], to predict the nucleation of an isolated crack [220]:

$$\frac{\sigma_c R}{2\gamma} = 0.1877 \left(\frac{2R}{h} \right)^{2/3} \left(\frac{GM\phi_{\text{rcp}} R^3}{2\gamma} \right)^{1/3} \quad (4.1)$$

where σ is the critical stress, R is the particle size, γ is the surface tension of the solvent, h is the film thickness, G is the shear modulus, M is the coordination number and ϕ_{rcp} is the particle volume fraction at random close packing. The equation predicts that thicker films crack at lower stresses and was found to be in relatively good agreement with experiment [220, 225].

Singh and Tirumkudulu showed that for hard particles, the CCT, which is the same as h_{max} , is set by the balance of the critical stress for cracking and the biaxial stress at the maximum attainable capillary pressure, as shown in Equation 4.2 below [225]. The term containing the maximum capillary pressure, P_{max} , which depends on the wetting angle of the solvent on the particles, θ , as shown in Equation 4.3 below, was predicted satisfactorily from a power law fit of experimental data from a range of water-based polymer and ceramic colloidal films.

$$h_{\text{max}} = 0.64 \left(\frac{GM\phi_{\text{rcp}} R^3}{2\gamma} \right)^{1/2} \left(\frac{2\gamma}{(-P_{\text{max}})R} \right)^{3/2} \quad (4.2)$$

$$\frac{(-P_{\max})R}{2\gamma} = \frac{3\cos\theta}{2} \frac{\phi_{\text{rcp}}}{1 - \phi_{\text{rcp}}} \quad (4.3)$$

The study of cracking in coatings continues to be important in many fields, such as fuel cells [226, 227], printing [228, 229], bio-medicine [230–235], nanoparticle self-assembly [236] and more [237].

For LIBs, a small body of research on electrode cracking has been slowly building from 2017. Du et al. showed that cracking in NMC electrodes led to severely increased internal resistance before and after calendaring [216]. The CCT was almost doubled by addition of alcohol to the slurry, which lowered the surface tension to enable relatively crack-free deposition of water-based NMC electrodes up to $\sim 25 \text{ mg cm}^{-2}$ [216]. Ibing et al. developed a new binder system consisting of CMC, PAA and PEO in equal amounts [238]. Although the adhesion force to the substrate was reduced from 200 to 51 N cm^{-2} in comparison to CMC only, the new binder system enabled slurry solid contents of up to 65 wt.% and deposition of NMC electrodes of $\sim 60 \text{ mg cm}^{-2}$ with performance similar to that of NMP-based equivalents [238].

Rollag et al. studied crack formation in NMC electrodes at different drying rates [239]. Using a novel polymerised SBR binder, hairline microcracks appeared in water-based NMC electrodes between $11\text{--}15 \text{ mg cm}^{-2}$ at 20°C and increased in length, width and number at 23 mg cm^{-2} . Increasing the drying temperature to 45°C and 70°C generated hole-type cracks of $\sim 100 \mu\text{m}$ in diameter, which increased in number and size with mass loading [239]. Kumberg et al. studied the formation of cracks in graphite anodes in response to drying rate [240]. The CCT had no relation to the drying rate before a critical rate of $3 \text{ g m}^{-2} \text{ s}^{-1}$ for electrode thicknesses ranging from 89 to $512 \mu\text{m}$ and containing 2 wt.% CMC and 4 wt.% SBR. The limiting factor to electrode thickness was binder migration, i.e. preferential concentration of binder along the evaporation direction of solvent in the electrode. This occurred for both CMC and SBR at all electrode mass loadings and became

more severe with increasing drying rate, significantly reducing the adhesion force to the substrate [240].

Lee et al. studied whether cracks could be utilised for improving the energy storage kinetics of thick NMC electrodes [241]. Crack density was controlled by mixing DMF or acetone into NMP-based slurries. The ionic conductivity increased with crack density, due to the formation of low tortuosity channels through the electrode, while the internal resistance increased considerably when compared with a non-cracked electrode. The combination of these properties led to the deliberately cracked electrodes having relatively poor rate performance [241]. A significant challenge here, aside from increased internal resistance, is that crack spacing increases with electrode thickness, while an improvement in ionic conductivity through cracks would be expected to improve by decreasing the crack spacing.

In this thesis, layer-by-layer spray deposition is investigated as an alternative deposition technique to slurry casting in order to avoid electrode cracking. Stable water-based suspensions containing electrode materials are spray deposited onto metal foils. A comparison is then made between the structure and performance of spray deposited LFP-based electrodes and those manufactured using a standard slurry casting technique.

4.2 Materials and methods

This section describes the methods specific to this chapter not otherwise already described in Chapter 3. Suspension characterisation and electrode thickness and mass measurement used methods outlined in the previous chapter.

4.2.1 Slurry and suspension preparation

Although previous work within the group had successfully produced high performance spray deposited electrodes, the immaturity of the process means that experimental optimisation

of suspensions was still required for each new active material to be studied. Previously, the processing route for suspension production was somewhat non-standard and not applicable for conventional electrodes, so direct comparison with slurry cast electrodes was not possible. In this section, more careful direct comparison of slurry cast and spray deposited electrodes is undertaken for the first time with a shared, standard slurry or suspension preparation route. Additionally, a comparison is made between variants of the spray deposition route and for a variety of suspension compositions.

Two main processing routes, slurry and ultrasonic, were studied to assess their advantages and disadvantages for preparing suspensions suitable for spray deposition. Aqueous processing was favoured for several reasons: (1) the trend in battery manufacturing towards non-toxic and cheap aqueous solvents compared to NMP, (2) the ability of common aqueous binders to act as dispersion aids, and (3) lower solvent evaporation temperature. The different processing routes are summarised schematically in Figure 4.2, showing key processes employed, including: pestle & mortar (PM), ball mill (BM), ball mill with alcohol (BMA), ball mill then ultrasonication (HYB), ultrasonication (UL), ultrasonication with alcohol (ULA), ultrasonication with an alternative commercial water-based binder (AB) and ultrasonication with a mixed organic solvent of NMP/IPA (ORG) routes. Aqueous and organic suspensions had an LFP:binder:CB ratio of 87:3:10 and 8:1:1, respectively, and a final mass concentration of 1 wt.% in solution (1g per 100 ml). PM was mixed in an agate pestle and mortar; BM, BMA and HYB routes were mixed using the planetary ball mill with 10 mm ZrO₂ milling media and all other routes were mixed (including HYB) using ultrasound.

Slurries (BM and BMA) were prepared at 300 rpm using a two step process outlined in Figure 4.2a: (1) CB and 2.5 wt.% CMC aqueous solution were mixed for 15 minutes and then (2) LFP and DI water were added to the CB-based slurry and mixed for a further 15 minutes. In step (2), DI water was added until the slurry reached a mass concentration of

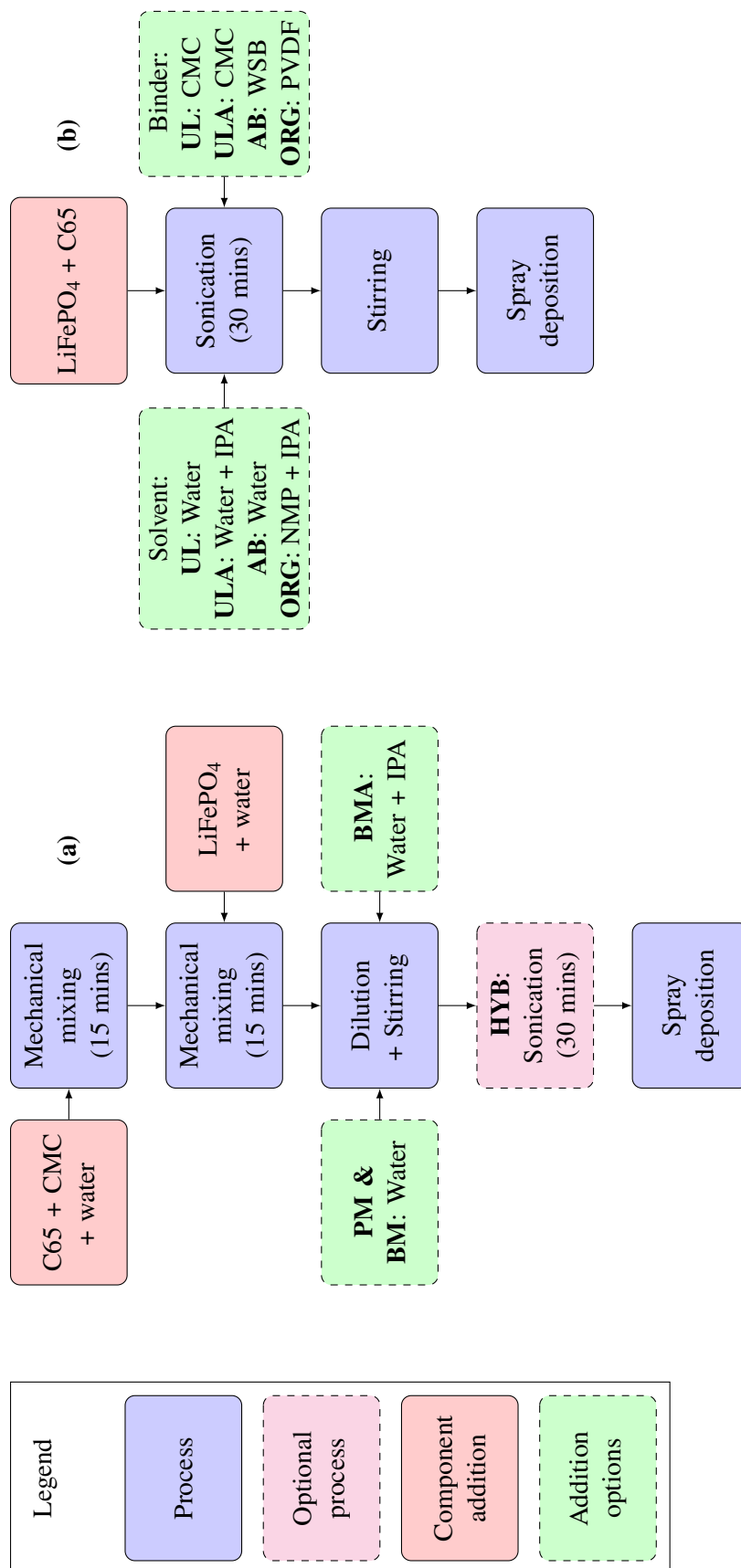


Figure 4.2: Flow charts outlining the processing routes of PM, BM, BMA, UL, ULA, AB and ORG. Squares of blue with solid outlines describe a mixing or spray process, pink with dashed outlines describe an optional process for a labelled route, red with solid outlines are linked to process steps that require addition of components and green with dashed outlines describe addition steps that differ depending on the labelled route.

40 wt.%. The resulting slurry was then diluted to a 1 wt.% solid concentration using either DI water (BM) or IPA:DI water (BMA) at a final ratio of 20:80 vol.%. For the PM route, the ball mill was substituted by a pestle & mortar. In the dilute mixing routes UL, ULA, AB and ORG (Figure 4.2b), active and conductive powders were stirred into 100 ml of dilute binder solution (0.03 wt.% binder for aqueous or 0.1 wt.% for ORG) and sonicated for 30 minutes at 70% amplitude in an ice water bath. Once the slurries and suspensions were mixed and diluted to the final mass concentration of 1 wt.%, they were placed onto a magnetic stirrer for 5 minutes before spray deposition. Solvent mixtures contained 100 vol.% water for PM, BM, UL and AB, 20:80 vol.% IPA:DI water for BMA and ULA, and 10:90 vol.% NMP:IPA for ORG. The binders for AB and ORG were a commercial water-based binder (WSB) and PVDF, respectively, while all other routes used CMC. The HYB route followed the same route as BM, but was sonicated after slurry dilution, a hybrid of the mechanical and ultrasonic routes. For CB:CMC suspensions, either the BM or UL route was followed without addition of active material. For slurry cast electrodes in Section 4.3.4, the BM route was used up until the dilution step. Although these variants produce some complexity, as shown subsequently, they can lead to significant effects on electrode performance.

4.2.2 Electrode deposition and drying

Spray deposition was performed using the basic principles described in Section 3.1.3. The temperature of the substrate was 130 °C, the flow rate of the suspension was $\sim 4.5 \text{ ml min}^{-1}$ and the atomisation pressure was 0.4 bar. After deposition, the Al foil was removed from the heated substrate and moved to a vacuum oven at 120 °C overnight. Composite slurry cast electrodes were deposited and dried using the doctor blade and multi-step drying method described in Section 3.1.4.

4.2.3 Crack characterisation

A common and defective feature of cathodes processed in aqueous solvents was cracking during the drying step. In order to quantify this behaviour statistical image analysis of electrode surfaces was performed in Matlab using code written in-house to measure crack intensity, width and length. Figure 4.3 describes the process: (a) a grayscale image was imported into Matlab, (b) a binary image was produced from the grayscale image, (c) "morphological opening" with a 3x3 square structuring element was performed to remove noise, (d) remaining noise was removed by a foreground pixel area filter set whose setting was dependent on a threshold value, up to the mean particle diameter (d_{50}) of the particle size distribution, (e) the clean binary image was overlayed onto the original grayscale image for manual comparison, and (f) the cracks were skeletonised to obtain their length. Once step (d) was complete, the continuous sections of foreground pixels were separated into 'grains'. Each of the grains should delineate a specific crack in the image, and the crack width can be calculated from dividing the grain area by the grain length calculated in step (f). A dimensionless crack intensity factor (CIF) was calculated from the summed area of all grains in the image divided by the total area. The code was based on crack analysis by Rollag et al. [239] up to step (e). For step (f), Rollag et al. used a simple estimation that identified grain boundary pixels and then the furthest distance between them was used to estimate a crack length. In this work, the grains were instead skeletonised to account for the crack branching and curvature observed in Figure 4.3.

The binary image in step (b) was created using Otsu's method of grayscale thresholding, with the default Matlab function 'imbinarize' [242]. The threshold was selected based on the user's visual assessment of the successful identification of a crack to noise ratio, and was therefore subject to human error. As the threshold was decreased, the edges of cracks could not be resolved, whereas as the threshold was increased, more noise was generated. Therefore several thresholds were selected and averaged to give an estimation of the sensitivity of computed values. Morphological opening, in step (c), is the process of

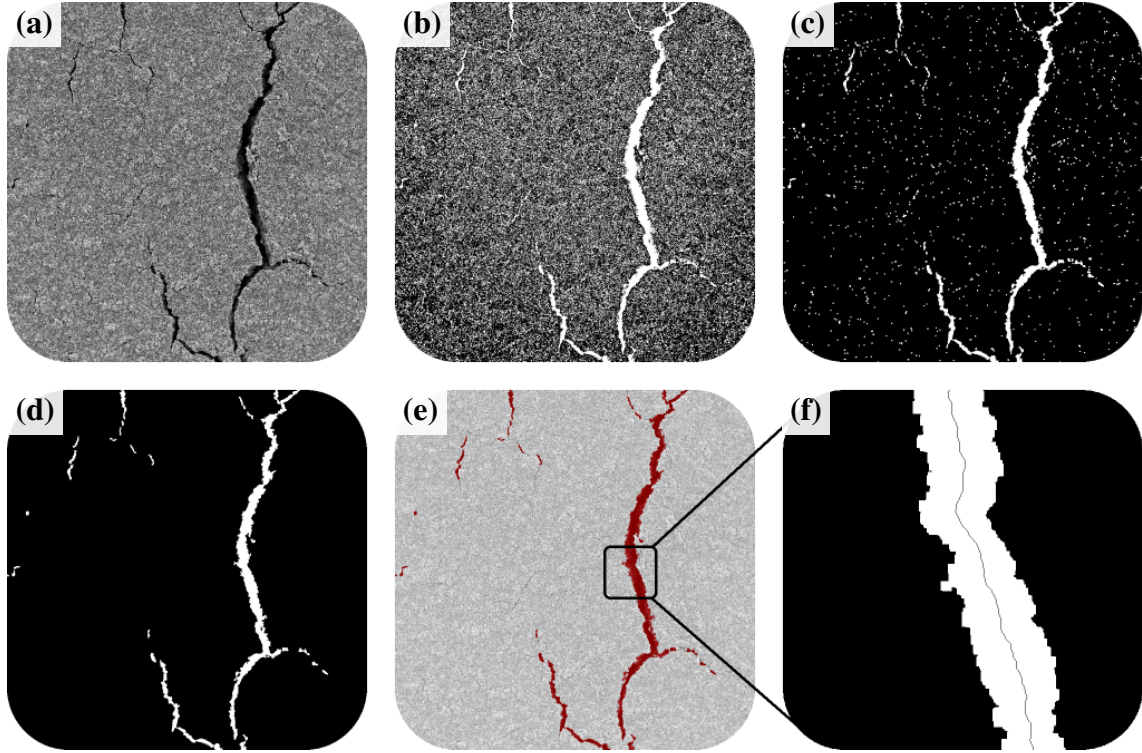


Figure 4.3: Image processing steps performed in Matlab to calculate cracking statistics: (a) importing the original grayscale image, (b) binary image generated using a threshold, (c) the binary image after morphological opening to remove "salt and pepper" noise, (d) pixel removal based on the mean particle diameter to remove non-crack foreground pixels, (e) final binary image overlaid back onto (a) for manual comparison, and (f) zoomed in skeletonisation of the identified crack to allow calculation of length and width.

erosion and then dilation of the binary image (Figure 4.4). For each pixel in the image, the erosion operation sets the value of the central pixel to 0 if any pixel of the overlaid structuring element was equal to 0. For a 3x3 structuring element, this means the central pixel will be set to 0 if any neighbouring pixels have value 0. Dilation then does the reverse of this, if a pixel has a neighbouring pixel set to 1, then that pixel is set to 1. Therefore, the opening operation aims to remove small salt and pepper noise while maintaining accurate crack edges.

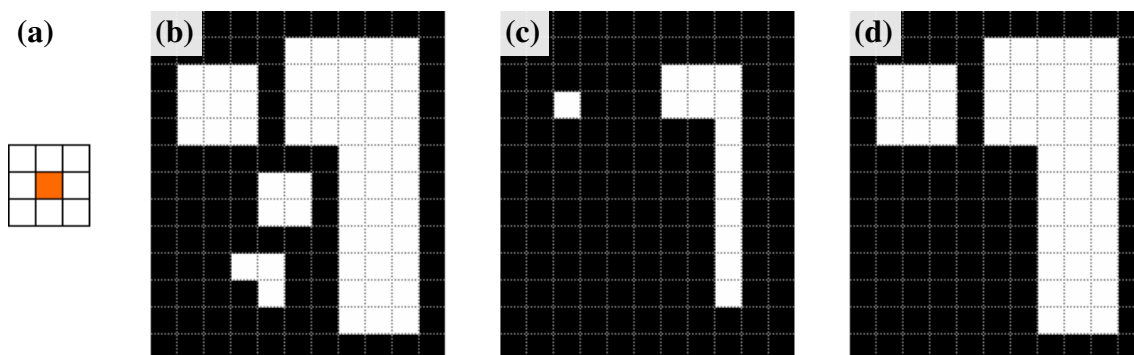


Figure 4.4: A visual representation of the opening morphological process: (a) a 3x3 square structuring element, with the target pixel filled in orange, (b) a binary image, (c) erosion of the binary image and (d) dilation of the eroded binary image. With the structuring elements overlaid for each pixel in the image, erosion sets the central pixel to 0 if any pixel in the structuring element contains a 0 value (in this case neighbouring values). For dilation, the opposite of erosion, the central pixel is set to 1 if any pixel in the structuring element has a value of 1.

4.2.4 Electrochemical characterisation

Electrochemical characterisation was performed using the methods described in Section 3.4. For rate capability, LFP coin cells were galvanostatically charged and discharged for 5 cycles at various C-rates between 0.1 C and 10 C, then charged for 2 more cycles at 0.1 C. EIS measurements were performed after the first 5 cycles at 0.1 C, in the discharged state between 1 MHz and 0.01 Hz. Long term rate cycling was performed at 0.5 C for 100 cycles after rate cycling.

4.3 Results and discussion

4.3.1 Suspensions

Suspension properties were characterised to relate particle size distribution, and its evolution over time, to physical and electrochemical properties of the electrode film.

Figure 4.5a shows the particle size distribution (characteristic diameter or d-values) of aqueous suspensions processed by ball milling (BM, 30 mins), ultrasonication (UL, 30 mins) or combinations of the two techniques (HYB, 10 and 20 min of ball mill and

sonication respectively). Ball milling did not effectively break down agglomerates in the CB suspension that had $d_{50} = 2 \mu\text{m}$ and $d_{90} = 6.4 \mu\text{m}$, suggesting that either the milling ball diameter was too large (10 mm), the mixing time was too short (30 min), or the milling RPM was too low (350 RPM), or a combination of the three. However, ultrasonication reduced the agglomerate diameter by roughly 6 times that of ball milling, to $d_{50} = 0.32 \mu\text{m}$ and $d_{90} = 1.3 \mu\text{m}$. But, due to carbon black's hydrophobic nature, trying to incorporate all the carbon black into a dilute CMC solution (0.015 wt.%) tended to produce inconsistent suspensions, with some measurements of d_{90} up to $100 \mu\text{m}$. In essence, the difference was due to the tendency of the non-wetting CB to float on top of the slurry or suspension. In BM, the balls forced non-wetted CB into the viscous CMC laden slurry, eventually allowing CMC adsorption and stabilisation. In the dilute suspension, shear forces were applied by cavitation within the suspension, but did not seem to create enough agitation on the surface to incorporate some stubborn non-wetted CB agglomerates. Therefore, the hybrid route was developed, CB-HYB, where carbon black was incorporated into a concentrated CMC solution (2.5 wt.%) by ball milling, and was then ultrasonicated after dilution to efficiently reduce the agglomerate diameter to a $d_{90} < 1 \mu\text{m}$.

Figure 4.5b compares an LFP:binder suspension (mixed by BM) and various LFP:binder:CB composite mixtures. All the mixing techniques yielded similar distributions. The LFP:binder suspension had the highest d_{10} and d_{50} values, as expected from the lack of small CB particles. The particle size distribution was similar to that supplied by the manufacturer, indicating that the BM process did not significantly alter or damage the LFP particles. Pestle & mortar (PM) produced a slightly higher $d_{90} = 11 \mu\text{m}$ compared with the other techniques ($d_{90} = 6\text{--}8.5 \mu\text{m}$), which was due to the difficulty in applying homogenous shear forces to agglomerates by hand. The addition of 10 wt.% CB to the LFP suspension with BM, HYB or AB generally resulted in a halving of the average agglomerate diameter. The mixing procedures using ultrasonication, HYB and AB, developed suspensions with relatively small agglomerate diameters of $d_{10} = 0.4 \mu\text{m}$ and $d_{50} = 1.4 \mu\text{m}$, compared with

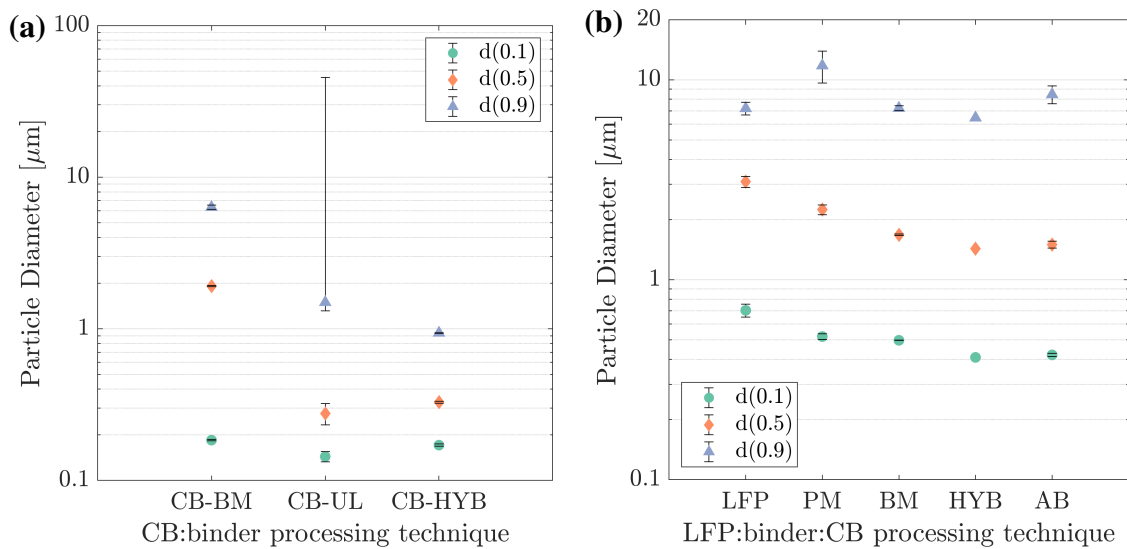


Figure 4.5: Average diameter $d(0.1)$, $d(0.5)$ and $d(0.9)$ measured by laser diffraction of suspensions for a variety of processing routes of (a) CB:CMC and (b) LFP:binder and LFP:binder:CB. Carbon black suspensions in (a) were processed by the BM, UL, and HYB routes described previously, but without addition of LFP. LFP:binder:CB suspensions were processed by PM, BM, HYB, and ultrasonication with an aqueous binder, AB. An LFP:binder suspension (LFP) processed by BM was also measured for comparison. Error bars show the standard deviation from 5 measurements.

the slurry based mixing that yielded a $d_{10} = 0.5 \mu\text{m}$ and a $d_{50} = 1.7\text{--}2.2 \mu\text{m}$. However, ultrasonicated suspensions showed a $d_{90} = 6.5\text{--}8.4 \mu\text{m}$, similar to that of BM with a $d_{90} = 7.2 \mu\text{m}$. Therefore, while ultrasonication was more efficient at breaking up agglomerates in CB suspensions, both ultrasonication and ball milling were effective in reducing the overall agglomerate diameters in LFP:CMC:CB suspensions. Interestingly, the BM process on LFP:CB:binder produced a smaller d_{50} than both the LFP:binder by BM and CB-BM suspensions. This suggests that the hard and small LFP particles acted as extra 'milling balls' and allowed the BM process to reduce the CB agglomerate size more effectively than in the absence of LFP particles.

The agglomerate diameter distributions were studied over time, i.e. their stability, as shown in Figure 4.6. Figure 4.6a shows the agglomerate diameter distributions of suspensions dispersed by BM, HYB and HYB followed by stirring for 30 minutes on a magnetic stirrer (HYB 30m). As described earlier, initially the ultrasonicated suspensions

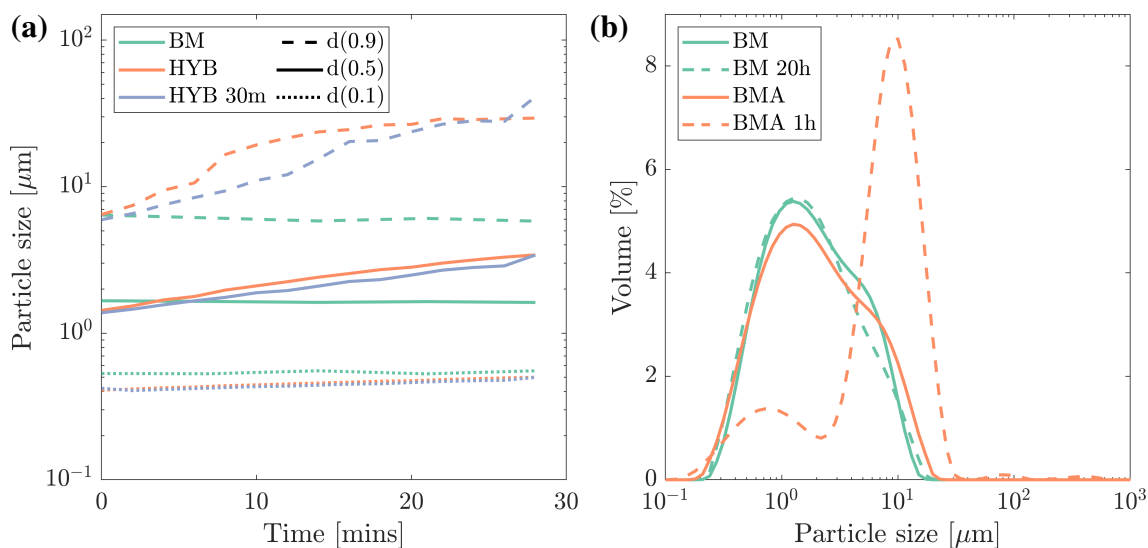


Figure 4.6: Average diameter $d(0.1)$, $d(0.5)$ and $d(0.9)$ evolution over time of LFP:binder:CB suspensions (a) BM, HYB and HYB 30m and particle size distributions of (b) BM, BM 20h, BMA and BMA 1h.

had a distribution shifted to lower diameters than those processed by BM. However, during the measurement, the agglomerate diameter of ultrasonicated suspensions increased while the BM suspension agglomerate diameters were stable or slightly reduced. The starting distribution of both HYB and HYB 30m were similar, suggesting that the agglomerates increased in diameter during the measurement in the Mastersizer, but were more stable when stirred in a glass beaker. The suspension ultrasonicated with the alternative commercial binder (AB) had relatively stable agglomerate diameters similar to that of BM, indicating that the instability arises from the combination of CMC binder and ultrasonication.

Figure 4.6b compares the agglomerate diameter distributions of a ball milled suspensions when diluted with water or an aqueous solvent containing 20 vol.% IPA. When the solvent was solely water (BM), the distribution was approximately stable over 20 hours of magnetic stirring (BM 20h). When the mixed solvent was used, the d_{50} of the suspension increased dramatically over 1 hour, from $1.6 \mu\text{m}$ to $7 \mu\text{m}$.

There was also some interaction between suspensions and the plastic tubing of the Mastersizer observed after multiple experiments. Plastic tubing was easily cleaned after transporting water-only ball milled suspensions, while the ultrasonicated and alcohol

containing suspensions left a residue. This might explain why the agglomerate diameter of ultrasonicated suspensions increased as the measurement was performed. For suspensions containing IPA there was a similar increase in agglomerate diameter during measurements in addition to the agglomerate diameter increasing between measurements when stored in a glass beaker, indicating a more severe stability issue.

4.3.2 Deposition

In general, thin layers deposited with IPA were substantially darker than those without, leading to the exploration of whether there were differences in the deposition mechanism. Aqueous suspensions of LFP:CMC:CB (87:3:10) were deposited onto Al current collectors with water (LFPW) and a mixture of water and 20 vol.% of IPA (LFPA). Electrodes comprising of only 1, 4, 8 and 16 ‘layers’, which were defined by the number of passes of the spraying nozzle across the current collector, were fabricated.

Figures 4.7a and c compare plan view SEM micrographs of LFPW and LFPA suspensions deposited onto Al current collectors at 130 °C. A single layer of deposition shows that deposited material initially formed distinctive circular patterns with particles relatively evenly distributed within the circle. The perimeter of each circle comprised a ‘wall’ of more agglomerated material, magnified in the inset Figures 4.7b and d for LFPW and LFPA respectively. It is reasonable that each circle was a discrete droplet from the atomised spray, with the solid content rapidly pushed to the perimeter of the droplet as it impacted and then dried. Within the walled perimeter, particulate agglomerates of up to 10 µm were resolved, consistent with the diameter distributions presented in Section 4.3.1. Further deposition resulted in a progressively more homogenous surface layer, as shown in Figures 4.7e and f. The 8 layer LFPW electrode, Figure 4.7e, showed agglomerated boundaries, in the left and bottom right, on either side of which the current collector can still be seen. In Figure 4.7f, after 16 layers of deposition, the current collector was fully obscured and the electrode surface became more regular, similar to that of the relatively homogenous 4 layer

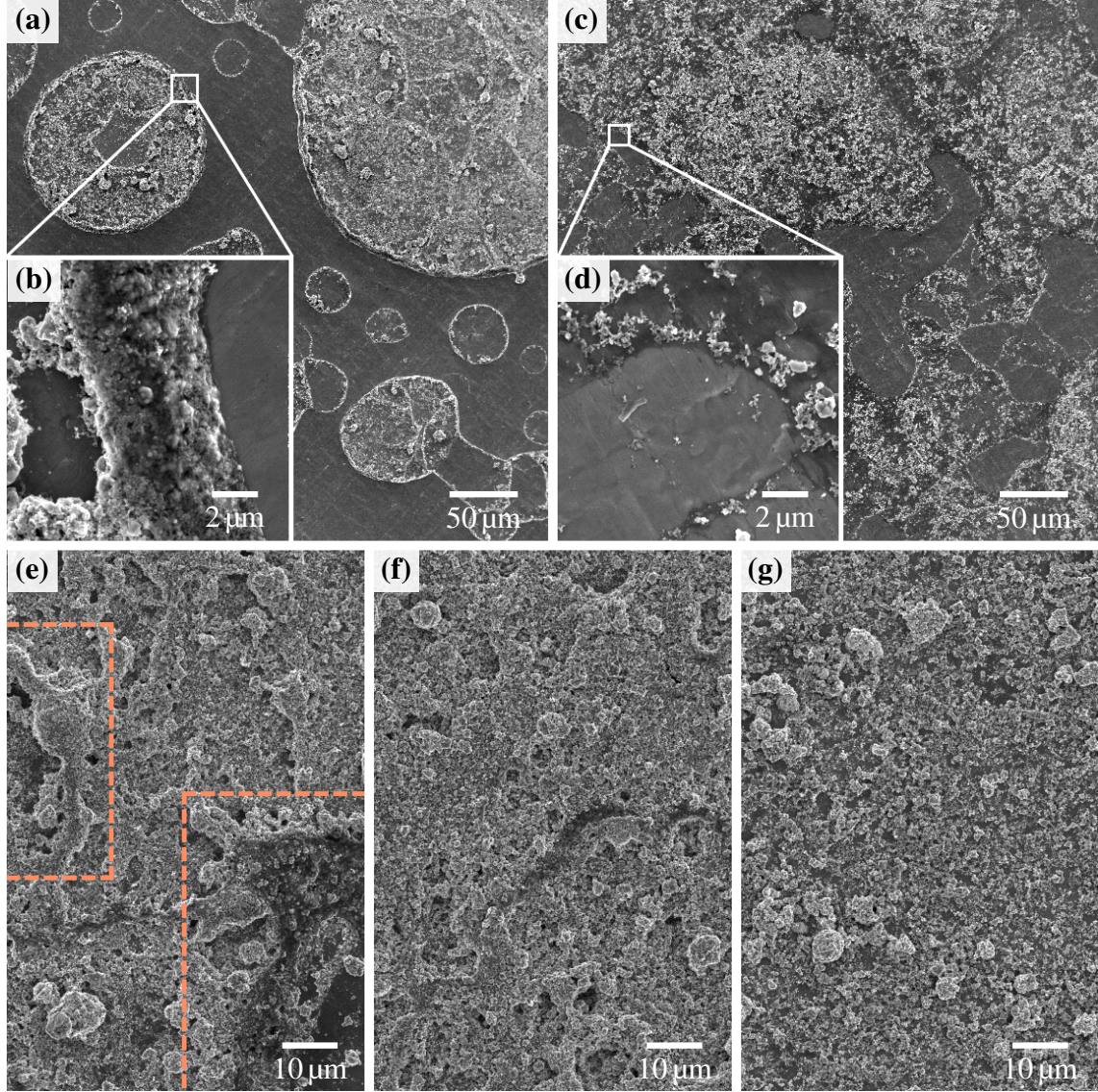


Figure 4.7: Plan SEM images of LFP:CMC:CB suspensions deposited onto Al substrates with (a) 100 vol.% DI water, LFPW, and (c) 80:20 vol.% DI water:IPA, LFPA. Inset images (b) and (d) show magnifications of the droplet boundaries. Below, 8 and 16 layers of LFPW (e,f) and 4 layers of LFPA (g) show the development of the electrode surface as layers are deposited. Agglomerated boundaries are outlined by orange dashed lines in (e).

deposition of LFPA in Figure 4.7g.

