Understanding the Limitations in Battery Components for Improving Energy Density under Extreme Fast Charging (XFC) Conditions

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I am submitting herewith a dissertation written by Dhrupad Parikh entitled "Understanding the Limitations in Battery Components for Improving Energy Density under Extreme Fast Charging (XFC) Conditions." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Energy Science and Engineering.

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(Original signatures are on file with official student records.)
Understanding the Limitations in Lithium-Ion Battery Components for Improving the Energy Density under Extreme Fast Charging (XFC) Conditions

A Dissertation Presented for the Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Dhrupad Parikh
August 2021
ACKNOWLEDGEMENTS

Success is failure turned inside out -

The silver tint of the clouds of doubt,

And you never can tell how close you are,

It may be near when it seems so far,

So, stick to the fight when you’re hardest hit

It’s when things seem worst that you must not quit.

- Don’t Quit by Edgar Albert Guest

I would like to acknowledge the honor and privilege it has been to be able to work in the Energy Storage and Conversion Manufacturing Group at Oak Ridge National Laboratory and the Bredesen Center for Interdisciplinary Research. The completion of this dissertation would not have been possible without the support, and guidance of several people and I would like to acknowledge my gratitude to these people. With this, I am deeply grateful to Dr. Lee Riedinger (Ex-director of Bredesen Center) for giving me this opportunity to perform research at Oak Ridge National Laboratory. I would also like to thank the staff members of the Bredesen Center for their continuous support and guidance.

With all my heart I would like to express gratitude to my advisor Dr. Jianlin Li for his continuous support, guidance, and motivation throughout my doctoral studies. His guidance helped me during my research and writing this dissertation. His kind and encouraging words, always kept my spirits high, no matter if the results were good or bad.
Along with technical and mathematical skills, he taught the tricks of life, which made decision making easier and helped me improve my personality.

Thanks are due also to my thesis committee members, Dr. David L. Wood III, Dr. Thomas A. Zawodzinski, and Dr. John Zhanhu Guo. Their insightful interjections during my qualifier & comprehensive exams were very helpful in guiding the second half of my life as a graduate researcher. I am grateful to Dr. Charl Jafta, Dr. Rachid Essehli, Dr. Linxiao Geng, Dr. Jaswinder Sharma, and Andrew Todd for sharing all the knowledge and tricks while collaborating on various projects and beyond research. I am also very grateful to all my colleagues at the lab, especially Blake Hawley, Alexander Kukay, and Kelsey Grady Livingston, for having long discussions regarding any doubts with the experiments/results and constantly motivating me during my research. I will make sure to take the lessons I learned from you with me wherever I go in the future.

With all my sincerity I would like to thank to my family members and close friends who have been the support pillars throughout my doctoral studies. This would not have been possible without the immense support my mother, Shilpa; my father, Pragnesh; my twin sister, Dhruti; and my brother-in-law Ruchitbhai. I would thank all my relatives, teachers and mentors who have taught me the fundamentals of life and science. A very special thanks to my girlfriend Ruhani Sagar. Her never-ending love and affection provided me with the strength and motivation to surpass all the hurdles. A huge shout out to the Google Hangouts Public who have been supporting me for the past 12 years, thank you so much Abhishek, Marm, Anand, Sai Mani, Kushan and Bhumil.
ABSTRACT

Presently, there are ~2 million electric vehicles (EVs) in US, which account for only less than 2% market share in automobile sector. The poor adoption of EVs is attributed to three key issues, range anxiety, charging time and higher cost of EVs. Most EVs take ~30 minutes to charge using DC Fast charger, with less than 200 miles. To change the consumer perception towards EVs, it’s important to reduce charging time to that of fueling a conventional IC engine vehicle with a range of more than 200 miles. To reach the U.S Department of Energy goal of extreme fast charging(XFC) along with high energy density >200 Wh kg$^{-1}$, a combined improvement in electrode architecture, electrolyte and separator membrane would be crucial.

This dissertation focuses on improving the energy density of lithium-ion batteries by understanding the bottlenecks in separator membrane, cathode design, and anode architecture under XFC conditions. We develop novel hybrid anode architecture via freeze tape casting with directionally aligned solid particles that improves that rate performance of graphite by ~20% at 5C rate. The enhanced rate performance is attributed to low tortuosity and shorter diffusion pathways of the freeze cast electrodes. Next, we investigate various cathode (LiMn$_{0.6}$Ni$_{0.2}$Co$_{0.2}$O$_2$) design parameters (electrode porosity and mass loading) for developing high energy density electrodes for XFC application. Increasing mass loading from 11.5 mg cm$^{-2}$ to 25 mg cm$^{-2}$ reduces the rate performance due to mass transport limitation and underutilization of thick electrodes. While, reducing the electrode porosity helps in improving rate performance and gravimetric energy density of the cell. In
regard to separator membrane, this work demonstrates that Celgard 2500 has excellent
electrolyte wettability, 2.23 Ω cm\(^{-2}\) less in resistance, attributed to the high porosity and
low tortuosity of Celgard 2500 and improved rate performance at 3C. To address this issue
of thermal shrinkage and self-discharge, separators are coated with ceramics that lead to
high electrolyte wettability, excellent thermal stability (0.6% shrinkage vs 5.8% for
uncoated membrane) at 130°C and lower self-discharge after 350 hours. These results
indicate that, separator membrane, cathode design, and anode architecture play a
significant role in enabling XFC.
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CHAPTER 1
INTRODUCTION
1.1 Energy Storage and Electrification

The world’s energy demands are growing continuously and is predicted to increase by 50% from 2020 to 2040. These demands arise from various sectors for different applications such as agriculture, transportation, electricity, industries, and residential/commercial buildings. Simultaneously, we rely on fossil fuels as one of the prominent sources of energy. However, combustion of fossil fuels lead to the emission of greenhouse gases into the atmosphere. Global warming and climate change are direct consequences of the accumulation of greenhouse gases mainly CO$_2$ and present as a threat to the environment.

The transportation sector is one of the major sources of CO$_2$ emission and hence alternative energy sources for automotive propulsion applications is one of the prime focuses of research throughout the world. As a result, there is an increasing focus on developing clean renewable energy sources. The renewable sources such as solar, wind, and ocean energy are “green” sources of energy, but these are inherently intermittent in nature. Hence, a wide range of stationary energy storage technologies would be required for renewable energy to reach its full potential. Within the umbrella of energy storage technologies, batteries are likely to play a vital role.

In working towards tackling climate change, a huge change in the transportation will be required by transitioning from the current internal combustion (IC) engine cars to zero emission vehicles such as battery electric vehicles (BEVs), plug-in hybrid electric vehicles (PHEV), hydrogen fuel cell vehicles (FCEV) among many others. Developing renewable
energy storage sources and implementing the electrification of the transport sector will be critical in reducing the global CO$_2$ emission.

In order to achieve a sustainable future as described by the International Energy Agency (IEA), the transportation and power generation sector needs to contribute an overall CO$_2$ reduction of 21% and 42%, respectively, by 2050. That means three-fourths of all vehicles sales by 2050 would need to be electric and at least an additional 310 GW of grid storage to be deployed for renewable energy. Meeting the demands of both electrification of transportation sector and grid storage for renewable energy requires the development of new battery technologies that are much cheaper and higher in energy density.

Out of various zero emission vehicles, BEVs are one of the most promising due to their low cost and mature lithium-ion battery technology. Major automobile manufacturers across the world have committed to make huge investments in transitioning towards battery electric vehicles in the next 10 to 20 years. Table 1.1 shows the list of various automobile manufacturers across the world with their timeline to transition towards BEVs.

However, for the successful transition and implementation of EVs, one of the most crucial factors will be building a robust charging infrastructure. To support the efforts initiated by the EV manufacturers, the oil and gas industry has also pledged in transitioning towards carbon neutral by investing and developing charging infrastructure for electrification of the transportation sector. Presently, there are fewer companies across the world that offer different charging options such as the Level 2 (>40 minutes) and DC fast charging (>20 minutes) as shown in Table 1.2.
Table 1.1 Automobile manufacturers and their timelines for transitioning towards BEVs

<table>
<thead>
<tr>
<th>AUTOMOBILE MANUFACTURER</th>
<th>YEAR TO TRANSITION TO ZERO EMISSION VEHICLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General Motors</td>
<td>2035</td>
</tr>
<tr>
<td>2. Volkswagen Group</td>
<td>2026</td>
</tr>
<tr>
<td>3. Toyota</td>
<td>2040</td>
</tr>
<tr>
<td>4. Ford</td>
<td>2035</td>
</tr>
<tr>
<td>5. Honda Motor Co.</td>
<td>2040</td>
</tr>
<tr>
<td>6. Volvo</td>
<td>2030</td>
</tr>
<tr>
<td>7. Jaguar</td>
<td>2025</td>
</tr>
<tr>
<td>8. Hyundai Motor Co.</td>
<td>2040</td>
</tr>
<tr>
<td>9. Lincoln</td>
<td>2030</td>
</tr>
<tr>
<td>10. Mercedes-Benz</td>
<td>2040</td>
</tr>
</tbody>
</table>
Table 1.2 Charging stations in the U.S. as of November 2020

<table>
<thead>
<tr>
<th>CHARGING STATION COMPANIES</th>
<th>NUMBER OF EV CHARGING STATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ChargePoint</td>
<td>30,000</td>
</tr>
<tr>
<td>2. EVgo</td>
<td>1,100</td>
</tr>
<tr>
<td>3. Blink Charging</td>
<td>23,000</td>
</tr>
<tr>
<td>4. Electrify America</td>
<td>600</td>
</tr>
<tr>
<td>5. Volta</td>
<td>1,830</td>
</tr>
<tr>
<td>6. RWE and Daimler</td>
<td>500</td>
</tr>
<tr>
<td>7. NewMotion and Shell</td>
<td>30,000</td>
</tr>
<tr>
<td>8. Powershare and BP</td>
<td>7,000</td>
</tr>
<tr>
<td>9. EVBox</td>
<td>700</td>
</tr>
<tr>
<td>10. G2Mobility and Total</td>
<td>10,000</td>
</tr>
</tbody>
</table>
1.2 Significance of Fast Charging in Lithium-ion Batteries

According to the recent reports, the current EV market share is only ~4% of the IC engine vehicles. The poor adoption of electric vehicles is mainly due to two major factors, a) range anxiety and b) longer charging time. Currently, BEVs rely mainly on residential and workplace charging which are categorized as Level 1 and Level 2 alternative current charging points with a charging time in the order of tens of hours as shown in Figure 1.1. Direct current fast charging (DCFC) is another viable option that adds 80-100 miles of driving range with 20 minutes of charging. However, the number of DCFC stations are significantly low in comparison to the number of EVs on road.

Low cost EVs like the Chevy Bolt and Hyundai Ionic are only able to deliver less than 120 miles on a single charge of 30 minutes. While EVs such as Lucid, Volvo, and Rivian are able to add a little close to 180 miles with a 15 minute charging time, however, they are tremendously expensive. Even the fastest Tesla superchargers take up to 20 minutes to add 200 miles on a single charge. The current state-of-the-art fast charging capabilities are far from offering a similar refueling experience as conventional IC engine vehicles. To accelerate the mass adoption of EV, it is necessary to speed up the fast-charging goals such that the EV charging time could be matched with refueling of an IC engine vehicle while delivering more than 250 miles on a single charge. Hence, the U.S. Department of Energy has identified extreme fast charging (XFC) as a critical challenge for quicker transitioning towards EVs, resulting in curbing greenhouse gas emission, and ensuring greater energy security.
Figure 1.1 Comparison of charging requirements (time and power) for various charging stations with regards to XFC
As the automobile market gears up on shifting towards electric vehicles with various automakers making huge investments in manufacturing BEVs, it is imperative to develop batteries that are cheaper, and can deliver high energy density under fast charging conditions. The U.S. Advanced Battery Consortium (USABC) has defined specific goals for low-cost fast charge of EVs that would deliver high energy density with 15 minutes charge time for 80% of the pack capacity. The key metrics target as per USABC regarding cost and energy density are US$75 kWh⁻¹, 550 Wh L⁻¹ and 275 Wh kg⁻¹ should be regarded as a standard for battery packs used in EV application [1].

For widescale automotive applications, lithium ion batteries are limited by volumetric and gravimetric energy density, as well as with charging times (>15 minutes). There is room for a lot of improvement with better engineering of electrode (cathode and anode) design, modifying separator membranes, and exploring novel material that can deliver high energy density and avoid issues such as lithium plating. The aim of this work aligns with the above discussion and focuses on improving the energy density and extreme fast charging capabilities of LIBs by understanding the bottlenecks in anode, cathode and separator membrane from material, architecture, and design perspective.

1.3 Limitations of Fast Charging

The present lithium ion battery chemistry in liquid electrolyte is unable to achieve XFC goal without adversely affecting the cell performance and safety. As batteries are charged at high rates, they lead to various issues in the cell such as increase in overpotential, electrode underutilization, lithium plating, excess heat generation, and many more. Before
delving into the details of these issues related to fast charging, it is important to understand the working of a lithium ion battery.

A lithium ion battery cell is composed of a negative electrode and a positive electrode as shown in Figure 1.2. These electrodes are separated by a separator membrane which has a finite ionic conductivity and negligible electronic conductivity. The cell is filled with electrolyte that facilitates the mobility of ions. The potential difference between the two electrodes drives the ions from one electrode to the other. The current collectors transfer the electrons through the external circuit. The commercially available lithium ion batteries commonly contain graphite as a negative electrode material. At the same time, lithium iron phosphate, lithium cobalt oxide, spinel or their derivatives are commonly used positive electrode material. A typical electrolyte is 1:1 by volume mixture of ethylene-carbonate (EC) and ethylmethyl-carbonate (EMC) with 1M LiPF₆ salt. Polyolefins have proven stable over time and are universally used in lithium ion cells as separator membranes.

The functioning of a lithium ion battery is based on the lithium insertion mechanism. While discharging, a lithium atom leaves the negative electrode leaving an electron behind and enters the electrolyte in the ionic form. This lithium ion travels through the electrolyte towards the positive electrode where it gains an electron and thus is converted back to the atomic state. This atomic lithium is inserted and stored in the positive electrode material. The electron travels through the external electrical circuit and thus we get external current.
Figure 1.2 Schematic of a conventional Lithium-ion battery showing the anode, cathode, separator membrane, electrolyte, and current collectors
The successful implementation of XFC would require significant efforts in research and development of batteries across multiple levels, right from electrode-electrolyte chemistries to cell design engineering to pack level improvements. From the aspect of cell chemistry, there are two major limitations to extreme fast charging, a) mass transport limitation and b) charge transfer kinetics. These limitations are mainly governed by three key mechanisms described in Figure 1.3, ion transport 1) in the electrolyte including solvation/desolvation processes, 2) through porous electrode and bulk active material, and across electrode/electrolyte interface - solid electrolyte interphase (SEI) film.

A schematic representation of these limitations at the electrolyte-anode interface are shown clearly in Figure 1.4 showing the solvation and desolvation (breaking of the solvation shell) processes in the electrolyte, the diffusion through the SEI layer which requires the highest activation energy and the diffusion through the bulk anode, graphite in this case. The electrolyte properties such as the transference number and ionic conductivity play a significant role in governing the solvation-desolvation processes, while the nature of salt and its molar concentration govern the SEI layer formation as well as the lithium ion diffusion through the SEI interphase. For instance, short-chain esters demonstrate inferior oxidation stability than baseline electrolytes and the resulting solid electrolyte interphase (SEI) is less favorable. A judicious selection of additional film-forming additives is needed for ester-rich electrolytes. Therefore, in order to effectively address these challenges, improvements in multiple aspects would be required for achieving the U.S. DOE goal of extreme fast charging.
Figure 1.3 Various factors contributing to the mass transport and charge transfer limitation in a lithium ion cell

Figure 1.4 Schematic of lithium intercalation and charge transfer process from cathode to graphite anode through electrolyte
Figure 1.5 shows a chart with various limiting factors in LIB components (electrodes, electrolyte, and separator membrane) affecting the high rate capability application. For instance, to address the issues with the mass transport limitation in the electrolyte phase, the electrolyte properties would play a crucial role. The transference number and the ionic conductivity/diffusivity of the electrolyte would significantly affect the fast charging capability of LIBs in terms of concentration polarization and lithium plating. To further tackle the mass transport limitation, tailoring the electrode porosity and tortuosity could enhance the rate performance via reducing the lithium ion diffusion pathways through the electrode. Electrode engineering is another facet that needs to consider for developing high energy density electrodes for high rate capability application.

In case of the sluggish intercalation kinetics and charge transfer limitation, improvements in the electrolyte is required to tackle two major concerns, a) accelerate the solvation-desolvation processes, b) lower the resistance across the SEI layer as it requires highest activation energy for the lithium ion to diffuse through it.

1.4 Research Objectives

As discussed in the earlier sections, for EVs to reach their full potential and compete with IC engine vehicles, it is critical to tackle the two main issues, range anxiety and charging time. The U.S. Department of Energy has identified a goal for extreme fast charging (XFC) of LIBs with a charging time of less than 15 minutes while delivering greater than 200 Wh kg\(^{-1}\) energy density.
Figure 1.5 Limiting factors for fast charging application in different battery components
In this dissertation, it is demonstrated that different battery components such as cathode, anode, and separator membrane contribute to the limiting factors for fast charging. The mass transport and charge transfer kinetics are the two major factors which can be further divided into different process such as solvation-desolvation process, Li-ion diffusion through the SEI layer, bulk diffusion through the porous electrode and the active material, and Li-ion diffusion through the tortuous separator membrane.

One of the major challenge during fast charging is Li-plating on graphite that is significantly influenced by all the factors mentioned above. Chapter 3 addresses the issue of lithium plating on graphite electrode by attempting to understand the influence of different electrode properties such as porosity, mass loading, and particle size on the onset and nucleation of Li-plating. The correlation of lithium dendrite morphology (mossy vs whisker structures) and electrode porosity is also explored. In order to tackle the issue of Li-plating during fast charging, it is critical to understand the bottlenecks in various battery components and determine a combined way of making improvements in all these sections in order to enhance the lithium-ion diffusivity for fast charging application.

To begin with, Chapter 4 addresses one of the main battery components that is a limiting factor for fast charging, the anode. This chapter investigates two different aspects of anode, 1) novel electrode architecture via freeze tape casting of graphite; 2) exploring a new material (titanium niobium oxide (TNO) - TiNb$_2$O$_7$) for high rate capability in order to address the issues with lithium plating on graphite. In the first part, a novel hybrid electrode architecture is developed via aqueous processing of graphite. Freeze tape casting
is used for developing this novel architecture, that imitates a roll-to-roll process, and creates an electrode with directionally aligned solid particles that improve the lithium-ion diffusivity due to the lower electrode tortuosity. Electrochemical performance will be carried out to understand the improvements that could be leveraged with the help of freeze casting.

In the second part, a new material is explored mainly to address the never-ending issue of lithium plating with graphite based chemistries. TNO comes from the same family as lithium titanium oxide (LTO) and has the advantage of high redox potential vs Li as well as higher theoretical capacity (387 Wh kg\(^{-1}\)) than graphite and LTO. Taking advantage of these properties, TNO based pouch cells will be tested under XFC conditions. To understand the swelling of pouch cells during long-term cycling and to understand the degradation in capacities, an operando gassing study is also performed to determine the reason for failure after 300 cycles. To tackle the gassing behavior, a protective barrier coating is developed on the TNO to reduce the gas evolution during low and high current cycles.

After addressing the anode, chapter 5 focuses on cathode design which is crucial for improving the energy density of LIBs under extreme fast charging conditions (total charging time = 10 minutes). This chapter reports a systematic investigation on optimizing NMC622 cathodes for XFC application. A matrix of 4 mass loadings and porosities (16 conditions) are investigated. All electrodes are calendared to different electrode thicknesses to obtain the target porosity and mass loading. In addition, the influence of charging
protocol on the gravimetric and volumetric energy density under XFC was also evaluated. Impedance spectroscopy was further used to characterize the electrode tortuosity and diffusion length for understanding the implications of the rate performance.

The final piece of puzzle looks into one of the important battery components. Separator membranes play a crucial role in maintain the safety of Li-ion cell by preventing electric short circuit, while facilitating Li-ion diffusion through the membrane. Several separator properties such as porosity, thickness, tensile strength, and thermal stability are important to consider while selecting a membrane for various applications. Chapter 6 correlates the physical properties of separator membrane to the electrochemical performance and high rate capability. The two widely used separator membranes, Celgard 2325 and Celgard 2500, with different porosity and polymer structure (tri-layer vs single layer) are used to understand their physical properties such as electrolyte wetting, contact angle, and thermal stability, and correlate with the electrochemical performance under fast charging conditions. Impedance spectroscopy further used to characterize the ionic resistance and tortuosity of the membranes.

While single layer membranes show excellent rate performance, they are prone to lack in thermal stability and self-discharge. In chapter 7, binary ceramic coating are applied on one side of thin single layer membranes to understand their impact on thermal conductivity, thermal shrinkage, electrolyte wettability, and self-discharge. Impedance spectroscopy and electrochemical rate performance are carried out to better understand the
influence of ceramic coatings on separators. Finally, Chapter 8 discusses the summary of the experimental results that have been discussed in this dissertation work.
CHAPTER 2
EXPERIMENTAL TECHNIQUES
2.1 Material Property Characterization

2.1.1 Scanning Electron Microscopy

Scanning electron microscopy is an optical technique to characterize morphology of materials at the nano-scale. SEM images are generated by capturing reflected/knocked off electrons from the sample surface and thus can provide information regarding morphological features of the investigated material. In addition to morphological information, energy dispersive spectroscopy (EDS) mapping can be used to track distribution of elements within the sample.

2.1.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is a surface sensitive technique used to probe elemental compositions on the surface, chemical state, as well as the electronic structure. XPS employs photoelectric effect to investigate these parameters wherein monochromatic X-rays near an absorption edge of element of interest are impinged on the sample and the energy of the emitted electrons are measured by the detector. At the absorption edge, the energy of the emitted shows a significant change in the measured intensity enabling to quantify the surface concentration of the elements. In addition, depending on the valence of the elements in the probed material, the binding energy of the emitted electrons shift enabling to quantify the electronic structure and valence of the elements of interest. While XPS is primarily a surface sensitive technique, if coupled with ion-beam etching, depth resolved measurements can be carried out. It should be noted that almost all XPS
measurements are carried out under ultra-high vacuum conditions. In addition to assessing elemental distribution and valences, XPS can also provide information regarding surface chemical bonds across different elements by carrying out appropriate fittings. XPS can be used to detect elements Z>2, with detection limits typically in parts per thousand range.

2.1.3 Contact Angle Measurements

Contact angle is defined as the angle made by the liquid-vapor interface in contact with the solid surface. Contact angles provide information regarding the interaction strength between the liquid and the solid with a low contact angle indicating strong affinity and higher wettability and vice versa. The contact angle is typically given by the Young’s equation:

\[ \gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos \theta = 0 \]

where, \( \gamma_{SG} \) is the solid-gas interfacial energy, \( \gamma_{SL} \) is the solid-liquid interfacial energy, \( \gamma_{LG} \) is the liquid-gas interfacial energy and \( \theta \) is the contact angle. Contact angle is measured typically by optical experiments wherein a dense solid material is kept on a horizontal stage with a controlled quantity of liquid dropped on the surface of the material investigated. Subsequently, the drop on the surface is imaged with a high-resolution camera and the contact angles are estimated through software using basic geometrical fittings.
2.1.4 *Thermal stability*

Thermal stability of materials is typically investigated by exposing the separator samples in a vacuum oven for a certain period of time. In this measurement a specific quantity of material is heated in a controlled environment while measuring the mass change of the sample over time. This measurement allows for estimating information related to physical changes in the shape and size of the separator membrane.

2.1.5 *Rheology*

Rheology measurements are carried out to assess viscoelastic properties of the slurries made for electrodes. Unlike solid or liquid materials where stress within materials are linked only to deformation and rate of deformation respectively, viscoelastic fluids mechanical response depends on both deformation and rate of deformation. Generally, viscosity for any fluid can be described by a power law formula,

\[ \eta = m^*\gamma^{(n-1)} \]

Where \( \eta \) is the viscosity, \( m \) is a flow-consistency constant, \( \gamma \) is the shear rate and \( n \) is the flow behavior index. For \( n=1 \), the viscosity of the material does not depend on shear rate and such fluids are called Newtonian fluids. For \( n>1 \), the fluids show an increase in viscosity with increasing shear rate and are described as shear-thickening or dilatant fluids. For \( n<1 \), the fluids show a decrease in viscosity with increasing shear rate and are described as shear-thinning or pseudoplastic fluid. Typically, three kinds of measurements
are performed on electrode inks. Shear sweeps are run from high shear rate to low shear rate to estimate the shear-rate dependent viscosity of the material. Frequency sweeps are carried out at different angular frequencies and constant oscillation amplitudes to estimate the time-duration of agglomerate. Amplitude sweeps are carried at a constant angular frequency in the linear viscoelastic region at a range of oscillation amplitudes. The oscillation and amplitude sweep both provide information regarding internal structure of the slurries in terms of storage and loss moduli.

2.2 Electrochemical Characterization Techniques

2.2.1 Coin Cell Assembly

Coin cell batteries were assembled using standard cell making procedures. Positive and negative electrodes were punched from slot-die coated electrodes. Depending on cell configurations: symmetric, Li-half cell or full cells can be assembled.

For symmetric cells two punches of the same electrode are utilized in the coin cell assembly. Li-half cells employ a working electrode which is the material under investigation and Li metal foil as the counter electrode. Full cells employ a cathode material (NMC) as the positive electrode and graphite/TNO as the anode material. Typical size of cathode is 12 mm, while anodes are generally kept larger (14 mm). Cell balancing requires tailoring the loadings of the individual electrodes to achieve the required negative to positive electrode capacity ratios (N/P), which is generally kept as 1:2. The cathode and anode are sandwiched by a separator membrane, typically Celgard 2325 except mentioned
Figure 2.1 Exploded view of the coin cell parts and assembly steps
otherwise. A controlled amount of liquid electrolyte is dropped on to the trilayer assembly of cathode | separator | anode. This trilayer configuration is assembled inside a coin cell casing and sealed for further electrochemical testing.

2.2.2 Pouch Cell Assembly

Pouch cells were assembled using the standard procedure. Single-sided and double-sided electrodes were cut using with pilot-scale die-punching machine. The electrodes are calendared before punching and vacuum dried at 90°C overnight before assembling. Aluminum and nickel tabs are welded on the punched cathode and anode respectively using an ultrasonic welder. The electrodes are put together in an aluminum laminated pouch cell material. A separator membrane is used to separate the cathode and the anode. A multilayer jelly roll is prepared using a semi-automatic stacker and assembled into a pouch cell. Electrolyte is filled into the pouch cell before vacuum sealing it. After assembling the pouch cell, it is put into the test fixture under certain pressure. Once the formation cycle is completed degassing is performed on the pouch cells followed by second round of vacuum sealing.

2.2.3 Galvanostatic Charge and Discharge

Cycling performance of batteries is tested by galvanostatic charge and discharge methods. In this method, a controlled current is applied to the cells until specified voltage cutoffs are reached. During charging, a positive current is applied which leads to transport of Li ions from the cathode to the anode and increase in the voltage of the cell. The charging
is cut-off when the upper voltage cut-off for the cathode material is reached. Subsequently, a negative current is applied during which Li ions migrate from the anode to the cathode resulting in voltage drop of the cell which is continued till the lower voltage cut-off is reached. The capacity of the cell is obtained by integrating the current with the total duration of charge and discharge of the cell.

\[
Q_{\text{charge}} = \int_{t=\text{charge}} i \, dt; \quad Q_{\text{discharge}} = \int_{t=\text{discharge}} i \, dt
\]

Specific capacity of the cell is obtained by normalizing the charge and discharge capacity to the active material/cell mass depending on application. Typical testing protocols involve carrying out charge-discharge cycling over multiple cycles and different current density to obtain information regarding performance stability and rate capabilities of the battery.

### 2.2.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy is a technique that is used to probe dynamic processes in the battery with time scales ranging from $10^{-6}$ s (1 MHz) to ~h/min (1 mHz). For this technique a sinusoidal voltage with low amplitude (~10s of mV) is applied at a range of frequencies mentioned. This results in a sinusoidal response of the resulting current which is measured by the potentiostat. Based on the applied sinusoidal voltage and
Figure 2.2 Physical processes occurring in a battery system which can be probed by electronic impedance spectroscopy
the measured current, the complex impedance of the tested device is evaluated, and is given as,

$$Z = \frac{V}{I} = \frac{V_0 \sin(\omega t + \phi)}{I_0 \sin(\omega t + \phi)}$$

The impedance can be modelled using equivalent circuit elements, viz. resistor, capacitor, inductor, constant phase element, Warburg diffusion, among others to extract physical descriptors for the system. EIS is primarily used in this thesis as a characterization tool for total cell resistance and for estimating diffusion coefficients.
CHAPTER 3 LITHIUM PLATING MORPHOLOGY ON GRAPHITE ELECTRODE
3.1 Introduction

Lithium-ion batteries (LIBs) have seen an unprecedented rise for energy storage application in the past few years [2,3]. LIBs are a crucial technology for the electrification of the transportation sector because of their superior rate performance and high energy density [4,5]. However, issues related to range anxiety and fast charging need to be addressed to enhance the mass acceptance of electric vehicles [1]. Extreme fast charging (XFC) is one of the key factors to achieve a charging time equivalent to conventional vehicles [6]. Graphite is one of the widely used anodes for current LIBs. However, it is the rate limiting electrode during XFC because higher charging currents lead to lithium plating on graphite anodes [7,8].

Significant efforts have been undertaken to understand the mechanism of lithium plating [9–13]. Lithium plating is an undesirable side reaction on the anode that significantly degrades the life-time of a LIB and cause drastic safety concerns [14]. Thermodynamically, lithium plating becomes favorable on graphite particles in regions where the local potential drops below Li/Li$^+$ potential. This happens mainly due to the mass transport and charge transfer limitations in the electrode and electrolyte [15,16]. Each of these limitations contribute heavily to plating depending on the temperature, electrode design parameters (tortuosity, porosity, active material loading), particle size, and nature of the electrolyte [17–20].

Electrochemical techniques such as voltage relaxation and high precision coulometry have been used extensively to detect plating during charging [21–25]. Dahn
and coworkers developed a high precision charger to detect the presence lithium plating by accurately measuring the coulombic efficiency of any cell because the efficiency drops to 99.5% once plating takes place [23]. While these techniques are easy to implement, they provide little information about the onset lithium plating [26]. Other techniques such as electron paramagnetic resonance (EPR), nuclear magnetic resonance spectroscopy (NMR) and neutron diffraction (ND) are used to detect lithium metal, [27–30]. Wan et al carried out a time-resolved detection of lithium plating using operando EPR spectroscopy that can deconvolute the coulombic inefficiency of plating/stripping process, and quantify the amount of dead lithium [26]. Zinth et al used neutron diffraction to detect lithium plating by observing the peaks of LiC₆ and LiC₁₂ at different state of charge during a charge-discharge process [31]. While these can effectively detect lithium plating, they do not shed light on the morphology and reversibility of lithium on graphite particles.

In this work, we developed a unique platform to carry out operando video microscopy studies that enables us to visualize in-situ lithium plating behavior on graphite electrode. The unique cell design enables to effectively couple the electrochemical response of the system with continuous optical images of the electrodes from a plan-view perspective. The plan-view (top-view) enables us to observe the onset of lithium nucleation on graphite particles, track the growth of lithium whiskers/dendrites in real-time, and understand the reversible behavior of lithium plating-stripping on graphite. The results provide qualitative insights into the coupled behavior of surface electrochemistry and the plating behavior of lithium during a charge-discharge process on graphite anode.
3.2 Experimental Methods

Slurry preparation and electrode fabrication was completed at the U.S. Department of Energy (DOE) Battery Manufacturing facility at Oak Ridge National Laboratory [32]. Superior graphite SLC1520T and GrafTech APS19 graphite particles were used to make the slurry for the anode. The negative electrode was composed of 92 wt% graphite, 5 wt% polyvinylidene fluoride (PVDF, Kureha 9300) and 3 wt% carbon black (powder grade, Denka small). N-Methyl-pyrolidine (NMP) was used as the solvent and the slurry was tape-casted on the copper foil (10 µm thickness) using a doctor blade. The as-coated electrodes were dried at 120°C under vacuum overnight before being assembled into coin cells with lithium metal as the counter electrode.

Figure 3.1 shows the operando setup, (a) shows a single channel potentiostat (S150, Bio-Logic) was used together in sync with a unique in-situ setup and Keyence optical microscope (VHX and VHZ-250R) to capture the real-time images of lithium plating on graphite [33]. A closer look of the in-situ set with graphite electrode and Li-metal is shown in Figure 3.1 (b). The coin cells were assembled in an argon filled glove box with 1.2 M LiPF₆ in EC/EMC (3/7 wt) electrolyte and Celgard 2325 as the separator. The coin cells were cycled between 0.005 to 1.5 V (VSP, Bio-Logic) for the formation process at 0.1C for three cycles before lithiating the electrode to 100% state-of-charge (SOC) as shown in Figure 3.1 c and d. The lithiated electrodes are extracted from the coin cells in the glove box and the lithiated graphite electrode was re-assembled in the unique cell with Li metal to perform the operando video microscopy studies as shown in Figure 3.1 (b).
Figure 3.1 In-situ Li-plating setup (a) A single channel potentiostat, Keyence optical microscope, and the in-situ cell are synced together, (b) Top-view of the in-situ Li-plating setup, (c) Fully lithiated graphite electrode (100% state of charge), (d) Closer view of the fully lithiated graphite electrode
Once the fully lithiated electrodes and the Li metal are placed in their respective positions in the slot, a constant current is applied to in order to push lithium ion from the Li metal to the graphite electrode. Continuous images are taken (every 15 seconds) at a fixed spot on the graphite electrode to observe the Li plating nucleation and morphology on different electrode design parameters (porosity - 50% vs 25% and mass loading - 7 mg cm$^{-2}$ vs 15.6 mg cm$^{-2}$).

3.3 Results and Discussion

Previous studies in literature have employed Li-Li symmetric cell for understanding the lithium plating behavior and dendrite morphology [34–37]. While lithium plating is one of the major issues with graphite based chemistries in LIBs, there is little information regarding the nucleation of plating and the morphological evolution of dendrites. It is important to note that these morphologies depend significantly on the cell configuration, stack pressure, and presence of separator [9].

For example, coin cells have highly pressurized internal volume that could lead to compressive stresses on the lithium dendrites, flattening its topography at the electrode-separator interface as observed in post-mortem results. The resulting compressed lithium is often referred as ‘mossy Li’ layer, while no description is available for the initial nucleation and growth of the mossy dendritic structures [38]. This has led to the generalization of “dendritic Li growth” on graphite, without understanding the mechanistic origins of the inhomogeneous nucleation of needle-like or mossy dendrite formation during
the initial cycles, which is plastically deform while under compression. For better understanding of the lithium nucleation behavior on graphite and the consequent lithium morphology evolution, it is necessary to develop operando cells to visualize the lithium dendrite growth on graphite particles [26,37].