When a droplet settles on a substrate, the liquid forms into a hemisphere with a ‘contact line’ at the perimeter or three phase interface of droplet liquid, surrounding air and solid substrate. Under equilibrium, the sessile droplet height is determined by the liquid contact angle with the substrate, the surface tension and the droplet volume. Whether the contact line is ‘pinned’, i.e. fixed in place, or unpinned, i.e free to move, as shown in Figure 4.8, plays a significant role in how solute or suspended particles within the droplet will be incorporated into the structure. For an unpinned droplet, evaporation of liquid at the liquid-air interface causes the droplet surface to recede towards the centre of the droplet, with a reduction in droplet height and radius, as shown in Figure 4.8a. Therefore, assuming a uniform distribution of suspended particles, particles are deposited principally in the centre of the droplet once a critical concentration of suspended solids is reached (due to evaporation of the liquid component). However, to maintain the constant radius of a pinned droplet, liquid from the centre must flow outwards to replenish liquid lost at the perimeter, as shown in Figure 4.9a. This flow carries the suspended material from the centre to the disc periphery, which is subsequently deposited onto the surface in a "coffee ring" pattern once a critical concentration of suspended particles is reached, as shown in Figure 4.9b and c [243, 244].

The deposition of material within the coffee-ring may relate to two factors: (1) a surface active polymer (such as CMC) will encourage physical interaction of the coated particles with the underlying surface before they are transported to the droplet contact line, and (2) near the end of drying, the contact line can break free and particles deposit across the substrate as the contact line recedes [244, 245]. For Al and Cu foil substrates, the contact line breaks once the contact angle of the evaporating droplet reaches $\sim 10^\circ$ [246]. Therefore, both of these mechanisms could help facilitate the relatively uniform deposition of material within the coffee-ring for the LFPW suspension.

In practice, the impact, spreading and drying behaviour of a suspension droplet will

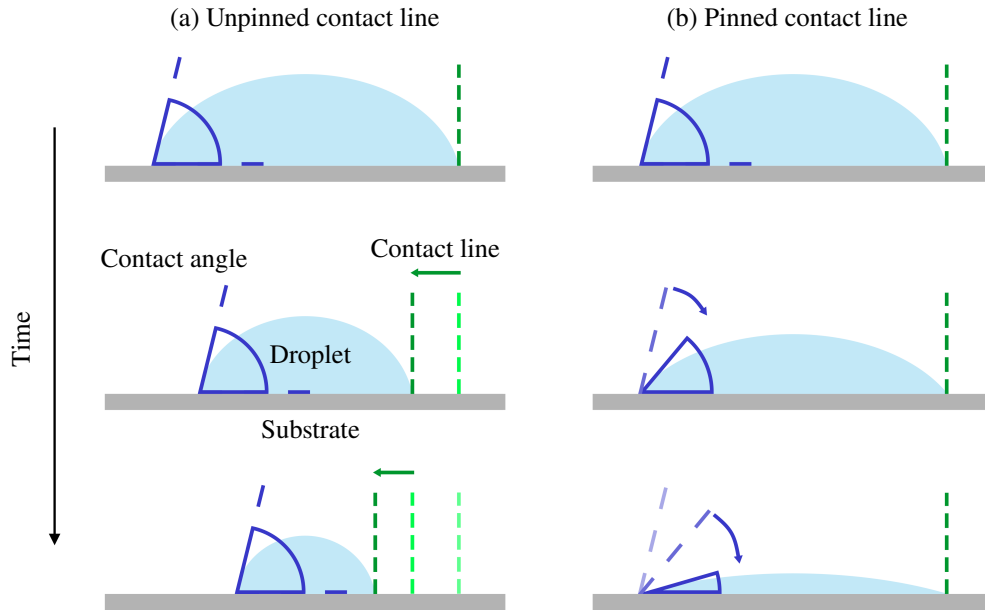


Figure 4.8: Basic evaporation mechanisms of a liquid droplet on a impermeable substrate. With an unpinned contact line, the contact angle between the droplet edge and the substrate stays constant, as the radius of the droplet decreases. For a droplet with a pinned contact line, the contact angle must reduce in response to the radius of the droplet being constant.

also depend on its velocity and the porosity of the substrate [247]. Pack et al. showed that the coffee-ring effect was suppressed on a porous substrate if the liquid component fully wicked into the substrate, or the time for particle motion to the pinned contact line was greater than the evaporation time of the residual drop volume [248]. During deposition of LFPW, the substrate surface transitions from non-porous to porous, i.e. the foil surface initially and then the previously deposited particle layers, with the liquid component of a deposited droplet then wicking into the porous under-layer. At this point, a coffee-ring will only continue to form if the time for particle motion to the droplet edge is less than the time for the fugitive liquid component to either evaporate and/or wick into the porous surface. Therefore, subsequent layers obscure the coffee-ring formations once these conditions are met, as seen in Figure 4.7f.

In contrast to LFPW, LFPA showed no sign of coffee-ring formation, so that either the droplets were unpinned, or the radial flux within the droplet was reduced [244, 249]. This might, for example, arise due to a Marangoni flow, which can be generated in a

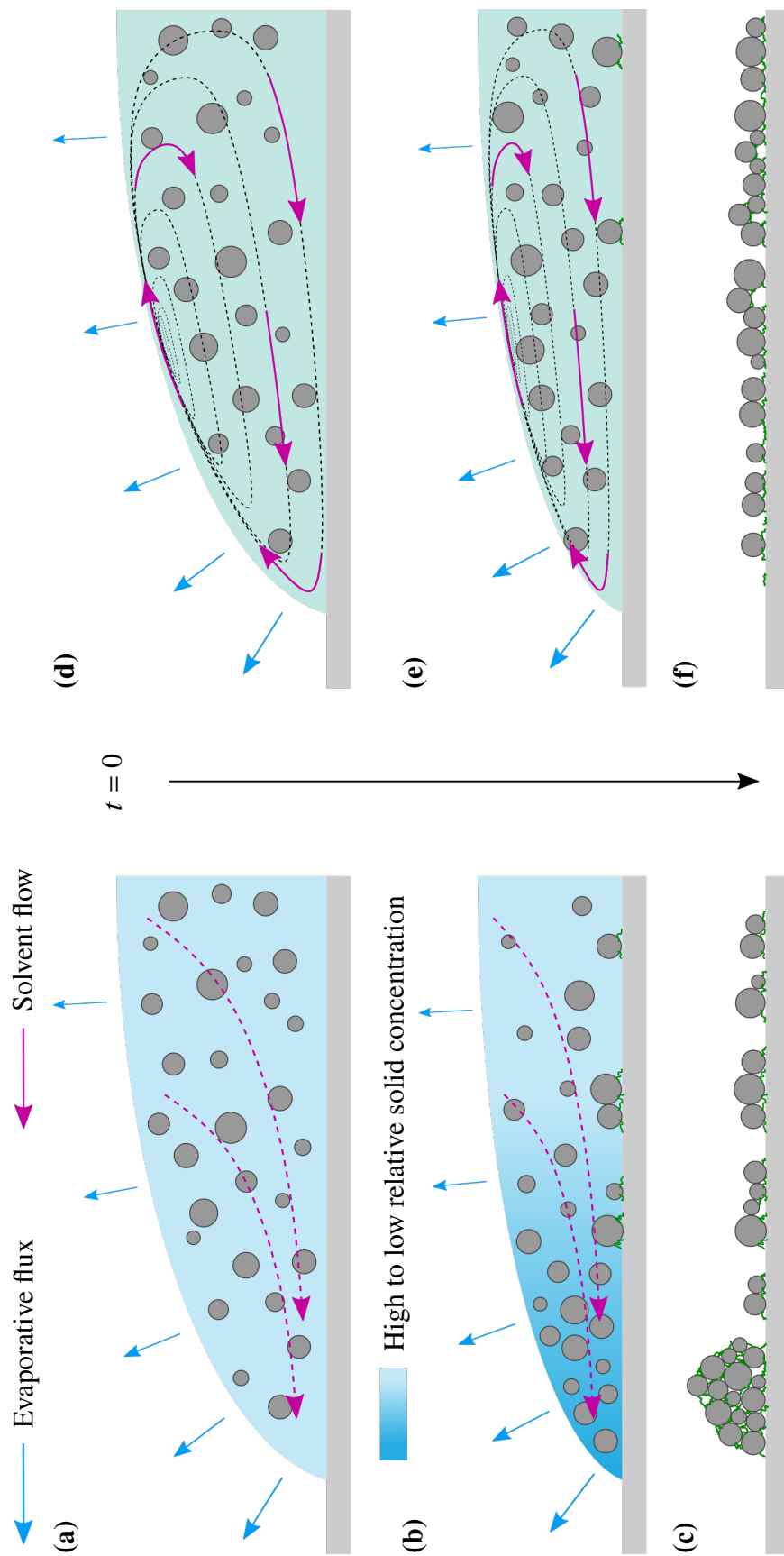


Figure 4.9: Drying and particle deposition mechanisms for pinned contact line droplets without (a) and with (b) significant Marangoni flow. Particle deposition homogeneity is improved with a Marangoni flow counteracting the flow to the droplet edge caused by evaporation. Blue arrows indicate evaporative flux, while purple arrows show the corresponding redistribution of solvent in the drying droplet. Some particles can adhere to the substrate during drying due to the surface active polymer (CMC).

droplet of mixed solvents with different boiling temperatures, such as water and IPA. Upon evaporation, the concentration of the high boiling point liquid (in this case 80 vol.% water) increases near the edge of the droplet in response to the greater evaporation rate, and a surface tension gradient is generated between the centre and perimeter of the droplet. A flow from high to low surface tension regions, shown in Figure 4.9d, will occur if the Marangoni Number, $M = \Delta\gamma L / \nu D$, is large enough, where $\Delta\gamma$ is the difference in surface tension, L is the length scale, ν the viscosity and D is the diffusion coefficient. De Gans and Schubert showed that two solvents with a smaller difference in surface tension than IPA and water used here can generate a Marangoni flow large enough to counteract the evaporative flow [249]. Therefore, for LFPA, it is reasonable that a surface tension gradient induced flow may counteract the evaporative flow, and subsequently, the solid component was deposited in a relatively homogenous pattern, as shown in Figure 4.9e and f.

To quantify how the Al surface changes with the deposition of electrode materials, surface profilometry was used on Al foil as supplied, after 1 pass of LFPA and LFPW suspensions and after 40 μm of deposition, with the results shown in Table 4.1 and Figure 4.10. R_a , the arithmetic average deviation from the mean line of the profile, and W_a , the arithmetic average deviation of waviness from the mean line, were measured on each surface from 5 evenly spaced profiles.

Table 4.1 shows that the non-shiny side of Al foil had low and consistent R_a and W_a ($\sim 0.1 \mu\text{m}$), and hence contributed little to electrode roughness. The W_a for LFPW layers after 1 pass was $\sim 0.9 \mu\text{m}$ and larger than that of LFPA at $\sim 0.5 \mu\text{m}$. Figure 4.10 shows representative profiles of LFPW (left) and LFPA (right) after 1 pass. For LFPW, there was some relatively large peaks of up to $\sim 6 \mu\text{m}$, spaced hundreds of microns apart, and are suggested to be the agglomerated 'walls' at the perimeter of each droplet, as shown in Figures 4.7a and b. On the other hand, LFPA generally had a maximum peak height of $\sim 3 \mu\text{m}$, slightly larger than the d_{50} of the feedstock suspension of $\sim 2 \mu\text{m}$. LFPA and LFPW electrodes deposited to 40 μm thickness had an R_a of ~ 0.7 and $\sim 0.8 \mu\text{m}$ and the same W_a of

Table 4.1: A comparison of LFPA and LFPW spray deposited electrodes after 1 pass across an Al foil substrate and after 40 μm of deposition. Measurements were averaged from 5 profiles per surface. Ra is the arithmetic average deviation from the mean line and Wa is the arithmetic average deviation of waviness from the mean line.

Surface	Ra (μm)	Wa (μm)	Ra (μm)	Wa (μm)
Al foil	0.1 ± 0.0	0.1 ± 0.0		
	<u>1 pass</u>		<u>40 μm</u>	
LFPA	0.3 ± 0.0	0.5 ± 0.1	0.8 ± 0.1	1.4 ± 0.5
LFPW	0.4 ± 0.0	0.9 ± 0.1	0.7 ± 0.1	1.4 ± 0.1

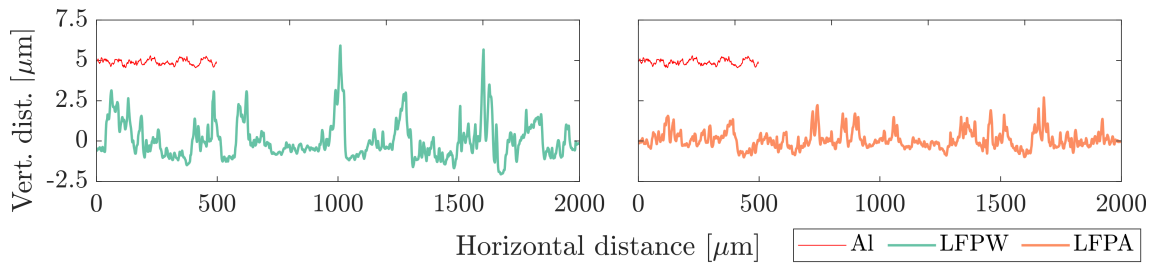


Figure 4.10: Surface profilometry comparison of LFPA and LFPW on Al foil after 1 pass of the spray head. The 500 μm profiles in red are of the uncoated Al foil.

$\sim 1.4 \mu\text{m}$. However, Wa for the 40 μm thick LFPA electrode varied significantly, which was likely related to the relative instability of the LFP suspensions containing IPA, as already shown in Figure 4.6.

For the LFPW suspension, there was a relatively strong coffee-ring effect on an Al foil substrate. After multiple layers, a typical porous electrode formed, which obscured and suppressed any ongoing coffee-ring effect. Therefore, the mixed solvent system with IPA improved the deposition homogeneity initially due to a greater Marangoni flow, but the poor suspension stability caused the deposited electrode layers to become more heterogeneous over time as agglomerates form in the suspension, as shown previously in Figure 4.6b.

4.3.3 Effect of suspension processing on LFP-based electrode performance

Several mixing procedures were compared to determine the optimum route to process aqueous electrode suspensions for spray deposition, shown in Table 4.2: pestle & mortar (PM), ball mill (BM), ball mill with alcohol (BMA), ball mill then ultrasonication (HYB), ultrasonication (UL), ultrasonication with alcohol (ULA), ultrasonication with an alternative commercial water-based binder (AB) and ultrasonication of 8:1:1 LFP/CB/PVDF in NMP/IPA (ORG).

Suspensions consisting of the same solid components and relative fractions (LFP:CMC:CB) produced electrodes of similar weight (6.3 mg cm^{-2} for PM, BM, HYB and UL). Changing the binder or solvent reduced the electrode weight to 5.9, 5.8 and 5.7 mg cm^{-2} for AB, ULA and ORG respectively, presumably through a slightly reduced deposition rate (perhaps dependent on each binder's adhesive force to the substrate) since flow rate and spray time were fixed at 4.5 ml min^{-1} and 16 min, respectively. The PM, BMA and AB electrodes had a higher initial porosity (60–62 %) than other aqueous electrodes (55–58 %) and this correlated with their larger agglomerate diameter (d_{90}) in suspension, as shown in Figure 4.5b. While there was some variation in this initial porosity of electrodes, all CMC-based spray deposited electrodes calendered to a narrow range of porosities of $52 \pm 1 \%$, while AB and ORG electrodes reached a similar $\sim 54 \%$ porosity.

Slurry mixed electrodes had a capacity of 147 mAh g^{-1} or slightly larger at 0.1 C while electrodes processed using dilute ultrasonication had capacities of 140 mAh g^{-1} or less. At 10 C, slurry mixed electrodes had capacities of 48 mAh g^{-1} or greater and 40 mAh g^{-1} or less with ultrasonication. Electrodes deposited in water/IPA, BMA and ULA, reached capacities of 140 and 10 mAh g^{-1} at 0.1 C and 10 C respectively, regardless of mixing technique. The ORG electrode obtained the same specific capacity of the best aqueous-based electrodes but had comparatively poor higher rate performance (only

Table 4.2: Physical and electrochemical characteristics of spray deposited electrodes processed using a variety of solvent, binder and mixing combinations.

Processing route	PM	BM	BMA	HYB	UL	ULA	AB	ORG
Solvent additive (20 vol.%)	–	–	IPA	–	–	IPA	–	IPA
Electrode mass (mg cm^{-2})	6.3	6.3	6.1	6.3	6.3	6.0	5.8	5.7
Active mass (mg)	6.2	6.2	6.0	6.2	6.2	5.9	5.8	5.2
Initial porosity (%)	60	56	62	58	55	55	60	81
Calendered porosity (%)	53	52	52	52	52	51	54	54
0.1 C capacity (mAh g^{-1})	147	148	140	139	134	140	136	147
10 C capacity (mAh g^{-1})	48	49	10	40	35	10	40	20
Mixing technique	Slurry				Ultrasonication			

20 mAh g^{-1} at 10 C). Qualitatively this behaviour is not unusual as PVDF-based LFP electrodes are commonly reported to have worse rate performance than their CMC-based counterparts [250, 251].

Figure 4.11 groups electrochemical performance data from Table 4.2 according to processing technique and solvent. The x-axis shows the 10 C capacity of each electrode relative to its own maximum capacity at 0.1 C. The y-axis is the capacity of each electrode at 0.1 C relative to the type of electrode with the highest capacity at 0.1 C, which was BM. Figure 4.11 shows that suspensions processed in water by slurry mixing provided the highest specific capacity at 0.1 C (99–100 %) and rate capacity at 10 C (33 %). Reducing the agglomerate diameter of slurry mixed suspensions by ultrasonication resulted in a similar rate capacity (30 %) but a reduction in specific capacity (94 %). Dispersion by ultrasonication without slurry pre-mix provided similar performance, with a rate capacity of 25–30 % and specific capacities of 91–92 %. Alcohol addition before dilute ultrasonication and dilution of the ball milled slurry reduced specific capacity (95 %) and resulted in a severe reduction of rate capacity (6 %).

To explain these qualitative trends, some key differences between the mixing techniques should be noted: (1) slurry mixed electrodes were dispersed at higher concentrations

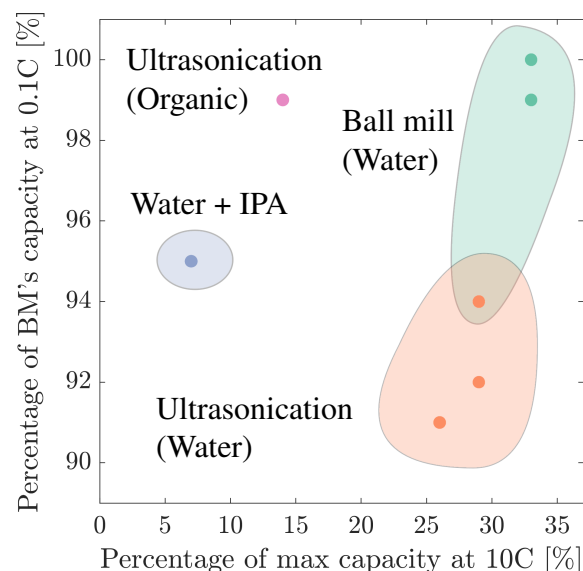


Figure 4.11: A scatter plot grouping electrochemical data from Table 4.2 by processing variations.

of CMC relative to liquid loading than dilute ultrasonication, (2) the ultrasonication step provided higher shear forces evidenced by its efficiency in reducing carbon black agglomerate diameter [252] and (3) dispersions in NMP and water differed fundamentally because while the aqueous dispersions relied on a surface active species to stabilise the suspension, the NMP-based dispersion stability was controlled by the properties of the solvent alone. In regards to (1) and (2), when the BM suspension was ultrasonicated after dilution (HYB), the specific capacity was reduced to near that of those processed only by ultrasonication (UL and AB).

Bockholt et al. studied the effects of intensive high shear mixing against a reference mixing technique and found that intensive mixing produced electrodes with well-dispersed conductive additive, but poor long range conductivity pathways and regions of electrically isolated active material [253]. While this could be partly remedied either by adding conductive graphite or including a high force calendaring step, the less intensively mixed electrodes used for comparison provided the optimum performance under each condition. Haselrieder et al. studied the affects of varying shear forces with processing technique, and found a complex interplay between electrode performance and the pore size distribution

associated with carbon black agglomerates [254]. For LiFePO_4 specifically, significant variations in specific capacity of electrodes have been attributed to the dispersion of components in an aqueous slurry [250, 255]. Additionally, in previous studies, high shear forces were usually applied mechanically to a slurry, while in this work shear was applied using ultrasonication to much more dilute suspensions. Ultrasonication is known to cause polymer chain scission, and could alter how the binder interacts with, and disperses the suspended particles i.e. the efficiency of the binder may be reduced by physical degradation [256].

Previous data showed that ultrasonication reduced agglomerate diameter, which might be expected to increase capacity and rate performance (by better structural homogeneity), but in general it had the opposite effect. One possibility might be the concept of "over-mixing" in which the LFP (unlike the CB) starts to either agglomerate itself or the surface becomes coated with other species in the suspension, such as the insulating binder, so that ionic/electronic conductivity in the composite electrode is undermined. The reduction in CB agglomerate diameter, clearly shown in Figure 4.5a, may eliminate the long range conductive bridging effect that the larger CB agglomerates within the composite electrode. Since LiFePO_4 has poor electronic conductivity [257], and relies on the percolating network of conductive additives to realise its theoretical capacity, these aspects may combine to cause the difference in capacity between BM and UL electrodes.

The addition of IPA to aqueous slurries has been associated with slightly improved electrochemical performance [258]. With the dilute suspensions required for spraying, IPA addition reduced both the specific capacity and the relative rate performance of LFP at 10 C. As shown in Figure 4.6b, the agglomerate diameter of BM was increased within 1 hour of adding the IPA and severe agglomeration was visible by eye. Therefore it can be reasonably concluded that this agglomeration was the significant factor in the reduced performance of BMA and ULA electrodes.

Based on the previous three sections, the BM method produced homogeneous LFP

electrodes at conventional thicknesses with the best electrochemical performance and stability in suspension compared to other mixing techniques for spray deposition. However, BM was relatively poor at depositing thin homogeneous electrode layers ($< \sim 10 \mu\text{m}$). Suspensions with addition of IPA had improved homogeneity of initially deposited layers and are therefore more suitable to generating thin layers of materials, at the expense of worse suspension stability and worse electrochemical performance.

4.3.4 Physical comparison with aqueous slurry cast electrodes

Following on from the greater understanding of the spray deposition process developed in the previous sections, spray deposition is now compared to slurry casting using a shared BM processing route. In this section, the physical properties of spray and slurry coated electrodes are compared, the results of which are then translated to potential advantages in electrochemical performance, as outlined in the next section.

Cracking of thick ceramic and polymer granular coatings has been studied for many years with the aim of reducing the amount of organic binder required and/or being able to realise thicker coatings [219]. Cracking has been observed in NMC electrodes when organic solvents are replaced with more environmentally sustainable water-based alternatives [215, 216], which hampers the efforts of Li-ion battery manufacturers who would like to reduce their processing costs, environmental impact and use of toxic solvents. The well-established cracking mechanism was described and simplified schematically earlier in Figure 4.1.

Equation (4.4) below relates critical film thickness (CCT) to physico-chemical properties, expressing the tendency of a coating to crack due to surface tension as a function of the arrangement and type of constituent particles, and is a simplification of Equation (4.2), based on experiment [223, 225]:

$$h_{max} = 0.41 \left(\frac{GM\phi R^3}{2\gamma} \right)^{1/2} \quad (4.4)$$

Here, h_{max} is the CCT, G is the shear modulus of the particles, M is the coordination number, ϕ_{rcp} is the particle volume fraction at random close packing, R is the particle radius and γ is the solvent-air interfacial tension [219, 225, 259]. Equation (4.4) was derived for binder-free mono-disperse particulate systems, and can be applied without specific experimental mechanical data. Chiu et al. observed that the CCT of an alumina suspension increased linearly with PVA binder content [219]. A CCT range for LFP electrodes will be determined, bounded by an estimate of the minimum (binderless) CCT established by Equation (4.4) and a maximum value determined by experimental results.

This section also compares the physical properties of spray deposited LFP-based electrodes against 'reference' slurry cast electrodes. To directly compare the deposition techniques, a consistent and shared mixing process was required to make the feedstock slurries/suspensions as comparable as possible. The previously described ball mill mixing process (BM) was used for slurry cast electrodes, which were then simply diluted with DI water for spray deposition. Slurry cast electrodes were pre-dried at room temperature for 12 h before oven drying as high evaporation rates have previously been linked to cracking [219, 239]. The slurry displayed characteristic shear thinning behaviour and had a viscosity of 1.4 Pa s at 100 s⁻¹, comparable with similar examples in the literature when considering the particle size and composition [260–262].

Figure 4.12 compares how the electrode areal density and thickness affected the appearance of slurry and spray processed electrodes. Figure 4.12a displays the relationship between mass loading and thickness of slurry cast and spray deposited electrodes. In general, the slurry cast electrodes delaminated at thicknesses greater than 70–80 µm, while spray deposited electrodes had no upper thickness limit and had a near constant as-sprayed porosity of 56 %.

Figures 4.12b-d show plan view SEM micrographs of the surface of slurry cast electrodes at areal densities of 3, 6, and 11 mg cm⁻². At 3 mg cm⁻² (23 µm), cracks formed in "triplets" from a central point with an angular displacement of ~120° spacing (Figure 4.12b). The isolated cracks had lengths and widths of 25–50 µm and 4 µm respectively. At 40 µm thick (6 mg cm⁻²), the largest cracks were longer (<250 µm), wider (6 µm) and started to form a continuous network (Figure 4.12c). At 80 µm (11 mg cm⁻²), a network of parallel and perpendicular cracks caused the electrode to split into separate 'tiles' that were prone to spontaneous delamination (Figure 4.12d); the cracks were ~35 µm wide and up to several centimetres in length. Figure 4.12e is an SEM micrograph of the surface of a spray deposited electrode at a mass loading of 17.2 mg cm⁻². The surface of the spray deposited electrode was free of macro-defects and indistinguishable from a much thinner damage-free slurry cast electrode surface.

Figure 4.13 shows results from statistical image analysis that was employed to quantify the cracks in SEM images, such as those in Figure 4.12. Figure 4.13a shows the distribution of crack widths at different electrode thicknesses, normalised to the number of cracks in a 13 µm thick electrode. Each electrode had a crack width mode at ~2.5 µm, due to many small cracks distributed across the surface. The area under the curves indicated that the total number of cracks had an approximately inverse relationship with thickness. The inset plot (Figure 4.13b) compares measurements of maximum crack width by manual and statistical image analysis. The maximum crack width at 51 µm thickness was 11 µm, which was roughly two times that at 42 µm thickness (6 µm) and 3 times that at 23 µm thickness (4 µm). The manual and statistical measurements agreed well for thicker electrodes, but for thinner electrodes the manual measurement gave a smaller maximum width because: (1) manual measurements were taken from three points along the crack while the statistical analysis considered the whole crack length, (2) the widest crack in the manual measurement was determined by eye, and (3) the width measurement of small cracks in the statistical analysis will be disproportionately affected by noise. As the crack width increased, the

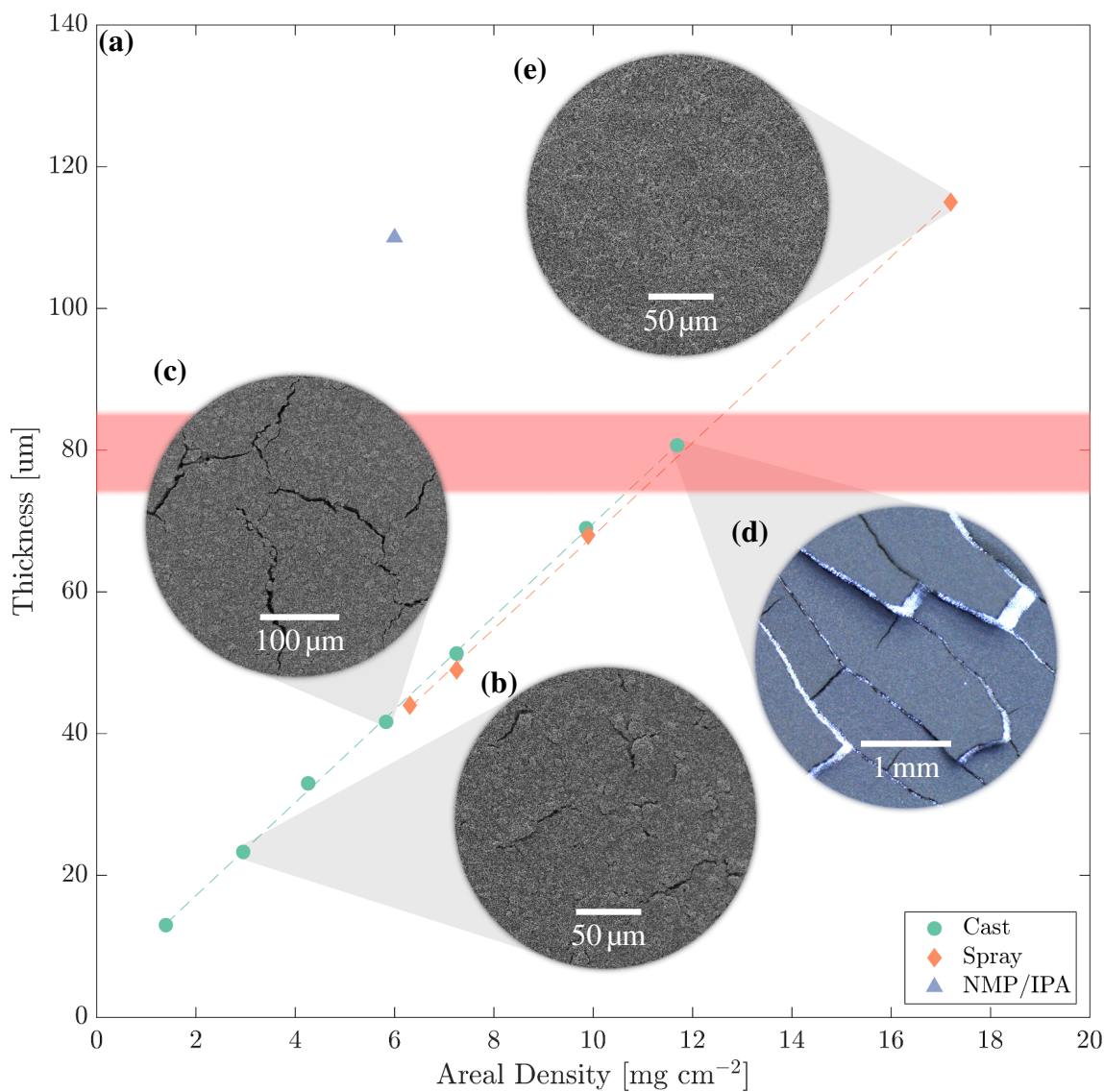


Figure 4.12: Electrode thickness against areal density for slurry and spray deposited LFP-based electrodes, (a), and planar SEM images of the electrode surfaces, (b-e). Images (b-d) are slurry cast electrodes 3, 6 and 12 mg cm⁻² respectively. Image (e) is a 17.2 mg cm⁻² spray deposited electrode. An agglomerated NMP/IPA LFP suspension was deposited to provide a comparison to the physical similarity of spray and slurry deposited electrodes.

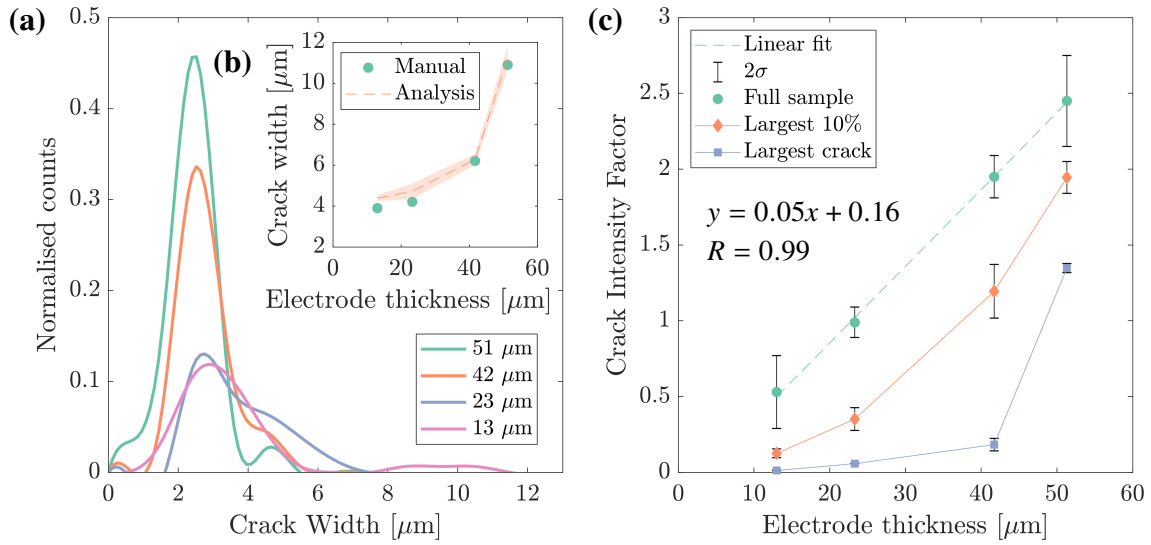


Figure 4.13: Statistical image analysis (SIA) results showing (a) crack width distribution for slurry cast electrodes, (b) maximum crack width measured by manual and SIA techniques and (c) crack intensity factor versus electrode thickness with sampling varied from the largest crack by area, the largest 10 % and the full electrode.

statistical analysis parameters and noise affected the measurement less, indicated by the blue filled region showing the standard deviation of average crack width estimated at different threshold values.

Figure 4.13c compares the crack intensity factor (CIF) as a function of electrode thickness, with a 2σ deviation plot as the error bar. The CIF is a measure of the area of the surface covered by cracks divided by the total surface area. The CIF increased linearly with thickness and, when combined with the previous analysis, the average area per crack increased as the number of cracks decreased. For 13 μm and 51 μm thick electrodes, the largest 10 % of cracks accounted for 24 % and 80 % of the CIF respectively. The largest single crack accounted for 50 % of the CIF for the 51 μm electrode, and this decreased to 10 % for the 42 μm electrode. Therefore, the largest 10 % and largest single crack contributed larger proportions of the total CIF, leading to a network of a few large cracks and electrode delamination. At the slurry cast electrode delamination threshold of $\sim 80 \mu\text{m}$ and 12 mg cm^{-2} , the estimated crack width was 35 μm , or roughly half the thickness. In the other direction, extrapolating a linear fit to the CIF, shown in Figure 4.13, gives a critical

cracking thickness of 3.1 μm . Applying a 95 % confidence interval gives an approximate thickness of less than 10 μm for a CIF of 0, i.e. the CCT of the LFP electrode. Therefore, recalling the particle diameter distribution in Figure 4.5, to a first level of approximation, to deposit an electrode (of this composition) with no cracking, the thickness of each layer should be of the same magnitude as the d_{90} of the active material.