The lithium plating behavior for high porosity (25%) graphite electrode with 7 mg cm$^{-2}$ loading is shown in Figure 3.2. Initially, the electrodes are fully lithiated in a coin cell and then disassembled in the glove box. The 100% lithiated electrodes are then assembled into the in-situ setup with a thin lithium metal foil (320 µm) as shown in Figure 3.1 (b). A constant current of -25 µA is applied to the lithiated graphite for ~20 hours in order for lithium plating to take place. The galvanostatic voltage response in Figure 3.2 (a), exhibits a characteristic voltage decay associated with the slow depletion of salt concentration at the electrode surface.

For low porosity (25%) electrodes with smaller pore size and smaller surface area, it is presumed that the local current density is higher near the electrode surface. Once lithium nucleation begins on the graphite particle, and lithium plating occurs on the electrode surface, the higher current densities would lead to higher ionic flux at the electrode/electrolyte interface, causing the fracture of the solid electrolyte interphase (SEI) film on the lithium plated surface as shown in the schematic in Figure 3.3. As the SEI breaks, it exposes fresh Li, creating more sites for Li deposition, and result into formation mossy dendrite structure as shown in Figure 3.2 (b)-(d). This agrees with the previous studies in literature regarding the mossy dendrite growth reported for lithium metal anodes.
Figure 3.2 Lithium plating on 25% porosity and 7.0 mg cm$^{-2}$ mass loading graphite electrode (a) voltage profile at a constant current = 25 µA lithiation process for ~20 hours, (b) different morphology of lithium plating on graphite with predominantly mossy dendritic structure, (c) and (d) majorly mossy structure with needle-like dendrites at certain locations.
Figure 3.3 Schematic representation of different dendrite morphologies.
suggesting that it follows a root-growth mechanism [38,39]. Videos pertaining to the mossy structure evolution on 25% porosity electrodes are found in the supporting information.

Likewise, in case of high porosity electrode (50%) with 7 mg cm\(^{-2}\) mass loading, the galvanostatic voltage profile in Figure 3.4 (a) shows considerable divergence from the smooth decay profile observed for high porosity condition. The larger pore sizes for the high porosity electrode have a higher surface area, and as a result local current densities are lower at the surface. The low current densities tend to keep the SEI layer intact on the nucleated Li metal, allowing the SEI layer to continuously evolve on the Li metal without fracturing. This would result into whiskers or needle-like structure (see video in supporting information) with a tip-growth mechanism as shown in Figure 3.4 (c) and (d), that are also in agreement with the models described by Steiger et al. and Wood et al. [36,40].

Additional experiments with higher mass loading (15.6 mg cm\(^{-2}\)) show similar outcome pertaining to the lithium plating morphology (mossy vs needle-like structure) on graphite electrode.

### 3.4 Conclusion

In-situ experiments are carried out to understand the lithium plating and morphology evolution on graphite electrode. While the goal of the study was to understand the Li plating behavior under fast charging condition, the experiments were conducted at low currents due to the limitation with the experimental setup.
Figure 3.4 Lithium plating on 50% porosity and 7.0 mg cm$^{-2}$ mass loading graphite electrode (a) voltage profile at a constant current $= 25\, \mu$A lithiation process for 18 hours, (b) different morphology of lithium plating on graphite with predominantly needle-like dendritic structure, (c) close view of the red section in (b) showing the mossy dendrite surrounded by several needle-like dendrites, (d) close view of the blue section in (b) showing needle-like dendrites
However, crucial information pertaining to the nature of lithium plating and dendrite growth is obtained from this study. It is observed that the growth of the dendritic structures on graphite mainly depend on the local current densities.

- Mossy dendrite structure obeys the root-growth mechanism, and it is predominant for low porosity electrodes (25%) mainly due to the high local current densities near the electrode surface that cause the breakage of SEI layer on the plated lithium, creating fresher sites for Li deposition, and leading to the growth of a mossy structure.

- Needle-like dendrite morphology is more likely for high porosity (50%) electrodes with larger pore sizes mainly due to low local current density, which allows the SEI on the nucleated Li metal to evolve while accommodating the expansion of Li without any fracture. The needle-like structure obeys the tip-growth mechanism.

- The mossy and needle-like morphologies do not change while varying the electrode loading from 7 to 15.6 mg cm$^{-2}$. However, for higher loadings, the lithium morphology is different for low porosity - 25% (mossy structure) and high porosity - 50% (needle-like structure).

These results shed lights on the morphology of lithium plating on graphite without the presence of a separator membrane, which is crucial in understanding the nucleation behavior and dendrite propagation mechanism during lithium plating, which is unavoidable under fast charging conditions.
CHAPTER 4
GRAPHITE ANODE ARCHITECTURE FOR IMPROVED RATE PERFORMANCE AND EXPLORING A NOVEL MATERIAL FOR HIGH RATE CAPABILITY
4.1 Introduction

The previous chapter discussed the main issue with graphite based chemistries, lithium plating. A unique setup is used to understand the lithium nucleation and dendrite morphology on graphite electrode under a constant current. Two different morphologies are observed with different porosity electrodes. Whiskers are observed with high porosity electrodes mainly driven by the low local current density while mossy structures are observed with the dense electrodes due to the high local current densities. While the issue of lithium plating is still challenging and unresolved, this chapter addresses the ways through which the mass transport limitation could be addressed with graphite based chemistries and explore a novel material in order to improve the rate performance.

Graphite is the most commonly utilized anode material with a theoretical capacity (372 mAh g\(^{-1}\)) [41,42]. However, it undergoes irreversible capacity loss due to forming a solid electrolyte interphase (SEI) layer and lithium plating at higher charge rates due to the low lithiation potential and mass transport limitation [43,44]. Lithium plating and subsequently dendrite formation are prominent with graphite anode due to their close electrochemical potential with lithiated graphite as shown in Figure 4.1 (a) [9,14,45]. This is a serious concern with the present LIBs chemistry that leads to safety hazards [7,15,46]. In terms of XFC application, previous studies in literature have shown that very thin graphite-NMC chemistries can achieve 6C charging, however one of their drawbacks is poor energy density and high cost ($/kWh) [33].
Figure 4.1 Crystal structure and Li plating after cycling on (a) graphite and (b) Titanium niobium oxide electrode
The major issues with achieving fast charging are mass transport limitation in the electrode and electrolyte as well as charge transfer at the electrode/electrolyte interface. With regards to electrolyte, there are several modifications in the electrolyte that could be implemented such as improving the ionic conductivity, increasing the transference number, and using solvents/salts that allow faster Li-ion diffusion through the SEI layer. In terms of the electrode, varying the design parameters such as porosity, tortuosity, and mass loading would in turn affect the Li-ion diffusion process at high currents. Hence, part of the focus of this study is developing a novel anode architecture that would enable faster Li-ion diffusion through the electrode. Freeze tape casting is used to create a unique architecture with aligned channels, that would lower the electrode tortuosity, leading to shorter diffusion pathways, and resulting to high rate capabilities.

There is also an interest in developing an anode material that is capable of high power and fast charging while avoiding lithium plating [47]. Previous studies in literature have mainly focused on engineering the electrode properties for LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{1-x-y}O\textsubscript{2}-Graphite based cell chemistries, design separators with coatings, and improve the electrolyte properties for achieving extreme fast charging [33,48–53]. Spinel titanium oxide (Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{2} - LTO) has been explored as a substitute of graphite for high rate capability, however, it suffers from poor electronic conductivity and low specific capacity for automotive applications [54–56].

Titanium niobium oxide (TiNb\textsubscript{2}O\textsubscript{7} - TNO) is another material that has drawn significant interest due to its high specific capacity (387 mAh g\textsuperscript{-1}) for high power
application [57–61]. Similar to LTO, the TNO-based anodes can avoid issues such as SEI formation and lithium dendrite growth due to their high voltage plateau (~1.6 V vs. Li/Li+) [62–64] while delivering much higher specific capacity [65–67]. Dai and co-workers developed TNO anode with a nanoporous interconnected network that was able to deliver a reversible storage capacity of 280 mAh g\(^{-1}\) at an average voltage of 1.66V, ensuring no lithium plating in LIB cycles [68]. Likewise, numerous other TNO oxides morphologies were developed such as nanofibers, nanowires, hollow structures, as well as meso and macro-porous microparticles that have achieved high rate performance and long cycle life [69–74]. Similar to LTO, cells with TNO anodes tend to suffer from significant amount of gas generation, which has not been fully investigated.

4.2 Freeze Tape Casting of Graphite Anode

4.2.1 Experimental Methods

As received SLC1520T graphite (Targray), polyvinylidene fluoride (PVDF, Kureha 9300) and carbon black (C45, Targray) were used to fabricate the conventional anodes using N-Methyl-pyrolidine (NMP) as the solvent and following the procedures reported previously [75]. The graphite anodes consisted of 92 wt% graphite, 5 wt% PVDF and 3 wt% carbon black. The as-coated graphite (~50% porosity) was dried at 120°C under vacuum overnight before being assembled into coin cells with Li metal as the counter electrode. One layer of Celgard 2325 was used as the separator in each coin cell.
The slurry preparation and electrode fabrication for the freeze tape casting (FTC) was carried out at the U.S. Department of Energy (DOE) Battery Manufacturing facility at Oak Ridge National Laboratory [32]. Superior graphite SLC1520T was used with styrene butadiene rubber (SBR, 40% solidity, Targray) and sodium carboxymethyl cellulose (Na-CMC, average MW = 250,000, Sigma Aldrich) to prepare the aqueous slurry. The anode composed of 90 wt% graphite, 7 wt% binder solution, 1.0% polyacrylic acid (PAA), and 2.0 wt% carbon black (C45, Targray). The PAA additive was helpful in stabilizing the slurry while mixing by reducing the bubble formation in the aqueous slurry due to the presence of SBR. The binder solution comprised of SBR and CMC in the ratio of 4:1. Deionized water was used as the solvent and the slurry was tape-casted on the copper foil (10 µm thickness) using a doctor blade to make single layer coatings. Figure 4.2 (a) and (b) shows the schematic of the benchtop freeze tape caster setup. The freezing bed can achieve a maximum temperature of -25°C.

The freeze bed was connected to a vacuum pump via a hose and a pressure gauge was used to monitor the pressure as shown in Figure 4.2 (a). A copper foil was laid on top of a mylar sheet that was attached to the roller, and a doctor blade was used to coat the slurry on the copper foil as shown in Figure 4.2 (b). A second mylar sheet was used to cover the coating in order to prevent it from drying. The coating moves through the freeze bed at a slow speed, creating specified channels for faster lithium ion diffusion. Once the ice crystals were formed the coated electrode was placed under vacuum for 6 to 8 hours to sublimate the ice. All the electrodes, conventionally coated and freeze tape casted
Figure 4.2 Benchtop freeze tape caster (a) Freeze bed, pressure gauge, vacuum valve, and roller of the freeze tape caster, (b) Copper foil on the mylar with a doctor blade to imitate roll-to-roll process for freeze casting
electrodes were dried at 120°C under vacuum overnight before being assembled into coin cells with lithium metal as the counter electrode. The mass and thickness of all the electrodes was measure by an analytical balance (Mettler) and a micrometer (Mitutoyo).

For rate performance testing, half cells were built with Li metal and formation cycle was carried out at C/10. The cells were then lithiated to 50% SOC before assembling them into symmetric cells in the glove box. For XFC testing, symmetric cells and cycled in the voltage window of -0.5 V to 0.5 V and the cells were charged using a CCCV protocol with various constant currents (5C, 5.5C, 6C, 6.5C, 7C, 8C, and 10C) followed by constant voltage until the current dropped below C/20 for a total charging time of 10 minutes. The cells were then discharged at C/3.

4.2.2 Results and Discussion

Figure 4.3 shows the rate performance in terms of the specific charge capacity of graphite anode with different porosity under XFC conditions. Three different porosity conditions are selected with 8.5 mg cm$^{-2}$ mass loading. All the cells performed well at low rate (0.1C) with almost identical charge capacities for different porosity conditions. As the charge rates are increased to 5C and beyond, a decrease in charge capacity is observed due to mass transport limitation during the fast charging conditions.

As shown in Figure 4.3, the charge capacity at XFC conditions (5C) was improved from 190 mAh g$^{-1}$ to 198 mAh g$^{-1}$ by increasing the porosity of the electrode from 25% to 35%. Further increasing the porosity to 50% only helps with little improvement in specific capacity to 205 mAh g$^{-1}$. In case of 25% porosity electrode, the specific charge capacities
Figure 4.3 Rate performance of conventionally coated graphite with different porosities (25, 35 and 50%) using symmetric cell configuration
degrade significantly as the currents increase from 5.5C to 10C. While in case of 35% and 50% porosity electrodes, a somewhat similar trend is observed in the degradation behavior of charge capacities with increase in charge rates. This suggests that increasing electrode porosity enhances the rate performance only up to a certain extent, mainly due to overcoming the mass transport limitation in the electrolyte phase across the electrode. Hence, it is also crucial to reduce the electrode tortuosity such that the Li-ion diffusion pathways could be shorter in order to achieve high rate performance under XFC conditions.

The top view of the conventionally coated and freeze tape casted electrodes are shown in Figure 4.4 (a) and (b). The structural difference in case of freeze casting is due to the growth of ice crystals in perpendicular direction to the copper foil, i.e., along the temperature gradient, entangling the solid particles and developing a directionally aligned structure as shown in Figure 4.4 (b). The solid particles are arranged in specified channels, leading to lower tortuosity electrode. The lower electrode tortuosity translates to shorter Li-ion diffusion length, resulting in improved rate capability at high currents. While in case of conventional coating, the graphite particles are randomly arranged, leading to a more tortuous pathway for Li-ion diffusion. It is also hypothesized that the electrolyte wetting, and electrolyte retention would improve significantly with FTC electrodes due to its high porosity and low tortuosity, in turn leading to better performance. The high porosity basically improves the wettability by shortening the wicking time [76].
Figure 4.4 Top-view optical microscope images of (a) conventional coated graphite electrode, (b) freeze tape cast electrode with specified channels.

Figure 4.5 Single layer freeze tape cast (a) Top-view of the electrode structure of the single layer FTC, (b) cycling of single layer FTC at 0.1C, (c) Electrode coating after the freezing and drying process, (d) Electrode delamination after cycling.
The top-view of the single layer FTC electrode with directionally aligned channels is shown in Figure 4.5 (a), and the voltage profile with the charge-discharge curves at 0.1C are shown in Figure 4.5 (b). The single layer FTC half cell shows excellent cycling at 0.1C for 5 cycles with an attainable capacity of ~340 mAh g\(^{-1}\). Similar voltage profiles were observed for conventional coated graphite electrodes at 0.1C. Overall, the freeze tape casting process doesn’t change the intrinsic electrochemical reaction of graphite.

As FTC electrodes are highly porous in nature, the electrode tends to flake and delaminate from the copper foil while punching, resulting into poor structural integrity. Different compositions of binder solution (5 to 10%) and CMC:SBR ratios with different coating thickness were tested for this study to determine the best possible combination for the single layer FTC. It was observed that thin slurry coatings with wet thickness from 150 to 300 µm show good structural integrity with extremely less to no flaking. To the contrary, thicker coatings with wet thickness from 350 to 600 µm demonstrate poor structural integrity even with 10% binder content.

Figure 4.5 (c) shows an FTC electrode after the freezing and drying process. The electrode doesn’t flake or disintegrate after punching and keeps the structure intact. For rate performance testing with symmetric cells, the graphite FTC electrodes are assembled into half cell with Li metal and charged to 50% SOC. The half cells are disassembled in the glove box and then assembled into symmetric cells. The single layer FTC electrodes tend to delaminate from the copper foil once disassembled from the coin cell, demonstrating poor structural integrity as shown in Figure 4.5 (d). This behavior suggests
that even though there is good cohesion among the solid particles, poor adhesion between the solid particles and the copper foil lead to weak lamination characteristics.

To address this issue, a dual layer hybrid FTC is developed, with a thin conventional coating (PVDF-NMP based slurry) as the bottom layer, and an aqueous FTC layer above the bottom layer. A schematic of the dual layer hybrid FTC electrode is shown in Figure 4.6 (a), where the bottom layer is conventionally coated graphite (calendared), while the top layer is achieved via freeze tape casting. The calendared bottom layer and the freeze casted top layer are shown in Figure 4.6 (c) and (d). The flexibility of the hybrid FTC coating and the punched electrode shown in Figure 4.6 (e) suggests that the structural integrity of the hybrid coating is excellent. The thickness of the bottom layer was fixed to ~ 50 µm, while the thickness of freeze cast layer was varied from 200 to 300 µm. Hybrid freeze tape cast coatings with variable areal loadings (2.5 to 3.0 mAh cm\(^2\)) were fabricated.

The XFC rate performance of the hybrid FTC was systematically compared with single layer FTC and conventional coated graphite electrode (35% porosity) in symmetric cell format. Electrodes were initially assembled into half cells and lithiated to 50% SOC after undergoing formation cycle. The half cells were disassembled in the glove box and symmetric cells were built with the 50% SOC electrodes. The symmetric cells were tested under XFC conditions while limiting the total charging time to 10 minutes.
Figure 4.6 Dual layer hybrid freeze tape cast (a) schematic of the dual hybrid FTC layer, (b) Hybrid FTC coating, (c) bottom layer of the coating - calendared, (d) top layer of the coating - freeze cast, (e) flexibility of the coating and electrode disk.
The rate performance in Figure 4.7 shows the performance of three different electrode configuration - convention coated (35% porosity), single layer FTC, and dual layer hybrid FTC. The rate performance of the conventional coated electrode is similar to the one discussed earlier in Figure 4.3. Interestingly, the single layer FTC electrodes performed the worst out of all in symmetric cell format, displaying lower charge capacity than the conventional coated electrode. This could be mainly attributed to the poor structural integrity and delamination issues with the single layer FTC graphite electrode, which lead to poor performance at high current. To the contrary, the hybrid FTC not only showed excellent structural integrity before assembling and after disassembling half cells, but it also improved the attainable charge capacity by ~20% at 5C rate. Higher charge capacity is also observed for 5.5C, 6.0C and 6.5C rate. This improvement could be mainly attributed to the well-defined channels that could reduce the electrode tortuosity, and in turn shorten the Li-ion diffusion pathways, resulting in better rate performance at high currents.

Figure 4.8 shows the Nyquist plot for the three different anode architectures carried out with symmetric cells at 0% state of charge. Multiple measurements were taken for one condition, to minimize the error, the connector and channel were kept same for all the experiments. The results in the Nyquist plot clearly show lower impedance for both the freeze cast electrodes vs the conventionally coated calendared electrode. The single layer FTC shows the lowest resistance due to its highly porous-less tortuous nature. While the hybrid FTC shows slightly higher impedance due to the presence of a thin conventionally coated bottom layer as discussed earlier. The conventionally coated electrode with 35%
Figure 4.7 XFC rate performance for conventional coated, single later FTC, and hybrid layer FTC graphite anode
porosity shows the highest impedance among all mainly due to the longer Li-ion diffusion pathways with the low porosity electrode where the solid particles are more interconnected, creating highly tortuous pathways. The diffusion length calculations also show that the single-layer FTC has the lowest diffusion length, however it did not show good rate performance mainly due to its poor structural integrity.

4.2.3 Conclusion

Performance of different graphite electrodes were evaluated under various extreme fast charging testing protocols with different anode architectures - conventional coating, single layer freeze tape cast coating, and dual-layer hybrid freeze tape cast coating. Symmetric cells were tested to study the rate performance of these electrodes under XFC conditions. It is demonstrated that,

- One of the best possible ways of developing a low tortuosity electrode with high structural stability is via hybrid freeze tape casting. The hybrid FTC electrode has dual layers, a thin bottom layer via conventional coating (calendared to ~35% porosity), and a top layer developed via freeze tape casting.
- The single layer freeze cast shows good structural integrity with thin coatings, but at the cost of low areal loading. The single layer FTC also demonstrate some delamination after cycling.
Figure 4.8 Nyquist plot and diffusion lengths for the three different anode architectures. The impedance spectroscopy is carried out using symmetric cells with 0% SOC.
• The hybrid FTC shows excellent rate performance under XFC conditions, with 
~20% improvement in the specific charge capacity at 5C. This can be attributed to 
the shorter diffusion pathways that are created by the aligned channels developed 
via freeze casting.

These results shed lights on the significance of a novel anode architecture and its 
scalability for extreme fast charging application.

4.3 Novel Material for XFC Application

4.3.1 Experimental Methods

The titanium niobium oxide (TiNb$_2$O$_7$ - TNO) particles were synthesized following 
the reported sol-gel method, and their SEM images are shown in Figure 4.9 [77]. A 
protective barrier coating was applied on the TNO particles and the surface coating of TNO 
with polyimide was accomplished in two steps following a US patent [78]. The resulting 
coated TNO was calculated to be 1 wt.% polyimide coating, assuming all the polyamic 
acid is converted to polyimide.

The rate performance of the TNO electrode was evaluated with NMC622 cathode 
using pouch cell format. The pouch cells were assembled in the dry room with a controlled 
environment at the U.S. Department of Energy (DOE) Battery Manufacturing R&D 
Facility (BMF) at Oak Ridge National Laboratory (ORNL). The pouch cells were 
fabricated using double-sided TNO and NMC622 electrodes, 1.2M LiPF$_6$ in ethylene 
carbonate (EC): ethyl methyl carbonate (EMC) (3:7 by weight) electrolyte and tri-layer
separator Celgard 2325. The details related to the electrode loading, porosity and pouch cell configuration are addressed in Table 4.1. The TNO electrodes (uncoated and coated) and NMC cathode (Targray) were fabricated using N-methyl-pyrrolidone (NMP) and polyvinylidene fluoride (PVDF) as the solvent and binder, respectively, and uniformly coated on an aluminum foil via a pilot-scale slot-die coater. Detailed fabrication procedures have been reported previously [79]. All the electrodes were dried at 120°C under vacuum overnight before assembling them into pouch cells. The TNO-NMC full cells were cycled in a voltage range of 3.2 to 1.0 V at various currents 5C, 5.5C, 6C, 6.5C, and 7C under XFC conditions (total charging time = 10 minutes). Formation process at 0.1C and degassing of the cells was performed prior to XFC testing.

The gassing behavior was also evaluated in TNO and NMC622 half cells and full cells to decouple the gas generation from the individual electrodes. The half cells and full cells were charged and discharged at 0.1C, 1C, 3C and 5C (1C=150 mA g⁻¹ of NMC or 200 mA g⁻¹ of TNO) rates. The NMC-Li and TNO-Li half cells were cycled in a voltage range of 4.4-3.0 V and 3.0-1.0 V respectively. While the TNO-NMC full cells were cycled in a voltage range of 3.2-1.0 V. All pouch cells were cycled at 0.1C for 1 cycle as the formation cycle for the gassing study. The lithium foils and electrolyte were stored in an argon-filled glove prior to use. All the pouch cells were sealed under vacuum.
Figure 4.9 SEM images of (a) uncoated TNO and (b) coated TNO

Table 4.1 Properties of the electrode, electrolyte, and separator used for pouch cell assembly

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition</th>
<th>Loading / porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>80 wt% TiNb$_2$O$_7$ (TNO) - uncoated and coated, 13 wt% C45 carbon black, 7 wt% PVDF, Al foil current collector with Al tab</td>
<td>12.5 mg cm$^{-2}$/ 35%</td>
</tr>
<tr>
<td>Cathode</td>
<td>90 wt% NMC, 5 wt% Denka carbon black, 5 wt% PVDF, Al foil current collector with Al tab</td>
<td>15 mg cm$^{-2}$/ 35%</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>1.2 M LiPF$_6$ in (ethylene carbonate (EC): ethyl methyl carbonate EMC 3:7 wt%)</td>
<td></td>
</tr>
<tr>
<td>Separator</td>
<td>Celgard 2325</td>
<td>39%</td>
</tr>
</tbody>
</table>
4.3.2 Results and Discussion

In order to investigate the electrochemical performance of TNO, 2 Ah pouch cells were fabricated and tested for XFC application. Figure 4.10 (a) shows the galvanostatic charge/discharge curves for the TNO-NMC 2 Ah cell in the voltage range of 3.2 to 1.0 V at different currents from 5C to 7C with a total charging time of 10 minutes. The charge-discharge capacities for these rates are shown in Table 4.2. The highest charge and discharge capacities are ~1.84 Ah and ~1.57 Ah at 6.5C respectively, as shown in Figure 4.8 (b), suggesting TNO anodes are capable of achieving high rate performance while delivering high capacity unlike graphite and LTO based anodes [56,80].

While TiNb\textsubscript{2}O\textsubscript{7} (TNO) shows excellent rate performance at high currents, one of the major issues with TNO based cell chemistry is significant gas evolution. Figure 4.11 (a) shows the swelling of 2 Ah pouch cell before and after long-term cycling (400 cycles) at 5C. Significant swelling is observed even after degassing was performed before beginning the long term cycling. This suggests that continuous side reactions could lead to significant gas evolution that would potentially result into degradation of the rate performance. To the best of our knowledge, only Cheng and co-workers reported the interphase layer formation and gas evolution on TiNb\textsubscript{2}O\textsubscript{7} anodes [81]. The authors show via XPS and TEM that SEI forms on TNO when TNO/Li half cells is cycled at 1C within a voltage range of 1.0-3.0 V. However, the nature of the gases evolved from the TNO surface was not discussed [81].
Figure 4.10 TNO-NMC pouch cell (a) rate performance at different currents - 5C, 5.5C, 6C, 6.5C, 7C, (b) rate performance at 6.5C (4 cycles)

Table 4.2 Charge and discharge capacities of TNO-NMC 2 Ah pouch cells at different currents. The capacities are an average of 4 cycles

<table>
<thead>
<tr>
<th>C-rate</th>
<th>Charge Capacity (Ah)</th>
<th>Discharge Capacity (Ah)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 5.0C</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>2. 5.5C</td>
<td>1.62</td>
<td>1.39</td>
</tr>
<tr>
<td>3. 6.0C</td>
<td>1.75</td>
<td>1.50</td>
</tr>
<tr>
<td>4. 6.5C</td>
<td>1.84</td>
<td>1.57</td>
</tr>
<tr>
<td>5. 7.0C</td>
<td>1.81</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Figure 4.11 Gassing behavior in TNO cells (a) gas evolution in 2 Ah TNO-NMC pouch cell after 400 cycles at 5C, (b) operando mass spectrometer setup for gas analysis
In this part of the work, an operando measurement of gases generated in TNO based pouch cells is systematically investigated and quantified using Mass Spectrometer (MS) for the first time. Three types of cells, TNO-LiNi\textsubscript{0.6}Mn\textsubscript{0.2}Co\textsubscript{0.2}O\textsubscript{2} (NMC) full cells, TNO-Li and NMC-Li half cells, are assembled and cycled to diagnose contribution of each electrode to the gas evolution. It has been demonstrated that TNO anodes release gases during the initial charge-discharge cycle at lower C-rate (0.1C and 0.2C) [77,81–83]. However, the nature of these gases and their quantity while cycling half / full cells under fast charging conditions are yet to be determined. In this study, real-time gas evolution from TNO and NMC based pouch cells is obtained from an operando MS setup (Figure 4.11). A wide range of \textit{m/z} scan from 2 to 100 were obtained every 30 seconds to identify the gases. Unique \textit{m/z} signals of 32, and 44 were observed corresponding to, O\textsubscript{2}, and CO\textsubscript{2}, respectively. In case of C\textsubscript{2}H\textsubscript{4}, \textit{m/z} = 27 is used after removing the contributions from the electrolyte solvents. Detailed description on analysis and identification of the gaseous species can be found elsewhere [84].

Calibration was performed for the set up with standard gases. The gas composition and the corresponding voltage profile for TNO-Li metal half cell as well as the gas evolution during voltage relaxation is shown in Figure 4.12 a and b, respectively. Firstly, the TNO-Li metal half cell is cycled between 3.0 to 1.0 V, as shown in Figure 4.12a. It must be noted that the discharge process in the TNO-Li half cell corresponds to the actual charging process in a practical lithium-ion full cell. It is observed that the main gaseous
Figure 4.12 Voltage profile and the corresponding background-corrected mass signals m/z = 44 (12CO₂), 32 (O₂), and 27 (C₂H₄) for (a) TiNb₂O₇-Li metal pouch cell cycled at 0.1C in the voltage range of 3.0-1.0 V; (b) TNO-Li pouch cell cycled at higher currents (1C, 3C and 5C)
species generated during the initial low current (0.1C) cycle were ethylene (C\(_2\)H\(_4\)), with minor contributions from carbon dioxide (CO\(_2\)) and oxygen (O\(_2\)).

From the plot in Figure 4.12 (a), CO\(_2\) evolution begins concurrently with onset of cycling in the first lithiation process as the lithium ions start moving towards the TNO anode during the discharge process at low current (0.1C). The intensity of CO\(_2\) increases from 0 to \(~1.8 \text{ nmol min}^{-1} \text{g}^{-1} \text{TNO}\) as the voltage drops from its open circuit voltage (OCV = 3.18 V) to \(~2.0\) V. Simultaneously, there is increase in concentration of C\(_2\)H\(_4\) and O\(_2\) to \(~2.0\) and \(~0.4 \text{ nmol min}^{-1} \text{g}^{-1} \text{TNO}\), respectively, at the beginning of the lithiation process. The rise in gases during the first cycle at an onset potential of \(~2.0\) V could be ascribed to the beginning of certain parasitic side reactions. Another peak for CO\(_2\) is observed along with the onset of C\(_2\)H\(_4\) and O\(_2\) formation as the cell voltage reaches close to 1.15 V towards the end of the discharge process (lithiation) as shown in Figure 4.12 (b). All the three gaseous species, C\(_2\)H\(_4\), O\(_2\), and CO\(_2\) peak towards the end of the discharge process with a maximum gas evolution of 32.8, 0.98 and \(~2.8 \text{ nmol min}^{-1} \text{g}^{-1} \text{TNO}\), respectively, as shown in Figure 4.12b. Similar trends in C\(_2\)H\(_4\), O\(_2\), and CO\(_2\) evolution are observed during the second cycle at 0.1C. It is hypothesized that the gas evolution during lithiation of TNO electrode might be due to electrolyte reduction on TNO surface. Equation 4.1 and 4.2 show the EC reduction reactions that lead to C\(_2\)H\(_4\) and CO\(_2\) formation at the TNO electrode [85]. Subsequently during the delithiation cycle, CO\(_2\) evolution is observed at an onset potential of \(~2.1\) V along with little contributions from C\(_2\)H\(_4\) and O\(_2\), which might be due to the side reactions and electrolyte decomposition at the Li-metal surface.
\[ n\text{EC} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}(-\text{CH}_2 - \text{CH}_2 - 0 -)_n\text{Li} \downarrow + n\text{CO}_2 \uparrow \] (4.1)

\[ 2\text{EC} + 2\text{Li}^+ + 2e^- \rightarrow (\text{CH}_2\text{OCO}_2\text{Li})_2 \downarrow + \text{C}_2\text{H}_4 \uparrow \] (4.2)

C\text{H}_4 generation is the highest among all gases during this lithium insertion process (discharge cycle). This might be attributed to the decomposition of EC component in the electrolyte as reported previously for graphite based cells [43], suggesting a possibility of SEI layer formation on TNO during the initial cycle (0.1C). It has been reported that the reduction decomposition potential for EC in 1.0 M LiPF\textsubscript{6} in EC/EMC (3/7 wt) was 0.9 V [86,87]. The detected decomposition products (i.e., CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{4}) indicates that the local potential could be lower than the lower cutoff voltage (1.0 V) and a layer similar to SEI could form on the TNO surface.

To verify our hypothesis, XPS analysis was conducted on the TNO powder and TNO electrodes as shown in Figure 4.13. The Ti 2p spectra shows two peaks at 459 eV and 465 eV, which is in good agreement with Ti 2p\textsubscript{1/2} and Ti 2p\textsubscript{3/2} of Ti\textsuperscript{4+} ions in TNO, respectively (curve a and b) [88]. At fully lithiated state (curve c), the peaks almost disappear with a slight hump at 456 eV during the first cycle. The peaks completely disappear at fully lithiated state after two cycles (curve e).

A similar behavior is observed with the Nb 3d spectra where the peak disappears at fully lithiated state after 2 cycles. This indicates that a layer, i.e. SEI, was formed during
Figure 4.13 Ti 2p, Nb 3d, C 1s XPS spectra of TNO (a) pristine powder; (b) electrode before cycling; (c) electrode at 100% lithiated state (cutoff at 1.0 V); (d) electrode at complete delithiated state (cutoff at 3.0 V); (e) electrode at 100% lithiated state after 2 cycles (cutoff at 1.0 V). The cycling is performed at 0.1C.
lithiation which reduced the intensity of Ti and Nb from the bulk. This layer grows with cycles and completely blocks the signal from the bulk after two cycles. During the delithiation process (charge cycle), the evolved gases keep reducing and also disappear when fully delithiated at 3.0 V, as shown in Figure 4.12 (a). Based on the XPS analysis in Figure 4.13, the spectra of Ti, Nb and C (curve d) are almost identical to the as-coated electrode after complete delithiation. This suggest that the preformed SEI layer during lithiation step becomes thinner if not completely disappeared at 3.0 V. The formation and dissolution of the SEI indicates a more dynamic process for TNO during lithiation and delithiation compared to a more stable one for the graphite counterpart [81]. TEM images shown in Figure A9 support our hypothesis on the formation of an SEI layer on TNO surface. Figure A9 a shows a thin interphase layer formed on the TNO surface after complete lithiation of the TNO electrode at 1V cutoff. Further cycling (two cycles) leads to a more diffused and thinner SEI on the TNO surface as shown in Figure A9 b.

For the C1s XPS profile, bonds of C-C from carbon black and C-F from PVDF are observed at 284 eV and 292 eV respectively for curve b. During the first cycle after full lithiation (curve c), the C=O double bonds appear at 287 eV and 289 eV, corresponding to LiCO₃ and RCOOLi, respectively, which are common components of SEI [43]. The C-F bond from PVDF disappears in curve c confirming an SEI layer forms and covers the surface of TNO electrode. This is consistent with Wu et. al, who confirmed an SEI layer on TNO anodes based on the double bonds in Li₂CO₃ and RCO₂Li at 50% and 100% lithiated state via XPS [81]. Likewise, at the delithiation state (curve d), the C-F bonds
reappear and the SEI related peaks disappear. The SEI related peaks at 287 eV and 289 eV appear again at 100% lithiation state after two cycles. Thus, it can be concluded that during the first lithiation cycle, dynamic evolution of a reversible SEI is observed on the TNO surface even at a high operating voltage (1.0 V).

At higher currents, an overall rise in gas generation is observed as shown in Figure 4.12 (b). As the currents are bumped up from 0.1C to 1C, gas generation is observed during the lithiation process, that continues over to the delithiation process in the first cycle. The slightly different behavior during the first cycle might be due to the combination of unstable plating-stripping at higher currents (1C vs 0.1C) in a TNO-Li metal half cell as well as the lag in sampling of gases (during delithiation) due to adsorption of gas on the pores of electrodes and solubility of electrolyte.

As the reaction proceeds to higher rates (3C and 5C), the intensity of gas evolution increases, allowing faster detection of gases. For instance, the bar chart in Figure 4.14 shows that as the charge rates are bumped from 0.1C to 1C, CO$_2$ levels increase ~10 times and C$_2$H$_4$ generation increases ~6 times, while a negligible change in the O$_2$ levels are observed at 1C. As the charge rate is bumped up further from 1C to 3C, the CO$_2$ evolution increases slightly, while a significant jump in C$_2$H$_4$ from 12.1 to 42.8 nmol min$^{-1}$ g$_{TNO}^{-1}$ (~4 times) is observed. Likewise, the bar chart in Figure 4.14 shows that O$_2$ evolution spikes by 11 times as the charge rate increases from 1C to 3C.