Using Equation (4.4), the CCT of aqueous LFP and NMC coatings deposited with the absence of binder was calculated from values of G , M , R and γ taken from literature, as shown in Table 4.3 [216, 263–269]. Packing fraction, ϕ_{rcp} , was estimated over a realistic range for as-cast LFP and NMC electrodes (40–60 %), with LFP and NMC electrodes more likely to be in the lower (40–50 %) and higher end (50–60 %), respectively. For LFP, CCT (h_{max}) was estimated to be $1.1 \pm 0.2 \mu\text{m}$ with water ($\gamma = 72 \text{ mN m}^{-1}$), and $2.3 \pm 0.5 \mu\text{m}$ with 20 vol.% IPA ($\gamma = 34 \text{ mN m}^{-1}$). For NMC, CCT (h_{max}) was estimated to be $53 \pm 11 \mu\text{m}$ with water, and $109 \pm 22 \mu\text{m}$ with 20 vol.% IPA. A significant difference in CCT between LFP and NMC arises due to their different mean particle sizes (3.5 and 10.8 μm) and assumed shear moduli (48 and 78 GPa).

There are a variety of options to increase the CCT based on equations developed previously in the literature: (1) increase proportion/strength of binder, (2) increase particle size, and (3) lower surface tension. However, (1) increases the inactive component of the electrode while also potentially lowering the bulk electrical conductivity; (2) is currently not practical for LFP because Li^+ diffusivity and accessible capacity are reduced considerably by anti-site defects as particle size is increased [77]; and (3) is unable to substantially increase the CCT of the LFP electrode, as evidenced in Table 4.3.

In layer-by-layer spray deposition, the crack-free surface, shown in Figure 4.12, indicated that the CCT was not reached even at a thickness of $\sim 120 \mu\text{m}$. Figure 4.14 shows a schematic diagram for the mechanism that facilitates these thick electrodes: (a) an atomised droplet containing suspended electrode particles is sprayed towards the heated electrode surface, (b) the droplet impacts the surface, spreads and the liquid component starts wicking into

Table 4.3: The physical properties used in Equation 4.4 to calculate the critical cracking thickness (CCT) for LFP (MTI) and NMC (Toda America) electrode coatings. Values for G [263–266], M [267, 268], γ [216] and R [269] are taken from literature. Packing fraction was estimated as a range of typical values for electrodes.

Active material	h_{max} (μm)	G (GPa)	M	ϕ_{rcp}	R (μm)	γ (mN m^{-1})
LFP	1.1 ± 0.2	48	6	0.5 ± 0.1	1.75	72
LFP (IPA 20 wt.%)	2.3 ± 0.5	48			1.75	34
NMC	53 ± 11	78			5.42	72
NMC (IPA 20 wt.%)	109 ± 22	78			5.42	34

the underlying porous electrode, and the solvent evaporates and (c) the capillary pressure generated by the wicking solvent exerts transverse tensile stresses on the particles in the wet layer.

Cracking will only occur if the solvent generates a wet layer depth (the distance the liquid wicks into the electrode before drying) greater than the CCT. Since cracking was not observed, assuming this mechanism operates, it is reasonable to conclude that the liquid does not wick to a depth greater than the CCT. Equation 4.4 estimated $h_{max} > d_{50}$, but this did not account for the possible effects of additional components in the drying electrode such as the carbon black and CMC. The analysis of CIF variation with electrode thickness was extrapolated to estimate $h_{max} = 0\text{--}10\ \mu\text{m}$, so a wet depth lower than $\sim 10\ \mu\text{m}$ provides a reasonable and simple explanation for the lack of cracking in spray deposited electrodes. Following this reasoning, increasing suspension mass loading and deposition temperature may reduce the volume of liquid that is able to wick into the previously deposited electrode, ensuring both crack-free, and relatively low-binder fraction electrodes.

4.3.5 Electrochemical behaviour of thicker electrodes enabled by spray deposition

This section compares the electrochemical properties of spray deposited electrodes with slurry cast equivalents. The same slurry base mixture was used for spray deposition-based

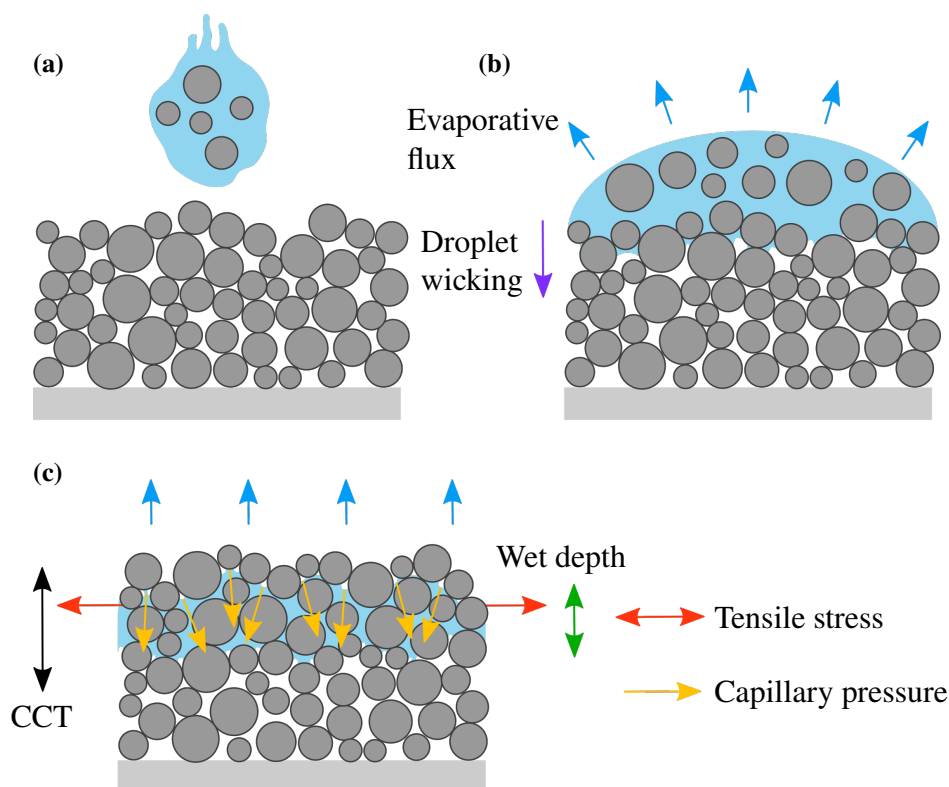


Figure 4.14: Atomised suspension droplets, impacting and drying on an electrode: (a) an atomised droplet containing electrode particles is sprayed towards the heated electrode, (b) the droplet impacts the surface, spreads and the liquid component starts infiltrating into the underlying porous electrode as liquid evaporates, (c) the capillary pressure generated by the solvent infiltrated into the porous electrode exerts biaxial stress on the particles in the wet layer.

and slurry cast electrodes. Figures 4.15a-b show the rate performance of a slurry cast electrode (SL) and two spray deposited electrodes (SP1 and SP2). SP1 had similar mass loading to SL (6 mg cm^{-2}), while SP2 had a much higher mass loading of 17.2 mg cm^{-2} , significantly greater than can be achieved by slurry casting (maximum $10\text{--}11 \text{ mg cm}^{-2}$) if delamination was to be avoided. All electrodes were calendered to the same final porosity of $\sim 52\%$.

Figure 4.15a shows the specific capacity of electrodes between 0.1 and 10 C. SL and SP1 exhibited almost exactly the same performance at all C-rates. SP2 displayed similar capacity to SL and SP1 until 5 and 10 C, where the capacity was lower by approximately 50% and 75% respectively. The decrease in rate performance is typical when mass loading, and consequently thickness, is steadily increased [165]. Figure 4.15b shows the volumetric

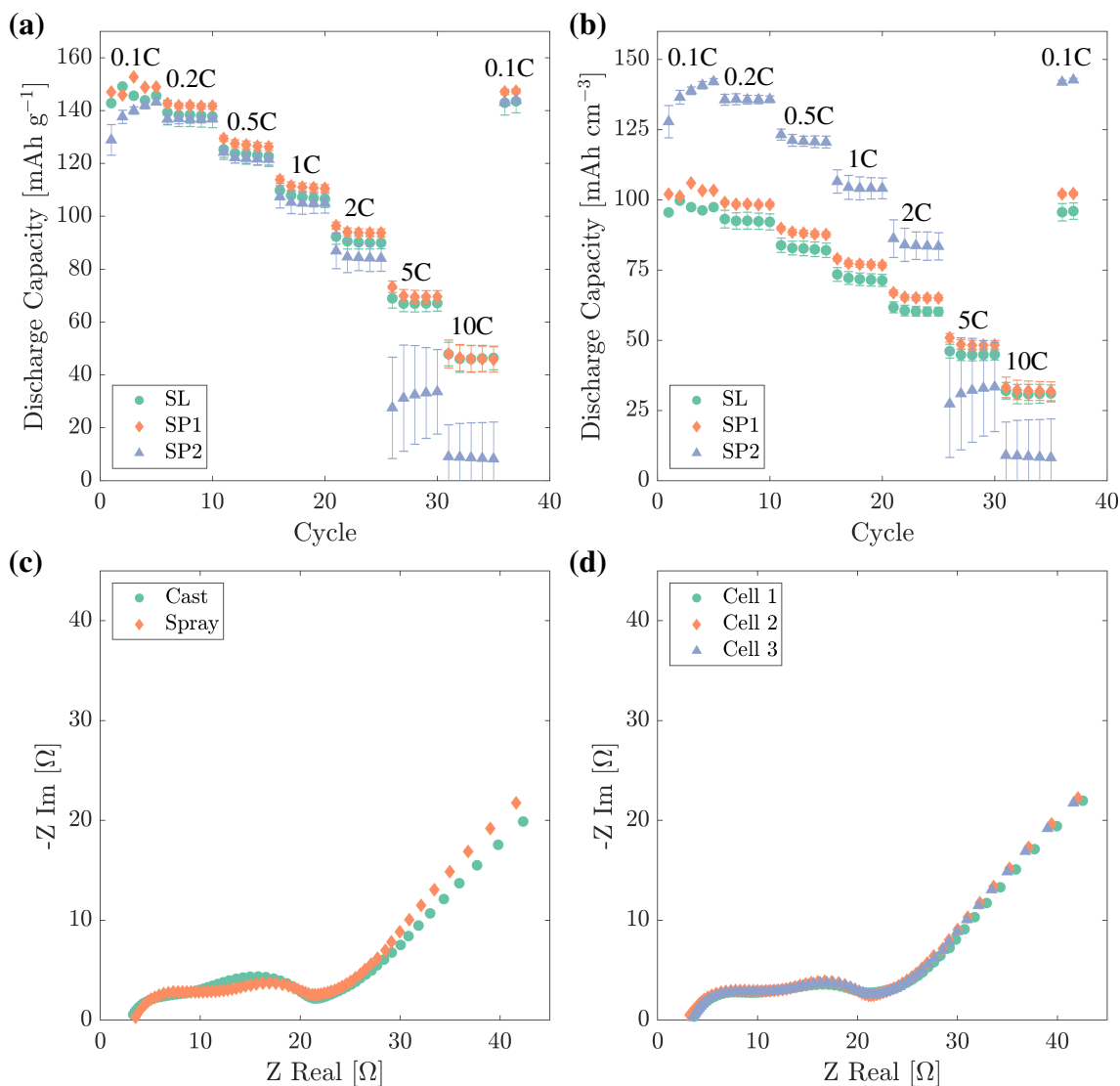


Figure 4.15: Electrochemical characterisation of slurry (SL) and spray (SP) deposition-based electrodes. SL and SP1 electrodes had a coat density of 6 mg cm^{-2} , while SP2 had a coat density of 17.2 mg cm^{-2} . C-rate performance of half cells in terms of (a) specific capacity and (b) volumetric capacity taking into account the volume of inactive material in a cell (half the thickness of both current collectors and the thickness of the separator). Nyquist plots of (c) SL and SP electrodes after C-rate testing and (d) three spray deposition-based cells after C-rate testing.

capacity of electrodes between 0.1 and 10 C, when all inactive components in the cell are taken into account (carbon, binder, half the thickness of both current collectors, and the thickness of the separator). SP2 had a capacity of 142 mAh cm^{-3} at 0.1C, representing almost a 40 % increase over the capacity of SP1 of 103 mAh cm^{-3} . The difference in capacity between SP2 and the thin electrodes decreased steadily to 28% at 2C ($83 \text{ vs } 65 \text{ mAh cm}^{-3}$), and became negative at 5 and 10 C. At these higher C-rates, the active material had become effectively inactive due to restricted Li ion and/or electronic mobility through the much thicker electrode, i.e. most regions were starved of Li ions (or electrons) and no longer contributed any capacity. This shows one of the clear advantages of very thick electrodes, unachievable by slurry casting, for high capacity applications, rather than high power.

Figures 4.15c and 4.15d compare the Nyquist plots from EIS measurements of SP1 and SL and multiple SP1 cells respectively. Figure 4.15c supports the rate performance data in Figures 4.15a and 4.15b, showing that SP1 and SL electrodes exhibited almost exactly the same EIS response at high to middle frequencies with a small deviation in the early/middle to low frequency tail (diffusion and differential capacity). Figure 4.15d displays similar EIS measurements of three nominally identical SP1 cells, in which the responses were essentially identical showing that spray deposition can provide reproducible electrodes.

Cells were cycled for 100 cycles at 0.5 C, as shown in Figure 4.16, to determine their stability after rate testing. Discharge capacity is presented as a percentage of the initial 0.5 C rate of each electrode. After 100 cycles, SL1 and SP1 had retained $92 \pm 1 \%$ capacity, while SL2 had $89 \pm 1 \%$ capacity. The slightly lower capacity retention of SL2 was expected due to its greater thickness, which may lead to more polarisation resistance induced side reactions and increased mechanical degradation [165]. At the start of cycling, all electrodes had a coulombic efficiency of 99 %. The SP2 electrode maintained this efficiency throughout, while the SP1 and SL electrodes decreased in coulombic efficiency to 97.5 % and 96.5 % on the 100th cycle, respectively. Overall, the cycling response of 100

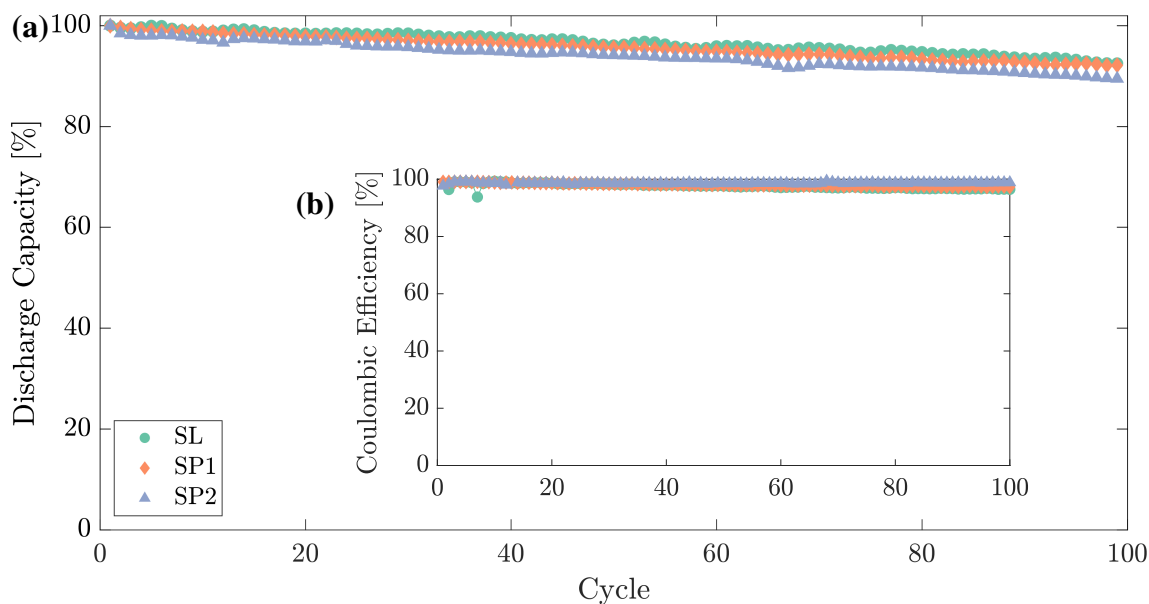


Figure 4.16: Long term cycling of SL, SP1 and SP2 electrodes at 0.5C after C-rate testing. The first cycle at 100% capacity was performed at 0.1C. Capacities reduced by the same relative value for each electrode over the test.

cycles was broadly similar, even for the comparatively thick and high coat weight spray deposition-based electrode.

4.3.6 The design space for sprayed electrodes

The layer-by-layer spray deposition technique enlarges the design space for Li-ion battery electrodes and cells because structures such as layered, graded and patterned electrodes can be readily achieved in a laboratory environment (Figure 4.17), with (at least in theory) the potential to scale-up to roll-to-roll manufacturing. Involving the author, Figure 4.17a shows unpublished work of a sprayed graphite electrode with a honeycomb pore structure, where bi-solvent drying and self-assembly was exploited to reduce the pore tortuosity of the electrode, resulting in greater ion mobility through the thickness. Further, Figure 4.17b is an EDX map taken from the cross-section of a sprayed, graded $\text{LiFePO}_4\text{-C}$ electrode, where the C (conductive additive) fraction was controlled to increase steadily with distance from the separator [201]. This arrangement or 'structuring' of the electrode constituents

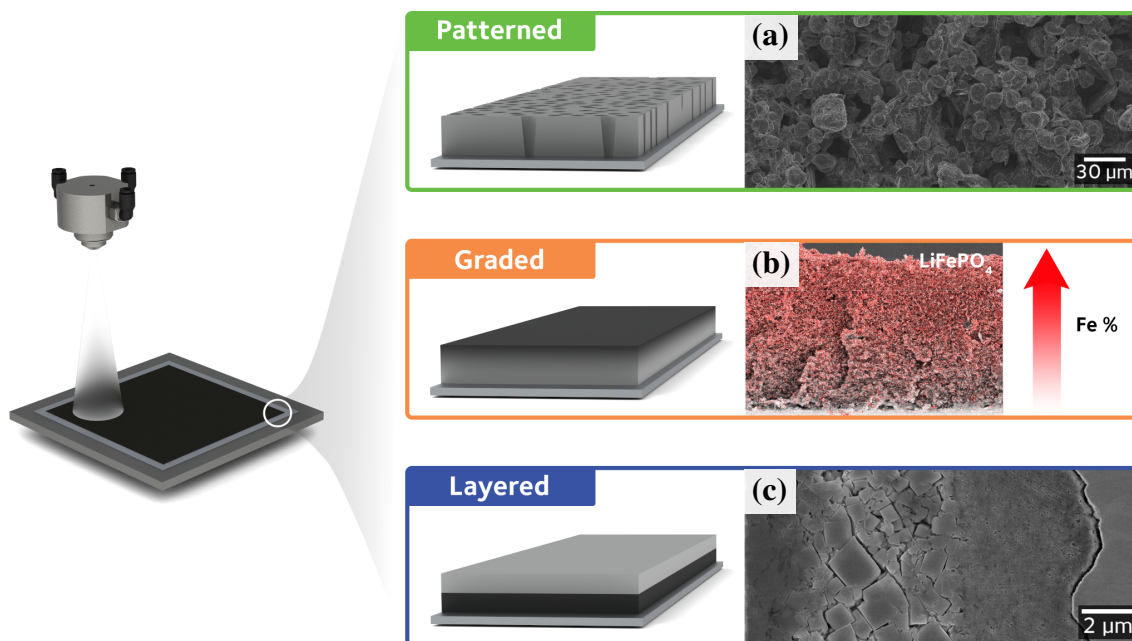


Figure 4.17: Potential, current and past avenues of research and applications for spray deposition. In-house generated examples of patterned, graded and layered structures for improved lithium-ion kinetics or novel cell configurations.

led to benefits in C-rate performance and capacity degradation [201]. Finally, Figure 4.17c shows a cross-section of a concept for a solid-state cell, where the layers from left to right are a prussian blue analogue (PBA) cathode, PBA electrolyte, PBA anode and a copper current collector. Other work from members of the group have also shown the efficacy of layered electrodes to increase cell energy and power density [197, 202, 207]. These results indicate that spray deposition increases the design space of electrodes and can lead to higher performance electrodes, as suggested in Figure 4.18. Beyond the scope of this thesis, research is also focused on simulating the performance of these and other structured electrodes (since the design space is so large/flexible, trial-and-error is impractical) to guide optimisation of performance. In practice, slurry casting cannot provide the control or flexibility to manufacture many preferred designs or structures, providing an opportunity for spray deposition and related techniques.

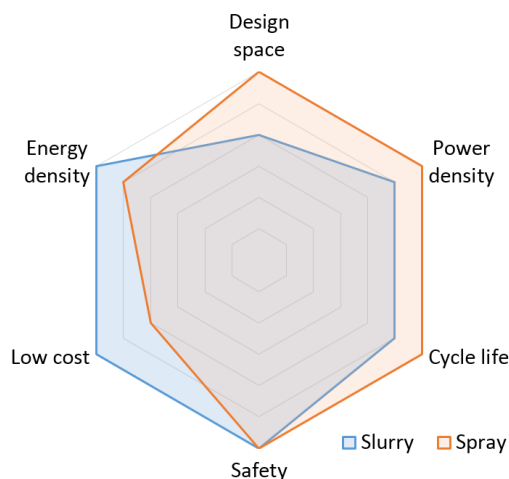


Figure 4.18: Proposed advantages and disadvantages of spray deposition for LIBs.

4.4 Conclusions

A layer-by-layer spray deposition process has been investigated, from the mixing of electrode components in suspensions suitable for stable atomisation to the electrochemical testing of cells. Suspensions containing LiFePO_4 , carbon black and binder with aqueous or organic solvents were processed using either ball milling, dilute ultrasonication or a combination thereof. The microstructure of electrodes deposited onto Al foil substrates, was studied by SEM. Electrodes of increasing thicknesses were slurry cast and spray deposited from the same slurry for direct comparison. Several electrode structures, such as multiple layers, graded and patterned electrodes enabled by spray deposition and otherwise difficult to manufacture were briefly introduced.

Spray deposited LFP-based electrodes processed by ball milling in water produced the highest capacity and best rate performance (148 and 50 mAh g^{-1} at 0.1 and 10 C , respectively) of the electrodes studied. Electrodes using NMP had similar capacity but inferior rate performance (147 and 20 mAh g^{-1} at 0.1 C and 10 C respectively), in agreement with the literature. Ultrasonic mixing in aqueous systems resulted in lower maximum capacity ($\sim 92 \%$) and rate performance inferior to slurry processing ($35\text{--}40 \text{ mAh g}^{-1}$ at 10 C). This may have originated from 'over-mixing' when active and insulating components

agglomerate to reduce electrode electronic and ionic conductivity, and/or a significant reduction in the size of CB agglomerates led to the loss of long range conductive bridging. Use of IPA in dilute LFP suspensions caused agglomeration of particles and resulted in severely reduced rate performance (10 mAh g^{-1} at 10 C). Both of these performance deficits were suggested to arise from poor physical contact between the active material and conductive additive, leading to electronically isolated regions of active material.

Initial deposition behaviour of suspensions and the tendency to form uniform electrode structures was determined mostly by the liquid solvent behaviour, although the mass/density of particles being deposited and/or their affinity to the binder may also play a role. Taking these effects into consideration and after optimisation, it was facile to manufacture reproducible LFP-based cathodes by spray deposition.

Ball milled LFP:CMC:CB aqueous slurries produced similar performance whether spray deposited or slurry cast at mass loadings of roughly 6 mg cm^{-2} ($\sim 148 \text{ mAh g}^{-1}$ and 50 mAh g^{-1} at 0.1 and 10 C , respectively). However, slurry cast electrodes formed cracks at all mass loadings between $1.5\text{--}10 \text{ mg cm}^{-2}$ and completely delaminated at $10\text{--}11 \text{ mg cm}^{-2}$ and $70\text{--}80 \mu\text{m}$ electrode thickness. This is known to be due to capillary pressure forming in the thick, drying coating. A critical cracking threshold, h_{max} , was estimated at $<10 \mu\text{m}$ for the LFP slurry used here, using a combination of analyses from literature and statistical image analysis. However, the layer-by-layer spray deposition technique was able to manufacture macro crack-free electrodes to apparently almost any practical thickness. This was because the critical cracking thickness (h_{max}) was not breached at any point because of the thin, layer-by-layer deposition and incremental, step-by-step drying nature of the process. A crack-free spray deposition-based electrode with a mass loading of 17.2 mg cm^{-2} and thickness of $115 \mu\text{m}$ maintained similar specific capacity and slightly lower capacity retention ($89 \pm 1 \%$) when compared with 6 mg cm^{-2} spray deposition-based and slurry cast electrodes ($92 \pm 1 \%$), but produced a significant improvement in volumetric capacity at rates between 0.1 and 2 C ($>\sim 30 \%$ at $0.1 - 2 \text{ C}$ currents).

This work shows that spray deposition can produce high performance electrodes with reproducible behaviour when compared with industry-type slurry cast counterparts. Layer-by-layer deposition can deposit electrodes to thicknesses above that of aqueous slurry casting without cracking or delamination. In the next chapter, layer-by-layer spray deposition is used to explore the effects of discretely layered particle size and porosity within LFP electrodes, and whether this provides benefits over uniform, single-layer electrodes.

Chapter 5

Spray deposition of layered LFP electrodes

5.1 Introduction

Overall Li-ion battery performance derives from compromises made between specific energy, specific power, cycle life, safety and cost. For example, in terms of electrode structure, specific energy can be increased by using a thicker electrode, due to a greater proportion of active material compared with inactive components. However, specific power will decrease due to increased diffusion lengths for Li ions in the electrolyte. Therefore, the performance of a battery is due not only to the combination and fraction of constituent electrode materials but also to their geometrical arrangement.

Due to the complex, multi-material (and porous) nature of the electrode structure, and the difficulty in directly measuring certain cell properties, significant modelling effort has been expended to understand better these inter-related factors governing overall performance. Unlike empirical models, such as equivalent circuit and neural network models, mechanistic models can provide insight into why and how certain parameters affect performance, albeit such models are often computationally expensive. For a complicated system like a LIB cell or even a single electrode, an efficient model will usually be tailored towards a specific purpose, and the insights gained will only be as good as the

particular model formulation, parameter estimation, input data, numerical implementation and simulation process. Physical experimental is usually necessary for model calibration and to estimate some key parameters not available from theory. Generally such models end up with a significant number of free or fitting variables.

Newman et al. developed the most established mathematical model for Li-ion cell processes, commonly referred to as the pseudo-two-dimensional (P2D) model [270–275]. The electrolyte is modelled using concentrated solution theory, which accounts for Li^+ and X^- transport [270]. The electrode is modelled as a homogenous multiphase system based on porous electrode theory i.e an array of spherical monodisperse particles of solid phase surrounded by the electrolyte phase [271, 272]. Zhang et al. improved computational efficiency and provided a basis for microscale modelling by developing the single particle model (SPM), where the electrode layer is represented by a single particle. The distribution of current, voltage and electrolyte concentration are ignored, so the isolated particle model is only valid for low C-rates, thin and highly conductive electrodes [182, 276, 277]. The P2D and SPM models have been extended further to predict geometrical, particle size distribution, thermal, SEI growth and stress effects on battery systems, and have been coupled with homogenisation techniques for multi-scale modelling of LIBs [278–288]. Although proven to be acceptably accurate for modelling the overall performance of common LIBs, homogenous models have drawbacks, including an inability to predict the degradation or dynamic effects triggered by local heterogeneity, which can lead to significant inaccuracy when modelling real cells under high current rates or long term cycling, and some difficulty in modelling materials with multiple solid phases during charge and discharge, such as LFP and graphite [289–292]. In response, heterogeneous models have been developed to provide insight into local effects that contribute to overall processes in LIBs [293–295]. However, due to their relative simplicity, efficiency and accuracy, combinations and variations of P2D and SPM models remain the most widespread in the literature.

For electrodes with uniform particle radii and porosity distributions, Fuller et al. used a P2M model to show that there was a relationship between increased thickness or decreased porosity in electrodes and the mobility of Li^+ in the electrolyte, which underpins the compromise between energy and power density [296]. Newman et al. showed that a P2M model could optimise electrode porosity and thickness to maximise specific energy for any discharge time [297].

From the limited understanding gained on the relationship between structure and performance in the rather limited design space of homogenous through-thickness properties, it has been suggested that deliberately layered, graded and low tortuosity structures (i.e. heterogeneous electrodes) may partly overcome the typically kinetic compromise between energy and power [298, 299]. Ramadesigan et al. used a 1D analytical model to optimise electrodes of a fixed amount of active material, and suggested that ohmic resistance and its variance in graded porosity electrodes could be reduced by 15–33 % and 40 %, respectively, compared with an optimised homogeneous electrode [300]. Golmon et al. developed a multiscale model based on P2M and SPM, which could model stress developed in particles during charge and discharge [301]. Increasing the porosity and particle size at the separator-electrode interface reduced the maximum stress in the cathode particles during the high reaction rate period, i.e. initial charge or discharge, and increased Li^+ concentration towards the current collector [302]. With a stress constraint, compared with a single layer optimised electrode, the porosity-only and porosity-particle size varying electrodes showed an increase in usable capacity of 67 % and 70 % in full cells. This model suggested that the effect of particle size position was negligible (at least in terms of their model) compared with much more pronounced effects due to variations in porosity [301]. Dai and Srinivasan argued that by removing the constraint on the thickness in the P2D model, as established in previous analyses [300, 301], there was no difference in the liquid phase polarisation or energy density of cells with uniform or non-uniform porosity [303]. Du et al. supported Dai and Srinivasan's findings, calculating that any specific

energy increase due to structuring was negligible, while a decrease in specific energy due to poor structuring can be substantial, i.e. a relatively low porosity fraction next to the separator [304].

Alternatively, some simulations have suggested that multi-layer electrodes may be effective at reducing phenomena associated with the ageing of LIBs. Meyer et al. modelled the state-of-charge (SOC) of large and small particles next to the separator and next to the current-collector concluding that large particles next to the separator might result in a more homogenous load and overpotential through the electrode thickness and potentially reducing ageing effects [305]. Taleghani et al. similarly found that larger particles next to the separator produced a more uniform SOC distribution, but regardless of the particle size, the layer next to the separator should always have a greater porosity than the layer next to the current collector to reduce potential and concentration drops in the electrolyte [306]. Suthar et al. used a P2D model with intercalation stress, Li plating and SEI side reaction sub-models to show that greater porosity near the separator in low tortuosity graphite anodes may not alter the discharge capacity but could reduce capacity fade, while both factors were improved in anodes with high tortuosity [307]. Muller et al. found that a graphite anode with greater porosity near the separator could avoid the 'sudden-death' effect, effectively doubling the cell life-time [308]. Qi et al. suggested that optimisation for a single objective function, i.e. only specific energy, artificially limited the advantages of multi-layer designs [309]. A two layer electrode could reduce ohmic resistance by 4.4 %, while a graded electrode may reduce it by up to 6.5 %. Compared with a uniform electrode, a two layer electrode had a lower ohmic resistance, a lower average overpotential and a lower standard deviation of the overpotential. Hosseinzadeh et al. used coupled 3D full cell and thermal models to suggest that a graphite anode with greater porosity at the separator gained 8 % and 2.6 % specific energy and power [310]. Although the specific energy of the cathode did not increase, one scenario showed a 4–14 % reduction in heat generation during discharge.

Despite the large number of simulation studies, experimental validation has been limited by manufacturing difficulties and compounding of variables, such as poor interfaces between layers in multi-layer slurry cast electrodes and an inability to vary particle size independently of porosity [311]. Liu et al. showed that a two layer $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode with greater porosity at the separator reduced capacity fade after 50 cycles by ~8 % in full cells and ~5 % in half cells compared to uniform electrodes. The improvement was suggested to be due to more uniform distribution of the SEI layer [312]. However, there were differences in the average porosity and the thickness of the conventional and layered electrodes, which is difficult to avoid and makes meaningful "back-to-back" comparison difficult. Aside from porosity and particle size, Cheng et al. showed that the power density and ageing of LFP/LTO full cells showed significant improvement when conductive carbon and binder were graded to greater proportions near the current collector in both electrodes, using a spray deposition technique [200, 201]. The improvement was suggested to be due reduced contact resistance and more uniform overpotential leading to a thinner SEI layer (assessed by X-ray photoelectron spectroscopy) formed during cycling.

The positioning of different particle sizes in different parts of the electrode from the experimental point of view has largely been overlooked, no doubt partly because of a lack of a suitable fabrication route. In this chapter, LFP cathode electrodes comprised two sub-layers, each with its own particle size distribution and porosity, were investigated and performance compared with a uniform, blended mixture of the same particles. LFP was selected as a model material due to its clearly defined voltage plateau and ohmic drop, associated with the ratio between particle surface area and volume, and its availability in different particle sizes. The porosity of the two layers after calendaring was different, which allowed for investigation of not only cathodes with greater porosity next to the separator (compared with a uniform electrode), as previously explored in the literature, but also electrodes of greater porosity next to the current collector, which are a relatively unexplored arrangement - especially experimentally.

5.2 Materials and methods

This section provides details of the methods specific to this chapter expanding on those already described in Chapter 3.

5.2.1 Powder characterisation

X-ray diffraction (XRD, D8, Bruker) was performed on as-received LiFePO_4 (LFP) powders from Hydro-Quebec (HQ) and MTI Corporation (MTI) between 2θ values of 10° and 90° . The morphology and size of primary particles of each powder was estimated from SEM images (6500F, JEOL).

5.2.2 Suspension preparation

Electrode layers were spray deposited from suspensions of LFP with mass fractions of 87:3:10 of active material (AM), binder (CMC; carboxymethyl cellulose salt) and carbon black (CB). LFP slurries were firstly mixed using ball milling (BM), as described by the BM route in Figure 4.2a in Section 4.2.1. Slurries of either MTI or HQ LFP were prepared at 350 rpm using 10 mm ZrO_2 milling balls and a two step mixing process: (1) CB and 2.5 wt.% CMC aqueous solution were mixed for 15 min, and then (2) LFP and DI water were added to the CB-based slurry and mixed for a further 15 min. In step (2), DI water was added until the slurry reached a mass concentration of 40 wt.%. The resulting slurry was then diluted further to 1 wt.% solid concentration using DI water and agitated by a magnetic stirrer for 2 hours immediately before spray deposition. A slurry containing both HQ and MTI was also prepared by BM, with the same overall HQ:MTI ratio as in the layered electrodes, which was determined to be approximately 47.5:52.5 % by mass.

5.2.3 Suspension characterisation

Suspensions were characterised using laser diffraction particle size analysis (Mastersizer 2000, Malvern Instruments) to assess the primary and/or secondary particle diameters of MTI and HQ LFP, and the stability of the suspensions after mixing, according to the method outlined in Chapter 3. The stability of suspensions was measured by particle size analysis at 30 minutes, 2 hours and 20 hours after dilution of the ball milled slurries and the suspensions were kept agitated by magnetic stirrer between measurements.

5.2.4 Electrode deposition and drying

Spray deposition was performed based on the approach described in Section 3.1.3. The temperature of the substrate was maintained at 130 °C, the flow rate of the suspension was $\sim 4.5 \text{ ml min}^{-1}$ and the atomisation pressure was 0.4 bar. For HQ-only and MTI-only electrodes, either the HQ or the MTI-based suspension was spray deposited until a thickness of $\sim 80 \mu\text{m}$ was reached. For the structured electrodes, termed MTI/HQ and HQ/MTI, based on deposition order of the two powders, $\sim 40 \mu\text{m}$ of either the MTI or HQ suspension was first deposited onto the current collector, and directly afterwards a second layer of HQ or MTI suspension was deposited to give a total thickness of $\sim 80 \mu\text{m}$ before calendaring. The $\sim 80 \mu\text{m}$ Mix electrode, based on a mixture of MTI and HQ LFP, was formed in a single operation from the mixed HQ + MTI suspension. After deposition, the Al foils coated with the different electrodes were removed from the heated substrate, calendared to the same average porosity and moved to a vacuum oven at 130 °C overnight before cell assembly.

5.2.5 Electrochemical characterisation

Electrochemical characterisation was performed using the methods previously described in Section 3.4. For rate capability, coin cells were galvanostatically charged and discharged for 5 cycles at various C-rates between 0.1 C and 10 C, then cycled 2 more times at 0.1

C. EIS measurements were performed after the relatively slow 0.1 C recovery cycles of rate cycling, in the discharged state between 1 MHz and 0.01 Hz. Long term cycling was performed at 0.5 C for 200 cycles after rate cycling and EIS.

The plateaux within the LFP voltage profiles were analysed by dQ/dV analysis for both rate and cycle data. For voltage profiles with two peaks, a merged peak was calculated by using the matlab function 'interp1' with a spline to coarsen the discharge profile, gaussian smoothing was applied, then the dQ/dV profile was calculated, and 'interp1' with a spline was applied again to interpolate the position of the merged peak. The Matlab function islocalmax/islocalmin were used to identify peaks and make sure there were no erroneous peaks identified.

5.3 Results and discussion

As discussed previously, experimental work on through-thickness structuring of Li-ion electrodes has mostly focused on two-step deposition/calendering of slurry cast electrode layers, with a different volume fraction of porosity in the two layers. Experimentally a layered electrode with a higher relative fraction of porosity in the "top" layer is relatively simple to achieve, and has been suggested to be beneficial when compared with a conventional uniform electrode [300, 306–309, 312, 313]. However, the performance of a structure involving a simple reversal of the two layers has not been reported. In addition, some studies have suggested that binder and conductive additive migration during drying, and the two-step calendering process of two-layer structured slurry cast electrodes, may lead to delamination and/or increased resistance at the internal inter-layer interface [311, 314].

Figure 5.1 shows schematic cross-sections of electrodes with uniform (at the electrode thickness scale) and various deliberate heterogeneous arrangements of sub-layers with different porosity fractions. Figures 5.1a-c show electrode structures that might be achieved in a single deposition step and a single calendering step. In previous studies, to achieve the

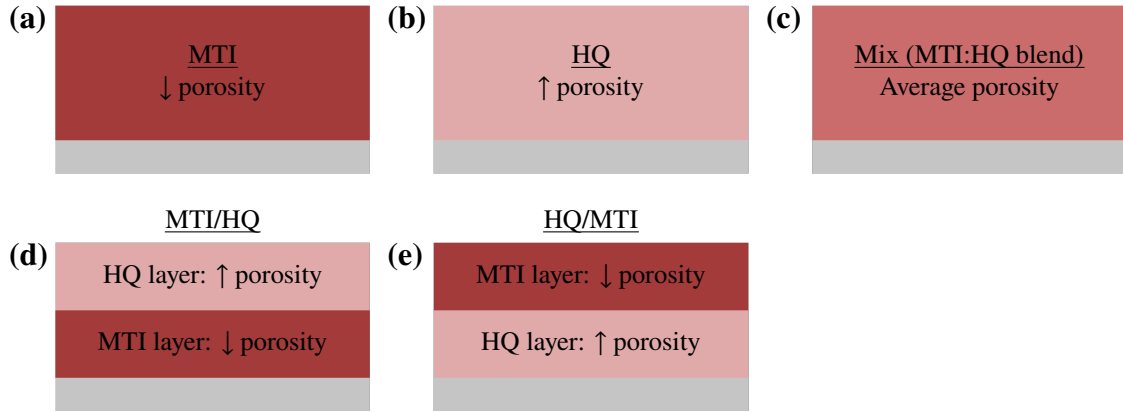


Figure 5.1: Schematic cross-sections of electrodes with homogenous and heterogeneous through-thickness porosity profiles: (a) homogeneous and relatively low porosity fraction, (b) homogeneous and relatively high porosity fraction, (c) homogeneous, average porosity, (d) heterogeneous porosity, with a lower porosity layer on the current collector and a higher porosity layer next to the separator and (e) heterogeneous porosity with the layers of (d) but reversed in order of deposition.

porosity profile shown in Figure 5.1d, the first layer was deposited, calendered, and then a 2nd layer was deposited and calendered to a lesser degree to create a difference in porosity between the two layers. However, using the same approach to achieve the (inverse) porosity profile shown in Figure 5.1e, the more severe calendering step to achieve the lower relative porosity of the 2nd, top layer would induce further deformation (and reduction in porosity) in the prior, more weakly calendered lower layer. This sequence would then simply result in the uniform porosity profile shown in Figure 5.1c. In this thesis, a different approach is taken in that the two layers comprised different particle diameters (HQ and MTI LFP powders), which calendered to slightly different porosities, regardless of whether in the lower or upper layer. Thus, all arrangements (a) to (e) were achieved.

Overall, the effect of two coupled variables on the electrochemical performance of layered electrodes were assessed: the through-thickness distribution of 1) particles of differing diameter (different surface area to volume ratio) and 2) the porosity, compared with mixed electrodes of the same materials. Although the electrodes here were manufactured using the layer-by-layer spray deposition technique, manufacture of similar electrodes might also be practical with slurry deposition [312].

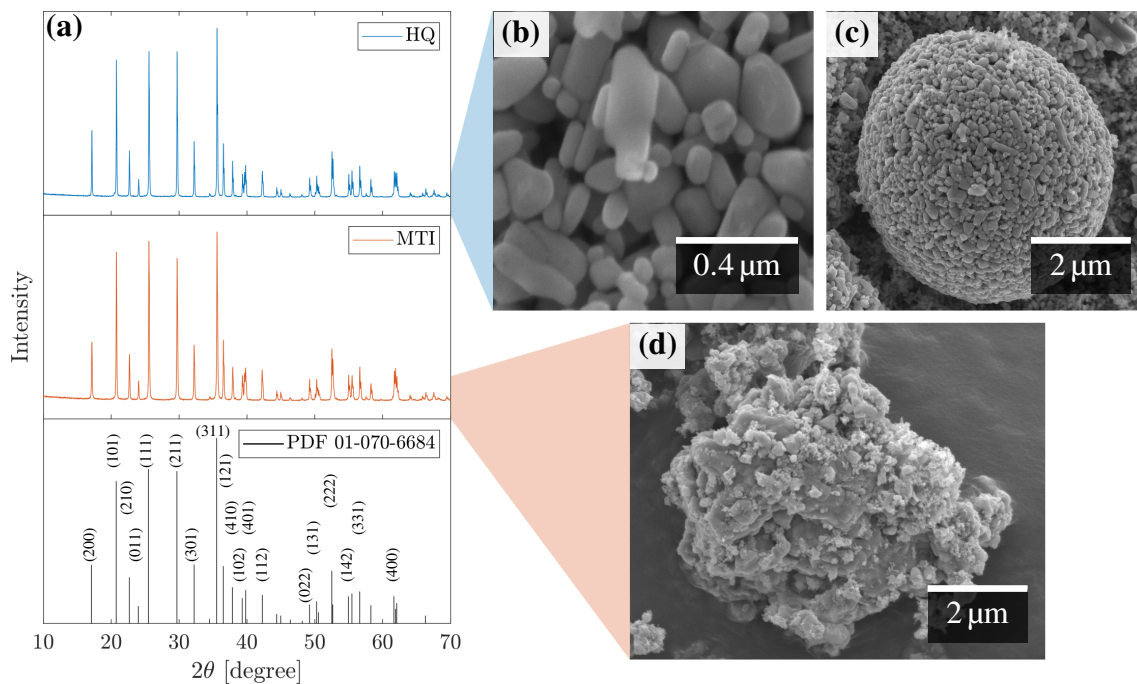


Figure 5.2: XRD and planar SEM micrographs of HQ and MTI LFP powders: (a) XRD spectra, from top to bottom, of HQ, MTI and the LFP powder reference peaks, (b) HQ primary particles, (c) HQ secondary particles and (d) MTI particles.

5.3.1 Powder characterisation and suspension properties

Figure 5.2a shows XRD spectra of the HQ and MTI supplied LFP powders, and the reference powder diffraction file for LiFePO_4 (Triphylite, PDF 01-070-6684). HQ LFP contained a non-stoichiometric minor phase of Fe_3PO_7 , while MTI contained both Fe_3PO_7 and $\text{Li}_{0.6}\text{FePO}_4$. However, based on the weak peak intensities, these minor phases were likely present only in negligible fractions. Overall, the HQ and MTI powders were judged crystallographically similar.

Primary particle size was assessed by SEM, as shown in Figure 5.2b-d. HQ LFP comprised primary particles, shown in Figure 5.2b, that were 50–200 nm in their smallest dimension. The smooth primary particles formed porous, spherical secondary particles that were several microns in diameter, as shown in Figure 5.2c. MTI LFP particles, in Figure 5.2d, consisted of rough-surfaced aggregates, estimated to be in the size range of 500 nm to several microns in diameter.

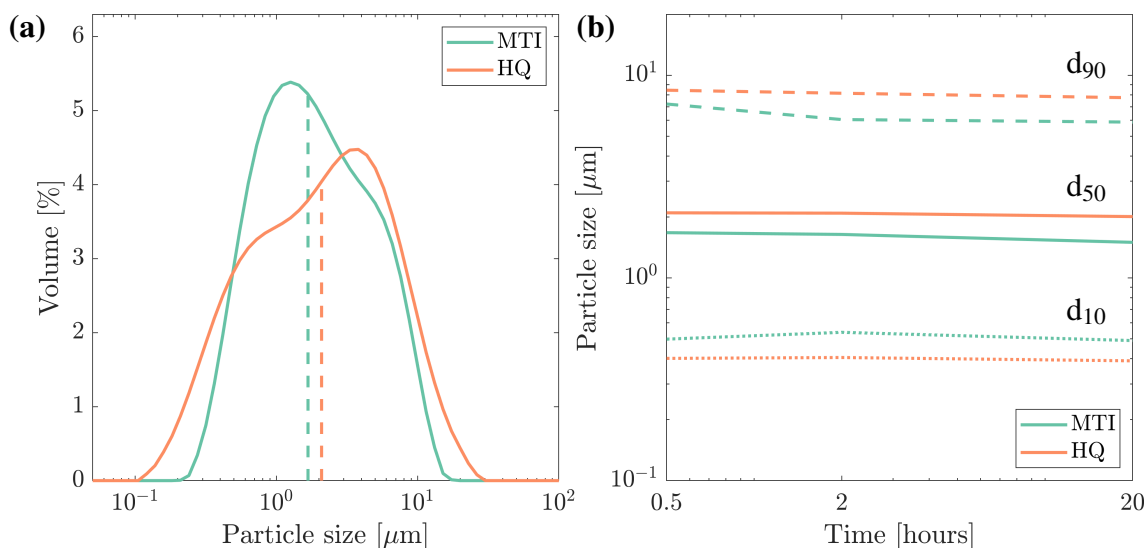


Figure 5.3: Particle size analysis of MTI and HQ LFP powders mixed with CMC and CB in a 87:3:10 ratio: (a) particle diameter distributions after 2 hours of mixing on a magnetic stirrer and (b) d-values of suspensions over a period of 20 hours.

Suspensions of MTI and HQ LFP were characterised using dynamic light scattering (DLS) to compare particle size distributions (PSD) and suspension stability, as shown in Figure 5.3. Suspensions had the same mass ratio of constituent materials as those used to manufacture electrodes. Figure 5.3a shows that the suspended particles/agglomerates in the MTI and HQ suspensions had similar mean particle diameters of ~1.6 and ~2 μm, respectively. Considering the same two-step ball mill mixing technique was used to produce the suspensions, the carbon black distribution was expected to be similar for both powders and any significant differences in the particle size distributions (PSDs) were due to the differences in the active material distribution. The HQ powder produced a slightly broader distribution, with a minimum particle diameter of 0.1 μm, which was consistent with the SEM observations, and a maximum secondary particle diameter of up to 20 μm, which was consistent with the manufacturer information. Therefore, although there was a significant difference in primary particle diameter between the two powders, the secondary particle diameters were approximately similar.

Figure 5.3b shows measurements of d₁₀, d₅₀ and d₉₀ powder diameters for MTI and HQ suspensions after ball mill mixing, measured at 0.5, 2 and 20 hours during agitation

Table 5.1: Thickness, areal density and estimated porosity of electrodes MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI. Error bars equal 1 standard deviation from the mean.

Electrode ¹	Thickness ² (μm)	Areal density (mg cm^{-2})	Porosity ² (%)
MTI-only	63 ± 1	10.0 ± 0.1	52.5 ± 0.8
HQ-only	68 ± 1	9.5 ± 0.1	58.0 ± 0.7
Mix	64 ± 1	9.6 ± 0.1	54.9 ± 0.7
MTI/HQ	66 ± 1	10.0 ± 0.1	54.8 ± 0.7
HQ/MTI	65 ± 1	9.8 ± 0.1	54.9 ± 0.7

¹ MTI-only = MTI powder only, HQ-only = HQ powder only, Mix = MTI:HQ blend, MTI/HQ = MTI then HQ layered, and HQ/MTI = HQ then MTI layered.

² After calendering.

with magnetic stirring. The suspended particles had approximately stable diameters over the period, with only a slight shift towards smaller particle diameters in the first 2 hours. Therefore suspensions were stirred for 2 hours before spray deposition to allow for an approximately steady suspension state.

5.3.2 Physical properties of electrodes

Spray deposited electrodes were characterised by mass, thickness and areal density. Each layered electrode, as shown in Figures 5.1d and e, were designed to have the interface boundary between layers at the same through-thickness position, and the overall mass ratio of MTI:HQ was 52.5:47.5 wt.%, regardless of sub-layer position. The ‘Mix’ electrode, shown schematically in Figure 5.1c, was sprayed from a single suspension of MTI:HQ with the same mass ratio.

Table 5.1 shows the physical properties of spray deposited electrodes after calendering. MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI electrodes had thicknesses of 63, 68, 64, 65 and 66 μm , areal densities of 10, 9.5, 9.6, 10, $9.8 \pm 0.1 \text{ mg cm}^{-2}$, and porosities of 52.5, 58, 54.9, 54.8 and 54.9 %. The thickness ($65 \pm 1 \text{ }\mu\text{m}$) and areal density ($9.8 \pm 0.1 \text{ mg cm}^{-2}$) of the HQ/MTI electrodes were approximately the mass weighted average of the MTI-only

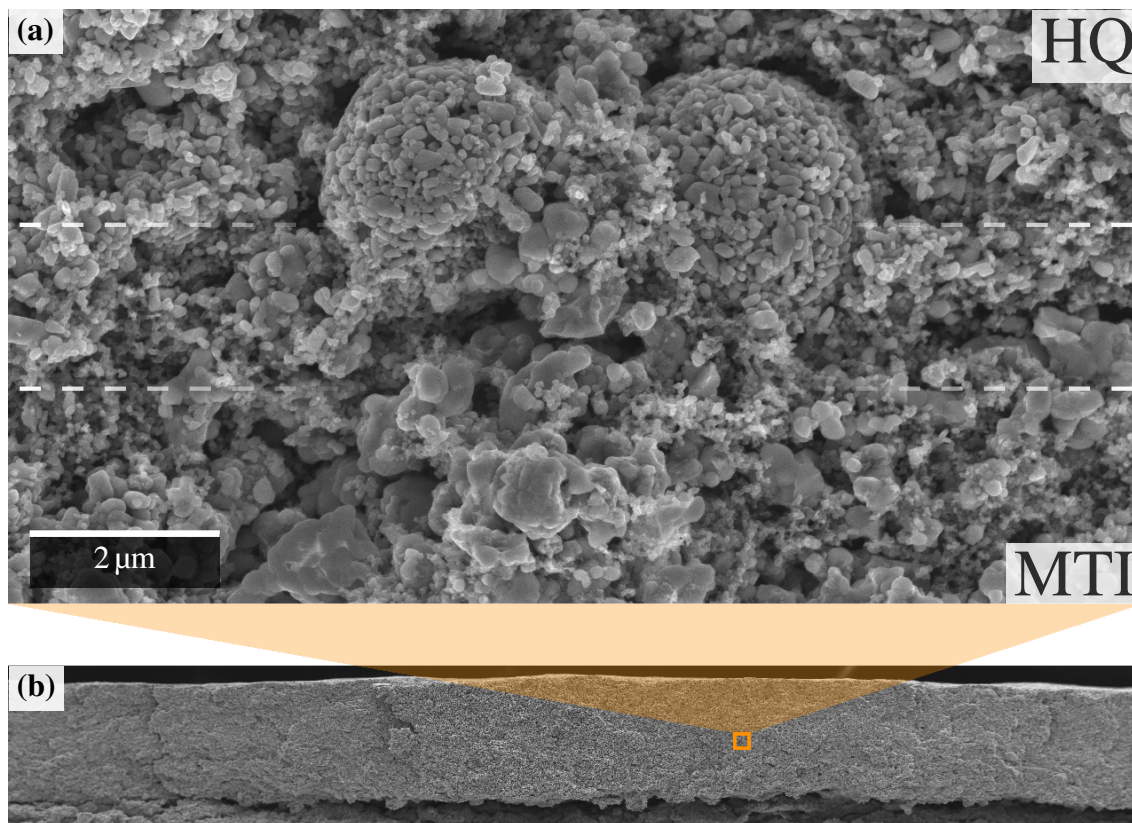


Figure 5.4: Cross-section of a calendered MTI/HQ electrode, consisting of lower layer of MTI LFP particles on the current collector and an upper layer of HQ LFP particles, at (a) higher and (b) lower magnification.

and HQ-only electrodes. The average porosity of electrodes correlated with the average primary particle diameter: the greater diameter MTI-only electrode calendered to a lower porosity of 52.5 %, while the smaller diameter HQ-only electrode calendered to a higher porosity of 58 %, and the Mix, HQ/MTI and MTI/HQ electrodes, as might be expected, calendered to a porosity in between at $\sim 55 \pm 1$ %.

The calendered MTI/HQ electrode was cross-sectioned by manual mechanical fracture to observe the internal sub-layer boundary, as shown in Figure 5.4a. There was slight inter-mixing zone between the HQ and the MTI layers, of $\sim 2 \mu\text{m}$ thickness. At a lower magnification, as shown in Figure 5.4b, the calendered electrode had a relatively uniform thickness, at least over this frame width of $500 \mu\text{m}$.

5.3.3 Electrochemical properties of electrodes

Electrochemical properties of the LFP electrodes were studied at low current density, high current density and under sustained longer term cycling, and the relationship to the electrode structure is discussed. LFP, within a near 'zero current' (i.e. a low current density approximating no distance effects), has a distinctive flat voltage plateau [315]. This plateau results from the two-phase reaction that occurs with (de)insertion of Li within the active material. An LFP particle can be thought to be 'stable' in the solid solution region where x is approximately <0.05 or >0.95 in $\text{Li}_{1-x}\text{FePO}_4$, with an 'unstable' spinodal region in-between. There is an energy barrier to overcome to enter into the spinodal region, but once accessed there is a strong driving force to continue (de)insertion until the stable region on the other side of the spinodal region is reached [316]. There is evidence that this energy barrier is overcome due to surface adsorption induced coherency strain, which leads to the barrier to enter the spinodal region scaling with the volume to surface area ratio of the active particles [317]. Therefore, the voltage plateau can only be flat with a single particle size and no distance effects, such as concentration polarisation [318]. For LFP with a particle size distribution, the voltage plateau, and hence the transformation, is spread over a sloped voltage profile, which depends on the width of the particle size distribution and the thickness of the electrode. Traditional cathode particles react via solid solution reaction, and at low current density the distribution of current over the cell is homogenised (as concentration polarization nears zero) and near 100 % of active particles are active. For LFP, at low current densities, only a small proportion of LFP particles are able to transform, as the energy barrier of larger particles is not met, so the current is not homogeneously distributed [319–321]. Based on this, it has been predicted that a bimodal distribution of LFP would result in a voltage profile with two voltage plateaus, one for lithiation of smaller particles and one for lithiation of larger particles [318].

Rate testing – The rate performance of cells was assessed between 0.1-10 C, as shown in Figure 5.5. The error bars represent a 2σ deviation from the mean. Figure 5.5a shows

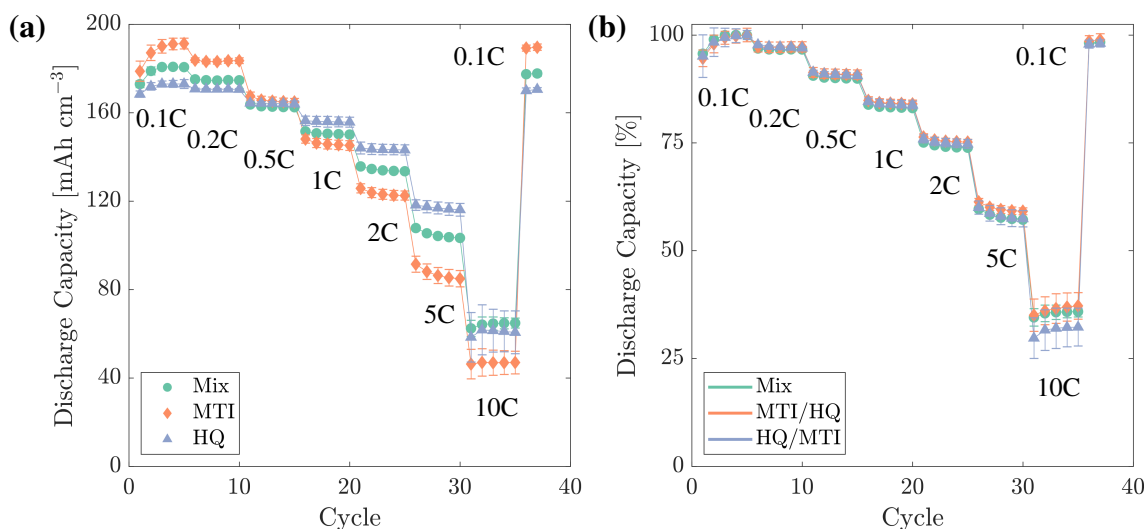


Figure 5.5: Galvanostatic rate cycling comparisons of MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI electrodes between 0.1-10 C with (a) Mix, MTI-only and HQ-only in terms of volumetric capacity and (b) Mix, MTI/HQ and HQ/MTI in terms of capacity relative to their 0.1 C capacity.

the capacity of MTI-only, HQ-only and Mix electrodes as C-rate was increased. The volumetric capacity at 0.1, 0.2, 0.5, 1, 2, 5 and 10 C was: 191, 184, 165, 145, 122, 85 and 47 mAh cm⁻³ for MTI-only; 173, 171, 164, 156, 143, 116 and 61 mAh cm⁻³ for HQ-only; and 181, 175, 163, 150, 134, 103 and 65 mAh cm⁻³ for Mix. MTI-only electrodes had a slightly higher capacity by volume than HQ-only electrodes between 0.1 and 0.5 C because of the slightly lower porosity (52.5 vs 58 %). However, the smaller particle size of HQ-only provided 7, 17, 37 and 29 % greater volumetric capacity than MTI-only at the higher rates of 1, 2, 5 and 10 C. The improved rate performance of HQ compared to MTI can be related to the lower particle size, and consequently smaller diffusion distances for full intercalation within the particles. To estimate whether the Mix electrode performed similarly to an average of HQ-only and MTI-only electrodes, the weighted average performance based on a 52.5:47.5 MTI:HQ electrode was calculated. Between 0.1 and 5 C, Mix performed at 100 ± 2 % of the expected average rate performance. The 10 C capacity of HQ-only was due to poorly performing cells and was judged an outlier.

Figure 5.5a shows the percentage of 0.1 C capacity retention of Mix, MTI/HQ and HQ/MTI electrodes as C-rate was increased. Between 0.2 and 10 C, the capacity retention

of Mix was 97, 90, 83, 74, 57, 36 %; MTI/HQ was 97, 91, 84, 75, 59, 37 %; and HQ/MTI was 97, 91, 84, 75, 57, 32 %, respectively. Applying a 2σ confidence interval, MTI/HQ performed slightly better than Mix at 2 and 5 C, while the difference between MTI/HQ and HQ/MTI did not reach 2σ at any rate, even though HQ/MTI had a lower average capacity at all rates.

Low current density – Figure 5.6b shows that the voltage profiles of HQ-only and MTI-only electrodes were typical of LFP particles at 0.1 C, where, upon discharging, the voltage drops to ~3.4 V and remained approximately constant until the current limit was reached, leading to a sharp decline in voltage. The voltage plateau of the MTI-only electrode at 3.393 V (± 1 mV) was lower than that of the HQ-only electrode at 3.407 V (± 1 mV), as expected from the larger particle size [317].

Mix, HQ/MTI and MTI/HQ electrodes had an initial plateau at a potential similar to that of HQ-only. At ~45 % capacity, there was a relatively sharp drop in voltage to a second plateau at a potential similar to that of MTI-only. The voltage step aligns quite well with the estimated mass ratio of 47.5/52.5 for HQ and MTI in the structured electrodes. The shape of these voltage profiles suggests that the two-particle electrodes discharge the majority of HQ particles before the MTI particles, i.e. in sequence based on particle size.

Figure 5.6e is a schematic of the process of sequential discharge of different particle sizes. Two voltage profiles are shown, relating to the discharge of MTI/HQ (orange, higher initial voltage) and HQ/MTI (green, lower initial voltage). The HQ particle layer in MTI/HQ was near the separator, while the HQ particle layer in HQ/MTI was near the current collector. Since the HQ particles in HQ/MTI were further away from the lithium source, the discharge plateau associated with HQ occurred at a slightly lower voltage, as shown in Figure 5.6c. In this case the top layer of MTI particles in HQ/MTI could be thought of as increasing the thickness of the separator layer. Once many HQ particles are discharged, the reaction current cannot be supplied by HQ particles alone and in response the voltage drops further to a point where the barrier to enter the spinodal region of larger

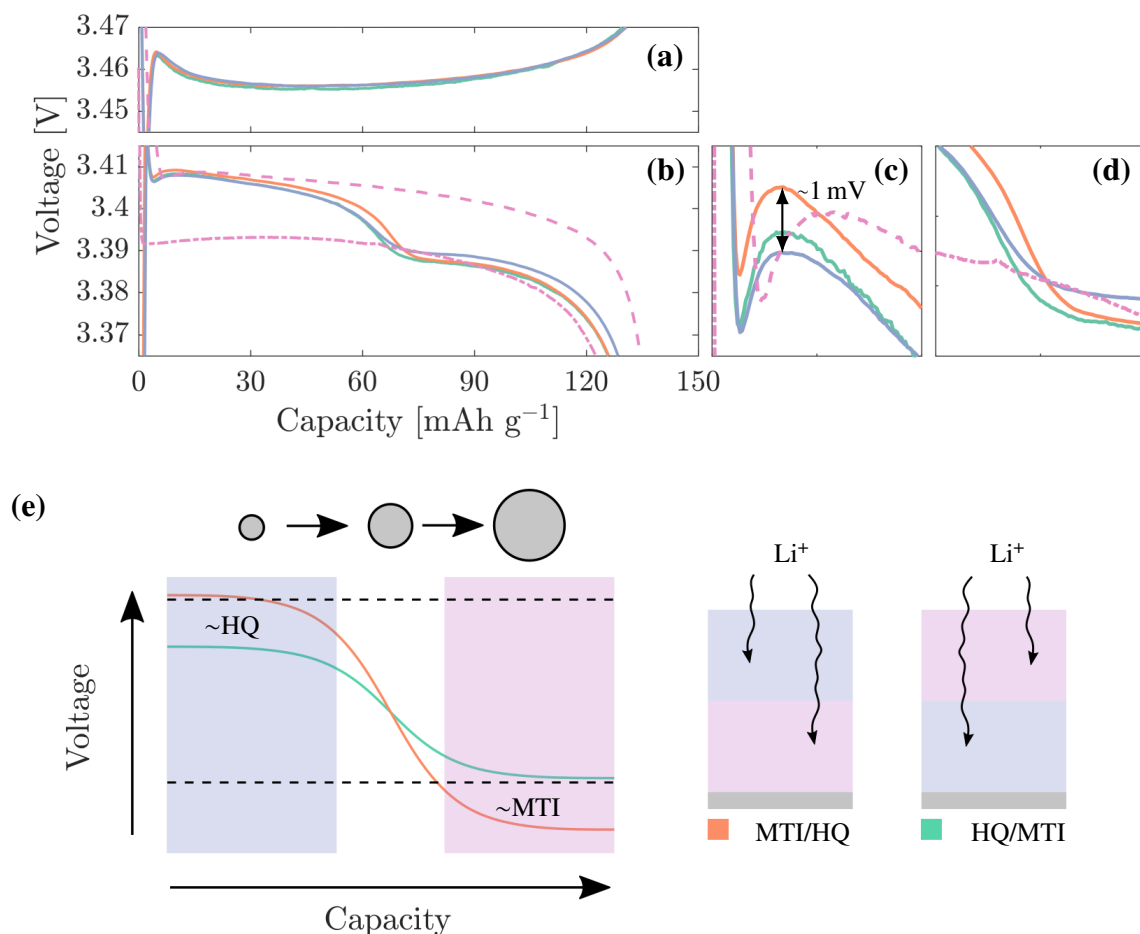


Figure 5.6: Voltage profiles of MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI electrodes cycled between 2.6 and 4 V showing (a) the charge step and (b) discharge step at 0.1 C, zoomed in views of (c) the reaction onset voltage during discharge and (d) the kink observed in electrodes containing both HQ and MTI particles. A schematic is shown in (e) relating the voltage profile shape to the position of the HQ and MTI particles in the two-layer electrodes.

MTI particles is overcome, leading to the development of the second voltage plateau. In MTI/HQ, the MTI particle layer was near the current collector, so a larger voltage drop was observed than in HQ/MTI, as shown in Figure 5.6d. Therefore, the HQ/MTI had a narrower distribution of overvoltage throughout discharge, but, at least at low rates, the same average potential as MTI/HQ and Mix. Although the difference between the plateaux of MTI/HQ, Mix and HQ/MTI was relatively small at 0.1 C, dQ/dV analysis shown later shows this pattern at 0.2 - 1 C also.

Interestingly, only a single voltage plateau was observed during charge in the Mix,

HQ/MTI and MTI/HQ electrodes, as shown in Figure 5.6a. Based on the dQ/dV analysis, it was found that the average difference in voltage between the HQ-only and MTI-only dQ/dV peaks upon discharge was 14 mV at 0.1 C, while during charge it was only 2 mV. Therefore, during charge, the SOC increased more simultaneously than sequentially in the Mix, MTI/HQ and HQ/MTI electrodes at all current densities. It is not clear why this asymmetry between charge and discharge exists, however recent studies on size-dependent phase morphologies may provide suggestions. It has been shown that the phase morphology of LFP particles during discharge and charge varies with particle size. Below 200 nm, the phase morphology of LFP has been observed to be symmetric during charge and discharge, i.e. the particle core is delithiated while the perimeter is lithiated at 50 % lithiation [322]. For particles above 200 nm, morphological asymmetry was identified between charge and discharge, where discharge promoted a delithiated core, while charge promoted a lithiated core, especially at low current density. The difference in phase morphology is important as the Li diffusion activation energy for LiFePO_4 and FePO_4 are significantly different, at 0.5 eV and 0.27 eV, respectively [323]. It may be that during charge the Li extracted from the lithiated core of the micron sized LFP particles (MTI) can diffuse through the low activation FePO_4 phase, while the opposite may be true during discharge. For HQ, a roughly symmetric response to charge and discharge might be expected due to the <200 nm particle size. However, the phase morphology and (de)insertion mechanisms are complex and further study is required to understand the mechanism without significant assumptions.

High current density – Figure 5.7 displays the voltage curves of electrodes between 3.41 and 3.24 V at (a) 1 C and between 3.41 and 2.6 V at (d) 5 and 10 C. At 1 C, the voltage step was difficult to identify in HQ/MTI, and was less pronounced in MTI/HQ and Mix. The second plateau of MTI/HQ and Mix still roughly occurs at the same potential as the MTI-only voltage plateau. By 5 to 10 C, the voltage step cannot be identified by eye in any of the discharge profiles.

To more accurately identify the relative position of the voltage plateaux of each electrode

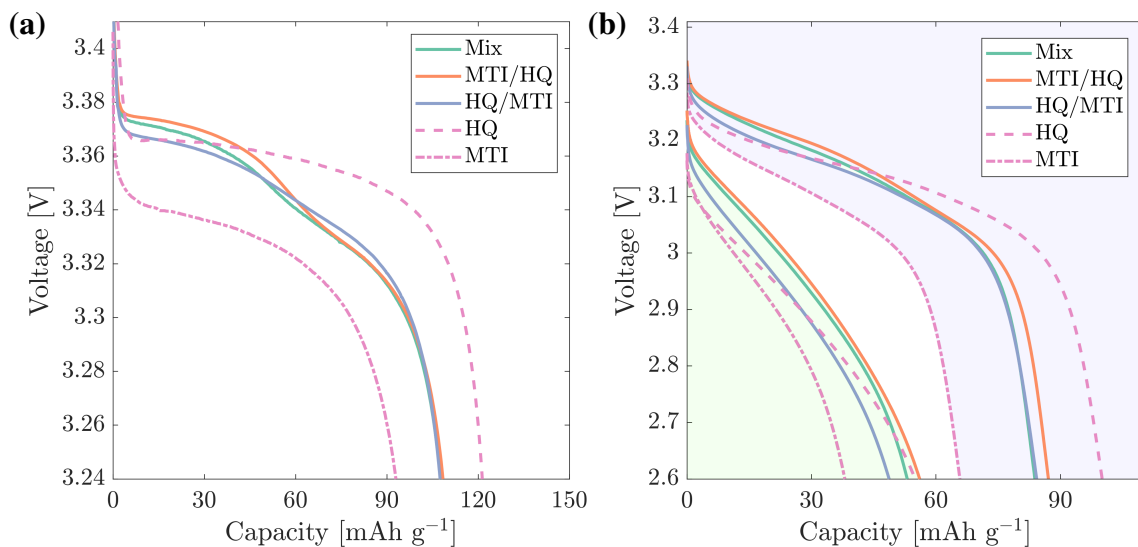


Figure 5.7: Voltage profiles of MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI electrodes cycled between 2.6 and 4 V at (a) 2 C, and (b) 5 and 10 C. Note that the voltage range displayed for (a) is 3.24–3.41 V, while for (b) it is 2.6–3.41 V.

as current density increased, dQ/dV analysis was employed, as shown in Figure 5.8. In Figure 5.8a and b, the two plateaux in the Mix electrode were identified as separate peaks, with the first peak being sharper and higher in magnitude than the second peak, perhaps arising from a narrower primary particle size distribution in the HQ material. A merged peak was calculated so that an overall potential could be determined for the electrodes with two peaks during discharge.