It is also observed that at each individual current, the gas generation follows the trend C$_2$H$_4$$>$CO$_2$$>$O$_2$ for the TNO half cells. The increase in gas generation could be
Figure 4.14 Gas evolution at different currents (0.1C, 1C, and 3C) for TNO-Li half cell.
attributed to the increased rate of the side reactions on the surface of TNO electrode due to higher current density, leading to formation of more products such as CO₂, C₂H₄, and O₂. The substantial increment in gas evolution at 1C rate could potentially lead to further capacity degradation. However, the gas evolution decreases when further increasing the current from 3C to 5C, as shown in Figure A8, which could be due to a shorter lithiation period for SEI formation which overweighs the higher kinetic from a higher current.

As mentioned previously, NMC is used in this study as the cathode material. The cathodes were dried in the vacuum oven before assembling into pouch cells with lithium metal as the reference electrode. The voltage profile and gas composition for NMC-Li metal cell are shown in Figure 4.15 (a) and (b), respectively. The onset potential for CO₂, C₂H₄, and O₂ evolution is ~4.2 V during the delithiation process [89]. The CO₂ generation rate is ~0.1 nmol min⁻¹ g⁻¹ NMC at 4.2 V, while a dramatic rise in the CO₂ concentration (~4.5 nmol min⁻¹ g⁻¹ NMC) is observed once the cell reaches a cutoff voltage of 4.4 V. The CO₂ concentration peaks to ~7.18 nmol min⁻¹ g⁻¹ NMC as shown in Figure 4.15 (b). While NMC cathode is the major contributor to the CO₂ generation, it is also possible that the reduction of the electrolyte solvent component on Li-metal surface could lead to CO₂ evolution as shown in equation 1.

Previous studies in literature suggest that the increase in CO₂ concentration at 4.4 V can be attributed to a couple of factors such as surface oxygen reacting with the electrolyte, decomposition of carbonate impurities (LiCO₃) on the surface of NMC particles, or electrochemical oxidation of the electrolyte [89–91].
Figure 4.15 Voltage profile and the corresponding background-corrected mass signals m/z = 44 ($^{12}$CO$_2$), 32 (O$_2$), and 27 (C$_2$H$_4$) for (a) NMC-Li metal pouch cell cycled at 0.1C in the voltage range of 3.0-4.4 V; (b) NMC-Li metal pouch cell cycled at higher currents (1C, 3C, and 5C).
The CO$_2$ generation rate, according to our results, was significantly influenced by the cutoff voltage, where CO$_2$ concentration increased dramatically when the voltage increased from 4.2 to 4.4 V. It must also be noted that the CO$_2$ generation rate remained high during the initial few minutes of the discharge cycle, which is in agreement with the work by Renfrew and McCloskey [92]. This indicates that the oxidation of the surface carbonate (Li$_2$CO$_3$) species on NMC particles, shown in equation 4.3, might be one of the major contributors to CO$_2$ generation as they are typically around 0.1 % by weight [93,94].

$$2\text{LiCO}_3 \rightarrow 4\text{Li}^+ + e^- + 2\text{CO}_2 \uparrow + \text{O}_2 \uparrow \quad (4.3)$$

The gas concentration of O$_2$ and C$_2$H$_4$ peaks at approximately 0.22 and 1.75 nmol min$^{-1}$ g$_{\text{NMC}}^{-1}$ towards the end of the discharge process (4.4 V), respectively. The possibility of lattice oxygen release could be ruled out because the cutoff voltage is limited to 4.4 V, and lattice oxygen evolves at $>$4.6V for NMC [84,89,95]. Hence, the O$_2$ and C$_2$H$_4$ generation at 4.4 V are mainly due to the decomposition of impurities at the cathode surface (LiCO$_3$) and reduction of electrolyte solvents at the Li-metal anode, respectively [84,96].

At higher currents, the gas evolution for all three species shows a completely similar profile with same onset potential but different generation rate, as shown in Figure A9 b. It is observed that the CO$_2$ generation rate dropped from ~7.18 to ~0.85 nmol min$^{-1}$ g$_{\text{NMC}}^{-1}$, while O$_2$ and C$_2$H$_4$ rates increased. Also, the rise in the generation rate is observed once the voltage increases beyond 4.2 V and reaches the upper cutoff voltage of 4.4 V. This could be attributed to the more reducing environment at the Li anode, leading to increased evolution of O$_2$ and C$_2$H$_4$. The gas evolution decreases as the current is further
increased from 1C to 5C, because the Li anode is subjected to a lower local potential for a short time. While O₂ and C₂H₄ increased, a dramatic decrease in the CO₂ generation is seen because all the surface carbonate impurities might have decomposed in the first cycle where CO₂ generation was maximum, as shown in Figure 4.15 (a). As the charge rates are further bumped from 3C to 5C, the gas evolution decreases showing the same profile for all three gases.

Gas evolution and voltage profile of the TNO-NMC full cell is shown in Figure 4.16 (a) and (b). The gas evolution profiles at low current (0.1C) in Figure 4.16 (a) shows that C₂H₄ generation is the highest among all the gases during the charging process when the cell potential reaches 3.2 V. Small amounts of O₂ and CO₂ are generated during this process. While, during the discharge process towards the cell potential of 1.0 V, CO₂ generation is significantly higher than other gases with little quantities of O₂ and C₂H₄. Figure 4.16 (b) shows that the rate gas evolution decreases at higher currents.

When lithium ions move towards the TNO anode during the charging process, the onset of C₂H₄ generation begins at ~1.5V and it peaks at the end of charging process as the cell potential reaches the cutoff voltage of 3.2 V. Approximately, 12.55 nmol min⁻¹ g⁻¹ of C₂H₄ and 0.25 nmol min⁻¹ g⁻¹ of O₂ are generated at the end of process. This suggests that the electrolyte decomposition takes place during the charging process at low currents, forming a passivating SEI layer on the anode. Likewise, a dramatic rise in CO₂ generation (~74.33 nmol min⁻¹ g⁻¹) is observed towards the end of the discharge process.
Figure 4.16 Voltage profile and the corresponding background-corrected mass signals m/z = 44 (\(^{12}\)CO\(_2\)), 32 (O\(_2\)), and 27 (C\(_2\)H\(_4\)) for TiNb\(_2\)O\(_7\)-NMC full cell cycled in the voltage range of 3.2 to 1.0 V and at varying c-rates (a) 0.1C; (b) 1C, 3C, and 5C.
The O₂ generation is almost three times higher than the charge process, close to 0.69 nmol min⁻¹ g⁻¹ NMC. C₂H₄ evolution peaked to ~5.06 nmol min⁻¹ g⁻¹ NMC at the beginning of the voltage relaxation period after the discharge process, suggesting further electrolyte decomposition on the cathode side, leading to formation of cathode electrolyte interphase (CEI). Gas generation in lithium ion batteries during the first formation cycle is partly responsible for irreversible capacity loss, lower coulombic efficiency, active material surface degradation, and poor cycle stability [90,97–99]. Considerable gas evolution at high current (>1C) was also observed in this work, that could potentially degrade the cell performance. To tackle this issue, a protective barrier coating on the TNO particles was developed to reduce gas evolution in a lithium-ion cell.

Figure 4.17 (a) and (b) show the voltage profile and gas evolution behavior for the coated-TNO half cells. Figure 4.17 (a) shows that the CO₂, O₂ and C₂H₄ gas evolution decreases significantly once the protective barrier coating is applied to the TNO particles and the onset of gas evolution is influenced by the voltage at the anode. At 0.14C, CO₂ evolution begins at the end of the charge cycle (delithiation process) at ~2.6 V, and peaks to ~1.45 nmol min⁻¹ g⁻¹ TNO. Whereas C₂H₄ evolution begins at the end of the discharge cycle (lithiation process) as the voltage drops close to 1.14 V, and peaks to ~6.8 nmol min⁻¹ g⁻¹ TNO, as shown in Figure 4.17 (b). O₂ generation was almost constant throughout the cycling process, close to 0.6 nmol min⁻¹ g⁻¹ TNO. With the protective barrier coating on TNO particles, the rate of CO₂ and C₂H₄ evolution dropped by almost 2 and 5 times, respectively, at 0.1C versus the uncoated TNO-Li half cell discussed in Figure 4.12.
Figure 4.17 Voltage profile and the corresponding background-corrected mass signals m/z = 44 (^{12}CO_2), 32 (O_2), and 27 (C_2H_4) for (a) Coated TiNb_2O_7-Li metal (coated-TNO) pouch cell cycled at 0.08C in the voltage range of 3.0-1.0 V; (b) Coated TNO-Li metal half cell cycled at higher currents (1.4C, 4.1C, 5.9C)
XPS spectra shown in Figure 4.18 confirms that the gas evolution in coated-TNO half-cell leads to interphase formation. The disappearance of the Ti peaks in the Ti 2p spectra and the appearance of RCOOLi, Li$_2$CO$_3$, and C=O signals in the C 1s spectra (during the lithiation process) in Figure 4.18, confirms the formation of an SEI layer. In addition, the much stronger peaks of Li$_2$CO$_3$ and C-O single bond in curve e than those in curve c prove that the SEI layer grows thicker on the coated-TNO during cycling. Further TEM analysis also confirms the formation of a more uniform SEI layer on the coated-TNO after cycling, as shown in Figure A10.

A similar gassing behavior is observed at higher currents (1.4C, 4.1C and 5.9C) where CO$_2$ and C$_2$H$_4$ generation rate reduces to 1.5 and 5.5 nmol min$^{-1}$ g$_{NMC}^{-1}$ from 12.3 and 42.6 nmol min$^{-1}$ g$_{NMC}^{-1}$, respectively. This dramatic reduction in gas evolution with coated-TNO at both low and high currents suggests that formation of a uniform SEI layer leads to decrement in electrolyte decomposition and the pertaining side reactions on the TNO anode surface decreases significantly with the help of the protective barrier coating. Likewise, in case of the coated TNO-NMC full cell, a drastic drop in CO$_2$, O$_2$ and C$_2$H$_4$ gas generation rate is observed at both high and low currents, as shown in Figure 4.19. The CO$_2$, O$_2$ and C$_2$H$_4$ gas evolution begins towards the end of the first low current (0.1C) charge cycle, and peaks at 0.52, 0.31, and 3.45 nmol min$^{-1}$ g$_{NMC}^{-1}$, respectively, towards the end of lithiation process as shown in Figure A11.
Figure 4.18 Ti 2p, Nb 3d, C 1s XPS spectra of coated-TNO (a) pristine powder; (b) electrode; (c) electrode at 100% lithiated state (cutoff at 1.0 V); (d) electrode at complete delithiated state (cutoff at 3.0 V); (e) electrode at 100% lithiated state after 2 cycles (cutoff at 1.0 V). The cycling is performed at 0.1C.
Figure 4.19 Voltage profile and the corresponding background-corrected mass signals m/z = 44 ($^{12}$CO$_2$), 32 (O$_2$), and 27 (C$_2$H$_4$) for Coated TiNb$_2$O$_7$-NMC full cell cycled in the voltage range of 3.2-1.0 V.
The bar chart in Figure 4.20 clearly shows that the protective barrier coating helps reduce the gas evolution at both low and high currents. The CO$_2$ and C$_2$H$_4$ generation rate decreased by ~98% and ~72%, respectively at low current (0.1C), suggesting a major reduction in electrolyte decomposition at the anode. Further reduction in gas evolution is evident at higher currents (1C and 3C) with coated TNO. The improvement in lowering the gas evolution could prove to be extremely crucial in enhancing the rate performance of high-power fast charging lithium-ion batteries. The application of a protective barrier coating on TNO particles is a significant step towards improvement of TNO based anodes as the next generation lithium-ion battery for achieving extreme fast charging.

To further verify the benefits of the protective barrier coating, the rate performance data of TNO-NMC full cell for both scenarios (with and without coating) is shown in Figure 4.21. The full cells are cycled at varying charge rates (0.1C, 5C, 6C, 6.5C, and 7C) and a fixed discharge rate (0.3C) with a CCCV protocol and a fixed total charging time of 10 minutes. It is clearly evident from the plots in Figure 4.20 and 4.21, the coated-TNO not only reduces the gassing behavior in TNO-NMC cells, but also improves the rate performance at higher charge rates. We observe a ~20% improvement in the specific discharge capacity of the coated TNO-NMC full cells at higher charge rates (150 vs 125 mAh g$^{-1}$). This improvement in specific capacity with coated TNO could be attributed to the reduced gassing behavior which lowers the electrolyte decomposition at low/higher currents as seen in uncoated TNO, resulting into less capacity degradation during cycling.
Figure 4.20 Comparison of gas evolution in uncoated and coated TNO full cell at different currents.
Figure 4.21 Rate performance comparison for uncoated and coated TNO in a full cell format with NMC cathode. Varying charge rates (0.1, 5, 6.6.5 and 7C) and fixed discharge rate (0.3C) are used.
4.3.3 Conclusion

Titanium niobium oxide (TiNb₂O₇ - TNO) has proven to be a promising material for high rate capability applications. It’s high redox potential (1.5 V) and high theoretical capacity (387 mAh g⁻¹) makes it suitable for extreme fast charging application due to its ability to avoid lithium plating. TNO-NMC622 2 Ah pouch cells are built and tested for XFC (10 minutes total charging time). Excellent charge-discharge capacities are observed at 6C, 6.5C and 7C with capacity retention of greater than 83% at high currents. Long-term cycling revealed dramatic capacity degradation after 300 cycles and severe gas evolution at the end of 400 cycles at charge rate of 5C, 6C, 6.5C and 7C with a constant discharge at 0.33C.

To address the gassing behavior during the cycling of TNO based anodes, half-cell and full-cell configurations are investigated via operando mass spectrometry analysis. A detailed quantitative view on gas evolution during the lithium insertion/extraction process at low currents and high currents is provided. The main gases generated during the cycling process are C₂H₄, O₂, and CO₂. During the low current cycle (0.1C), formation of a reversible SEI film on TNO surface was observed during the lithium insertion process. The SEI film tended to dissolve during the lithium extraction from TNO. At higher rates (1C, 3C, and 5C), more significant gas evolution is observed in both TNO half-cells and TNO-NMC full-cells. A protective surface coating is applied on the TNO particles that significantly reduced the gas evolution. The rate of CO₂ and C₂H₄ evolution is lowered by almost 2 and 5 times respectively, at 0.1C in half-cell configuration, while the mitigation
of gases is more pronounced in full-cell configuration at both low and high currents. XPS and TEM analysis confirmed that a more uniform SEI layer is formed on the coated TNO after cycling, that resulted in less electrolyte decomposition.
CHAPTER 5 UNDERSTANDING THE IMPACT OF CATHODE DESIGN ON ENERGY DENSITY
Foreword

This chapter contains material modified from the following research paper published in the *Journal of Power Sources*:

D. Parikh, T. Christensen, J. Li, Correlating the influence of porosity, tortuosity, and mass loading on the energy density of LiNi_{0.6}Mn_{0.2}Co_{0.2}O_{2} cathodes under extreme fast charging (XFC) conditions, J. Power Sources. 474 (2020) 228601.

My contributions to this paper were the following: (1) performing background research to frame the research question, (2) executing experiments, and (3) drafting and revising the manuscript. My colleague, Tommiejian Christensen is the co-author, and her contributions were following: (1) assisting with coatings and experiments, (2) Data analysis. My adviser, Jianlin Li, is the other co-author on this paper. His contributions were the following: (1) assisting in experimental design, (2) imparting guidance on the structure of the paper, and (3) revising the manuscript before submitting to the journal.

5.1 Introduction

The rapid development of Li-ion batteries (LIBs) and the significant drop in its cost by 80% has led to the emerging rise in the market of electric vehicles (EVs) [3,100,101] although the EVs still only account for ~1.7% of annual vehicles sales [4,102]. Range anxiety and longer charging time have been reported as the key factors for the wide scale adoption of EVs [103]. Presently, the charging time for battery electric vehicles is significantly longer than the refueling of the conventional internal combustion engine.
vehicles[101]. For the wide scale adoption of EVs to increase, it is necessary to reduce the charging time. The United States Department of Energy has defined a specific goal for extreme fast charging (XFC) of electric vehicles where the charging time should be \( \leq 10 \) minutes with a gravimetric energy density of \( > 200 \text{ Wh kg}^{-1} \) and volumetric energy density of \( > 550 \text{ Wh L}^{-1} \) at cell level [1,2,104]. The gravimetric and volumetric energy density metric are critical based on different application that require high/low power density [6]. For EV application, both energy densities are important due to the constraint in the weight and volume of a battery pack [105].

The main components of a LIB are anode, cathode, liquid electrolyte, and a porous separator membrane. During the charging process, lithium ions travel from the cathode to the anode via liquid electrolyte, which includes several diffusion steps 1) solid diffusion through active material particles, 2) diffusion across the electrode/electrolyte interface, and 3) through porous electrodes via electrolyte. Each step contributes to the barrier of enabling extreme fast charging. Cells with LiNi\(_x\)Mn\(_y\)Co\(_z\)O\(_2\) (NMC) and graphite chemistry are capable for fast charging but the electrodes need to be very thin [33,52,106]. This suggests that the rate limiting step in extreme fast charging of high-energy batteries with thick electrodes is the lithium ion diffusion in electrolyte which was due to electrolyte depletion and long diffusion length induced from the porous electrodes and separator [48]. Enhancement of electrolyte properties such as transference number and ionic conductivity could improve the fast charging capabilities [33,49,107].
Graphite is the state-of-the-art anode material in LIBs. However, it is susceptible to Li plating due to the proximity of the LiC_x potential to that of Li^+/Li, which limits the charging current density and also results in capacity fade [46,108]. The plated metallic lithium can cause electrolyte decomposition and Li inventory loss from cathodes [1,31]. The plated lithium can further form dendrites and cause internal short circuits as well as form dead lithium on the anode, that could pose safety concerns for a LIB. Thus, extensive efforts have been made to improve the fast charging capability of graphite anode and alleviate Li plating via surface coating [80], utilizing graphene-like-graphite [109], and minimizing electrode tortuosity [110].