Figures 5.8c-e show the dQ/dV peak potential, P_1 , P_2 and P_c for Mix, MTI/HQ and HQ/MTI electrodes between 0.1 and 10 C. MTI-only and HQ-only electrode peak measurements were provided for comparison, however HQ was not included at higher rates as the cells had significant outliers. As current density increased, P_1 decreased, as shown in Figure 5.8c. The decrease in P_1 with current rate was expected due to increased polarisation losses, i.e. surface and concentration overpotential. MTI/HQ had the highest P_1 at all tested rates with 3.408, 3.404, 3.391, 3.370, 3.330, 3.205 and 3.091 V, Mix was slightly lower with 3.407, 3.403, 3.389, 3.369, 3.326, 3.187 and 3.073 V, and HQ/MTI was substantially lower with 3.407, 3.402, 3.386, 3.362, 3.310, 3.149 and 2.999 V. The difference between MTI/HQ and HQ/MTI at 10 C was significant, with the voltage peak

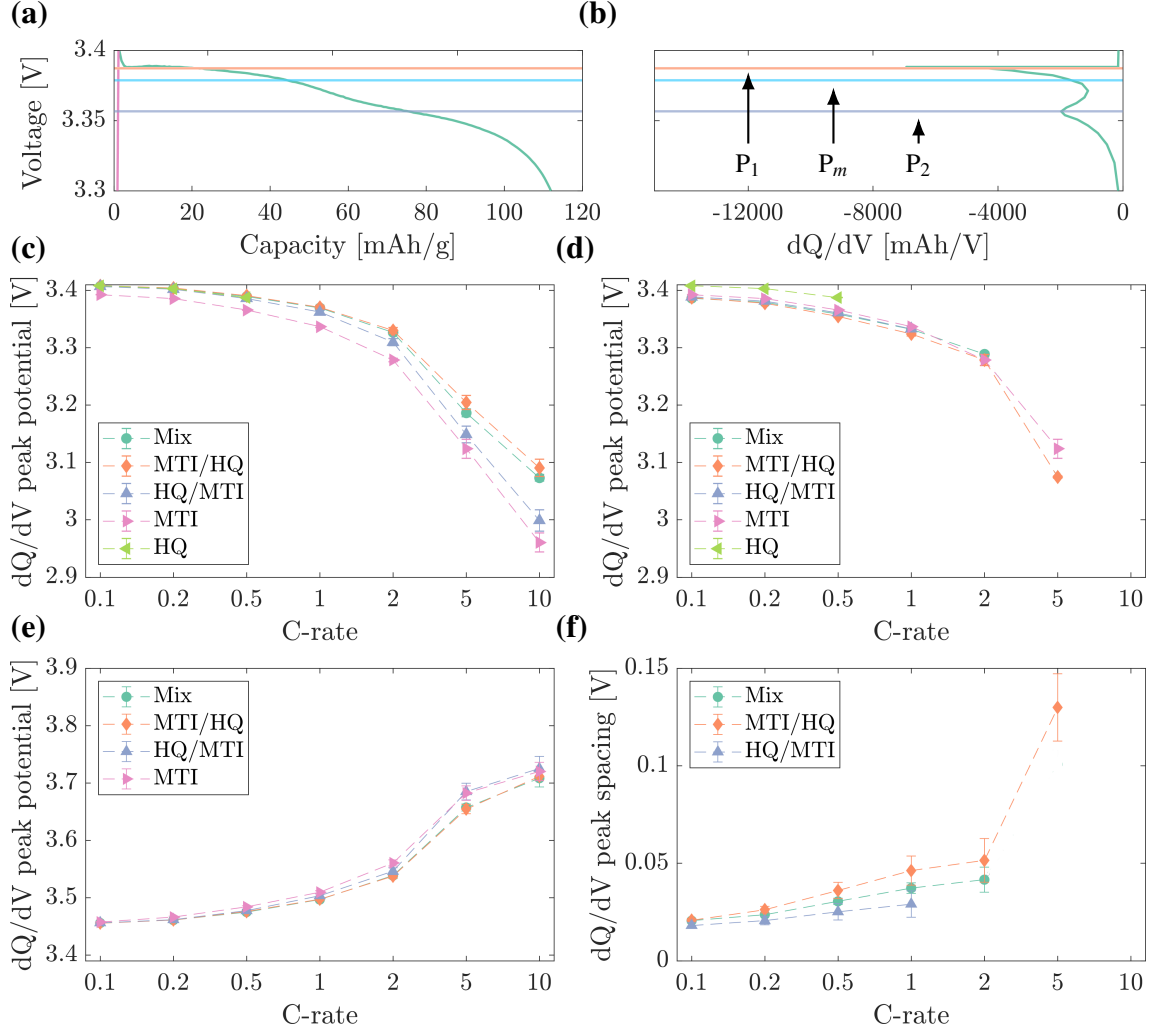


Figure 5.8: dQ/dV analysis of electrodes between 0.1 and 10 C. (a) A discharge voltage profile of the Mix electrode at 0.5 C side-by-side with (b) the corresponding V vs dQ/dV plot. The MTI electrode discharge peak potential is provided as comparison (P_m). The first peak potential during discharge (P_1) is shown in (c), the second peak potential during discharge (P_2) is shown in (d) and (e) shows the charge peak potential of Mix, MTI/HQ and HQ/MTI (P_c). The difference between the potential of the first and second peak in Mix, MTI/HQ and HQ/MTI is shown in (f). The first peak potential of HQ is included in (d) to provide a visual comparison.

for HQ/MTI almost ~90 mV lower.

Figure 5.8d shows the second dQ/dV peak potential for Mix, MTI/HQ and HQ/MTI electrodes. P_2 follows the opposite pattern compared to P_1 , where HQ/MTI had the highest potential with 3.389, 3.381, 3.361 and 3.333 V, Mix was similar with 3.386, 3.379, 3.359 and 3.332 V, and MTI/HQ was slightly lower with 3.387, 3.378, 3.355 and 3.324 V.

The relationship between P_1 and P_2 is shown in Figure 5.8f. A second peak could only be measured for HQ/MTI until 1 C, for Mix until 2 C, and for MTI/HQ until 5 C. As observed earlier from the voltage profiles, the plateaux of HQ/MTI had a smaller difference in voltage than those of MTI/HQ at all measurable current densities, while Mix was situation between the two, due to its random distribution of the two particle types.

Based on the sequential loss of the second dQ/dV peak, it could be that the discharge transitions from a sequential, particle size-based process to a simultaneous, reaction front process [319–321, 324]. As current density increases, transport limitations set in, which leads to a concentration gradient of Li^+ forming across the cell. In the cathode, the electrolyte near the separator will be able to maintain a higher ion concentration, and hence higher current density than electrolyte near the current collector [306]. In the case of HQ/MTI, this means that larger particles near the separator may be able to transform at the same time as smaller particles near the back of the electrode, where Li^+ ions are depleted and the Li ion flux into active particles cannot maintain the required current. This can be described in the voltage profile as the least favourable HQ transforming at a lower relative voltage, and the more favourable MTI transforming at a higher relative voltage, merging the voltage plateaux into a single entity. Therefore the voltage step became less defined as simultaneous discharging of MTI and HQ particles started to occur. In MTI/HQ, the HQ particle layer was near the separator, where Li concentration can be replenished more efficiently, so the sequential discharge process was maintained until slightly higher current densities.

Figure 5.8e shows the potential of the dQ/dV peak during the charge step of Mix,

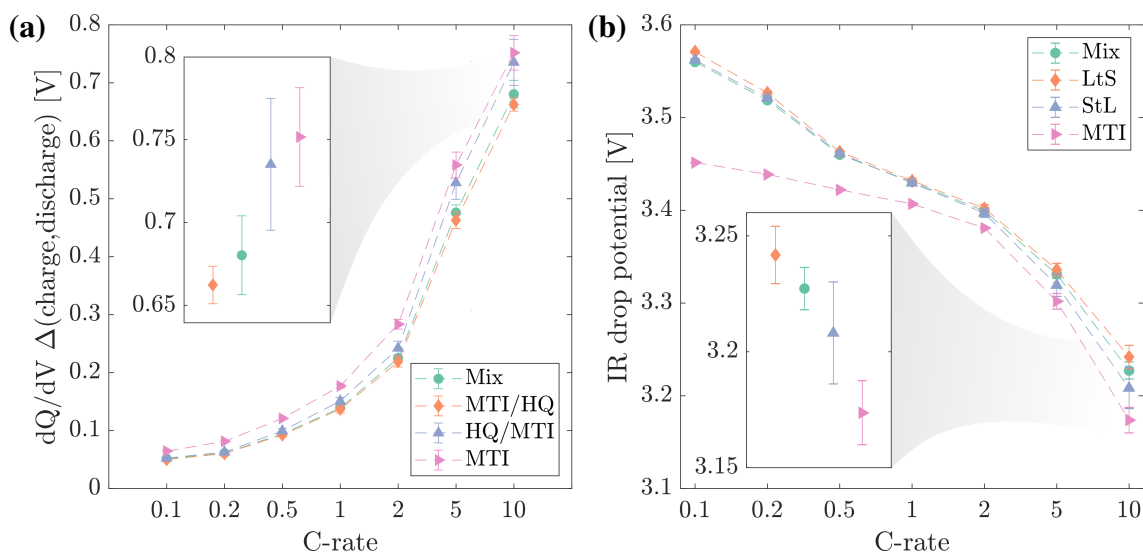


Figure 5.9: The difference between the charge and discharge steps measured by dQ/dV peak position in (a), and (b) the IR drop after charging between 0.1 and 10 C.

MTI/HQ, HQ/MTI and MTI. At low current density, all electrodes had the same dQ/dV peak potential at ~3.46 V during charge. As current density increases, there was a slight separation of MTI and HQ/MTI towards higher voltages, indicating slightly more resistance to charging than Mix and MTI/HQ.

Figure 5.9a shows the difference in voltage between the merged dQ/dV discharge peak and the charge peak of Mix, MTI/HQ and HQ/MTI between 0.1 and 10 C. The difference in voltage between the dQ/dV discharge and charge peak of MTI is provided for comparison. MTI/HQ had the lowest difference in voltage, with 50, 60, 92, 137, 219, 463, and 662 ± 11 mV, for Mix the difference was slightly higher, with 51, 61, 94, 139, 225, 476 and 680 ± 24 mV, while for HQ/MTI, the difference widens significantly, with 52, 63, 99, 151, 242, 527 and 735 ± 40 mV. Figure 5.9b shows the IR drop after charging between 0.1 and 10 C. A similar pattern is observed, where the drop is greater for HQ/MTI than MTI/HQ.

The difference between MTI/HQ and HQ/MTI could be due to two possible effects. Previous models calculated that greater porosity near the separator was an advantage in electrodes of two layers consisting of particles of different size [306]. The electrolyte near

the current collector maintained a higher Li concentration when the layer near the separator was more porous, which reduced the potential drop, aiding intercalation. The results found here align with this model, as a lower average overvoltage was measured for MTI/HQ than for HQ/MTI at all tested current densities. However, the difference in porosity near the separator was relatively small, with 58 % for the HQ layer in MTI/HQ and 52.5 % for the MTI layer in HQ/MTI.

Although Mix, MTI/HQ and HQ/MTI should have the same effective surface area, the distribution within the electrode was different. At high current density the depletion of Li ions in the electrolyte near the current collector may restrict intercalation into nearby HQ or MTI particles. This would result in loss of active HQ for HQ/MTI and loss of active MTI for MTI/HQ. In fact, the effective diffusion coefficient of LFP is found to be greater in smaller particles, due to the probability of 1D diffusion pathways being blocked by defects. In this case, the active surface area and average diffusion coefficient of the HQ/MTI electrode would be reduced more than that of MTI/HQ, even if other polarisation losses were equal. Therefore, the combination of lower porosity in the layer near the separator, and the greater loss of active surface area and effective diffusion coefficient near the current collector at high rates are likely both responsible for higher overvoltage observed in HQ/MTI.

Electrochemical impedance spectroscopy – EIS measures the resistive and capacitive response of a system to an external alternating voltage or current bias over a range of frequencies. In a Li-ion intercalation electrode, different kinetic and electrochemical mechanisms operate over different time scales, which can often be resolved using EIS. However, to quantify the magnitude of these respective mechanisms, an equivalent circuit model must be fitted to EIS data, the details (or elements) of which should be to some extent physically justified. Although EIS is a well-established technique within Li-ion battery research, the relationship between impedance response and physical mechanisms is still being refined, especially in the case of porous intercalation compounds [325–329].

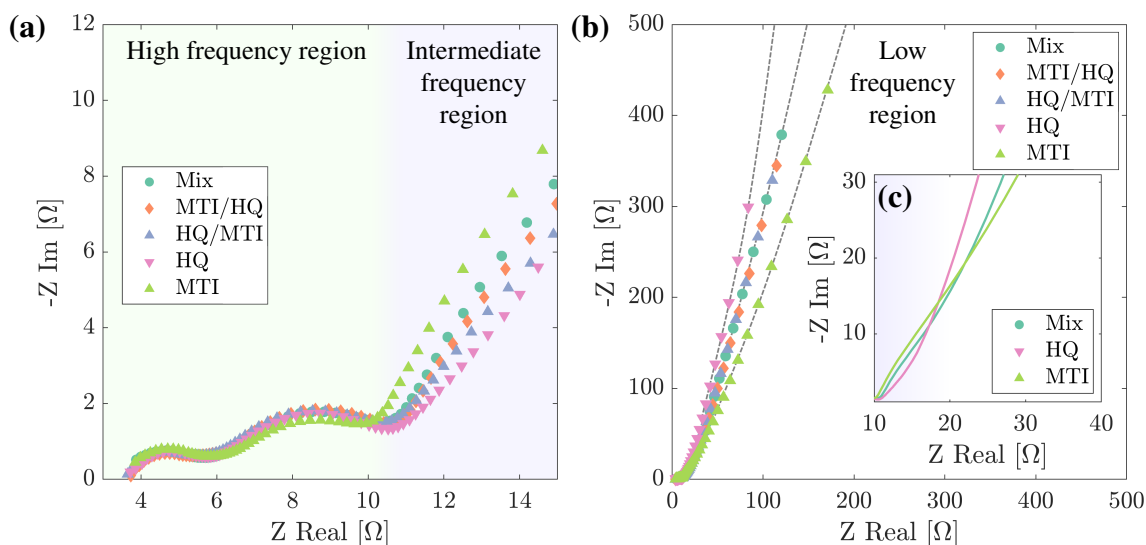


Figure 5.10: Electrochemical impedance spectroscopy measurements of MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI electrodes between 1-10⁶ Hz with a 10 mV perturbation after rate cycling. (a) The high and mid frequency response of cells, (b) the low frequency response and the mid-low frequency transition into a blocking condition (inset) and (c) the equivalent circuit model.

This is especially true of LFP-based cathodes, where several typical assumptions have been challenged in the last decade [325, 330].

EIS was performed on half cells after rate cycling with a two point potentiostat. The half cells were in a discharged state after rate testing and a 30 minute rest period, and then subsequently tested with a 10 mV perturbation between 0.1-10⁶ Hz. Figure 5.10a shows representative spectra of cells in the 1-10⁶ Hz frequency range. Several equivalent circuit models from the literature were fitted to the spectra, but the fits measured only small differences in several aspects between the electrodes [326, 328, 331]. Therefore, interpretation of the spectra is discussed based only on those differences judged significant. Furthermore, simple equivalent circuits may not be valid for porous electrodes consisting of multiple or graded layers with deliberately spatially varying microstructure and properties (porosity, tortuosity, conductivity, etc...), as equivalent circuits imply homogenous elements making up the electrode. Additional elements could be added to equivalent circuits for the hetero-electrodes but this simply increases the number of fitting parameters and lacks a strong justification for a particular element.

As shown in in Figure 5.10a, all electrodes displayed a similar EIS response, with two semi-circles followed by a near-linear diffusion "tail". The two semi-circles have previously and widely been attributed to impedance at the cathode-Al foil interface and at the solid electrolyte interphase (SEI) on the Li counter electrode [325, 326]. The charge transfer impedance at the electrolyte/particle interface is usually relatively low in LFP-based electrodes, and operates on a similar time scale to the anode SEI impedance and the transition to the diffusion region [326, 328].

All of the electrodes have an 'anomalous' diffusion region, as shown in Figure 5.10b, where the near-linear region deviated from the classic 45° semi-infinite Warburg slope [332]. The anomalous diffusion regime has been suggested to arise from particles with a distribution of diffusion lengths and a difference between the ionic diffusivity in the electrolyte and solid phases [327, 333]. It has also been suggested to strongly correlate with the tortuosity of the electrode [334]. The HQ-only electrodes response was steeper (i.e. more capacitive) than that of MTI-only electrodes, which likely corresponded to the smaller average primary particle size and greater porosity of the HQ-only electrodes, but may have been affected by variations in other unmeasured properties such as the pore size distribution and pore tortuosity [327, 333–338]. Based on this, it follows - and as observed - that the gradients of the near-linear regions for the two-powder electrodes Mix, MTI/HQ and HQ/MTI were between those of the HQ-only and MTI-only electrodes.

Therefore, although the EIS response of cells qualitatively showed differences between the tested electrodes in the intermediate to low frequency region, any further analysis should depend on identifying a valid equivalent circuit (or alternative) description of the multi-layer porous electrodes. Using a reference electrode to remove the contribution of the Li anode from the overall cell response may considerably improve the information gained from the technique.

Long term cycling - Cells were cycled for 200 cycles at a rate of 0.5 C directly after the EIS measurements, as shown in Figure 5.11. The initial 0.5 C capacity of each cell was set

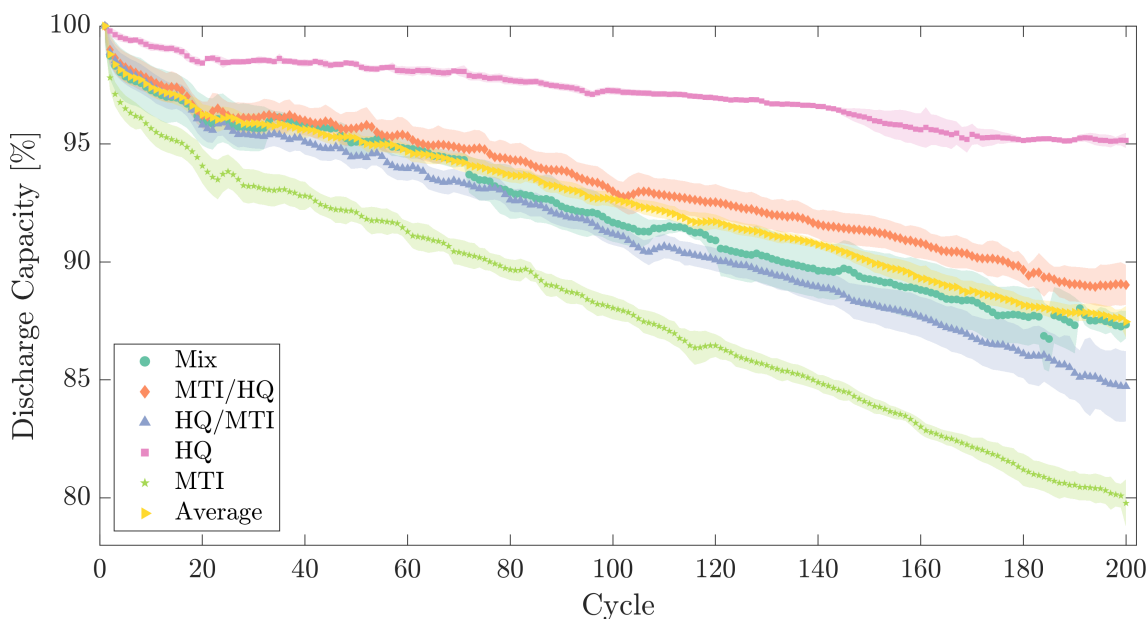


Figure 5.11: Long term galvanostatic cycling of MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI coin cells at 0.5 C for 200 cycles with a 95 % confidence interval shown by the shaded area. An "average" trace based on the MTI-only and HQ-only electrode traces was calculated for comparison to the two-powder structured and powder mix electrodes.

as the 100 % capacity, and subsequent cycle capacities were expressed as a percentage of this initial capacity. The shaded area surrounding the respective discharge capacities of each set of electrodes shows a confidence interval of 95 %.

The final capacities of MTI-only, HQ/MTI, Mix, MTI/HQ and HQ-only electrodes were 80, 85, 87, 89 and 95 %, with a MTI-HQ average of 87 %. As expected from the rate performance and cell voltage profiles, HQ-only had a significantly lower capacity loss per cycle of 0.022 % compared with MTI-only of 0.083 %, i.e. approximately a factor of four difference. Mix had a capacity loss per cycle of 0.056 %, close to the expected average of the MTI-only and HQ-only electrodes of 0.053 %. MTI/HQ had a capacity loss per cycle of 0.046 %, a 18 % improvement over Mix, while HQ/MTI had a capacity loss per cycle of 0.065 %, a 16 % decrease in capacity retention per cycle.

Voltage profiles during long term cycling – To understand why the capacity fade differed between MTI/HQ, Mix and HQ/MTI electrodes, the voltage profiles during cycling were analysed. During cycling, side reactions, binder degradation and mechanical pulverisation

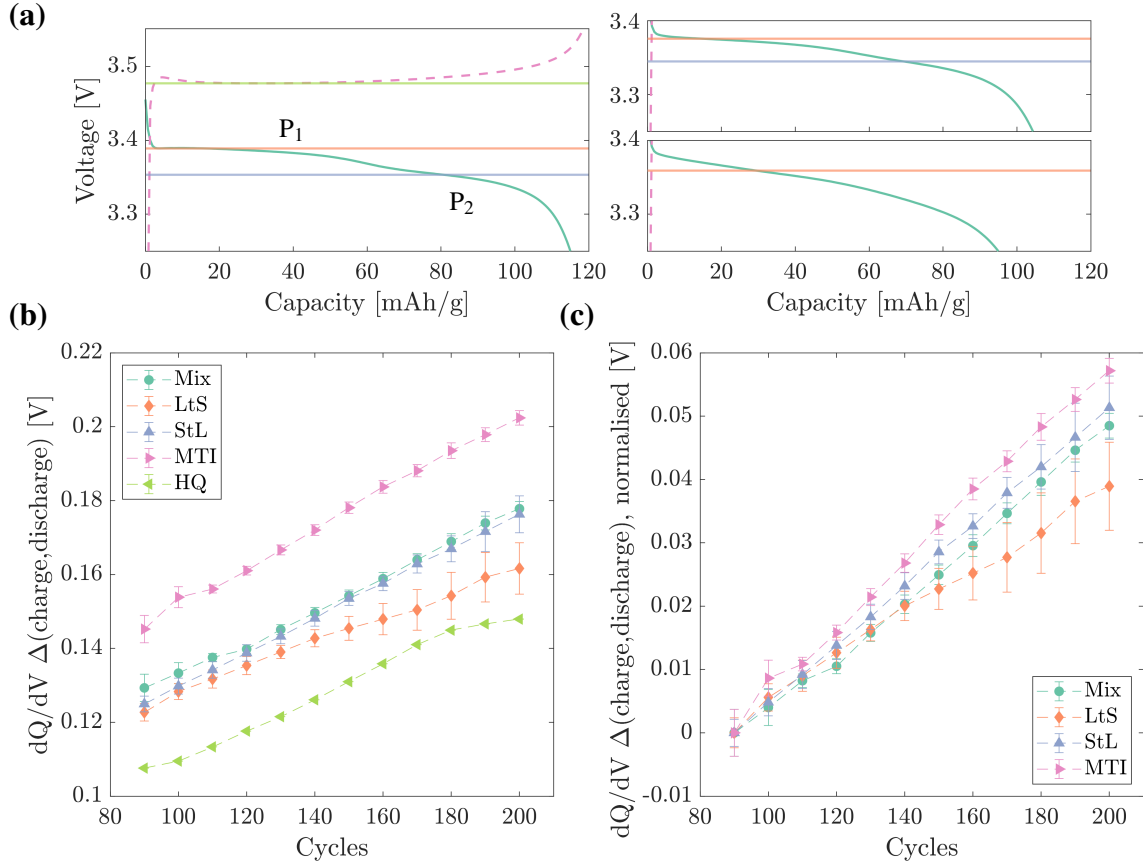


Figure 5.12: (a) Voltage profiles and dQ/dV peak potential lines of the Mix electrode discharged after 10 cycles, 100 cycles and 200 cycles at 0.5 C between 2.6 and 4 V, and (b) the absolute and (c) relative difference in voltage between the charge and discharge dQ/dV peaks from cycle 90 to 200.

due to the strains of intercalation may increase the overall impedance of the electrochemical cell. As a result, the polarisation of the cell required to overcome the increasing barrier to intercalation will increase, which in turn can lead to heating, which may then in turn further accelerate these unwanted processes. Therefore, limiting the polarisation "creep" of Li-ion cells is a critical issue [339]. A favourable electrode structure, i.e. one that facilitates efficient ion kinetics, might also advantageously reduce or spatially homogenise the growth of the impedance and subsequent overpotential, compared with a more uniform electrode structure.

Figures 5.12a shows the voltage profiles of the Mix electrode during discharge at 0.5 C after 10, 100 and 200 cycles. After 10 and 100 cycles, the two plateaux were still evident.

However after 200 cycles the potential of the second dQ/dV peak could not be measured. This pattern was also observed for MTI/HQ and HQ/MTI, although it occurred earlier in the cycling process for HQ/MTI and later in the cycling process for MTI/HQ. This may indicate that the degradation induced polarisation occurs heterogeneously, causing the previously well-defined sequential discharge of different particles sizes to merge across the intermediate voltage range between the two plateaux.

Figure 5.12b shows the absolute difference in the dQ/dV peak potential for charge and discharge for all cells between 90 and 200 cycles. Between 0-90 cycles, HQ-only, MTI/HQ, Mix and HQ/MTI electrodes had an overpotential growth of ~0.22 mV per cycle. The HQ-only electrode had the lowest difference in voltage at all cycles, while MTI had the greatest difference in voltage at all cycles. Therefore, as expected, MTI had worse polarisation losses than HQ, due to lower effective surface area, a larger transformation barrier and lower porosity in the electrode. MTI/HQ initially had a similar voltage difference between the charge and discharge dQ/dV peaks as HQ/MTI, but the difference in voltage increased considerably slower between 100 and 200 cycles. Figure 5.12c, shows the difference in voltage between the charge and discharge dQ/dV peaks calculated relative to the difference measured at cycle 90. MTI/HQ had the lowest rate of increase at 0.35 mV/cycle, followed by Mix with 0.44 mV/cycle, then HQ/MTI with 0.47 mV/cycle and then MTI-only at 0.52 mV/cycle.

Based on the capacity loss and increased polarisation observed during cycling, a few mechanisms, similar to those for rate performance, can be suggested. Firstly, any transport limitations should be slightly worse in HQ/MTI, as the MTI layer next to the separator is less porous than the HQ layer in MTI/HQ. Even if the electrodes had the same distribution of Li concentration throughout the electrode, in HQ/MTI, compared to Mix, a higher proportion of MTI particles may be active during discharge compared to HQ due the gradient of Li concentration across the electrode, while the opposite would be true for MTI/HQ. The capacity of the MTI-only electrode clearly degrades faster than that of the

HQ-only electrode, so a higher utilisation of MTI particles in HQ/MTI could cause greater degradation of capacity. This degradation is not only due to higher polarisation, but also due to a higher chance of fracture for larger LiFePO_4 particles at relatively low rate cycling [340].

Although previous literature has suggested that a larger particle size next to the separator would be favourable to homogenise the state-of-charge through the electrode thickness [305, 306], this work shows that this does not overcome the negative side effects of increasing particle size in LFP. This same result should not be generalised to many other common cathode materials such as NCA and NMC, as the intercalation processes and degradation mechanisms differ. For instance, optimised capacity retention is found in NMC by balancing the magnitude of surface reactions (i.e. reducing surface area to volume ratio) with mechanical strain (i.e. reducing particle size), which often results in micron sized particles offering the best performance. For LFP, there is minimal reaction with the electrolyte, and reducing particle size significantly reduces the transformation barrier, increases the Li diffusion coefficient and reduces mechanical degradation (which arises from the strain between the two phases of LiFePO_4 and FePO_4). Due to these differences, models outlined in the introduction may not accurately describe the processes occurring in structured LFP electrodes, as many are based on NMC, and specific models of LFP would be of considerable interest for future work.

5.4 Conclusions

A variety of two-layer structured or ‘hetero-’ electrodes and various comparator conventional structure or ‘homo-’ electrodes have been manufactured and their electrochemical performance investigated. In order to have two-layer electrodes with higher porosity next to the current collector and lower porosity next to the separator, two LFP powders with near identical crystal structures, confirmed by XRD, but with different particle size distributions

that catered to different porosities were chosen. All other aspects of the layers and electrodes (binder fraction, carbon fraction etc.) were kept constant. The two types of commercial LFP particles used were termed MTI and HQ, based on the supplier. The powders had primary particle diameters of 500–2000 and 50–200 nm, mean secondary particle diameters of 1.6 and 2 μm respectively, and similar secondary particle diameter distributions.

Five electrode structures of similar coating density of $\sim 10 \text{ mg cm}^{-2}$ were manufactured by spray deposition, including homo-electrodes of MTI and HQ (termed MTI-only and HQ-only), a mixed electrode of MTI and HQ (Mix), and two hetero-electrodes consisting of MTI then HQ and HQ then MTI layers deposited in the stated order (MTI/HQ and HQ/MTI, respectively). The overall porosity of the electrodes depended on the ratio of HQ and MTI particles, resulting in porosities of 52.5 ± 0.8 , 58.0 ± 0.7 , 54.9 ± 0.7 , 54.8 ± 0.7 and 54.9 ± 0.7 % for MTI-only, HQ-only, Mix, MTI/HQ and HQ/MTI, respectively. A discrete boundary formed between the HQ and MTI layers in MTI/HQ and HQ/MTI, with an approximately 2 μm inter-mixing zone at the interface.

In both rate and long term cycling, HQ-only and MTI-only electrodes had typical single plateau voltage profiles with overpotential behaviour dependent upon their particle size [318]. Mix, HQ/MTI and MTI/HQ electrodes displayed two stage voltage plateaux because they comprised two particle size distributions, with a steep voltage step during discharge occurring at ~ 45 % capacity, approximately in line with the mass ratio of HQ and MTI in the electrodes. The potential of these plateaux, measured using dQ/dV analysis, defined as P_1 and P_2 for the first and second plateau respectively, varied with the position of the HQ and MTI particles through the thickness of the electrodes. For example, P_1 was lower for HQ/MTI than MTI/HQ, as the HQ particles were further from the separator and their intercalation was more transport limited, while this same transport limitation was mirrored for MTI in MTI/HQ.

Galvanostatic cycling between 0.1 and 10 C showed that the Mix electrode had a

volumetric capacity that was the expected mass weighted average that of MTI-only and HQ-only electrodes. MTI-only electrodes had higher volumetric capacity at lower rates, due to lower porosity, while HQ-only electrodes had higher volumetric capacity at rates higher than 1 C due to significantly smaller primary particle size and higher overall porosity. The capacities of MTI/HQ, Mix and HQ/MTI electrodes as C-rate increased were surprisingly similar. However, the total overvoltage of Mix and HQ/MTI electrodes compared with MTI/HQ electrodes increased with C-rate, from an initial identical 1 mV at 0.1 C to 18 and ~90 mV at 10 C, respectively.

Electrochemical impedance spectroscopy data from cells after rate cycling were fitted to equivalent circuits. All electrodes produced an EIS response consisting of two well-defined semi-circles and a diffusion tail under distributed blocking conditions. However, it was difficult to draw any strong quantified conclusions because of uncertainty of the validity of equivalent circuits for hetero-electrodes and the similarity of the responses. In the intermediate and low frequency regimes, the gradients of near-linear tails varied, which was suggested to be due to the different distribution of diffusion lengths in the solid and liquid phases of each electrode (i.e. distribution of particle size and porosity, or tortuosity) [334].

Long term galvanostatic cycling was performed and after 200 cycles the capacity of MTI-only, HQ/MTI, Mix, MTI/HQ and HQ/MTI electrodes had reduced to 80, 85, 87, 89 and 95 %, with a percentage capacity loss per cycle of 0.083, 0.065, 0.056, 0.046 and 0.022 %, respectively. The long term cycling suggested that the electrode structure was favourable in order of MTI/HQ > Mix > HQ/MTI, principally suggested to be due to higher porosity at the separator and lower utilisation of MTI for MTI/HQ. During cycling, the change in voltage of the difference between the charge and discharge dQ/dV peaks was similar for all the electrodes before 90 cycles at ~0.22 mV/cycle but changed significantly after ~90 cycles to 0.35, 0.44, 0.47 and 0.52 mV/cycle for MTI/HQ, Mix, HQ/MTI and MTI-only, respectively. Therefore, the lower overvoltage for MTI/HQ can be attributed to

its greater porosity in the layer near the separator, which increases Li ion concentration towards the current collector, and potentially a lower utilisation of MTI particles, which were shown to degrade faster with cycling.

Although this work has shown that the MTI/HQ structure provided better capacity retention than the opposing HQ/MTI structure and a random mixture of HQ and MTI, the effect of different variables (i.e. distribution of particle size and porosity) could not be separated. Therefore, models specific to structured electrodes of LFP would be a useful addition to the literature to provide a deeper understanding of the mechanisms at play.

Chapter 6

Spray deposited oxide separators for sequential deposition of full cells

6.1 Introduction

A Li-ion battery (LIB) is composed of current collectors (Al and Cu), electrodes (anode and cathode, consisting of active material, conductive additive and binder), an electrolyte (a Li salt in an organic solvent mixture) and a porous separator. The separator is a membrane designed to stop electronic contact between the anode and cathode while providing pathways for Li transport, and this is conventionally achieved using an porous electronic insulator, in which the pores become filled with the Li-ion conducting electrolyte [341–343]. Therefore, it is favourable for these separators to have low electronic conductivity (to avoid anode-cathode short circuits), high affinity to electrolyte solvents, high thermal, mechanical and chemical stability, and have a thickness that seeks to minimise Li ion transport distance (typically 12–40 μm for commercial use) [343–348].

Most commercial LIB separators consist of microporous semi-crystalline polyolefins, commonly polypropylene (PP), polyethylene (PE) or combinations of both (i.e. bilayer and trilayer) [349–354]. Commercial PE and PP separators are manufactured using an extrusion process, either the dry process (e.g. Celgard) or a wet process [351, 355]. The dry process relies on forming pores between semi-crystalline lamellar and amorphous

regions in a polymer film by stretching, while the wet process relies on stretching before or after the removal of additives (which form pores on their removal) [351, 355]. For the dry process, the shape of the pores is characteristic to the technique, i.e. slit-shape pores, while the distribution and size of pores can be controlled by processing conditions [351]. Polyolefin separators have been favoured due to low cost, a mature manufacturing process, good electrochemical stability, acceptable mechanical strength and an intrinsic "thermal shutdown" method [346, 356, 357]. However, with the desire for higher performance and safety in LIBs, improvements to the poor thermal stability (shrinkage at 90 °C) and still often poor wettability is a necessity [41, 341, 358, 359].

Researchers have focused on two methods to produce separators with higher performance: (a) modification of existing polyolefins, and (b) identification and application of alternative materials and manufacturing techniques [353]. Surface coating, grafting and blending of conventional polyolefin separators to improve wetting, thermal, mechanical and chemical characteristics has been effective with polymers such as polyethylene oxide (PEO) [360, 361], poly(methyl methacrylate) (PMMA) [362], polydopamine [363, 364], poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [365], polyimide (PI) [366], hydroxyethyl cellulose (HEC) [367], polyethersulfone (PESU) [368], ceramics/inorganics such as Al_2O_3 [369–373], SiO_2 [374, 375], ZrO_2 [375], zeolites [376] and also combinations thereof [374, 377–381], to name just a few. However, the improvements imparted by these modifications are often coupled with a complicated manufacturing process, increased separator thickness, a decrease in porosity and/or de-bonding of modifying materials during cell assembly and cycling [343, 382, 383]. Lee et al. provide a comprehensive review of tabulated examples of the various modification techniques [343].

Because of the issues and compromises associated with polyolefin modification, there has been considerable research into alternative polymeric separators. High performance polymers, such as PI [384–386], polyether ether ketone (PEEK) [387], polytetrafluoroethylene (PTFE) [388] and polyphenylene sulfide (PPS) [389, 390] offer higher mechanical

strength, good chemical and electrochemical resistance and superior thermal resistance. Liu et al. showed that an electrospun PI/PVDF-HFP core/sheath separator could provide higher tensile strength (53 MPa), improved dimensional stability at 150 °C, and improved electrochemical performance over a Celgard PP separator [391]. However, manufacture of separators based on higher performance polymers can be challenging due to their poor solubility in common solvents. Liu et al. recently showed that the thermally induced phase separation (TIPS) technique could overcome this challenge by preparing a thin (~30 µm) PPS separator with high porosity (~70 %), excellent mechanical strength (~120 MPa tensile strength and ~7.5 GPa Young's modulus), high thermal stability (>200 °C) and improved electrochemical performance in LFP half cells over conventional PE [390].

Ceramic and inorganic separators have received increasing attention due to their high wettability, excellent thermal stability and comparatively high stiffness (to resist deformation) [346, 370, 392]. Common drawbacks include, in particular, the difficulty in creating a mechanically stable, thin, free-standing membrane and the often comparatively high material density (increasing the inactive mass in the cell) [393, 394]. Takemura et al. presented the first example of a free-standing ceramic-based separator [395], where Al₂O₃ particles of 0.01 and 0.3 µm were combined with PVDF in varying ratios. The thermal shrinkage of the resulting separator was negligible up to 150 °C and decreased with smaller particle size and a higher powder to binder ratio. Cells based on an optimised oxide separator had similar capacity retention to cells using Celgard separators over 500 cycles [395]. Zhang et al. produced a free-standing 37 µm Al₂O₃ separator from 100–300 nm particles, 6 wt.% SBR and 1 wt.% PEG2000 [396] and an aqueous process. On its own, SBR was unable to produce a free-standing film, while addition of 1 wt.% PEG and 6 wt.% SBR produced a mechanically stable membrane. A subsequent heat treatment at 55 °C to remove the PEG resulted in dimensional stability at 130 °C for 40 min, a ~0° contact angle with the electrolyte and improved rate performance in NMC/graphite full cells when compared with conventional PE [396].

Most ceramic/inorganic particle separators are formed using a slurry deposition method, so direct deposition onto the electrode is an obvious route to remove processing steps in the manufacture of LIBs. For example, Lagadec et al. stated, "With time, we expect separators to be viewed as a continuation of the electrodes themselves (perhaps even directly coated on them) with both structural and chemical functionality in mind." [397]. Jung et al. directly coated 1–5 μm $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) particles with 10–20 wt.% PVDF-HFP directly onto graphite-based electrodes [398]. A free-standing membrane of the same type had a thickness of 30 μm , a porosity of ~40 % and no dimensional change after 1 h at 150 °C. Although the separator displayed a relatively poor electrolyte uptake of ~20 %, the rate and cycle performance was improved over cells using PP separators. Significantly, the LLZO separator suppressed thermal runaway in a pouch cell during nail penetration tests, while the PP separator cell surged to ~280 °C. The thermal and dimensional stability of the ceramic particles stopped direct contact between the anode and cathode, suggesting that in some cases and in comparison to conventional separators, ceramic particle separators can improve cell safety [398].

Dai et al. directly coated a 60 μm layer of zeolitic imidazolate framework-4 (ZIF-4) with 5 wt.% PVDF onto an NMC electrode [399]. The ZIF-4 separator showed high dimensional stability up to 180 °C and improved specific capacity at low rates when compared to PP in NMC half cells. Blake et al. used ~50 nm Al_2O_3 with PVDF in a NMP/glycerol solvent mixture to manufacture a separator with improved wetting characteristics and similar rate and cycle performance as a Celgard 2325 separator [400]. The addition of glycerol induced porosity in the separator layer as it dried, without additional processing steps. Impressively, the separator slurry could be printed from a syringe in a custom 3D printer assembly, and, with a layer thickness of ~200 μm , enabled stable rate and cycle performance in an LFP-based half cell.

Taking direct deposition further, Singh et al. showed that a layer-by-layer spray deposition technique could enable spray painting of a functioning full cell including the

current collectors, anode, cathode and the separator [196]. The separator consisted of PVDF, PMMA and fumed SiO₂ at a ratio by weight of 27:9:4, deposited from a mixture of acetone and N,N-dimethylformamide (DMF), while the rest of the components were deposited from NMP. A separator thickness of 200 μm was said to be necessary to prevent internal shorting due to solvent penetration during deposition of the 2nd electrode onto the separator. Despite the relatively thick separator, the cells showed good performance in an LTO-LCO full cell for 65 cycles and could power LEDs after being printed onto the side of a mug [196].

The work described in this chapter advances previous examples of direct deposition of separators by providing a simple, potentially "greener" spray deposition route, paired with spray deposited cathodes and anodes, for the continuous layer-by-layer processing of full cell assemblies. An oxide-based separator, with thicknesses as low as ~5 μm, can be directly deposited onto electrodes, and also act as the substrate for the subsequent deposition of electrodes, while providing improved wetting, thermal, rate and cycle characteristics compared with a conventional Celgard 2500 PP separator.

6.2 Materials and methods

Materials used in this section have been described in detail in Chapter 3, but to recap: for electrodes, two types of LiFePO₄, termed MTI (d₅₀ 3.5 μm, MTI Corp.) and HQ (~100 nm primary particle size, Hydro-Quebec) were used as cathode active materials (AM) and Li₄Ti₅O₁₂ (LTO; <200 nm, Sigma Aldrich) was the anode AM. Carbon black (CB; C-ENERGY Super C65, Timcal Ltd.) was used as a conductive additive and sodium carboxymethyl cellulose (CMC; M_w 250,000, degree of substitution 1.2, Sigma-Aldrich) was used as the binder.

For spray deposited separators, oxide particles included Al₂O₃ <50 nm (AP50; Sigma Aldrich) and 250–450 nm (AP300; Alfa Aesar), and Y₂O₃ powder (Y₂O₃; 99.999 % pure,

MTI Corp.), while sodium carboxymethyl cellulose salt (CMC; M_w 250,000, degree of substitution 1.2, Sigma-Aldrich), polyacrylic acid (PAA; M_v 1,250,000, Sigma Aldrich) and styrene butadiene rubber (SBR; MTI Corp.) were used as dispersants and binders.

6.2.1 Electrode suspension preparation

Electrodes were spray deposited from suspensions containing LFP or LTO particles with component ratios of 85:5:10 and 90:5:5 of AM:CMC:CB, respectively. LFP and LTO slurries were mixed using the 'BMA' approach, previously described in Figure 4.2a of Section 4.2.1, with slight modifications. The modified BMA method was: (1) DI water, CB and CMC were mixed by ball milling for 15 min at 350 rpm using 10 mm diameter ZrO_2 balls, (2) AM and water were added until a slurry concentration of 40 wt.% solid was reached and then mixed for a further 15 min at 350 rpm, (3) a portion of the slurry was extracted and diluted with water to reach a solid concentration of 1 g/dL, (4) the suspension was agitated via magnetic stirrer, and (5) 1 minute before spray deposition, the solution was diluted with IPA to a solid concentration of 0.8 g/dL and solvent ratio of 80:20 vol.% water:IPA.

6.2.2 Separator suspension preparation

Suspensions to form a separator were prepared from mixtures of inert oxide particles of either Al_2O_3 or Y_2O_3 , together with a dispersant and SBR binder at a solid concentration of 0.4 g/dL. Suspensions for AP300 and Y_2O_3 with a oxide:dispersant:binder ratio of 94:1:5 were prepared as follows: (1) oxide powder, pre-dissolved dispersant and water were added into a ball mill and milled for 10 minutes at 350 rpm with 10 mm diameter ZrO_2 balls, (2) SBR solution was added, and the mixture ball milled for a further 10 min at 350 rpm, (3) slurry equal to 0.4 g of the solid component was diluted with water to a total volume of 80 ml and mixed for 1 min via magnetic stirring, (4) the diluted solution

was sonicated for 5 min, and (5) the suspension was magnetically stirred, and diluted with 20 ml of IPA to a final volume of 100 ml and a solvent ratio of 80:20 vol.% water:IPA, 1 min before the spray deposition process.

6.2.3 Suspension characterisation

Separator suspensions were characterised using a Zetasizer (Malvern Instruments) for which suspensions prepared up until step (4) of the previous section were diluted using an aqueous solution of NaCl for a final concentration of oxide particles and NaCl of 0.1 g/dL and 10 mM, respectively. Suspensions were magnetically stirred for 30 minutes before particle size and zeta potential measurements.

6.2.4 Electrode & separator deposition for half cells

Electrodes were deposited onto 0.5 mm stainless steel spacers, of known thickness and mass, by spray deposition. Separators were spray deposited directly onto electrodes pre-coated onto the stainless steel spacers. For impedance testing, separators were spray deposited directly onto stainless steel spacers. The hot plate temperature was 140 °C and 150 °C for deposition of electrode and separator layers respectively.

6.2.5 Electrode & separator deposition for full cells

Full cell deposition followed the same process as that for half cells up until the separator was deposited. Following this step, 3D printed polymer masks were placed around the electrode-separator coated spacers, and the counter electrode was then deposited. The mass of the spacer plus coatings was measured after each deposited layer so that the mass of each layer was known. The hot plate temperature was 140 °C and 150 °C for deposition of electrode and separator layers respectively.

6.2.6 Cell assembly

Cells were assembled according to the type of separator, the cell type and the characterisation techniques required, including separator-only cells, half cells and full cells for both conventional Celgard and spray deposited separators. Separator-only cells were assembled for linear sweep voltammetry and impedance testing.

Spray deposited electrodes, separators and combinations thereof were dried in vacuum for 12 hours at 150 °C in a vacuum oven (MTI Corp.) within a glove box with an Ar atmosphere of <0.1 ppm H₂O and < 0.1 ppm O₂. Half cells, using Celgard reference cells as an example, were assembled with the following components placed one after another in the centre of a stainless steel (SS) CR2032 coin cell cup (MTI Corp.): (1) a SS spacer coated with working electrode (0.5 mm thick, 15.5 mm diameter, MTI Corp.), (2) 75 µl of LiPF₆ EC/DMC=50/50 (v/v) electrolyte (Sigma Aldrich), (3) a Celgard 2500 separator (0.025 mm thick, 19 mm diameter), (4) 75 µl of LiPF₆ EC/DMC=50/50 (v/v) electrolyte (5) Li foil (0.6 mm thick, 16 mm, MTI Corp.) (6) an SS spacer, (7) an SS wave spring (0.3 mm height, MTI Corp.) and (8) a SS CR2032 coin cell cap (MTI Corp.). For Celgard full cells, the Li foil, i.e. component (6), was replaced with an SS spacer coated with a spray deposited counter electrode. For Celgard linear sweep voltammetry, an SS spacer replaced the spray deposited electrode, i.e. component (1) above. For Celgard impedance testing, both electrodes i.e. components (1) and (5) above, were replaced by SS spacers.

For spray deposited separator half cells, 150 µl of electrolyte was dispensed on top of an electrode-separator coated SS spacer and assembled from step (5). For 3-layer spray deposited full cells, an SS spacer coated with a working electrode, separator layer, and counter electrode was placed in the coin cell cup, 150 µl of electrolyte was dispensed on top and assembly continued from step (6). For linear sweep voltammetry, a SS spacer coated with a separator layer was placed in the coin cell cup, 150 µl of electrolyte was dispensed on top and assembly continued from step (5). For impedance testing, an SS spacer coated with a separator layer was placed in the coin cell cup, 150 µl of electrolyte was dispensed

into the cell, an SS spacer placed on top and assembly was continued from step (6).

The assembled cells were crimped using an MTI MSK-160E Electric Crimper and cleaned with ethanol after removal from the glove box. Cells were allowed to rest for at least 20 hours before initial cycling was performed.

6.2.7 Electrochemical Characterisation

Electrochemical characterisation, such as electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV), was performed using the basic principles described in Section 3.4.

Fitting of separator EIS data was performed according to an R-CPE equivalent circuit, where R is a resistor in series with a constant phase element (CPE). The effective resistance of the electrolyte through the separator was estimated from the intersection of a best-fit of the Nyquist plot fit with the real impedance axis (Z Real). The separator ionic conductivity was calculated from the effective resistance and physical measurements according to:

$$\sigma = \frac{d}{R_0 A} \quad (6.1)$$

where σ is the effective ionic conductivity, d is the separator thickness, R_0 is the effective resistance of the electrolyte and A is the separator area. LFP-Li coin cells were galvanostatically charged and discharged for 5 cycles at various C-rates between 0.1 C and 10 C, then 1 more cycle at 0.1 C. Long term rate cycling was performed at 1 C for 400 cycles after rate cycling. LTO-Li coin cells were galvanostatically charged and discharged for 3 cycles between 0.1 C and 1 C and cycled 5 times between 2C and 30C before 1 cycle at 0.1 C. Long term cycling was performed at 2 C for 400 cycles after rate cycling. Full cells were galvanostatically charged and discharged between 1 and 2.5 V following the same C rate and cycle scheme of the LTO half cells.

6.3 Results and discussion

The principal objective of this study was to assess the promise of spray deposited oxide layers in a simple electrode-separator-electrode integrated manufacturing sequence, which could enable the single step spray processing of LIBs. The spray deposited separators were optimised in terms of separator material, dispersant/binder and suspension solvent, and room for further optimisation remains. The proof-of-concept separators investigated here were tested with LFP positive electrodes to assess their ability to enable stable cycling of positive electrode-based half cells. The oxide-based separator that yielded the best performance was then characterised further and compared with the performance of a commercial Celgard separator in LTO-based negative electrode half cells for oxide separators of various areal densities. Spray deposited full cells with oxide separators were then deposited via single step processing, which at the time of writing is the first report of this type, as similar prior work has instead relied on direct deposition of much thicker and less stable gel or gel-based composite separators [196].

6.3.1 Initial optimisation of suspensions, substrate and deposition

This section outlines the optimisation process for the components to achieve a functional spray deposited oxide separator, i.e. controllable and reproducible thickness, acceptable roughness, balanced density/porosity, non-shortening and long cycle life. The optimisation steps were performed to allow the manufacture of reliable cells for subsequent more in-depth characterisation.

Dispersant selection – Dispersion of oxide particles in water was assessed as a function of several common aqueous thickeners and pH modifiers. Table 6.1 compares the zeta potential and particle diameter measurements for AP50, AP300 and Y_2O_3 particles suspended with various dispersants at a concentration of 1 wt.% of solids in the suspension.

AP50 particles had a zeta potential of 15.9 mV and an intensity weighted mean hydrody-

Table 6.1: Zeta potential and particle diameter analysis for Al₂O₃ (AP50 and AP300) and Y₂O₃ particles suspended in water using pH modification, PAA and CMC (at a concentration of 1 wt.% of solids in the suspension). All results were collected after 5 minutes of ultrasonication followed by 30 minutes of magnetic stirring unless otherwise stated.

Material	Dispersant	ZP ¹ (mV)	NM ² (nm)	Z-Average ³ (nm)	PDI ⁴
AP50	None	15.9 ± 4.9	159	421	0.49
	pH 4.3	37.6 ± 6.5	74	204	0.39
	PAA	-27.0 ± 8.4	93	225	0.35
	CMC	-19.9 ± 5.8	110	220	0.36
AP300	None	30.0 ± 8.8	225	260	0.1
	PAA	-43.5 ± 7.5	229	263	0.09
	CMC	-35.9 ± 6.7	225	258	0.08
Y ₂ O ₃	None	0.7 ± 3.6	3169	5281	0.29
	PAA	-19.0 ± 6.0	201	1054	0.90
	CMC	-19.9 ± 7.3	192	632	0.48
	CMC ⁵	-	144	439	0.39

¹ Zeta potential ² Number mean ³ Intensity weighted mean hydrodynamic diameter ⁴ Polydispersity index ⁵ 15 min ultrasonication

namic diameter (Z-average mean) of 421 nm with no dispersant at pH 7. On decreasing the pH to 4.3, the zeta potential of AP50 particles increased to 37.6 mV, suggesting greater suspension stability, and the Z-average mean reduced to 204 nm. Although altering the pH induced a more stable dispersion, acidic and alkaline conditions can corrode Al foil commonly used as the current collector, and large pH modifications were not seen as a viable option for direct deposition of the separator for LIBs. Carboxymethyl cellulose (CMC) is often favoured in the literature as an aqueous binder due to its low environmental impact. An AP50 suspension with 1 wt.% CMC had a reduced particle Z-average mean of 220 nm. However, a zeta potential magnitude of only (-)6.5 mV suggested that the CMC provided only limited stabilisation. Poly(acrylic acid) improved the zeta potential magnitude to (-)27.0 mV and provided an acceptable particle diameter of 225 nm for AP50

after a 30 minute equilibration period. The polydispersity of samples was in the order of $None > pH > CMC > PAA$, with a narrowing of the particle diameter distribution and the degree of agglomeration from left to right. Therefore, based on the similarity of the Z-average mean and the polydispersity index (PDI), but the improved (reduced) number mean diameter and (increased magnitude) zeta potential over CMC, PAA was determined to be a more effective dispersant for AP50.

The coarser diameter AP300 suspensions were stable under all tested conditions. With no dispersant, the suspension had a zeta potential of 30 mV and a Z-average mean of 260 nm. The PDI of the suspension was 0.1, indicating a narrow particle diameter distribution and a low degree of agglomeration. With PAA dispersant, the Z-average mean and PDI measurements were similar to those with no dispersant at 263 nm and 0.09, respectively. The zeta potential increased in magnitude to $(-)$ 43.5 mV, indicating a more electrostatically stable suspension. Similarly, CMC addition produced a suspension with a Z-average mean of 258 nm and a PDI of 0.08. The zeta potential magnitude was only slightly smaller at $(-)$ 35.9 mV. Therefore, for AP300, PAA was chosen based on the greater zeta potential magnitude compared with CMC or no dispersant.

The Y_2O_3 particles proved more difficult to disperse at neutral pH. The zeta potential without dispersant was 0.7 mV, resulting in a significantly agglomerated suspension with a Z-average mean of 5281 nm. With added PAA dispersant the zeta potential magnitude increased to $(-)$ 19.0 mV and the number mean diameter reduced to 201 nm, respectively. However, the Z-average mean was 1054 nm and the PDI was 0.9, indicating a particle diameter distribution containing agglomerates. CMC as a dispersant resulted in a zeta potential magnitude of $(-)$ 19.9 mV, similar to that of PAA, but significantly improved the Z-average mean and PDI to 632 nm and 0.48, respectively. CMC*, a CMC suspension with a 15 minute ultrasonication step instead of 5 minutes, improved the suspension further by reducing the PDI to 0.39, similar to that of AP50, with a further reduction in the number mean diameter to 144 nm, and Z-average mean of 439 nm. Although with

similar zeta potentials, CMC improved the dispersion over PAA, probably because of the shorter polymer chain length of 250,000 M_w compared with 1,250,000 M_v , as long chain polymers can act as flocculants by polymer bridging and depletion flocculation (i.e. too much unadsorbed polymer) [401].

Electrostatically, PAA was a satisfactory dispersant for AP50 and an excellent dispersant for AP300, but produced a highly flocculated suspension when added to Y_2O_3 . On the other hand, CMC provided substantially better dispersion for Y_2O_3 . Although the zeta potential induced by CMC for AP50 and AP300 was lower in magnitude than that of PAA, suspensions of either dispersant had similar Z-average means, which may be due to the shorter chain length of the CMC.

Binder optimisation – Styrene butadiene rubber (SBR) was selected as a model binder due to its known compatibility and widespread use in aqueous manufacture of LIB anodes. Optimisation of binder percentage was performed using AP50. At 2 wt.% SBR (Figure 6.1a), the sprayed oxide layer or coating tended to flake off in small circular areas, a phenomenon suspected to be caused by capillary induced delamination during drying, as described in Chapter 4. When the proportion of binder was increased to 5 wt.% or greater, the oxide particles maintained adhesion to the electrode layer and substrate (Figure 6.1b). Subsequently 5 wt.% SBR was sufficient to create mechanically stable layers for all oxide materials investigated.

Substrate selection – SS spacers were selected as substrates to facilitate; (1) consistent handling of samples while avoiding surface damage or inhomogeneities due to human error, and (2) simple, punch-less assembly into standard coin cells. In terms of assembling spray deposited full cells (with electrodes deposited on thin Al foil), an Li chip with diameter smaller than the separator must be used and alignment must be exact to avoid short circuits, as explained by the schematic shown in Figure 6.1d. Alternatively, a spacer raised the contact point of the Li foil into the middle of the cell, removing the chance of contact between the Li foil and the cell cup or working electrode (and short circuit), as explained

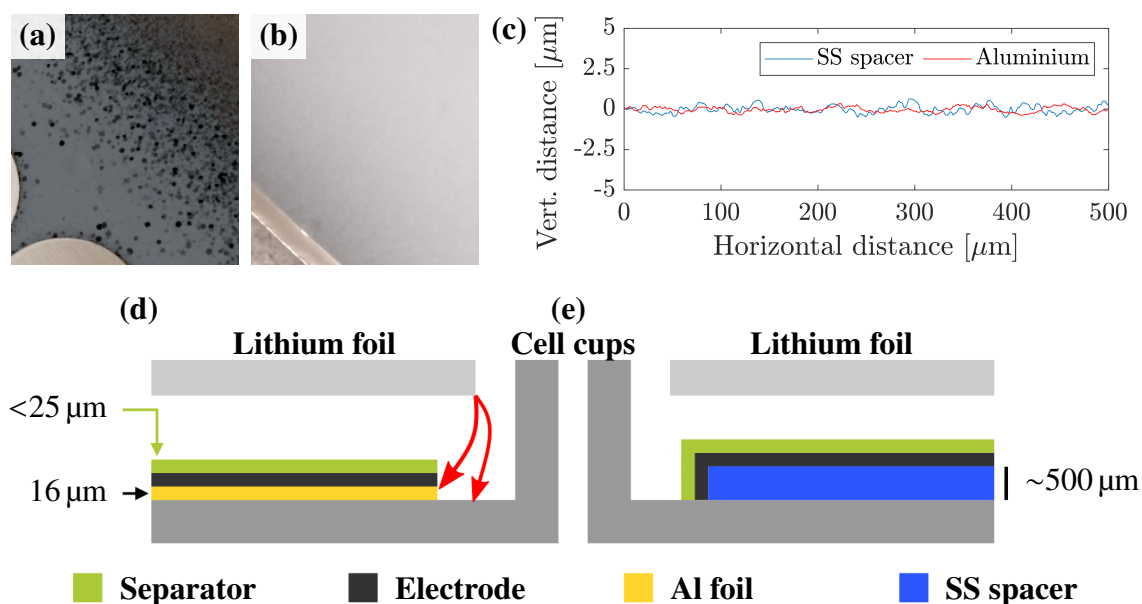


Figure 6.1: Optimisation of dispersant, binder, substrate and separator material for spray deposited cells. Optical microscopy of Al_2O_3 nanoparticle suspensions containing (a) 2 wt.% SBR and (b) 5 wt.% SBR by solid mass, deposited onto LFP electrodes. (c) Surface profilometry comparison of uncoated stainless steel spacers and Al foil. Schematic diagrams comparing spray deposited half cells assembled using (d) Al foil with the comparable routes for short circuits marked by red arrows and (e) a stainless steel spacer conformally coated with an electrode and oxide separator layer (reducing the probability of short circuits).

by the schematic shown in Figure 6.1e. A conformal coating of the separator onto the electrode and spacer also protected against contact with a misaligned Li foil, as shown in Figure 6.1e. In terms of full cells, it was assumed that punching spray deposited full cells could induce a short circuit by smearing material across the sides of the separator, potentially connecting the anode and cathode, and was avoided. The SS spacer and Al foil substrates were compared by surface profilometry in Figure 6.1c and were found similar.

Sprayed solvent optimisation – Figure 6.2 shows SEM plan view micrographs of $\sim 12\ \mu\text{m}$ thick sprayed Al_2O_3 deposited on top of a $\sim 20\ \mu\text{m}$ LFP-based electrode (coated on a SS spacer), and the corresponding surface profiles. A separator with a uniform structure and low roughness was desired (no "bumps" or cracks). Separators with excessively heterogeneous structures will result in a heterogeneous current density distribution, leading to localised heating and degradation of the electrode and separator, which could lead to

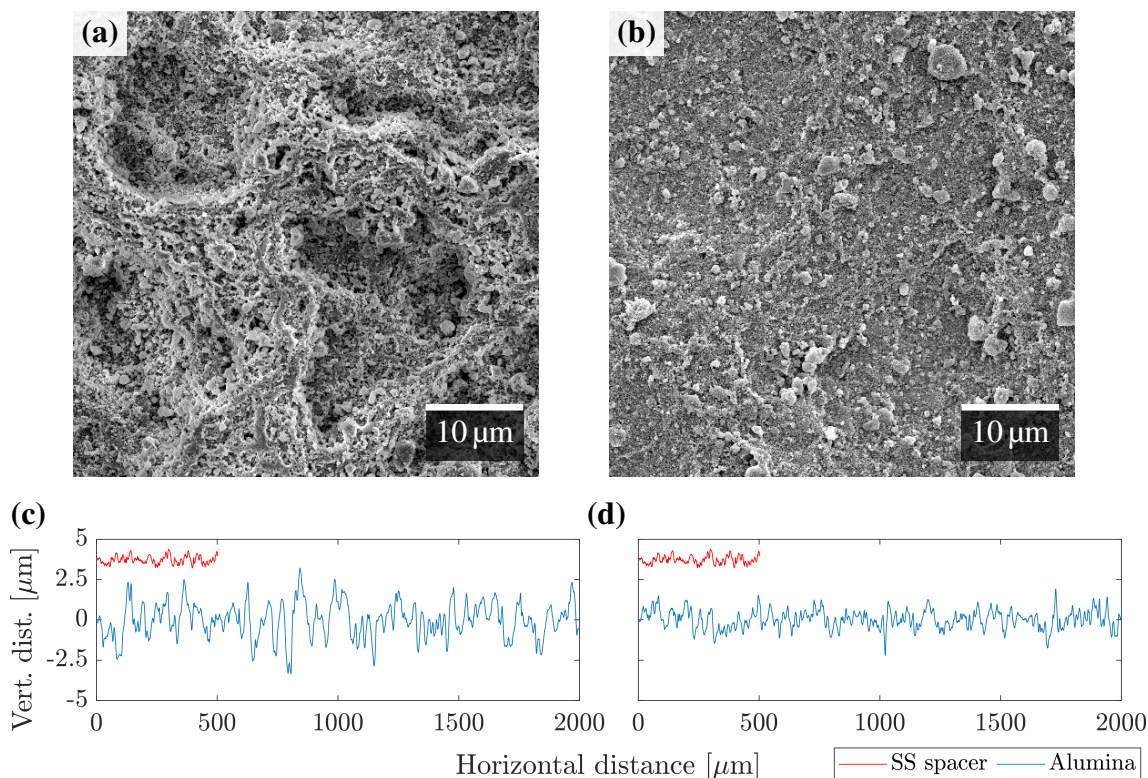


Figure 6.2: Plan-view SEM micrographs of AP50 layers deposited on top of sprayed LFP-based electrodes and corresponding surface profiles. AP50 was deposited from (a) water and (b) water:IPA 80:20 vol.% suspensions containing 1 wt.% PAA and 5 wt.% SBR of the total solid mass. Surface profiles of (a) and (b) are displayed in (c) and (d), respectively.

physical contact and short circuits between the anode and cathode [402, 403].

Figure 6.2a shows the surface of an AP50 separator deposited from water on a thin LFP electrode, with a morphology that was reminiscent of the 8 layer aqueous LFP-based electrodes deposited on Al foil, shown in Figure 4.7 in Chapter 4. Figure 6.2b is a plan-view image of AP50 deposited from water with 20 vol.% IPA, which had a qualitatively smoother surface. Some agglomerates persisted, most with a diameter of 1–3 μm , up to a maximum of $\sim 4 \mu\text{m}$.

Surface roughness scans of the AP50 coatings deposited with and without 20 vol.% IPA are shown in Figure 6.2c and d respectively, and Table 6.2 presents an overview of the roughness measurements of Al foil, SS spacer, APW and APM surfaces. R_p is the maximum height of roughness above a best-fit mean line to the data, R_v is the lowest point

Table 6.2: Roughness comparison of Al foil and SS spacer substrates and Al₂O₃ coatings deposited onto SS spacers with water and water with 20 vol.% IPA (averaged from 5 traces per sample). Rp is the maximum point of roughness above the mean line, Rv is the lowest point of roughness below the mean line, max(P2V) is the largest height difference between a neighbouring peak and valley, Ra is the arithmetic average deviation from the mean line and Wa is the arithmetic average deviation of waviness from the mean line.

Surfaces	Rp	Rv	max(P2V)	Ra	Wa
Al foil	0.4 ± 0.0	0.5 ± 0.1	0.9 ± 0.2	0.1 ± 0.0	0.1 ± 0.0
SS spacer	0.7 ± 0.0	0.7 ± 0.1	1.3 ± 0.1	0.2 ± 0.0	0.2 ± 0.0
AP50	3.1 ± 0.1	3.3 ± 0.2	5.3 ± 0.8	0.5 ± 0.0	1.0 ± 0.3
AP50 (IPA)	2.5 ± 0.1	2.0 ± 0.2	3.7 ± 0.7	0.3 ± 0.0	0.7 ± 0.2

of roughness below the mean line, max(P2V) is the largest height difference between a neighbouring peak and valley, Ra is the arithmetic average deviation from the mean line and Wa is the arithmetic average deviation of waviness from the mean line. Table 6.2, consistent with the micrographs, shows that the sprayed coatings increased the roughness and that 20 vol.% IPA offered the lowest coating roughness, and was thus preferred.

Oxide selection – Figure 6.3 shows plan-view SEM micrographs of sprayed (a) AP300 and (b) Y₂O₃, and higher magnification images of (c) AP50, (d) AP300, and (e) Y₂O₃ coatings. Figures 6.3a and b show that the Y₂O₃ coating had a more homogenous surface than AP300. Y₂O₃ particles were plate-like, and were estimated to be 0.1–3.5 µm in diameter and 50–250 nm thickness. The magnified SEM images of AP50, AP300 and Y₂O₃ in Figures 6.3c-e respectively suggested that AP300 had the most uniform surface morphology, consistent with its low PDI of 0.1 and relatively large zeta potential magnitude with PAA of (–)43.5 mV. Y₂O₃ showed little agglomeration of particles on the surface, although the particle diameter varied considerably in comparison to AP300, consistent with its relatively large PDI of 0.39. AP50 has a considerably smaller particle diameter than either AP300 or Y₂O₃, but had more agglomeration, as expected from a relatively high PDI of 0.35.

Figure 6.4 shows a cross-section SEM image from a 6–7 µm thick Y₂O₃ separator

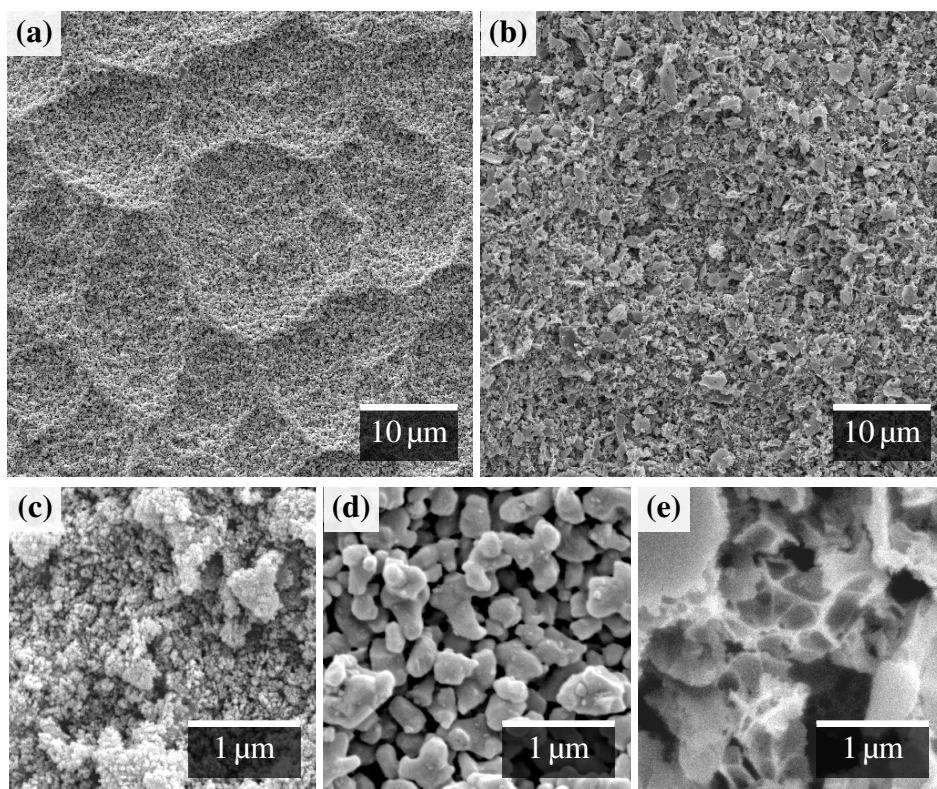


Figure 6.3: Plan view SEM micrographs of (a) AP300 and (b) Y_2O_3 coatings deposited on top of LFP electrodes. Oxide coatings were deposited from 20 vol.% IPA aqueous suspensions. Micrographs (c), (d) and (e) show the surfaces of AP50, AP300 and Y_2O_3 coatings, respectively, at higher magnification.

coating sprayed onto an LFP-based electrode. The overlaid EDX map in Figure 6.4a shows the distribution of three elements chosen to allow differentiation of the different materials: Y (red) for Y_2O_3 , Fe (cyan) for LFP, and C (dark blue) for CB. There was a small amount Fe and Y cross-contamination in the opposing layers, that was assumed to be generated by the destructive ion milling cross-sectioning process. The roughness of the separator surface, and also the interface with the electrode, as shown at higher magnification in Figure 6.4b, was estimated at $\pm 1 \mu\text{m}$, similar to that measured by surface profilometry. The LFP layer was porous and the interface with the SS substrate, shown at higher magnification in Figure 6.4c, had significant porosity, which suggested that a calendering step might be beneficial. Qualitatively, at this resolution, the pore size and distribution of pores were consistent over the cross-section, and there were no signs of delamination. The sprayed

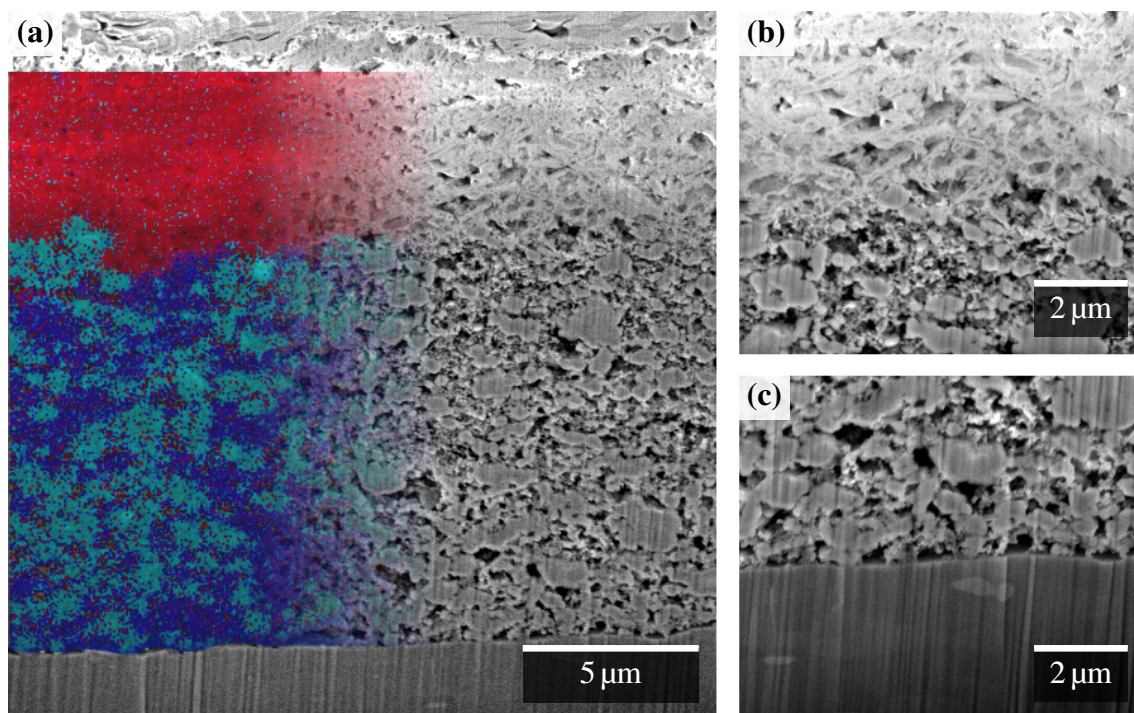


Figure 6.4: Cross-sectional images of a sprayed LFP-based electrode coated with a 6–7 μm Y_2O_3 separator. The interface of the LFP electrode with the Y_2O_3 layer and the substrate are magnified in (b) and (c) respectively. An EDX map is overlaid onto the cross-section (a) with the following colour key: Y (red) for Y_2O_3 , Fe (cyan) for LFP and C (dark blue) for CB.

separator apparently had conformal contact with the underlying electrode, with no obvious difference at the interface compared with the bulk electrode or separator layers, as shown in Figure 6.4a and b. Occasionally, there were some relatively large pores in the Y_2O_3 layer, 1 μm in at least one dimension, coinciding with off-angle stacking of larger plate-like Y_2O_3 particles (Figure 6.4b).