Common electrode materials, such as graphite and LiNi_xMn_yCo_{1-x-y}O_2, are capable of fast charging when the electrode thickness was very thin, which resulted in low energy density and high cost [111]. To increase electrode thickness and cell energy density, other manufacturing processes such as freeze casting [76,112] and magnetic templating [113] have been adapted to tailor the electrode architecture and enable fast charging, but they are not readily scaled up and yet economically viable. These efforts to achieve fast charging with high energy density have shown slightly detrimental influence on the cell cycle life [46] due to Li plating and increased temperature leading to accelerated SEI growth [13,114,115]. However, some studies also showed that high temperature (45°C) were useful in improving the cycle life for thick anodes [12,116] or while charging the cell at 2C rate [117].
While graphite anode is problematic in XFC, the cathode also deserves some attention especially if other anode materials with fast charging capability, such as lithium titaniam oxide [118] and niobium titanium oxide [56], are utilized. Previous studies on cathodes were mainly focused on optimizing electrode formulation including conductive additive [105], surface modification of the active material particles [119], and optimizing the stoichiometry and crystallite size of cathode materials [120]. A few studies also evaluated the correlation of electrode design (areal loading and porosity), and energy and power density. Gallagher et al. and Appiah et al. have systematically investigated on optimizing the areal capacities, electrode thickness and porosity of LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2 (NMC622) cathodes with help of modeling tools [108,121]. However, fewer insights were provided on the experimental aspect of varying the electrode architecture, and its influence on high rate capability [121,122]. A recent study by Huebner et al. focused on understanding the influence of electrode design (porosity and thickness) on electrochemical performance and lithium insertion kinetics of NMC622-based cathodes for high energy density cells at high rates. However, no work has considered the XFC [123–125].

This study reports a systematic investigation on optimizing NMC622 cathodes for XFC application. A matrix of 4 mass loadings and porosities were investigated. All electrodes were calendared to different electrode thicknesses to obtain the target porosity and mass loading. In addition, the influence of charging protocol on the energy density
under XFC was also evaluated. An optimal NMC622 cathode was identified as 11.5 mg cm\(^{-2}\) in mass loading, 35% in porosity and under 5C charging protocol.

5.2 Experimental Methods

As received LiNi\(_{0.6}\)Mn\(_{0.2}\)Co\(_{0.2}\)O\(_2\) (NMC622, Targray), polyvinylidene fluoride (PVDF, Solvay 5130) and carbon black (powder grade, Denka) were used to fabricate the NMC622 cathode using N-Methyl-pyrolidine (NMP) as the solvent and following the procedures reported previously [75]. The NMC622 cathode consisted of 90 wt% NMC622, 5 wt% PVDF and 5 wt% carbon black. The cathode was slot-die coated with varies mass loadings (11.5, 15.0, 20.0, and 25.0 mg cm\(^{-2}\)). The as-coated NMC622 cathode exhibited 50% porosity which was further tailored to 45%, 35%, and 25% via calendaring at 80°C. The porosity of these electrodes was obtained using the relation [123,126]

\[
\varepsilon = 1 - \frac{m_{\text{areal}}}{L} \left( \frac{\omega_{\text{AM}}}{\rho_{\text{AM}}} + \frac{\omega_{\text{B}}}{\rho_{\text{B}}} + \frac{\omega_{\text{CA}}}{\rho_{\text{CA}}} \right)
\]

(5.1)

where \(m_{\text{areal}}, \rho, \) and \(\omega\) are areal mass loading, density of coating, and mass fractions respectively. AM, B, and CA are active material, binder, and carbon additive respectively.

The cathodes were punched into 13 mm disks and dried at 120°C under vacuum overnight before being assembled into coin cells with Li metal as the counter electrode. Celgard 2325 was used as the separator in all coin cells. The coin cells were assembled in an argon filled glove box. The electrolyte was 1.2 M LiPF\(_6\) in EC/EMC (3/7 wt%).

For the electrochemical testing, the half cells were cycled within a voltage range of 4.3-3.0 V using a potentiostat (Maccor). The cells were first charged at C/5 (1C=175 mA g\(^{-1}\)) and discharged at C/3 to validate the cell performance before performing XFC testing where a
constant current and constant voltage charge was used with total charging time of 10 minutes. For XFC testing, the cells were charged using CCCV protocol with various constant currents (C/5, 5C, 6C, 7C, 8C, 10C, and 20C) followed by constant voltage at 4.3V (cut-off) until the current dropped below C/20 for a total charging time of 10 minutes. The cells were then discharged at C/3. The rate performance of the half cells was verified by cycling symmetric cells. The symmetric cells were assembled with both the electrodes being cycled to 50% state of charge (SOC). Eliminating Li anode in the symmetric cells excludes the contribution to kinetic properties from the anode. The cells were cycled in the voltage range of -1.3 to 1.3 V. Further, electrochemical impedance spectroscopy (EIS) was performed on the electrodes with symmetric cell configuration at open circuit voltage of approximately 120 mV. For this test, pristine electrodes with 0% SOC were used. The frequency range for the impedance measurement was 10 mHz to 600 kHz with an amplitude of 10 mV using a Biologic VSP potentiostat.

5.3 Results and Discussion

Figure 5.1 (a) and (b) shows the 3D plots of the specific discharge capacity and discharge energy density respectively with respect to different mass loadings and electrode porosity at XFC conditions. Sixteen NMC622 cathode conditions were shown in Table 5.1. All the cells performed well at low C-rate (0.2C) with almost identical specific discharge capacity. In case of fixed porosity, a small difference in discharge capacity was observed at 0.2C with increase in mass loading as shown in Figure 5.1(a). For instance, the specific discharge capacity reduced slightly at 0.2C when the mass loading is increased from 11.5...
to 25 mg cm$^{-2}$. This was most likely due to polarization with thicker electrodes; however, the effect was insignificant at lower current. With increasing current, a decrease in the discharge specific capacity is observed due to mass transport limitation during the fast charging condition. A similar trend was also observed for the charge specific capacity shown in Figure A7 (a).

The influence of mass loadings (mg cm$^{-2}$) and electrode porosity were studied to understand their combined effects on the specific capacity and energy density of the cell. As shown in Figure 5.1(a), the specific discharge capacity at XFC conditions (5C) for 50% porosity cathode the cell performance degraded from ~133 mAh g$^{-1}$ to 117 mAh g$^{-1}$ as the mass loading increased from 11.5 to 15 mg cm$^{-2}$. It dramatically dropped to 77 mAh g$^{-1}$ when the mass loading was further increased to 25 mg cm$^{-2}$, accounting for ~42% reduction in discharge capacity at 5C as loading was increased from 11.5 to 25 mg cm$^{-2}$. This behavior suggests significant polarization as well as underutilization of thicker electrodes at higher charge rates.

The rate performance of the cell was improved by reducing the electrode porosity to 45% and 35%. For example, at a fixed mass loading of 11.5 mg cm$^{-2}$ and 0.2C rate, the specific discharge capacity increased slightly from ~183 mAh g$^{-1}$ for 50% porosity cathode to 185 and 190 mAh g$^{-1}$ for the cathodes with 45% and 35% porosity, respectively. The improvement in the specific discharge capacities was more prominent at higher charge rates with reduction in electrode porosity. Up to 13% improvement in the specific capacity was observed at 5C and 6C rates for electrodes with 35% porosity.
Figure 5.1 3D plots for varying porosity and mass loading for (a) specific discharge capacity (mAh g$^{-1}$), (b) gravimetric discharge energy density (Wh kg$^{-1}$), and (c) volumetric charge energy density (Wh L$^{-1}$). The color bars represent the discharge specific capacities and energy densities for each figure.
“Figure 5.1 continued”

Table 5.1 NMC622 cathodes with various conditions

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<tr>
<th>Porosity (%)</th>
<th>Mass Loading (mg cm$^{-2}$)</th>
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<tr>
<td>50</td>
<td>11.5</td>
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<tr>
<td>45</td>
<td>15</td>
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However, further reducing the electrode porosity to 25% resulted in 12% degradation of specific discharge capacity at 5C from 148 mAh g\(^{-1}\) for 35% porosity to 136 mAh g\(^{-1}\). Similar trends were observed with specific charge capacity and gravimetric charge energy density where 11.5 mg cm\(^{-2}\) loading demonstrated superior performance at 5C and 6C rate as shown in Figure S5.1 (a) and (b). Similarly, the gravimetric discharge energy density at electrode level for the various mass loadings and porosity scenarios are shown in Figure 5.1(b), which was calculated using the energy normalized to the mass of the NMC622 cathode plus half of the Al mass as it was single-sided coating. Excellent energy density was observed, and it increased with increasing mass loading at low rate (0.2C). For example, the discharge energy density increased from 528 Wh kg\(^{-1}\) to ~550 Wh kg\(^{-1}\) with 50% porosity when the mass loading is increased from 11.5 mg cm\(^{-2}\) to 25 mg cm\(^{-2}\). Al foil with 15 µm corresponds to 4.05 mg cm\(^{-2}\), which accounts for 15.0 wt% and 7.5 wt% of the double-sided cathode with 11.5 mg cm\(^{-2}\) and 25 mg cm\(^{-2}\), respectively. Higher mass loading increased the mass fraction of active material in the whole cathodes which was fully utilized at low rate and contributed to the improved energy density.

However, higher mass loading resulted in lower gravimetric discharge energy density at XFC conditions as the cathodes were not fully utilized. For the same scenario (50% porosity), the gravimetric discharge energy density dropped to ~373 Wh kg\(^{-1}\) and ~230 Wh kg\(^{-1}\) when charging at 5C with total charging time of 10 minutes for 11.5 and 25 mg cm\(^{-2}\), respectively. Reducing porosity up to 35% was slightly beneficial to the discharge energy density, while further reducing it to 25% degraded the cell performance. For 35%
porosity, the energy density was improved to 405 Wh kg\(^{-1}\) and 255 Wh kg\(^{-1}\) at 5C for 11.5 and 25 mg cm\(^{-2}\) loading, respectively. Further reducing porosity to 25% resulted in lower energy density, 386 Wh kg\(^{-1}\) and 245 Wh kg\(^{-1}\) for 11.5 and 25 mg cm\(^{-2}\) loading, respectively. The optimal NMC622 cathode was 11.5 mg cm\(^{-2}\) and 35% in mass loading and porosity, respectively, and the optimal charging protocol was 5C, which delivered 148 mAh g\(^{-1}\) and 405 Wh kg\(^{-1}\) in capacity and energy density, respectively.

The volumetric discharge energy density (Wh L\(^{-1}\)) at electrode level is shown in figure 5.1(c), which was calculated by considering the volume of coating and half of the aluminum foil. Excellent volumetric energy density was observed at 0.2C which increased with decreasing the electrode porosity for all mass loadings as shown in figure 5.1(c).

For instance, when reducing the NMC622 cathode porosity from 50% to 25%, the volumetric discharge energy density increased from 1136 to 1554 Wh L\(^{-1}\) for 11.5 mg cm\(^{-2}\) mass loading. The benefit in improved volumetric discharge energy density from reducing the cathode porosity was also achieved at 5C. For example, the volumetric discharge energy density increased from 800 Wh L\(^{-1}\) to 1179 Wh L\(^{-1}\) at 5C for a mass loading of 11.5 mg cm\(^{-2}\) when the cathode porosity was reduced from 50% to 25%. Further increasing the C-rate or mass loading demonstrated adverse effect on the volumetric discharge energy density. Unlike the gravimetric discharge energy density where the optimal value was achieved at the NMC622 cathode with 11.5 mg cm\(^{-2}\) mass loading and 35% porosity and being charged at 5C, the best volumetric discharge energy density was at 11.5 mg cm\(^{-2}\) or 15.0 mg cm\(^{-2}\) mass loading and 25% porosity. As the volumetric energy density could be
more critical for electric vehicle application, these cathode parameters could be more valuable.

In the further analysis for simplicity, we will use the highest porosity case and the best performing scenario, which are 50% and 35% porosity with 11.5 and 25 mg cm\(^{-2}\) loading to understand the influence of porosity and mass loading on the rate performance. Figure 5.2 (a) shows the plot of specific discharge capacity with respect to charge rate. Reducing the electrode porosity from 50% to 35% with 11.5 mg cm\(^{-2}\) loading and at 5C contributed to ~11% improvement in specific discharge capacity (133 mAh g\(^{-1}\) vs 148 mAh g\(^{-1}\)). The enhanced performance at lower porosity for 11.5 mg cm\(^{-2}\) loading could be attributed to the better pore connectivity, lower electronic resistance, and shorter diffusion length for Li ion through the porous cathodes as shown in Table 5.2. However, the reduction in porosity from 50% to 35% was not effective with higher mass loading (i.e., 25 mg cm\(^{-2}\)) and it degraded dramatically as the currents increased. This suggests that Li-ion diffusion in the electrolyte phase was rate-limiting for thicker electrodes with higher loading [127–129].

The diffusion-limited current can be a good measure to qualitatively indicate the Li-ion diffusion limitation in the electrolyte phase or through the active material as the rate-limiting step at high currents [123]. Exceeding diffusion-limited current leads to increased overpotential, not fully utilizing the electrodes and a drastic drop in attainable discharge capacity [130].
Figure 5.2 (a) Specific discharge capacity, (b) Discharge energy density, with respect to C-Rate for 35% and 50% porosity cathode with 11.5 and 25 mg cm$^{-2}$ mass loading.
the areal capacity [130]. Although quantitative measurements are not shown in the present work, qualitatively based on specific capacities shown in Figure 5.1 (a) and 5.2 (a), 5C was the DLC for the cathode with 25 mg cm⁻² as no significant increase in discharge capacity was observed at higher rates whereas 7C was the DLC with 11.5 mg cm⁻² loading. Figure 5.2 (b) shows the plot of discharge energy density at varying c-rates. Thick cathodes with 25 mg cm⁻² loading showed highest energy density compared to other loading conditions at 0.2C due to the higher active material content. However, these cathodes degraded significantly under extreme fast charging conditions from 5C to 20C. As shown in Figure 5.2 (b), cathodes with 35% porosity and 11.5 mg cm⁻² loading show highest energy density of up to 405 Wh kg⁻¹ at 5C and 6C rates. This could be attributed to the higher achievable capacities, lower polarization and better pore network for low porosity and mass loading electrodes. As the electrode thickness increased due to the increase in mass loading, the cells energy density reduced drastically by ~38% from 405 Wh kg⁻¹ to 250 Wh kg⁻¹, suggesting mass transport in thicker electrodes is limited by the electrolyte phase as well as the impedance of electrons in the solid phase [131]. The evident difference in energy densities between two mass loading conditions (11.5 and 25 mg cm⁻²) is related to the poor rate performance of thick electrodes (25 mg cm⁻²) at high currents due to their longer diffusion pathways and underutilization of electrode. This led to low specific discharge capacity and high voltage and resulted in low energy.

For simplicity and ease of understanding, four cases one with best performing scenario (35%) and highest porosity (25%) are considered to interpret the results. Other
conditions were not considered due to their poor rate performance as seen in Figure 5.1(a). The EIS measurements were carried out to further understand the impact of these design parameters on the kinetic and mass transport limitations. Symmetric cells configuration with 0% SOC were assembled under blocking conditions as described by Landesfeind and co-workers [132].

Figure 5.3 shows the Nyquist plots for electrodes with varying porosity and mass loading conditions discussed above in Figure 5.2. The intercept of the semi-circle at the high frequency region (50 kHz) represents the ohmic resistance [76], while the semi-circle relates to the contact resistance at the cathode-current collector interface [133]. The ionic resistance through the electrolyte filled pores of the electrode corresponds to the 45° slope at the intermediate frequency. The steep slope (<90° phase angle) agrees with the transmission-line model with constant-phase element (TLM-Q) behavior as discussed by Landesfeind et. al [132]. The TLM-Q model is equivalent to the modified restricted diffusion element (Ma) in EC-Lab software. The impedance data fits well with the equivalent circuit shown in Figure 5.3. The fitting was performed using the ZFit tool in EC-lab. The ionic resistance ($R_{ion}$) was calculated using equation below, where $R_{total}$ is the total resistance, $R_{contact}$ is the contact resistance (or the high frequency resistance) [132,134].

$$R_{Total} = \frac{R_{ion}}{3} + R_{contact}$$  

(5.2)
Figure 5.3 Nyquist plots for the electrodes with 35% and 50% porosity with 11.5 and 25 mg cm$^{-2}$ mass loading. The impedance spectra was fit with the TLM-Q model shown by solid and dash lines.
The ionic resistance was further used to compute the electrode tortuosity ($\tau$), where $A$ is the electrode surface area, $d$ is the electrode thickness, $k$ is the electrolyte conductivity, and $\varepsilon$ is the electrode porosity.

$$\tau = \frac{R_{\text{ion}} \cdot A \cdot k \cdot \varepsilon}{2d}$$  \hspace{1cm} (5.3)

As shown in Figure 5.3, the ohmic resistance increases with higher mass loading. The contact resistance reduces with lower porosity (35%) for both the mass loading conditions due to better contact between the active material and carbon black particles as well as shorter diffusion length after they were calendared [123,135]. The contact resistance increases at higher loading, i.e., 11.1 $\Omega$ and 7.6 $\Omega$ at 50% porosity for 25 mg cm$^{-2}$ and 11.5 mg cm$^{-2}$, respectively as depicted by the semi-circle in Figure 3.

This can be attributed to the longer diffusion length for both electron and Li ion in the cathodes with higher mass loading. However, as the difference in contact resistance between different porosity was insignificant, the longer diffusion length of electron in thicker electrodes was the major contributor to the higher contact resistance. The diffusion length ($L$) through the porous electrode shown in Table 3 was computed using the equation below as discussed by Ebner et al. [20],

$$\tau = \left(\frac{L}{d}\right)^2$$  \hspace{1cm} (5.4)
The results indicate that for fixed loading conditions but varying porosity (35% and 50% porosity with 11.5 mg cm$^{-2}$), the lower porosity electrode exhibited a higher tortuosity than higher porosity electrodes.

However, the diffusion length in these lower porosity electrodes is shorter due to lower electrode thickness, which in turn resulted in better performance at higher charge rates. Rate capability and energy density also depend on other factors such as the electrode formulation, conductive additive, particle morphology, and cathode materials [130]. Appropriate selection of conductive additive, minimizing the inactive components while maintaining sufficient electronic conductivity, cohesion and adhesion can enhance rate performance [136]. Particle size and morphology is also crucial for the solid electrolyte interface and solid-state diffusion through particles.

Figure 5.4 (a)-(d) shows the plot for average charge and discharge voltage as well as the voltage difference of the two in the half cells at different c-rates. The first three cycles show the formation process at 0.2C while there are five cycles for each c-rate for 5C, 6C, 7C, 8C, 10C, and 20C. Figure 5.4 (a) shows the charge and discharge voltage curves for 35% and 50% porosity electrodes with 11.5 mg cm$^{-2}$ loading. A negligible difference in voltage for the charge-discharge process is observed at 0.2C for both porosity conditions shown by the first three cycles. Lower charge voltages are observed at 5C and 6C for 35% porosity in the next 10 cycles, suggesting that the cut-off voltage is reached quicker for 50% porosity electrode.
A slightly different behavior is observed for 25 mg cm$^{-2}$ electrodes in the first 10 cycles as shown in Figure 5.4 (c), where both 35% and 50% porosity electrode reached the cut-off voltage quickly in the first few cycles of charging at 5C and 6C. Consequently, as shown in Figure 5.4 (b) an average voltage difference of 0.1V was observed at low currents (0.2C) for the NMC622 cathode with 11.5 mg cm$^{-2}$ regardless the electrode porosity. However, the voltage difference increased from ~0.1V to 0.57V at 5C and gradually increased for the cathode with 50% porosity.

Reducing the cathode porosity to 35% significantly lowered the voltage difference at 5C (0.36V vs 0.57V) but the benefit became negligible at the end of 6C and beyond. The voltage difference further increased to ~0.7 V at 6C when increasing the mass loading from 11.5 to 25 mg cm$^{-2}$ as shown in Figure 5.4 (d), which was due to more severe mass transport limitation in thicker electrode. Unlike the one with 11.5 mg cm$^{-2}$ mass loading, reducing porosity didn’t reduce the voltage difference with 25 mg cm$^{-2}$ mass loading. Calendering can reduce the diffusion length as shown in Table 5.3.

For lower mass loading (11.5 mg cm$^{-2}$), the diffusion length was probably close to the critical diffusion length whereas it was much longer for the higher loading (25 mg cm$^{-2}$). Thus, the shorter diffusion length due to calendaring improved the cell performance at lower mass loading while the benefit was negligible for higher mass loading due to the much longer diffusion length as shown in Table 5.2.
Table 5.2 Tortuosity and diffusion length of cathodes derived from the EIS plots

<table>
<thead>
<tr>
<th>Porosity</th>
<th>Mass loading (mg cm(^{-2}))</th>
<th>(R_{\text{ion}}) (Ω)</th>
<th>Tortuosity</th>
<th>Diffusion length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>11.5</td>
<td>11.71</td>
<td>5.35</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>22.85</td>
<td>6.04</td>
<td>285</td>
</tr>
<tr>
<td>35%</td>
<td>11.5</td>
<td>11.92</td>
<td>5.69</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>27.83</td>
<td>6.18</td>
<td>241</td>
</tr>
</tbody>
</table>
Figure 5.4 Mean voltage and voltage difference profiles for different c-rates shown in terms of cycle number for varying cases of porosity and mass loading, (a) and (b) 35% and 50% porosity with 11.5 mg cm$^{-2}$, (c) and (d) 35% and 50% porosity with 25 mg cm$^{-2}$.
To verify that mass transport was limited by the cathode and not the Li anode, symmetric cells with two extreme mass loadings were assembled and cycled. Figure 5.5 shows the results of the rate performance of symmetric cells for the four conditions stated above, which were different with the performance of the half cells shown in Figure 1. The voltage profiles of the symmetric cells suggest that at higher charge rates, the cell potential reaches the cut-off voltage quickly due to the limitation of lithium ion transport. The cut-off voltage was reached significantly faster at higher mass loadings as shown in Figure 5.5 (c) and (d) due to higher ionic resistance. This led to underutilization of the thicker electrodes and resulted in less attainable capacity due to the longer constant voltage charging process.

Figure 5.6 (a) and (b) show the normalized discharge capacity at various c-rates to that at 0.2C from both half cells and symmetric cells. Lower normalized discharge capacity was observed for the symmetric cells compared to the NMC-Li half cell up to 8C for the 11.5 mg cm\(^{-2}\) loading as shown in Figure 5.6(a). This is attributed to longer diffusion length for Li ion in the symmetric cells as there were two cathodes compared to only one in the half cells. However, the symmetric cells performed slightly better than the half cells at >8C. The symmetric cells with 25 mg cm\(^{-2}\) mass loading outperformed the half cells at 5C and beyond as shown in Figure 5.6 (b), indicating the Li metal plating in half cells was the rate limiting step.
Figure 5.5 Charge and discharge voltage profiles with respect to capacity for the symmetric cells cycled within the voltage range of -1.3 to 1.3 V. (a) 35% porosity and 11.5 mg cm$^{-2}$ mass loading, (b) 50% porosity and 11.5 mg cm$^{-2}$ mass loading, (c) 35% porosity and 25 mg cm$^{-2}$ mass loading, (d) 50% porosity and 25 mg cm$^{-2}$ mass loading. Constant current constant voltage (CCCV) protocol was used for the cycling of the symmetric cells with total charge time of 10 minutes.
Figure 5.6 Normalized discharge capacity for half cells and symmetric cells with (a) 11.5 mg cm\(^{-2}\) loading for 35\% and 50\% porosity, (b) 25 mg cm\(^{-2}\) loading for 35\% and 50\% porosity
This was due to high resistance from the Li anode under high current density. The current density was 14.9 mg cm\(^{-2}\) and 19.7 mg cm\(^{-2}\) for 8C with 11.5 mg cm\(^{-2}\) and 5C with 25 mg cm\(^{-2}\), respectively. It has been demonstrated Li stripping-plating with NMC cathode was effective for current densities up to 2.2 mA cm\(^{-2}\) [138,139]. Higher current density resulted in deterioration of lithium metal, causing needle-like dendrite growth on the surface of lithium anode [140]. The resulting loose dead layer of lithium induces a high Li-ion diffusion resistance and causes a significant drop in the attainable discharge capacity. Thus, the discharge capacity and energy density in Figure 5.5 are either comparable or lower than the actual performance from the NMC622 cathodes.

5.4 Conclusion

Performance of NMC622 cathodes were evaluated under various extreme fast charging testing protocols with four mass loadings and porosities, respectively. Electrochemical impedance spectroscopy was used to correlate the influence of tortuosity and diffusion lengths with the rate performance of these cathodes. Symmetric cells were tested to confirm the diffusion limitation and the polarization behavior of the cathode half cells. It is demonstrated that:

- The best scenario was identified as 11.5 mg cm\(^{-2}\) with 35% porosity and 5C constant current constant voltage charge, and 11.5 mg cm\(^{-2}\) or 15.0 mg cm\(^{-2}\) with 25% porosity and 5C constant current and constant voltage charge for gravimetric and volumetric energy density, respectively.
• While increasing mass loading resulted to higher energy density at low currents (0.2C), no significant improvement was observed in specific capacity and energy density under extreme fast charging condition mainly due to the limitation in mass transport resulting in underutilization of the cathode.

• Reducing cathode porosity could improve discharge capacity and energy density for low mass loading (i.e., 11.5 mg cm\(^{-2}\)) and the effect is negligible for high mass loading (i.e., 25 mg cm\(^{-2}\)). For example, the specific discharge capacity and energy density were increased by 13% and 9%, respectively, when reducing the cathode porosity from 50% to 35%.

• Superior high rate performance from the symmetric cells indicated that Li metal plating in half cells was a significant factor in low rate performance under high current density.

These results shed lights on cathode design for extremely fast charging and the practical limitation from the cathode.
CHAPTER 6
INFLUENCE OF SEPARATOR MEMBRANE PROPERTIES ON ENERGY DENSITY
Foreword

This chapter contains material modified from the following research paper published in the *Journal of Electrochemical Society*:


My contributions to this paper were the following: (1) performing background research to frame the research question, (2) executing experiments, and (3) drafting and revising the manuscript. Other co-authors, Tommiejean Christensen helped with coating of electrodes and C.T. Hsieh helped in data analysis related to impedance spectroscopy. My adviser, Jianlin Li, is the other co-author on this paper. His contributions were the following: (1) assisting in experimental design, (2) imparting guidance on the structure of the paper, and (3) revising the manuscript before submitting to the journal.

6.1 Introduction

Proper selection of a separator is critical for better battery performance that can maximize energy and power density while maintaining required safety feature. As described in chapter 3, lithium plating in graphite based chemistries is a never-ending issue, especially under fast charging conditions. To avoid the failure of a lithium ion cell, it is important to study the physical properties of the separator membrane that might limit the lithium ion transport under while operating at high currents.
A separator, one crucial component of a lithium-ion battery (LIB), is a porous membrane which allows ionic transports between the electrodes while isolating the electronic flow [79,141]. One of the important characteristics of a battery separator is that it should be electrochemically stable towards the electrolyte and the electrodes. However, the presence of separator builds up the electrical resistance in a cell, which negatively affects the battery performance. The resistance in the separator is mainly ascribed to the resistance of electrolyte transport through the porous structure and is a function of the thickness, porosity, tortuosity, and surface fraction of pores of the separator. Usually in LIBs, the separator has a considerable influence on the transport of lithium ions. The conductivity and transference number in the electrolyte-filled pore space of separators are not only a function of the electrolyte properties but also the structure of the separator. Studies have shown that ionic conductivity reduces by ~5-20% in the pore space compared to the bulk electrolyte conductivity [142,143].

Several factors need be considered for selecting the best separator for a particular battery application such as separator thickness, electrolyte uptake, thermal stability, wettability, electrical resistance, porosity, tortuosity, and safety [144–146]. Correlating these properties to the electrochemical performance of the cells at high charge rates is the key to understanding the influence of separators on fast charging. Currently, majority of the literature is focused on modifying the separators by developing nanoparticle additives and coatings to improve their electrolyte wettability [147], mechanical strength and thermal
stability. Although these studies show improvement in the physical properties of the separator, their benefit to fast charging was not discussed.

Here, we report a detailed study comparing the electrochemical performance of Celgard 2325 and 2500 at higher rates (up to 10C) and correlate them to the physical properties of these separators. The highly porous structure of Celgard 2500 leads to better electrolyte uptake and wettability, lower resistance, and higher rate performance than Celgard 2325 with minimal tradeoff in thermal stability and self-discharge. This work provides another avenue in contributing to fast charging of LIBs.

6.2 Experimental Methods

As received Li[Ni_{0.5}Mn_{0.3}Co_{0.2}]O_2 (NMC532, Toda America), polyvinylidene fluoride (PVDF, Solvay 5130) and carbon black (powder grade, Denka) were used to fabricate the NMC532 cathode using N-Methyl-pyrolidine (NMP) as the solvent and following the procedures reported previously [75]. The NMC532 cathode consisted of 90 wt% NMC532, 5 wt% PVDF and 5 wt% carbon black with a mass loading of 27 mg cm^{-2} (3.9 mAh cm^{-2}). The as-coated NMC532 (~55% porosity) was dried at 120°C under vacuum overnight before being assembled into coin cells with Li metal as the counter electrode. One layer of Celgard 2325 or 2500 was used as the separator in each coin cell. Further details of these separators will be provided in the later sections.

The coin cells were assembled in an argon filled glove box. The electrolyte was 1.2 M LiPF_6 in EC/EMC (3/7 wt). For the electrochemical testing, the half cells were cycled
within a voltage range of 4.2-2.5 V using a potentiostats (VSP, Bio-Logic). The rate performance of the cells was characterized in both charge and discharge. When characterizing discharge capability, the cells were charged at constant current (C/3, 1C=160 mA g⁻¹) followed by a constant voltage charge at 4.2 V until the current dropped to C/20. Then the cells were discharged at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. During charge capability evaluation, the cells were charged by constant current at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C without the constant voltage charge step and discharged at C/3. Electrochemical impedance spectroscopy was carried out in a frequency range of 10 mHz to 500 kHz with an amplitude of 5 mV using the VSP potentiostats.

To understand different cell performance with various separators, the separators were characterized by including contact angle (electrolyte wettability), thermal stability, and electrolyte uptake. The contact angle experiment was performed using two different liquids, water and the electrolyte used in the coin cells by a goniometer (Rame-Hart 260-F4). The thermal stability was evaluated by the dimension change of the separators after being heated at different temperatures in air and time durations. The electrolyte uptake was characterized by thoroughly soaking the separators in the electrolyte for one hour. The mass of the separators was measured before and after electrolyte exposure. Electrolyte uptake was presented in mass percentage (%) or volume ratio where the absorbed electrolyte mass was normalized by the mass of separators, and the absorbed electrolyte volume was normalized by the separator volume, respectively. Morphology of the
separators was characterized by field emission scanning electron microscope (Zeiss Merlin FE-SEM).

6.3 Results and Discussion

6.3.1 Thermal and physical properties

Figure 6.1 a and b show the surface SEM images of Celgard 2500 and Celgard 2325 respectively. The Celgard 2500 is mono-layer membrane of polypropylene (PP), while Celgard 2325 is a tri-layer membrane separator with polypropylene-polyethylene-polypropylene (PP|PE|PP) configuration. Celgard 2500 has similar structure as Celgard 2325 but is more porous, consistent with the high porosity as shown in Table 6.1 [144,146,148]. The low Gurley number for Celgard 2500 indicates higher permeability.

Both separators have same chemistry (PP) on the surface which is pure dispersive in surface energy (35.3 mN m$^{-1}$) [149]. As shown in Figure 6.2, Celgard 2500 shows more hydrophilic behavior compared to Celgard 2325 with a smaller apparent contact angle with DI-water, which is hydrophilic. Assuming the surface energy of the PP is similar for both separators, the smaller contact angle with DI-water for Celgard 2500 indicates higher apparent surface energy, which is ascribed to the higher porosity (lower surface fraction of PP) and/or lower surface roughness [150]. As the electrolyte has a surface tension of 32.2 mN m$^{-1}$ with 38.0% polarity [151], the higher apparent surface energy of Celgard 2500 results in smaller contact angle with the electrolyte, indicating better surface wetting.
Table 6.1 Properties of separators

<table>
<thead>
<tr>
<th></th>
<th>Thickness (µm)</th>
<th>Porosity (%)</th>
<th>Gurley (s)</th>
<th>PP pore size (nm)</th>
<th>Puncture strength (gf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celgard 2500</td>
<td>25</td>
<td>55%</td>
<td>200</td>
<td>28</td>
<td>335</td>
</tr>
<tr>
<td>Celgard 2325</td>
<td>25</td>
<td>39%</td>
<td>620</td>
<td>28</td>
<td>&gt;380</td>
</tr>
</tbody>
</table>

Figure 6.1 SEM images of the surface of separators: (a) Celgard 2500, (b) Celgard 2325.
Electrolyte uptake was shown in Figure 6.3 where the absorbed electrolyte was normalized to the mass and volume of the separators, respectively. Celgard 2500 has almost double electrolyte uptake compared to Celgard 2325 attributing to its high porosity and pore volume, which would facilitate mass transport of lithium ion through the separator. The thermal stability of the separators plays a significant role on battery safety as high shrinkage may lead to cathodes and anodes uncovered and form short circuit.

The thermal shrinkage was measured in terms of the dimensional changes of the separator after being held at different temperatures for 10 and 20 minutes. The dimensional change pertains to the variation in the separator diameter after it is exposed to heat. Both separators show good thermal stability at 120°C with 3.0% and 1.75% shrinkage for Celgard 2500 and 2325, respectively, after 20 min heating. It was noted that the Celgard 2500 tends to fold when exposed to >100°C as shown in Figure 6.4 but didn’t shrink much in dimensions. Heating time also significantly affect the thermal stability. For instance, both separators exhibited higher shrinkage rate when exposed to 100°C for 20 min compared to the 120°C for 10 minutes.

6.3.2 Electrochemical performance

The ionic resistance associated with the separator was determined by electrochemical impedance spectroscopy. Both separators were soaked in electrolyte for over 72 hours before being sanwiched between spacers and assembled in a coin cell format. Special caution was paid to minimize additional electrolyte and ensure lithium ions
Figure 6.2 Contact angle measurements on Celgard 2325 (left) and Celgard 2500 (right) using water and electrolyte.