To assess the electrochemical performance of each oxide separator, half cells consisting of sprayed LFP/separator/Li foil were constructed. The initial half cell performances are shown in Table 6.3. Each separator layer was $\sim 11 \mu\text{m}$ thick, with a corresponding estimated areal density of $\sim 1.7 \text{ mg cm}^{-2}$, depending on the porosity of the deposited oxide layer. The estimated porosity of the Y_2O_3 layer was consistently higher because of the relatively inefficient packing of the higher aspect ratio Y_2O_3 particles, as observed in Figure 6.4b.

Cells constructed with AP50 deposited from a water-only solvent (WO) and AP300

Table 6.3: Physical properties of oxide separators, AP50 deposited from water-only (AP50 (WO)), AP50, AP300 and Y_2O_3 . ρ_{solid} is the theoretical density of the composite oxide:dispersant:binder separators. The functional cells (FC) column, lists how many of 3 assembled cells were able to charge and discharge on the first cycle.

Separator	ρ_{solid} (mg cm^{-3})	Areal density (mg cm^{-2})	Thickness (μm)	Porosity (%)	FC
AP50 (WO)	3.73	1.59 ± 0.05	12 ± 1	64 ± 4	0/3
AP50	3.73	1.70 ± 0.05	11 ± 1	59 ± 5	3/3
AP300	3.73	1.85 ± 0.05	11 ± 1	55 ± 3	0/3
Y_2O_3	4.73	1.70 ± 0.05	11 ± 1	67 ± 4	3/3

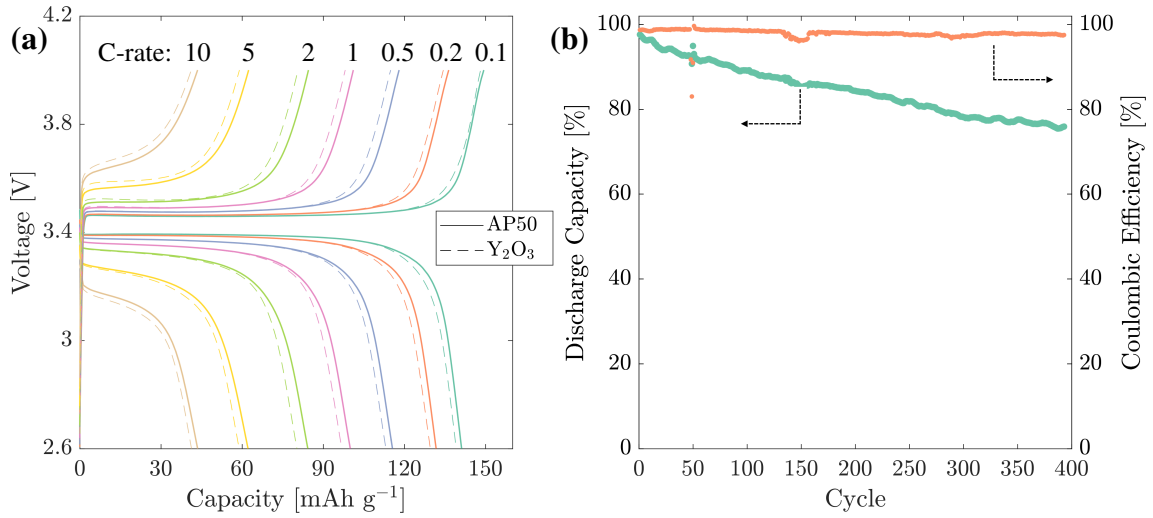


Figure 6.5: Voltage curves and long term galvanostatic cycling of LFP half cells with $\sim 11 \mu\text{m}$ AP50 and Y_2O_3 separators. (a) Voltage curves at C-rates between 0.1-10C and (b) long term cycling at 1C. The cells using AP50 (WO) and AP300 are absent as they were unable to charge on the first cycle, while the cells with Y_2O_3 separators were unable to charge after 10C.

charged continually without reaching the upper voltage cut-off, indicative of a short circuit. For AP50 (WO), the short circuit was attributed to a relatively high roughness, and therefore, comparatively large variation in the thickness of the separator layer (Table 6.2). For AP300, from Figure 6.3, the surface height variations (roughness) may have also been problematic in avoiding short circuits.

The rate performance of the cells with the better performing AP50 and Y_2O_3 separators was investigated between 2.6–4.0 V for 5 cycles at each C-rate between 0.1–10 C, followed

by 5 recovery cycles at 0.2 C. Figure 6.5a shows representative discharge curves for these AP50 and Y₂O₃ cells. The cells displayed typical discharge curves for LFP, with a long, relatively flat voltage plateau at ~3.4 V. As current density increased, cell polarisation shifted the plateau to a lower voltage on discharge and caused the plateau to begin to slant. LFP cells with AP50 and Y₂O₃ separators produced capacities of 141–44 mAh g⁻¹ and 139–41 mAh g⁻¹ at 0.1–10 C, respectively. However, after 10 C, the Y₂O₃ cells shorted and were unable to charge to the upper voltage cut-off, while AP50 cells successfully recovered to a capacity of 137 mAh g⁻¹ at 0.2 C. Both cell types had standard deviations in capacity of ~2 mAh g⁻¹ between 0.1–10 C.

Cycle stability of the AP50 cells was determined at 2 C for 400 cycles, as shown in Figure 6.5b. After 400 cycles, the cells retained 77 % of their original 2 C capacity, with percentage capacity lost per cycle of 0.057 ± 0.005 %. The coulombic efficiency reduced from 98.7 ± 0.2 % to 97.5 ± 0.3 %, but was generally stable apart from some minor events at 50 and 150 cycles.

6.3.2 Physico-chemical properties of spray printed Al₂O₃ separators

Given their encouraging proof-of-concept demonstration when sprayed onto a cathode, AP50 separators were then also explored to determine their physical properties, thermal stability, wettability, impedance and electrochemical performance in LTO-based (anode) half cells. An LTO anode is commonly paired with LFP due to their combined generally excellent high rate performance and cycle life. The LTO particles had an average particle size of (<200 nm). A commercial Celgard 2500 polypropylene monolayer separator was used for comparative purposes as either single layer PP and PE separators are the standard in previous literature. It should be noted however that the PP separator is relatively thick and more suited to high energy applications, which should be taken into account when electrochemical comparisons are drawn.

Physical characterisation – Separator thickness is an important parameter for LIBs, as

it contributes to safety (prevents short circuits, requires negligible electronic conductivity), impedance (i.e. degradation, heating and performance), dynamic response (ion mobility) and gravimetric and volumetric energy density of the cell (minimise inactive material thickness and mass). Generally, a thicker separator improves safety at the detriment of cell impedance, energy density and dynamic response. One potential advantage of direct deposition of a separator onto a pre-deposited electrode is that it lowers the risk of damage to the separator during manufacture, i.e. puncture and abrasion, due to a reduction in processing and transport steps. The risk may be mitigated further when both electrodes can be deposited immediately before and after separator deposition, i.e. integrated as part of a set of sequential steps.

Suspensions comprising of AP50, PAA, SBR in a 94:1:5 solid ratio and 80:20 vol.% water:IPA solvent were spray deposited onto SS spacers pre-coated with a $\sim 14\ \mu\text{m}$ LTO-based electrode. Figure 6.6 shows the resulting coated spacers, where (a) is the SS/LTO electrode and (b-d) are SS/LTO/AP50 electrode/separator composites, termed AS1, AS2 and AS3, with 5, 11 and $22\ \mu\text{m}$ thick AP50 separator layers, respectively. Table 6.4 compares the areal density, thickness and estimated porosity of the AP50 separators with a Celgard 2500 monolayer PP separator. The relatively high density of the Al_2O_3 ($3.95\ \text{g cm}^{-3}$) resulted in a higher mass per unit volume than the Celgard 2500 (PP assumed density of $0.9\ \text{g cm}^{-3}$). To obtain the same areal density, or better, than the Celgard 2500, the AP50 separator should be $\sim 7\ \mu\text{m}$ thick, i.e. approximately a third to a quarter of the Celgard thickness, assuming their porosities were similar. The porosity of the spray deposited Al_2O_3 -based separators was estimated as $58 \pm 3\%$, $59 \pm 5\%$ and $60 \pm 10\%$ for AS3, AS2 and AS1, respectively. As the thickness of the AP50 separators decreased, the proportional error in the thickness and mass measurement increased. Overall, the sprayed Al_2O_3 separators had slightly higher porosity than the Celgard 2500 porosity according to the manufacturer and literature [404, 405].

Figures 6.7a and b shows SEM images of AS1 and AS3 cross-sections. In each case, the

Table 6.4: A comparison of the thickness, mass, estimated porosity and pore size of a Celgard 2500 separator and three spray deposited Al_2O_3 -based separators of varying thickness [404, 405].

Sample	Materials	AD ¹ (mg cm ⁻²)	d ² (μm)	Porosity (%)	Pore size (μm)
Celgard	PP	1.13 ± 0.04	25 ± 1	55	0.21 x 0.06
AS1	AP50	0.74 ± 0.05	5 ± 1	60 ± 10	-
AS2	PAA	1.70 ± 0.05	11 ± 1	59 ± 5	-
AS3	SBR	3.44 ± 0.05	22 ± 1	58 ± 3	-

¹ Areal density ² Thickness

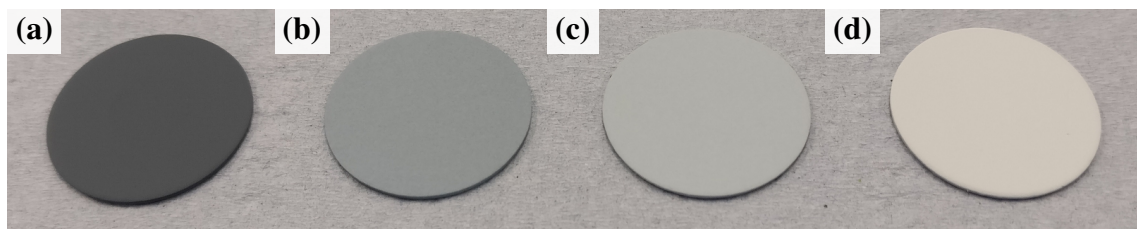


Figure 6.6: Stainless steel spacers coated with (a) an LTO electrode layer and (b-d) an LTO electrode layer coated with a ~5, ~11, and ~22 μm thick AP50 separator layer, respectively.

LTO-based layer was ~14 μm thick, and the Al_2O_3 -based layers were ~5 μm and ~22 μm. Similarly to the Y_2O_3 layer in Figure 6.4, the Al_2O_3 separator coated conformally onto the underlying sprayed LTO-based layer. AS1 had a roughness of ±1 μm, while AS3 was slightly rougher at ~±2 μm. AS1 had a few large pores of diameters of 200–300 nm, while AS3 had pores with diameters up to ~400 nm. However, the average pore size was significantly smaller and in general the lower magnification required to image a representative area was insufficient to resolve all the smaller pores, as suggested by Figure 6.7a.

Nitrogen gas surface adsorption (BET) was used to investigate the specific surface area and mesoporosity of AP50 and AP300 separator layers, which were spray deposited onto Al foil. The surface area of a pristine Al foil was firstly confirmed to be negligible. The BET isotherms of the Celgard, AP50 and AP300 are shown in Figure 6.8a. Celgard and AP50 displayed a hybrid shape between a classical type II and type IVa behaviour [406],

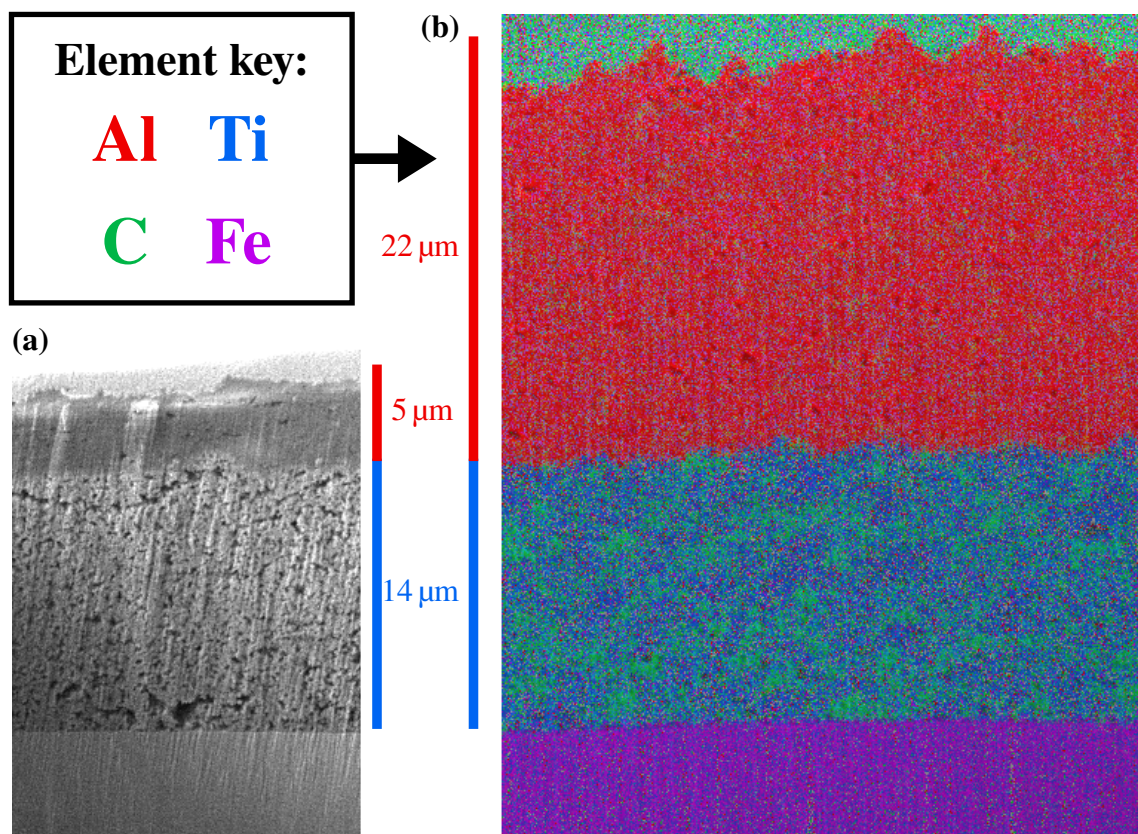


Figure 6.7: Cross-sectional SEM images of LTO-based electrodes coated with (a) a 5 μm Al_2O_3 separator (AS1) and (b) a 22 μm Al_2O_3 separator (AS3) with an overlaid EDX map. From bottom to top, the layers are stainless steel separator (purple), LTO (blue) and carbon black (green) electrode, Al_2O_3 separator (red), and Pt/C coating layer.

comprising adsorption-desorption hysteresis.

Type II behaviour is typical of non-porous or macroporous solids, as multilayer formation of adsorbed nitrogen appears to increase without limit as p/p^0 tends to 1. A type IVa isotherm is typical of mesoporous solids and is generated due to pore condensation, where the adsorbing gas condenses to a liquid-like state at a pressure below p^0 . However, a final saturation plateau, typical of a type IVa, was not observed, indicating structures with hybrid mesoporous-macroporous pore structures. Hysteresis is observed when mesopores exceed a critical width, roughly 4 nm according to non-local density functional theory (NLDFT) modelling [407], and occurs due to a difference in pressure between pore filling and pore evacuation. According to IUPAC, the hysteresis is due to a metastable adsorption

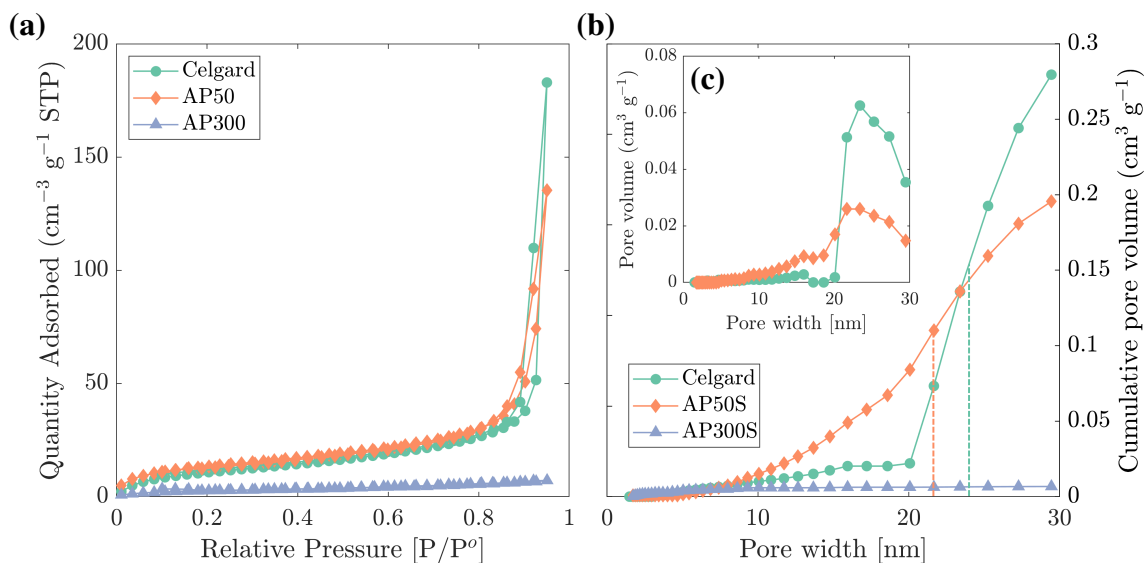


Figure 6.8: Nitrogen gas adsorption measurements and calculations for Celgard 2500, AP50S and AP300S separators. (a) BET isotherms and (b) NLDFT cumulative pore width distributions with dotted lines marking the average pore width and (c) inset incremental pore width distributions.

layer during pore filling and a thermodynamic equilibrium of the liquid-vapor transition during pore emptying [406].

Some powder and aggregate samples give Type II isotherms with H3 hysteresis (IUPAC classification [406]) arising from inter-particle capillary condensation within a non-rigid plate-like particle aggregate [408]. However, the AP50 and Celgard isotherms did not display the typical cavitation induced closure of the H3 hysteresis loop at 0.4–0.5 p/p^0 . In the case of AP50, the loop closed at 0.78 p/p^0 and the particles were not plate-like, as shown in Figure 6.3c.

H1 hysteresis is usually associated with a narrow range of uniform pores. However, it has also been attributed to networks of 'ink bottle' pores, where the pore size distribution is similar in width to the neck size distribution, and to spherical/cylindrical pore structures with wide openings through which there is immediate access to the vapor phase [406, 409]. In case of either classification, the distinctive isotherm of the AP50 separator most likely represents a porous powder bed with little to no pore blocking, and is also shown in the literature by porous and non-porous nanoparticles [410–412].

Specific surface area (SSA) was calculated from the BET isotherms. The AP300 separator had a surface area of $9.4 \text{ m}^2 \text{ g}^{-1}$ and no distinctive hysteresis loop, indicating little or no mesoporosity. The AP50 separator had an SSA of $44.4 \text{ m}^2 \text{ g}^{-1}$, likely due to the 'fluffy' morphology observed in Figure 6.3c, while the Celgard separator had an SSA of $41.3 \text{ m}^2 \text{ g}^{-1}$. The AP50 separator density of 3.77 g cm^{-3} was estimated to be approximately four times greater than Celgard at 0.9 g cm^{-3} , so the surface area per volume of separator was much higher. A high surface area could increase electrolyte uptake, however it also increases the area available for chemical side reactions.

Standard NLDFT models from the machine manufacturer's software package were fitted to the BET isotherms to calculate pore width distributions, as shown in Figures 6.8b and c. It should be noted that the results are presented on a per gram basis, which should be taken into account when comparing separators of differing density. The sprayed AP300 separator had a low cumulative pore volume of $0.007 \text{ cm}^3 \text{ g}^{-1}$ due to the lack of mesoporosity. The cumulative pore volume of Celgard and AP50 separators was 0.28 and $0.20 \text{ cm}^3 \text{ g}^{-1}$, respectively. The Celgard separator showed a narrower pore width distribution with an average pore diameter of 24.0 nm, with significant pore volume above 20 nm. The AP50 separator had an average pore width of 20.7 nm and had a broader pore width distribution (PWD) in the mesopore range, with minimum pore widths of <10 nm.

To estimate the volume of each component in the separators, a simple relation was used:

$$V_{\text{sep}} = V_{\text{solid}} + V_{\text{meso}} + V_{\text{macro}} \quad (6.2)$$

where on a per gram basis, V_{sep} is the volume of the separator, and V_{solid} , V_{meso} and V_{macro} are the volumes occupied by the solid, mesopore and macropore components of the separator, respectively, as shown for the Celgard and AP50 samples in Table 6.5. Table 6.5 reinforces some important comparisons between the AP50 and Celgard separators. As

Table 6.5: A comparison of the specific surface area of AP300, AP50 and Celgard separators, and the calculated proportion of pore widths in the Celgard and AP50 separators. On a per gram basis, V_{sep} is the volume of the separator, and V_{solid} , V_{pore} , V_{meso} and V_{macro} are the volumes occupied by the solid, total porosity, mesopore and macropore components of the separator, respectively, with units of $\text{cm}^3 \text{g}^{-1}$. $V_{meso,\%}$ and $V_{macro,\%}$ are the proportion of total porosity credited to meso and macropores, respectively.

Sample	SSA ($\text{m}^2 \text{g}^{-1}$)	V_{sep}	V_{solid}	V_{pore}	V_{meso}	V_{macro}	$V_{meso,\%}$	$V_{macro,\%}$
AP300	9.4	-	-	-	-	-	-	-
Celgard	41.3	2.47	1.11	1.36	0.28	1.08	0.21	0.79
AP50	44.4	0.60	0.27	0.34	0.20	0.14	0.59	0.41

long as the AP50 separator is chemically stable, its relatively high surface area per unit volume may be advantageous in terms of electrolyte uptake. The Celgard separator had a significantly larger pore volume per gram of material (V_{pore}) of $1.36 \text{ cm}^3 \text{g}^{-1}$, compared with AP50 at $0.34 \text{ cm}^3 \text{g}^{-1}$. The ratio of mesopores to macropores was 0.59:0.41 for the AP50 separator, compared with 0.21:0.79 for the Celgard separator. There is a possibility that V_{meso} is over-predicted due to the continued multilayer formation in the high pressure section of the isotherm for both Celgard and AP50 separators. However, the proportion of mesopores in the AP50 coating, assuming a monomodal pore distribution, suggested an average pore width near to that of the average particle diameter stated by the manufacturer.

Temperature stability – LIBs can undergo thermal runaway due to overheating and/or overcharging, leading to short-circuits, fire and even explosion. The separator plays an important role in reducing these risks. Part of the reduction of risk relies on ensuring the correct pore size distribution and porosity homogeneity to avoid localised heating effects and Li dendrite penetration. Another important aspect is the thermal properties of the separator to avoid pronounced thermal ageing (degradation) during normal charge/discharge that might lead to accelerated ageing under abnormal, localised heating conditions. Therefore, the thermal stability of the various separators was investigated using thermogravimetric analysis.

Figure 6.9 shows TGA plots for the Celgard 2500 separator (Celgard), poly(acrylic

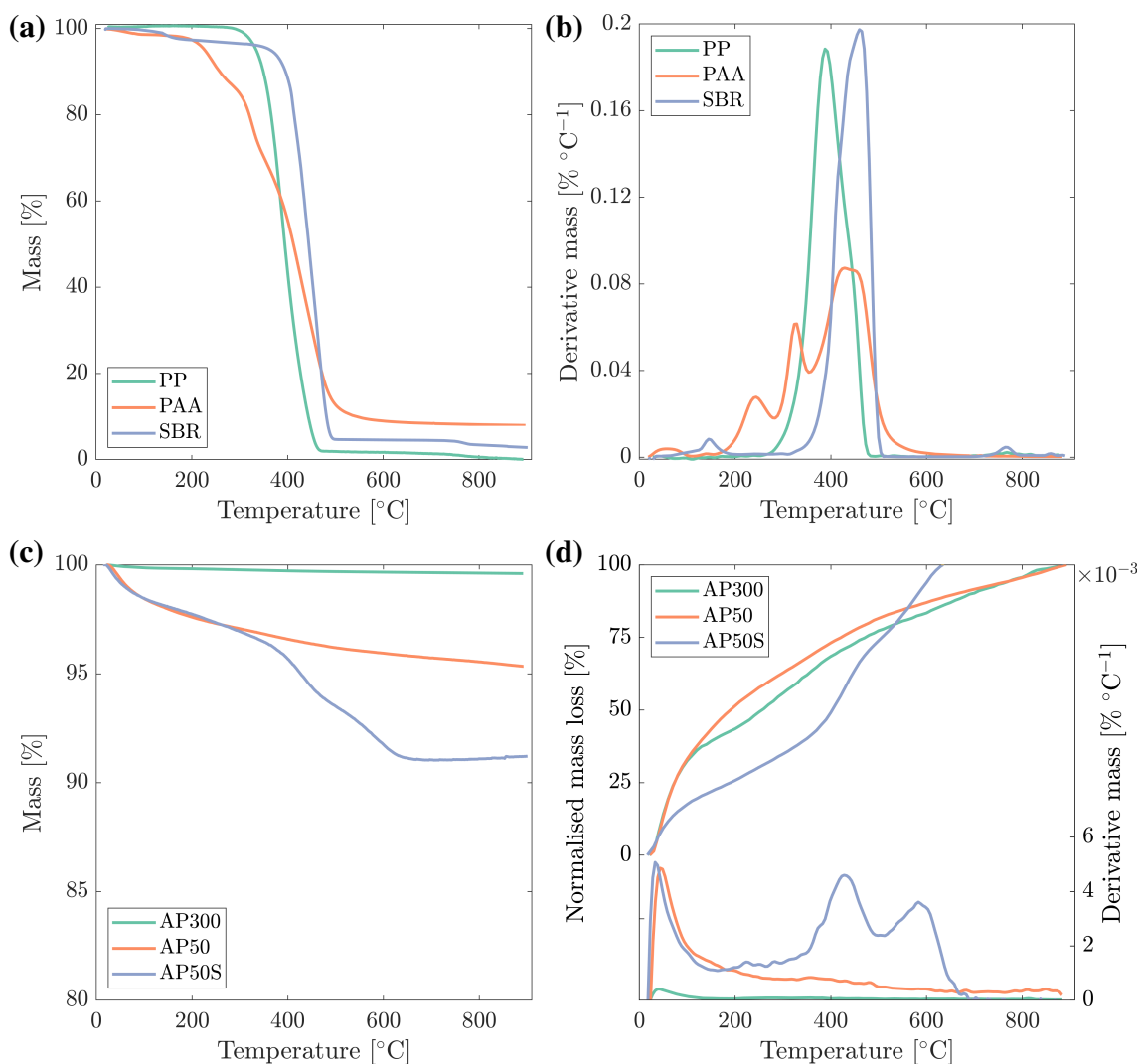


Figure 6.9: Thermogravimetric analysis of a Celgard 2500 separator and a spray deposited Al₂O₃ separator (AP50S) and requisite materials between 25-900 °C. (a) TGA and (b) DTG of Celgard 2500 (PP), poly(acrylic acid) (PAA), and styrene butadiene rubber (SBR). (c) TGA, (d, upper) normalised mass loss and (d, lower) DTG of 300 nm Al₂O₃ powder (AP300), 50 nm Al₂O₃ powder (AP50) and 50 nm Al₂O₃ separator (AP50S).

acid) (PAA), styrene butadiene rubber (SBR), 300 nm Al₂O₃ powder (AP300), 50 nm Al₂O₃ powder (AP50) and a spray deposited 50 nm Al₂O₃ separator (termed AP50S here) between 25–900 °C.

The raw TGA data and its differential for polymers, PP, PAA and SBR are shown in Figures 6.9a and b, respectively. PP decomposed in a single step at 252 °C, with a maximum rate of degradation (DTG peak) at 387 °C and was fully degraded at 482 °C.

Poly(acrylic acid) displayed four distinct DTG peaks, with the three high temperature peaks well-documented in the literature [413–416]. The other, first peak showing a 2 % loss between 50–130 °C, was simply evaporation of absorbed water. Stage 1 of polymer decomposition, a mass loss of 11 % in the range of 160–280 °C with a peak at 240 °C, was attributed to reversible anhydride formation, accompanied by a decrease in polymer ductility [417]. Stage 2, the peak at 330 °C, was due to decarboxylation of the anhydride and release of CO₂, and accounted for a mass loss of 22 %. Finally, a broad peak, related to chain scission of the polymer, occurred above 350 °C, and led to a further mass loss of 55 %. A mass of 10 % remained above 530 °C, which was due to a carbonaceous residue. Styrene butadiene rubber decomposed in a single step between 320–520 °C with a DTG peak at 460 °C and left a residual mass of 4.5 %. The small peak at 150 °C was most likely due to volatilisation of processing additives [418].

The AP300 powder in Figure 6.9c provided the baseline behaviour for as-supplied Al₂O₃, maintaining 99.6 % mass up to 900 °C. AP50 Al₂O₃ powder reduced in mass gradually to 95.3 % at 900 °C. Figure 6.9d shows the normalised mass loss against temperature (left axis) and the DTG (right axis). AP50 and AP300 showed some mass loss below 100 °C, which was attributed to evaporation of physically adsorbed water. In terms of normalised mass loss, 35 % of the loss occurred below 100 °C, suggesting that the difference between Al₂O₃ types was the surface area available for adsorption of water. Between 100 and 900 °C the normalised mass loss showed slightly differing behaviour. An equilibrium between aluminium oxide-hydroxides and Al₂O₃ occurs at approximately 370 °C (below 200 bar), and this may be identified as a small contribution in the DTG of AP50 and the normalised mass loss of AP300 [419]. Therefore, the slight differences above 150 °C were most likely due to slightly different hydroxide surface species.

The AP50 separator (termed AP50S here) was a composite of AP50, PAA and SBR, and displayed similar mass loss behaviour to AP50 powder until 300 °C, along with some underlying degradation of the PAA as expected. There were two large decomposition peaks

in Figure 6.9d, at 420 °C and 600 °C, the last of which in particular was not previously resolved in the individual constituent materials. Decomposition continued until a higher temperature (~720 °C) than the polymers by themselves (620 °C), potentially due to the reduced thermal conductivity of the composite separator or the degradation of some new species formed between the Al₂O₃, the Al₂O₃ surface species and/or one or more of the polymer components at lower temperature. At 900 °C, AP50 powder had 95.3 % of original mass remaining, while AP50S retained 91.2 %. This difference was slightly less than that expected due to the combined 6 wt.% of PAA and SBR in the oxide separator, but lies within the likely error of the technique.

Overall, polymer degradation behaviour was broadly similar, suggesting they would have very limited utility on their own above ~300 °C, although potentially cell rupturing gaseous products were released at even lower temperature. In contrast, Al₂O₃ particles in AP50 separators were stable even above 500 °C. Although the AP50 separator also required a minor fraction of the polymers that may shrink and partially degrade, physical separation would likely endure in a full cell. It is not suggested that normal operating temperatures of the cell assembly could be increased (although this might be considered), rather that a ceramic-based separator might extend overall life under normal operation and provide a much more robust response to the development of any thermal inhomogeneities.

Electrolyte wetting and uptake – The performance of polymer separators can be improved significantly by improving their wettability with the electrolyte [361, 420, 421]. A high contact angle (poor wetting) is usually expressed as a relatively high electrolyte resistance across the separator and even unfilled pores may result. An advantage of an oxide-based separator may be a greater intrinsic compatibility with common electrolyte solvents. Figure 6.10 shows contact angle measurements of a 50/50 v/v mixture of ethylene (EC) and dimethyl carbonates (DMC) on a Celgard 2500 separator, a SS spacer and SS spacer coated with an AP50 separator, with contact angles of $64.9 \pm 5.5^\circ$, $35.8 \pm 1.2^\circ$ and $\sim 0^\circ$, respectively. A coating of only 5 μm of Al₂O₃ reduced the contact angle of the SS

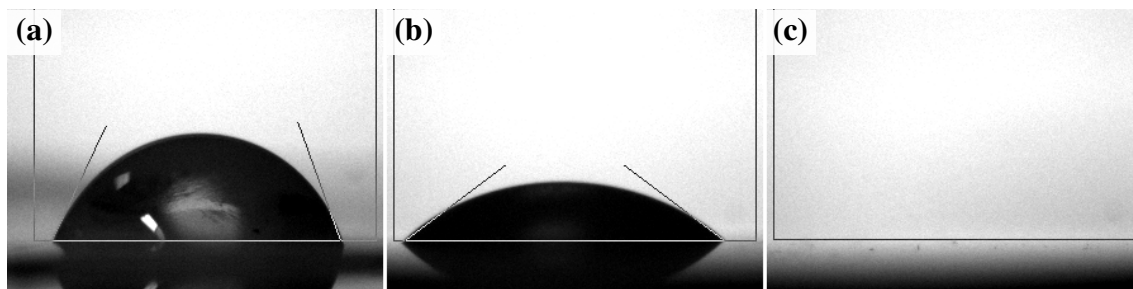


Figure 6.10: Contact angle measurements of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a 50/50 v/v mixture dropped onto (a) Celgard 2500, (b) a SS spacer and (c) a SS spacer coated with a spray deposited AP50 separator.

spacer from 36° to $\sim 0^\circ$.

6.3.3 Electrochemical properties of spray deposited Al_2O_3 -based separators

This section characterises the impedance, voltage stability and galvanostatic cycling of AP50-based and Celgard 2500 separators.

Separator impedance – Figure 6.11a shows Nyquist plots from electrochemical impedance spectroscopy (EIS) that were used to estimate the ionic conductivities of electrolyte soaked separators in SS/separator/SS coin cells. The equivalent series resistance scaled to area, determined by the intersection of a best-fit line to a Nyquist plot with the Z-real axis and normalised by the substrate area (1.9 cm^2) was 0.35, 0.54, 0.84 and $1.62 \Omega \text{ cm}^{-2}$ for 5, 11, and $22 \mu\text{m}$ thick AP50 separators and a Celgard separator, respectively. Figure 6.11b plots the equivalent series resistance against the separator thickness and shows an approximately linear relationship for the AP50 separator. The contribution from coin cell components and wiring to the equivalent series resistance of $\sim 0.4 \Omega$ was estimated from extrapolating to an AP50 separator of zero thickness, i.e. the intersect with the impedance y-axis in Figure 6.11c, similar to 0.35Ω determined previously [422]. Using Equation 6.1, the ionic conductivity of the AP50 separators was estimated as $1.00 \pm 0.04 \text{ mS cm}^{-1}$, approximately double that of the Celgard 2500 that was

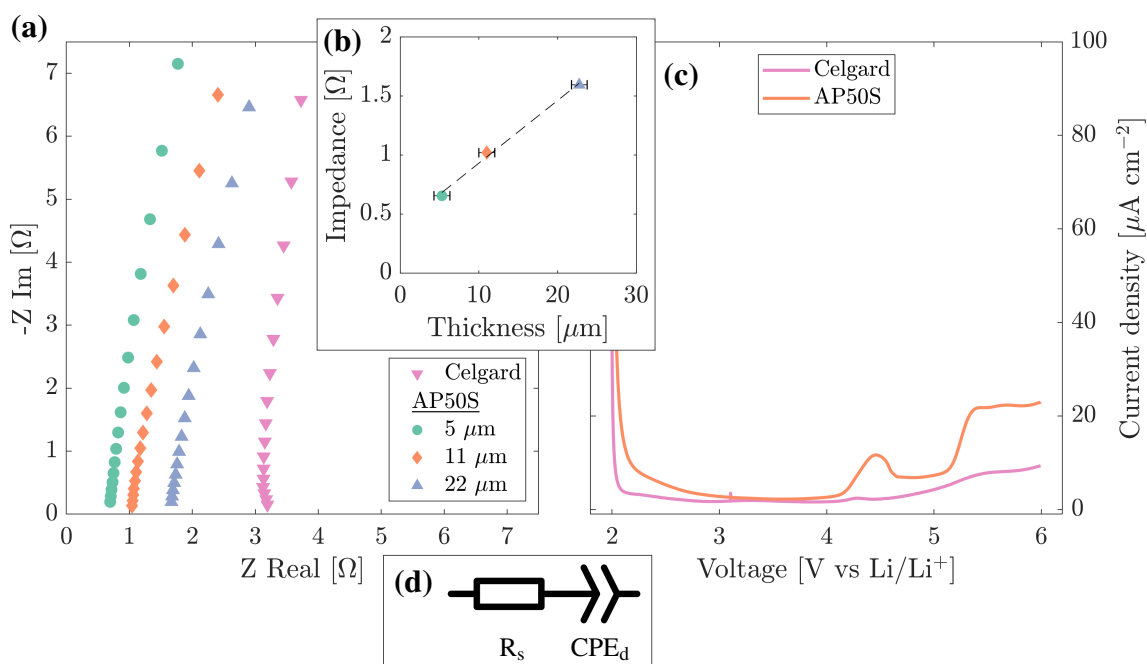


Figure 6.11: Impedance spectroscopy and linear voltage sweep response of separators soaked in a 1.0M LiPF₆ EC/DMC 50/50 v/v electrolyte. (a) Impedance spectroscopy between 10–200 kHz for Celgard and 5, 11, and 22 μm thick AP50 separators, (b) the relationship between equivalent series resistance and AP50S separator thickness, (b) linear voltage sweeps for Celgard and 11 μm AP50 separator.

estimated as $0.50 \pm 0.01 \text{ mS cm}^{-1}$. The higher ionic conductivity and lower equivalent series resistance was attributed to the superior wettability of the AP50 separator already shown.

Electrochemical stability – The stability of the separators under electrochemical conditions was studied using linear sweep voltammetry on SS/separator/SS coin cells in 1.0M LiPF₆ EC/DMC 50/50 v/v electrolyte, as shown in Figure 6.11b. The Celgard separator showed a current density of $\sim 1.7 \mu\text{A cm}^{-2}$ up to 4 V, and then a continual rise in current density after ~ 4.5 V. The small peak in current density at 4.2–4.3 V was due to the oxidation of water (based on standard hydrogen potentials) [423, 424]. The current density of the AP50 separator up to 4 V was $\sim 2.4 \mu\text{A cm}^{-2}$, slightly higher than that of the Celgard separator.

The water oxidation peak was relatively large at $11.6 \mu\text{A cm}^{-2}$ over 4.2–4.6 V, and was

likely due to the hydrophilic PAA dispersant and high surface area of the AP50 separator. The current density of AP50 reduced to $7.5 \mu\text{A cm}^{-2}$ at $\sim 5 \text{ V}$, close to $4.5 \mu\text{A cm}^{-2}$ of the Celgard separator. Above 5.1 V , the current density for the AP50 separator was ~ 2 times that of Celgard. Overall, the AP50 separator displayed adequate voltage stability up to 5 V but there may be room for further improvement with the use of more stable polymer binders and improved drying procedures.

Galvanostatic cycling – Half-cells consisting of LTO/separator/Li were fabricated and the rate performance of AS1 ($5 \mu\text{m}$ AP50 separator), AS3 ($22 \mu\text{m}$ AP50 separator) and Celgard 2500 cells investigated between 0.1 and 30 C , as shown in Figure 6.13a. AS1 and AS3 cells produced consistent capacities with a maximum difference in capacity of 2% at 30 C . Between 0.1 to 10 C , all cells had an initial discharge capacity of $170 \pm 2 \text{ mAh g}^{-1}$, with the largest difference in capacity of only 2.8% between AS1 ($136.2 \pm 1.0 \text{ mAh g}^{-1}$) and Celgard separators ($132.5 \pm 1.9 \text{ mAh g}^{-1}$) at 10 C . However, at higher rates, AS1 and AS3 outperformed the Celgard with an 8.1% improvement of $125.5 \pm 1.0 \text{ mAh g}^{-1}$ over $116.1 \pm 2.3 \text{ mAh g}^{-1}$ at 20 C , and a 27.8% improvement of $118.3 \pm 1.2 \text{ mAh g}^{-1}$ over $92.5 \pm 6.4 \text{ mAh g}^{-1}$ at 30 C . The AP50 separator performance had a relatively low standard deviation between cells, which arose due to the excellent wetting of the electrolyte and fine-scale microstructural uniformity of the spray deposited separators. Although AS3 retained similar capacity to AS1 up to 30 C , it was expected that a difference might emerge at even higher rates, due to differences in their impedances shown earlier in Figure 6.11a.

Cycle stability was assessed at 2 C over 400 cycles, as shown in Figure 6.13b. All cells had an initial capacity of $156 \pm 1 \text{ mAh g}^{-1}$ at 2 C on the first cycle (assumed as 100% capacity). After 400 cycles, AS1, AS3 and Celgard retained capacities of 97.5 ± 0.9 , 96.0 ± 0.4 and $91.4 \pm 1.4 \%$, with a capacity loss per cycle of 0.0068 , 0.0093 and 0.0209% , respectively. The two to three times greater capacity retention for the AP50 separators was ascribed to their significantly lower impedance and improved wetting compared with that of the Celgard separator; an assumed increased robustness to compression may also have

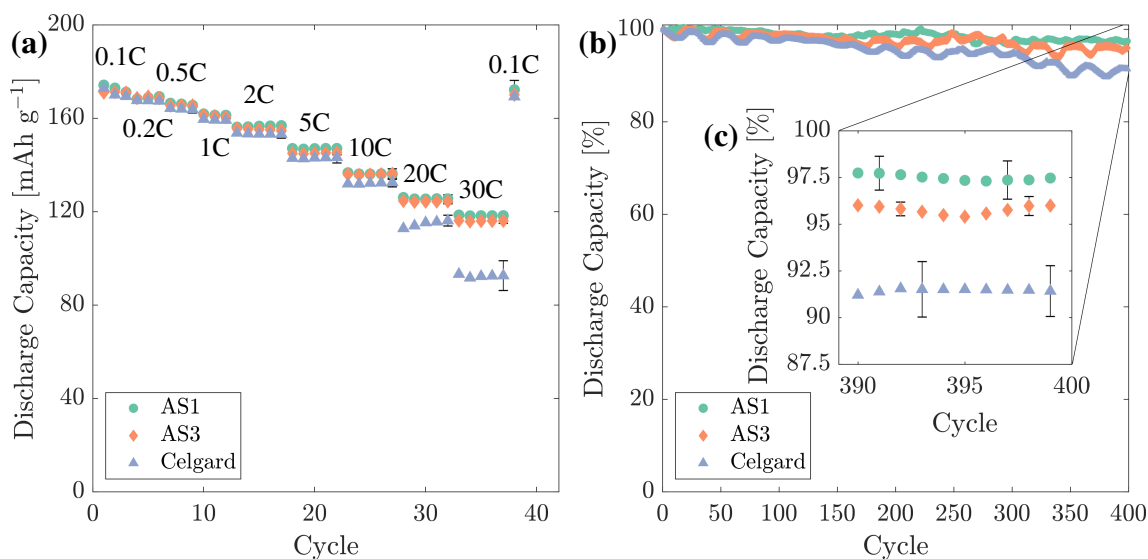


Figure 6.12: A comparison of LTO half cell performance using Celgard or AS separators. (a) Cycling performance between 0.1 and 30C, (b) long term cycling at 2C for 400 cycles and (c) a magnified inset of the last 10 cycles in (b).

been a factor.

It is worth recalling that the sprayed electrodes in the half cells tested here were not calendared and were relatively rough (1–2 μm). Nonetheless, the 5 μm AP50 separator (AS1) provided consistent, high performance enabled by the excellent conformal coating and even coverage provided by the layer-by-layer deposition technique.

6.3.4 Physical and electrochemical properties of full cells

Previous work has shown two advantageous properties of spray deposition: (1) ability to process multiple layers in a continuous operation, due to "on-the-fly" changing of deposition conditions and incremental drying of layers, and, (2) conformal coating of pre-sprayed substrates. Combining these attributes could enable coating of LIBs onto a variety of substrates, including non-flat geometries.

Figure 6.13 shows the processing steps for manufacturing Li-ion full cells by spray deposition: (a) electrode #1 (LTO-based) was deposited onto SS spacers, (b) an AP50 Al_2O_3 -based separator was deposited onto electrode #1, (c) 3D printed masks were

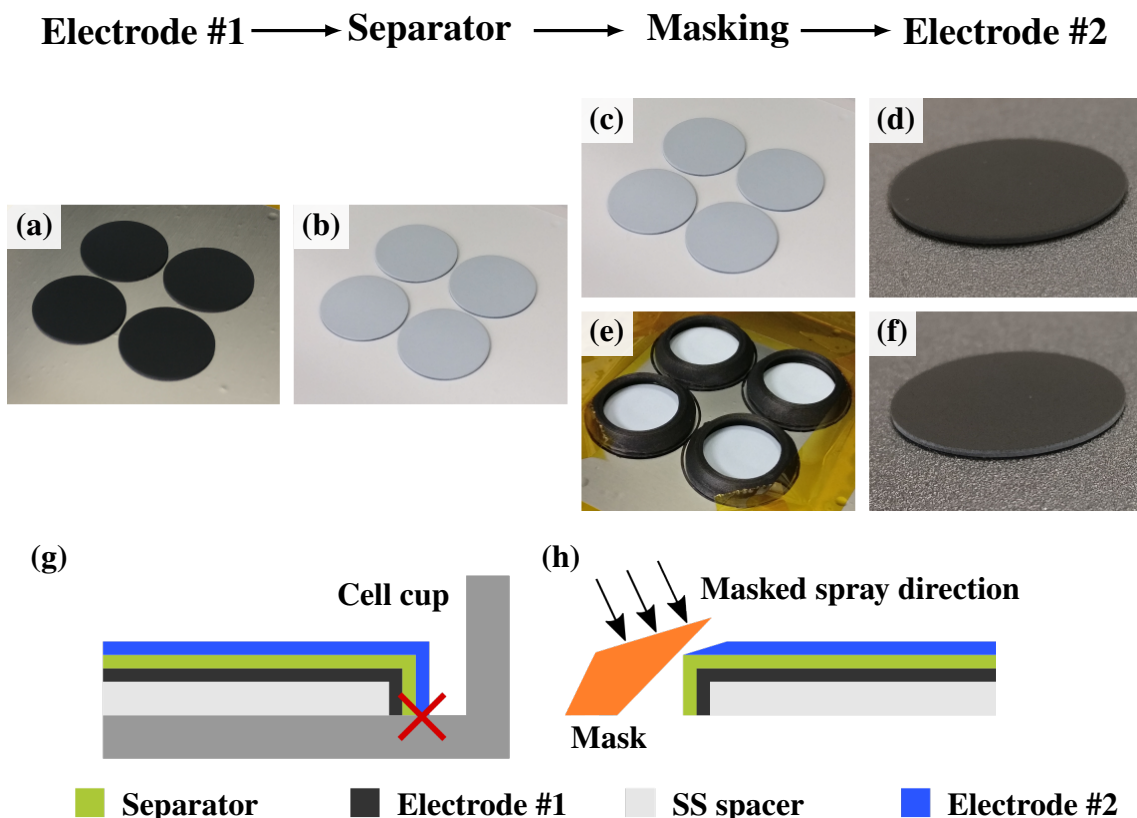


Figure 6.13: The process of manufacturing single step spray deposited full cells: (a) initial electrode layer deposition onto SS spacers, (b) oxide separator layer deposition, (c) 2nd electrode deposition without mask, (d) final full cell with a conformal 2nd electrode, (e) 2nd electrode deposition with 3D printed masks, (f) final full cell with 2nd electrode restricted from conformal coating. Schematic cross-sections of (g) the full cell without 2nd electrode layer masking and (h) the full cell with 2nd electrode layer masking, and the masking process.

positioned over the LTO/AP50 coated spacers, and (f) electrode #2 was deposited onto masked LTO/AP50. Figures 6.13c and d show how deposition without masks resulted in conformal coating of electrode #2 onto the side of the LTO/AP50 coated spacers, leading to short circuits on cell assembly, as shown in the schematic diagram in Figure 6.13g. Figure 6.13f shows the separator layer on the side of the spacer visible even after deposition of electrode #2 that prevented shorting, because of the masking arrangement shown schematically in Figure 6.13h.

Cross-sections of continuous deposition full cells (CDFCs) were examined by SEM imaging and EDX analysis, as shown in Figure 6.14. Ti (blue) differentiated the LTO, Al

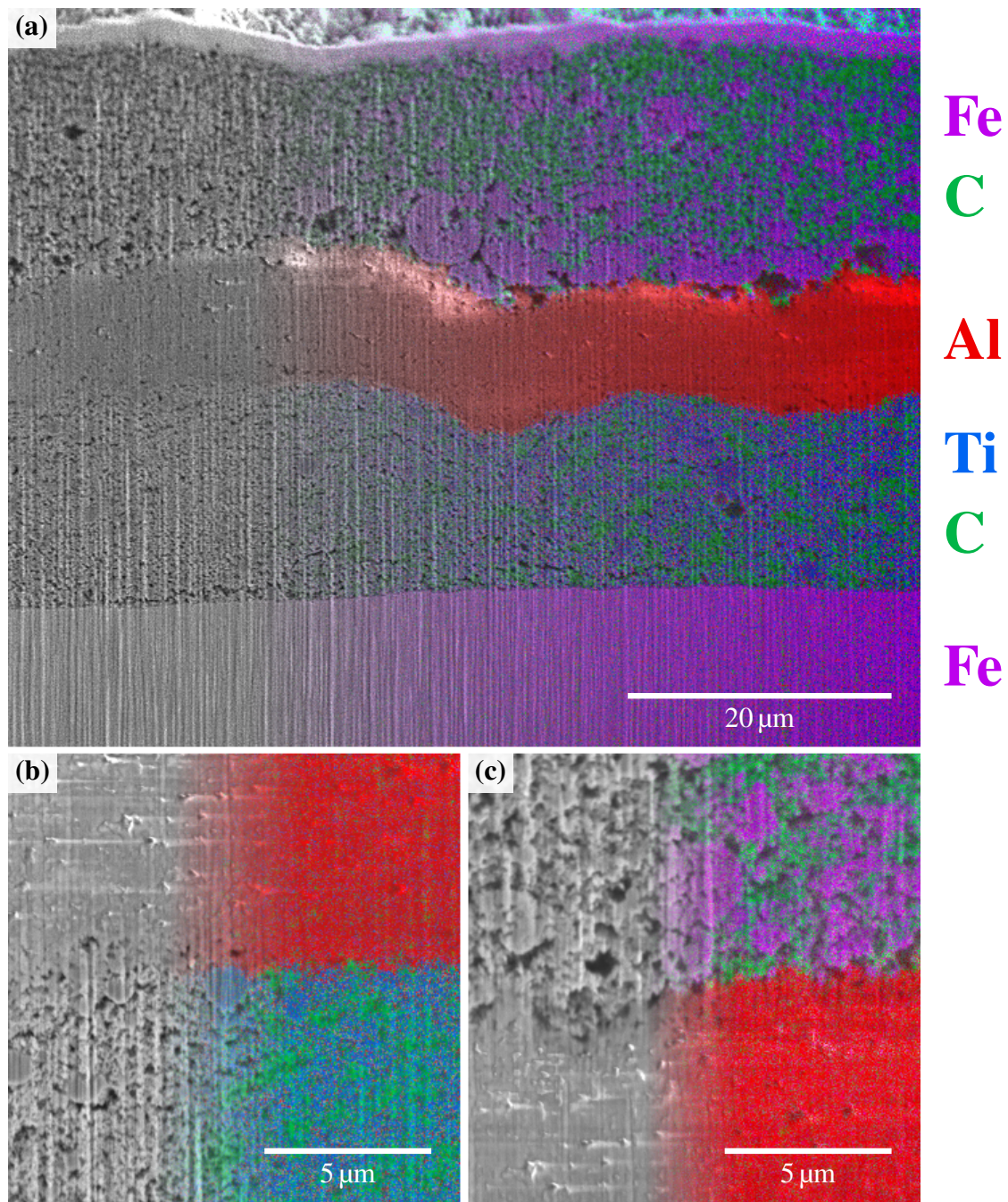


Figure 6.14: A cross-sectional SEM image of an SS/LTO/Al₂O₃ separator/LFP cell with an overlaid EDX map. The layers measure approximately $14.8 \pm 0.2 \mu\text{m}$, $9.7 \pm 0.7 \mu\text{m}$, and $17.7 \pm 1.7 \mu\text{m}$ in thickness for LTO, Al₂O₃ separator and LFP, respectively. The EDX element colour key is displayed on the right of the image.

(red) the Al_2O_3 separator, Fe (purple) the LFP and SS spacer, and C (green) in both the LTO (anode) and LFP (cathode). In this case the LTO-based layer had slightly larger variations in thickness of up to $4\text{ }\mu\text{m}$. Nonetheless, the AP50 separator layer conformally adopted the surface topography of the underlying LTO. The LTO/separator interface appeared to have excellent contact across its length while the separator/LFP interface appeared less consistent, with some pores of $2\text{--}3\text{ }\mu\text{m}$ diameter.

The LFP electrode layer had a generally consistent microstructure, with the impression of perhaps a slight concentration of large LFP particles at the interface with the separator. Larger particles might be preferred early in deposition if they had started to settle to the bottom of the suspension, from where the suspension was drawn for spraying. Figures 6.14b and c display magnified cross-sections of (b) the LTO/separator and (c) the separator/LFP interface. Overall, all the layers showed remarkably good particle packing and consistency of microstructure given the lack of any calendaring step.

Full cell rate testing, shown in Figure 6.15a and b, was performed between 0.1 and 30 C calculated based on the LFP cathode mass for both the continuous deposition full cells using an AP50 separator (CDFC) and the conventional full cells using a polypropylene Celgard 2500 separator (PPFC). Electrodes for CDFC and PPFCs were manufactured using spray deposition. An LFP:LTO capacity ratio of 1:1, according to the experimental 0.1 C capacities measured previously, was ensured by weighing the mass of cells during the spray step and adjusting deposition time as needed.

Figure 6.15a shows the typical voltage profiles of the LTO/LFP full cells, with the discharge plateau at roughly 1.85 V, steep changes of voltage near full and depleted lithiation and increasing polarisation as current density increased. At 0.1C, PPFCs and CDFCs had a capacity of $0.57 \pm 0.01\text{ mAh}$ and $0.55 \pm 0.01\text{ mAh}$, which aligned with the average active mass deposited of LFP of 4.1 and 3.9 mg, respectively. For rate comparison, the 0.1 C capacity was taken as 100 % capacity. Between 5 and 20 C, PPFCs had a greater capacity at the start of each set of 5 cycles, but lost a little capacity each cycle. CDFC capacity

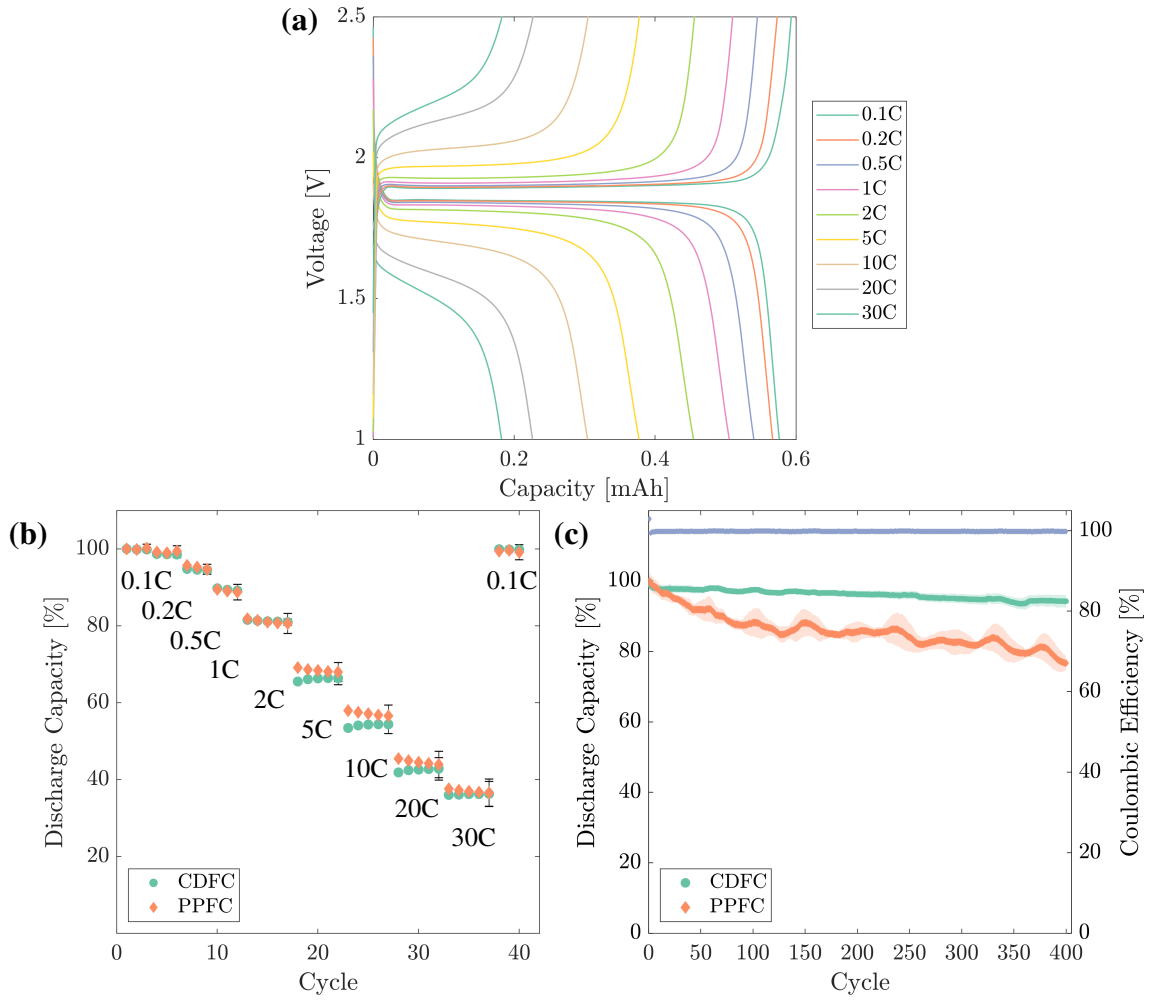


Figure 6.15: Electrochemical testing of SS/LTO/separator/LFP full cells manufactured using continuous spray deposition with an AP50 separator (CDFC) or conventional assembly using a polypropylene Celgard 2500 separator (PPFC). (a) Voltage profiles of a PP separator full cell, (b) Rate testing of full cells between 0.1 and 30 C with respect to the cathode active mass. (c) Cycle stability of cells over 400 cycles at 2 C.

slightly increased during each set of cycles, until PPFC and CDFC capacities were almost equal at 30 C at 0.2 mAh or 36 % of initial 0.1 C capacity. During the recovery cycles at 0.1 C, PPFC and CDFC cells recovered capacities of 99 % and 100 % of their initial 0.1 C capacity.

Cycle stability of the full cells was examined over 400 cycles at 2 C directly after the rate testing, as shown in Figure 6.15c. PPFCs and CDFCs had the same initial capacity of 0.44 mAh, reducing to 0.34 and 0.42 mAh after 400 cycles. The average coulombic

efficiency of both cells was 99.8 %. After 400 cycles, PPFCs and CDFCs retained 78.1 and 96.2 % of their initial 2 C capacity, respectively. PPFC displayed significant capacity loss between 0-100 cycles, 0.1 % per cycle, improving to 0.04 % per cycle between 100-400 cycles. Relating these values to LTO half cells with Celgard 2500 separators in Figure 6.12, the capacity retention for PPFC was almost 2 to 2.5x worse. It should be noted that the LFP capacity was intrinsically less stable than the LTO under long term cycling, so a slightly poorer capacity retention was expected. However, the CDFC capacity retention of 0.01 % was similar to the AS1 and AS3 half-cells of 0.007 and 0.009 %, respectively.

Therefore, the AP50 spray deposited separator enabled stable Li-ion cells to be fabricated using a single technique, with the anode, separator and cathode deposited on one another in a sequential process. These promising results should promote interest into comparison with more advanced commercial separator technologies (high rate and long life) and further refinement of the spray coated separator technique.

6.4 Conclusions

In summary, Al_2O_3 and Y_2O_3 -based separators were coated directly onto pre-sprayed Li-ion electrodes using a layer-by-layer (LBL) spray deposition technique. Initial optimisation of sprayed separators was performed by comparing separators containing oxide particles of varying chemistry, size and morphology based on galvanostatic cycling of LFP-based half cells. An optimised Al_2O_3 -based (50 nm particle diameter) separator was characterised further and compared with a commercial Celgard 2500 separator by electrochemical testing in LTO-based half cells. Finally, a novel full cell was manufactured in a continuous sequential deposition process, and oxide separator performance compared with a conventional full cell assembled with a Celgard 2500 separator.

A sodium salt of PAA at 1 wt.% of solid mass was effective at dispersing Al_2O_3 particles, and 1 wt.% CMC was favourable for Y_2O_3 , while 5 wt.% of SBR gave adequate

strength to the oxide separators on drying. Oxide separator surface morphology was qualitatively more uniform with a water/IPA 80:20 vol.% solvent, attributed to a greater Marangoni flow during drying that efficiently self-assembled the <100 nm particles. The separators conformally coated onto uncalendered pre-sprayed electrodes. Separators deposited from Al_2O_3 particles of average diameter 50 nm suspended in water, and 300 nm from a water/IPA mixture were unable to protect LFP-based electrodes against short circuits during half cell testing, while Y_2O_3 separators from a water/IPA mixture failed after high rate testing. 50 nm Al_2O_3 deposited from a water/IPA solvent formed separators (AP50) that enabled LFP-based half cells to retain ~80 % capacity after 400 cycles.

AP50 separators between 5 and 22 μm thick had consistent and similar porosity of ~58 %, excellent wettability (contact angle $\sim 0^\circ$), thermal stability to greater than at least 180 $^\circ\text{C}$, adequate electrochemical stability and high ionic conductivity of 1 mS cm^{-1} , which was double that of a commercial PP separator. Furthermore, LTO half cells with 5 μm and 22 μm AP50 separators showed improved rate performance and excellent cycle stability (0.007–0.009 % capacity fade per cycle) compared with Celgard 2500 (0.021% capacity fade per cycle), due to the improved compatibility of the electrolyte and separator.

A full cell manufactured in a continuous sequential processing step with a 10 μm AP50 separator (CDFC), the first of its kind, showed similar rate performance to a conventional Celgard 2500 full cell (PPFC) retaining 36 % of 0.1 C capacity at 30 C. After 400 cycles at 2 C, CDFCs displayed excellent capacity retention of 96.2 % of their initial 2 C capacity, compared with 78.1 % for the PPFCs, due to the lower impedance of the AP50 separator in the CDFC assembly.

Further avenues to improve the oxide separator were identified, such as selecting particles with lower density, improving the separator drying step and using a dispersant with better dispersive and thermal properties than NaPAA. Nonetheless, this work showed that a single deposition technique can be used to process both electrodes and separators for Li-ion batteries, and that cells manufactured using this assembly technique can have

similar or greater performance than those assembled with a Celgard 2500 separator.

Chapter 7

Conclusions

A scalable layer-by-layer (LbL) spray processing technique has been investigated for the fabrication of electrodes and separators for lithium ion batteries (LIBs) with novel arrangements of constituent materials. A variety of mixing methods were investigated for creating stable, well-dispersed water-based suspensions of LFP, CMC and CB. The optimal method was slurry mixing using a ball mill (BM) before dilution. Spray deposited LFP electrodes based on the BM mixing method had the same capacity ($\sim 148 \text{ mAh g}^{-1}$), rate performance (50 mAh g^{-1} at 10 C) and electrochemical impedance spectroscopy response as those manufactured by conventional slurry casting. Ultrasonic mixing of diluted suspensions and addition of IPA (30 vol.%) reduced suspension stability (i.e. induced agglomeration), and led to a reduction in specific capacity ($\sim 92 \%$) and/or rate performance ($\sim 6 \%$ at 10 C with IPA). The materials suspended in water:IPA (70:30 vol.%) initially dried to form a more uniform electrode layer than those suspended in water only, suggested to arise from a greater Marangoni flow generated from a surface tension gradient forming between the mixed solvents during evaporation.

Slurry cast LFP electrodes from water-based slurries cracked at a thickness of $\sim 10 \mu\text{m}$ and spontaneously delaminated from Al foil current collectors at a thickness of $70\text{--}80 \mu\text{m}$ ($\sim 10 \text{ mg cm}^{-2}$) due to capillary pressure generated during drying. Cracking was suggested to be more severe than observed in the literature for NMC-based electrodes due to the smaller LFP particle diameter and greater capillary pressure generated on drying. Spray

deposited electrodes were crack-free up to at least 115 μm because of sequential drying of each, much thinner suspension layer, approximately equal to the average particle diameter in the suspension. A 115 μm (17.2 mg cm^{-2}) thick spray deposited LFP-based electrode had a reduced capacity retention after 100 cycles when compared with thinner 6 mg cm^{-2} spray deposited or slurry cast electrodes, but provided a significant improvement in volumetric capacity at charge/discharge rates between 0.1 and 2C.

LFP-based electrodes with a through-thickness variation in local particle size and local porosity were produced. Whereas conventional LFP electrodes had a single voltage plateau during discharge, those containing two different particle size distributions had two distinct voltage plateaux which was suggested to be an observation of sequential discharge of barrier-limited active particles. Over 200 0.5 C charge/discharge cycles the electrode made from a mixture of the two distributions (Mix) lost 0.056 % of its original 0.5 C capacity per cycle, while an electrode with higher porosity and smaller particle size next to the separator, and lower porosity and larger particle size next to the current collector (MTI/HQ), lost 0.046 % capacity per cycle, an 18 % improvement. An electrode with the "inverted" arrangement of identical materials (HQ/MTI) lost 0.065 % capacity per cycle, a 16 % decrease.

At low C-rates, the average dQ/dV discharge peak of layered and conventional cells were similar (1 ± 1 mV), as expected since kinetic factors were less dominant at low current density. However, increasing the local porosity fraction and positioning the layer of smaller particles at the separator (MTI/HQ) decreased the average overvoltage during charge and discharge compared with other arrangements of the same materials. During long term cycling, the rate at which the overvoltage increased between 90 - 200 cycles was 0.35, 0.44, 0.47 and 0.52 mV/cycle for MTI/HQ, Mix, HQ/MTI and MTI-only electrodes, respectively. The lower rate at which overvoltage increased for MTI/HQ was suggested to arise due slightly greater Li concentration near the current collector due to the more porous HQ

particle layer near the separator (i.e. lower tortuosity) and lower utilisation of MTI particles, which degrade faster than HQ particles. While previous literature suggested that large particles next to the separator and small particles next to the current collector would be beneficial to electrode performance [305, 306], the experiments here suggested that these effects may not apply to LFP as there are significant disadvantages associated with large LFP particles.

A porous Al_2O_3 -based separator suitable for spray deposition was developed to enable the direct deposition of an electrode/separator/electrode full cell assembly in a single deposition operation. The optimised separator consisted of 50 nm Al_2O_3 particles, 1 wt. % polyacrylic acid (PAA) and 5 wt. % styrene butadiene rubber (SBR), deposited from an 80:20 vol. % suspension of water and IPA. Separators fabricated from 300 nm Al_2O_3 particles, 0.1–3.5 μm Y_2O_3 plate-like particles and water-only suspensions were unable to yield stable cells.

Al_2O_3 -based separators between 5 and 22 μm thick had consistent and similar porosity of ~58 %, excellent wettability (contact angle ~0°), thermal stability to greater than at least 180 °C, adequate electrochemical stability and high ionic conductivity of 1 mS cm^{-1} at room temperature, double that of a commercial PP separator. Analysis of the pore diameter distribution of the Al_2O_3 separator from N_2 gas adsorption suggested an average pore diameter similar to that of the manufacturer's stated average particle diameter of ~50 nm.

An LFP/LTO full cell manufactured in continuous sequential processing steps, with a 10 μm Al_2O_3 separator, the first of its kind, showed similar rate performance to a similar cell with a conventional PP separator, with a capacity of ~50 mAh g^{-1} at 30 C. After 400 cycles at 2 C, the Al_2O_3 separator cell had excellent capacity retention of 96.2 % compared with 78.1 % for the PP separator cell, due to the lower effective impedance of the thin, porous Al_2O_3 -based separator.

The flexible spray deposition approach has been shown to facilitate stable drying

of ultra-thick electrodes, layered electrodes that open a large design space for electrode structural design and improved performance, and relatively thin, porous inorganic separators with enhanced stability.

7.1 Further work

The spray processing technique has shown considerable versatility for Li-ion applications. Through-thickness layering and grading of electrode components (e.g. porosity and conductive additives) has improved the polarisation, SEI layer thickness, rate performance and capacity retention in a variety of different cathode and anode materials. However, due to the increased design space provided by arbitrary layered and graded structures, there are a considerable number of further avenues for potential investigation.

Large format electrodes can have non-uniform polarisation and heat generation, especially within the plane, which could be improved with areal and through-thickness spatial grading of components. If the maximum, average, and heterogeneity of heat generation within these larger format cells could be reduced then manufacturers might realise greater cell lifetimes and safety.

The Al_2O_3 -based sprayed separator showed promising performance in full cells, however the high density of Al_2O_3 and the relatively poor thermal properties of PAA were drawbacks. Lower density, microporous zeolites and polymer dispersants with higher temperature stability (e.g. a lower molecular weight sodium polyacrylate) might reduce the separator mass per unit volume nearer to that of polymer separators, and improve safety further.

Solid-state cells could benefit from thinner solid electrolyte layers and a more scalable production technique [425]. This could be partly enabled by the controllable deposition of thin layers of oxide particles directly onto electrodes, as shown in Chapter 6.

Slurry casting's principal advantage over all potential new manufacturing routes - even those that offer greater structural control or enlarged design space - is its very high

productivity. A more quantitative approach should be developed to allow assessment of the possible scale-up of new processes such as spray deposition, taking into account the possible value of the performance benefits.

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