Figure 6.3 Electrolyte uptake for two separators in terms of volume and normalized separator weight.
Figure 6.4 Thermal stability test for separators. Percentage decrement of the separator diameter at different temperatures and time duration: quantitative (top) and qualitative (bottom)
transporting through separator during measurement without bypassing the separator when
flooded electrolyte presents. Figure 6.5 (a) shows the Nyquist plots for the cell
configuration with all coin cell parts and electrolyte but without separator. The ionic
resistance is indicated by the intercept of the Nyquist curve on the horizontal axis. The
resistance through the cell with only spacers is approximately 0.632 Ω, while the resistance
through the cell with spacer plus electrolyte is 1.26 Ω. The increase in resistance is due to
the inclusion of electrolyte in the cell.

Figure 6.5 (b) shows the Nyquist plot for the two separators with ionic resistance
of approximately 7.51 Ω and 12.58 Ω for Celgard 2500 and 2325, respectively. This is
equivalent to 2.23 Ω cm$^{-2}$ less resistance due to Celgard 2500 separator. Based on the ionic
resistance, the tortuosities can be computed using the equation shown below [134], which
are found to be 2.89 and 3.92 for Celgard 2500 and 2325 respectively. The higher resistance
in Celgard 2325 is due to the longer path for lithium ions to cross through the separator.
The resistance can be presented in the following equation:

$$R = \frac{d \tau}{\sigma \varepsilon A} + R_{contact}$$  \hspace{1cm} (6.1)

where $d$ is the separator thickness, $\tau$ is the tortuosity, $\sigma$ is the electrolyte conductivity
9.24x10$^{-3}$ S cm$^{-1}$ [152], $A$ is the separator area, $\varepsilon$ is the porosity of separator, and $R_{contact}$ is
the contact resistance due to spacers. It is noted that the surface fraction of pores in
separator should be used in calculating tortuosity, which could be quite different from the
bulk porosity [24].

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Figure 6.5 Nyquist plots for cells with different configuration (a) coin cells plus electrolyte without separator (SS|electrolyte|SS) (b) coin cells with a separator soaked in liquid electrolyte previously (SS|separator|SS).
However, this number is not available. Thus, the calculated tortuosity is an approximate value and only for comparison purpose. The higher tortuosity of Celgard 2325 results in additional 25 µm diffusion length for lithium ion to shuttle between anode and cathode, resulting to longer lithium ion transport time through the separator. This also suggests that we could either reduce the overall diffusion length of the cell system by 25 µm, or increase the electrode thickness equivalent to the diffusion length which could further improve the energy density of the cell.

The effect of separators on rate performance was characterized in half coin cells with two different protocols between 2.5 and 4.2 V. One protocol was to evaluate the discharge rate performance with a constant charge (const CHG) at C/3 (CC) and a trickle current of C/20 while discharged at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. The other protocol was to gauge the charge rate capability where the cells were discharged (const disCHG) at C/3 while charged at C/5, C/3, C/2, 1C, 2C, 3C, 5C, 10C. It is noted that there was no constant voltage charge step in this protocol.

Figure 6.6 (a) and (b) show the voltage profiles under constant discharge protocol from coin cells with Celgard 2500 and 2325, respectively. The normalized capacity is the capacity ratio between a particular charge rate and 0.1C. Overall, the cells demonstrated excellent rate performance with ~4.0 mAh cm⁻². There charge capability was pretty identical at low charge rate (e.g. up to 1C) with both separators.
Figure 6.6 Voltage profiles for cells assembled with (a) Celgard 2500 - constant discharge cycle; (b) Celgard 2325 - constant discharge cycle; (c) Celgard 2500 - constant charge cycle; (d) Celgard 2325 - constant charge cycle. Rate performance of NMC532/Li half cell using Celgard 2325 and 2500 separator; (e) Discharge capacity retention; (f) Discharge capacity in mAh g$^{-1}$. 

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However, the cells with 2500 separator demonstrated dramatic improvement, corresponding to 57% and 47% increase over those with 2325 separator when charged at 2C and 3C, respectively. This indicates the separator could play a big role in improving charging capability and energy density. When further increasing the charging rate, the improvement was not significant which is most likely due to the dominant limitation of mass transport in the electrodes. Similarly, the cells with separator 2500 delivered much better discharge rate performance when discharged at 2C to 5C as shown in Figure 6.6 (c) and (d). The improvement was approximately 6%, 52%, and 60% for 2C, 3C, and 5C, respectively. capacity retention. ‘const CHG’ indicates constant charge protocol, ‘const disCHG’ indicates constant discharge protocol.

Figure 6.6 (e) and (f) show the electrochemical performance and capacity retention as a function of charge or discharge rate, respectively. Without the constant voltage charge step, capacity reduced quickly when increasing charging rate. The cells with 2500 separator always demonstrate identical or superior performance to those with 2325 separator regardless cycle protocols. For instance, cells with both separators demonstrated similar discharge capacity (160 mAh g\(^{-1}\)) at 0.1C. However, the cells with 2500 separator delivered a discharge capacity of 92 mAh g\(^{-1}\) (~60% capacity retention) compared to the ~60 mAh g\(^{-1}\) (37% capacity retention) with 2325 separator when charged at 2C. When charged at constant rate (C/3), the discharge capacity was higher especially at high discharge rate indicating significant portion of capacity came from the constant voltage charge step. The
cells with 2500 separator still outperformed those with 2325 separator. As shown in Figure 6.6 (f), the discharge capacity retention of the cells with 2500 separator was 82% and 90% compared to the 53% and 82% for those with 2325 separator at 3C and 2C, respectively.

Figure 6.7 (a) and (b) shows the plot of energy density in electrode level where the total weight of the cathode coating and Al foil was normalized to cell energy. The cells showed very high energy density at low rate due to the high areal loading. When charged at various rates without a constant voltage step, the cells suffered significant energy loss at high rate (≥ 2C). While the capacity retention was 89% at 2C for the cells with 2500 separator, the energy density retention was only ~70%.

The lower energy density retention as ascribed to the lower discharged voltage. The gap between charge and discharge energy was also increasing indicating higher polarization which was presented as the different between the average charge and discharge voltage in Figure 6.8. The voltage difference increased from ~0.2 V to > 1 V when increasing charging rate from 0.5C to 5C. The cells with 2325 separator showed even larger polarization, such as 1.25 V at 5C, 0.07 V higher than that with 2500 separator, which is ascribed to the extra 25 µm diffusion length according to the previous discussion. The higher values of voltage difference for 2325 and 2500 separator, 1.25 V and 1.18 V respectively, indicate that cathode and separator also contribute to the limited energy density in fast charging while the graphite anode is considered as the limiting factor [104,153]. When a constant voltage charge step was included, the voltage difference was much lower showing lower polarization.
Figure 6.7 Energy density (electrode level) at different test protocols: (a) constant discharge cycle; (b) constant charge cycle.
Figure 6.8 (a) Average voltage profiles at different charge rates for constant charge protocol. (b) Average voltage profiles at different charge rates for constant charge protocol.
Figure 6.9 Self discharge of the cells in terms of voltage vs time, after charging the cells to 4.2 V and allowing them to rest for 168 hours.
While rate performance will benefit from higher porosity and/or lower thickness of separator, self-discharge might increase as well. Figure 6.9 shows the self discharge of the cells after they were charged at C/5 CC to 4.2 V and held at 4.2 V for a total charge time of two hours. The cells with separator 2500 started showing higher voltage drop after 30 h. However, the voltage drop with both separators was not dramatic. At the end of 1 week rest, the voltage drop was ~60 and 50 mV for 2500 and 2325 separator, respectively.

6.4 Conclusions

In this work, the influence of separator on the rate performance and energy density was investigated and were corelated to the separator properties such as electrolyte uptake, contact angle, and porosity. The Celgard 2500 demonstrated better electrolyte wettability and ~2× in electrolyte uptake, 2.23 Ω cm\(^{-2}\) less in resistance with minimal penalty in thermal stability and self-discharge. As a result, it enabled superior rate performance, such as 57% and 47% improvement when charged at 2C and 3C respectively. This study provides important insights on the fast charging aspect of lithium ion batteries from the viewpoint of separator properties. It was also noted that the effect of highly porous separators on battery safety needs further investigation.
CHAPTER 7
CERAMIC COATING TO IMPROVE THE THERMAL STABILITY OF SEPARATORS
Foreword

This chapter contains material modified from the following research paper published in the *Journal of Power Sources*:


My contributions to this paper were the following: (1) performing background research to frame the research question, (2) executing experiments, and (3) drafting and revising the manuscript. Other co-authors, Charl Jafta helped with performing experiments, conceptualizing the idea, writing the manuscript, revising the manuscript before submitting to the journal. Bishnu Thapaliya helped in data analysis related to BET measurements. Jaswinder Sharma helped with thermal conductivity experiments and analysis. Harry Meyer III helped with XPS measurements and analysis. My adviser, Jianlin Li’s contributions were the following: (1) assisting in experimental design, (2) imparting guidance on the structure of the paper.

7.1 Introduction

Lithium ion batteries (LIBs) are widely regarded as the most promising technology of energy storage due to their high energy density, long cycle life, and superior rate performance.[4] The recent growing demands in the electrification of the transportation
sector have led to significant improvements in cathode, anode, electrolyte, and separator for high energy density LIBs.[2,3,53] This requires continuing improvement on battery safety which is suspect to the poor puncture strength and thermal stability of separator membranes.[142,154,155] A separator membrane is a pivotal part of a LIB that ensures safety by preventing the physical contact of the electrodes while allowing the mobility of the ions through it.[144,146] Commercial separators are composed of porous polymer layers or non-woven mats that are chemically stable towards the electrolyte and the electrode.[144] Ideally, a separator must have zero ionic resistance and electronic conductivity, high thermal stability, electrolyte uptake, as well as excellent mechanical properties.[127] However, the separators always contribute to a certain fraction of the ionic resistance which inadvertently degrades the cell performance.[48]

While microporous separators are widely used for lithium ion batteries[142], there are failure concerns of these membranes at high temperatures due to curling and shrinkage of the separators, specifically at temperatures greater than 110 °C.[48,156–159] In addition, separator membranes have been determined as the limiting factor for heat dissipation out of all the battery components due to their poor thermal conductivity.[160,161] Another important factor for a good separator is higher electrolyte uptake (wettability).[162] Polyolefin separators have also demonstrated poor electrolyte wettability and uptake, leading to low first cycle efficiency.[163,164] It is imperative to design separators with high thermal stability, conductivity, and electrolyte wettability to improve the safety and performance of LIBs.
Several studies are reported to address the issue of thermal stability and electrolyte wettability through various coatings, composite fibers, and different inorganic materials.[163,165–172] Zhang et. al developed a cellulose based nonwoven composite separator that showed excellent flame retardation characteristics with good thermal stability and rate performance.[164,173] Passerini and co-workers developed stable high temperature separators based on SiO$_2$ and hydroxypropyl guar gum using an environmentally friendly manufacturing process having high electrolyte uptake and thermal stability.[165] Jiang et. al developed a novel ceramic-grafted separator that demonstrated high thermal stability with negligible shrinkage at 150 °C.[156] While studies by Jung et. al and Lee et. al have applied atomic layer deposition and RF magnetron sputtering of Al$_2$O$_3$ nano-layer on separators respectively to improve their thermal stability.[174,175]

Hybrid aluminosilicate zeolite (ZSM-5) coating on PE separators and polysulfonamide based core-shell structured separators have also been developed by Mao et. al and Zhou et. Al, respectively, to improve the rate capability of the LIBs.[167,171] However, long cycle stability with these separators is yet to be demonstrated and more scalable processing methods need further development. Additionally, none of these studies have reflected on the thermal conductivity of the separators for safer LIBs. Thermal transport plays a crucial role in governing the stability and shrinkage of these membranes as it facilitates better heat dissipation, reducing the possibility of thermal stresses and hotspots.
Fewer studies in the past have focused on modeling the cooling of battery temperature while taking into account the thermal conductivity aspect.[176–178] However, these studies did not consider the thermal transport phenomena in battery components, especially separator membranes. To the best of our knowledge, only Yang and co-workers have addressed the issue of thermal stability of separators from the aspect of thermal conductivity in order to improve the thermal management and safety of batteries. [160] In their study, they developed a composite Al₂O₃/polymer separator membrane instead of coating them with a ceramic layer. This enabled thinner membranes with five times higher thermal conductivity. However, its ionic conductivity was considerably lower than commercially available separators, leading to poor rate performance.

In literature, ceramic coating on separator is mainly limited to one ceramic material partially due to the engineering complexity of coating thinner double layers without influencing the ionic transport and impedance growth across the membrane. Promising results have been demonstrated with various ceramic coatings. In this work, we aimed to develop a binary ceramic system to leverage the benefits of each ceramic. Al₂O₃ and TiO₂ were selected as Al₂O₃ has higher thermal conductivity while TiO₂ shows higher surface energy, which is expected to render higher thermal stability and electrolyte wetting, respectively. The binary ceramic system (Al₂O₃ and TiO₂) with various compositions were as coated layers on thin separator membranes to evaluate improvement in thermal stability, thermal conductivity, and electrolyte wettability without compromising its electrochemical rate performance at 2C. The slurries are prepared by mixing Al₂O₃ and TiO₂ with
Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) binder. Five various combinations of slurries are coated on one side of the porous separator. Due to the high affinity of ceramics with liquid electrolyte, all the coated separators showed excellent electrolyte wettability. All the coated separators demonstrated excellent thermal stability, with 100% Al₂O₃ coated separator showing the best performance. The improved thermal stability is attributed to the high heat dissipation characteristic of Al₂O₃ coated separator. The cross-plane thermal conductivity of the coated separators is evaluated using a thermal coefficient analyzer. The coated separators show ~3 times higher cross-plane thermal conductivity than the uncoated separator.

7.2 Experimental Methods

A schematic of a scalable process for coating ceramic on separator is shown in Figure 7.1. The ceramic powders, Al₂O₃ (150 nm, Advanced Materials) and TiO₂ (50 nm, Advanced Materials) were mixed into five different weight ratio mixtures: i. 100/0, ii. 0/100, iii. 50/50, iv. 75/25 and v. 25/75 (Al₂O₃/TiO₂). PVDF-HFP (Sigma Aldrich) was the binder. The ceramic mixtures were made into slurries by adding 39 wt.% of a ceramic mixture to a PVDF-HFP in N-methyle-2-pyrrolidone (NMP) solution. The PVDF-HFP is 1 wt% in the slurry. These ceramic slurries were then tape casted onto an uncoated Entek separator (a monolayer UHMWPE), with the doctor blade having an opening of 15 μm. The coated separators were dried at 50 °C in a dry room, resulting in a coated ceramic thickness of 10 μm ± 2 μm. Monolayers are tape casted instead of double layers in order to
Figure 7.1 Steps for coating ceramic slurry on separator membrane (a) ceramic slurry preparation and (b) roll-to-roll compatible coating process. Scale bar is 12 microns
maintain an optimal separator thickness, allowing effective ionic transport. The viscosity of the ceramic slurries were measured using a rheometer (Discovery HR-3, TA Instruments). A concentric cylindrical geometry (bob diameter = 28.05 mm, bob length = 42.01 mm) was used for determining the viscosity measurements at various shear rates. Calibration was carefully done before acquiring the measurements.

The cathode slurry was prepared by mixing LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2 (NMC622, Targray), carbon black (powder grade, Denka) and polyvinylidene fluoride binder (PVDF, Solvay 5130) with NMP solvent and coated the NMC622 slurry following the procedures reported in our previous work.[75] The NMC622 cathode was composed of 90 wt% active material (NMC622 particles), 5 wt% PVDF and 5 wt% carbon black. The mass loading of the as-coated cathode was 11.5 mg cm$^{-2}$ (2.1 mAh cm$^{-2}$). The as-coated NMC622 (~50% porosity) was dried at 120°C under vacuum overnight before assembling them into coin cells with Li metal as the counter electrode. The electrolyte was 1.2 M LiPF$_6$ in ethylene carbonate (EC)/ ethyl methyl carbonate (EMC) (3/7 wt). The uncoated and ceramic coated separators, as seen in Table 7.1, were used to assemble half cells. The half cells were cycled within a voltage range of 4.3 V to 3.0 V using a potentiostat (VSP, Bio-Logic).

The rate performance of the cells was characterized with both the charge and discharge at C-rates, C/10, C/2, 1C and 2C. Electrochemical impedance spectroscopy was carried out in a coin cell with a separator membrane sandwiched between two spacers. The impedance is measured in a frequency range of 1 MHz to 10 mHz with an amplitude of 5 mV using a VSP potentiostat. To understand the electrochemical performance with various
Table 7.1 Different coating scenarios for separators

<table>
<thead>
<tr>
<th>Separator Name</th>
<th>Al$_2$O$_3$ wt%</th>
<th>TiO$_2$ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sep1</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Sep2</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Sep3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Sep4</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Sep5</td>
<td>25</td>
<td>75</td>
</tr>
</tbody>
</table>
separators and correlate them with their physical properties, the separators were characterized by measuring contact angle (electrolyte wettability), thermal stability (shrinkage), and thermal conductivity. Two liquids, deionized (DI) water and electrolyte, were used to carry out the contact angle measurements of the separators using a goniometer (Rame-Hart 260-F4). The surface and cross section morphology of the different coatings on the separator were characterized by field emission scanning electron microscope (Zeiss Merlin FE-SEM), while their elemental composition was determined using energy-dispersive x-ray spectroscopy (Burker Inc).

The thermal stability of the separators was obtained as a function of the dimension change of the separators after being exposed to heat at different temperatures and time durations. The thermal conductivity tests were carried out using a thermal coefficient analyzer (Transient Plane Source: TPS 2500S, Hot Disk) as shown in Figure A1. Thin Film module was used with Kapton Sensor#7854 with an input power of 2 W. For the measurements, the sensor was sandwiched between two pieces of the same separator, which were further sandwiched between two steel disks provided by the manufacturer. 1 Kg brass weight (provided by manufacturer) was put on the sandwiched assembly in order to make a good contact of the separators with sensor. Three drops of ethanol were added to the separator-sensor-separator assembly in order to fill the separator pores with ethanol.

7.3 Results and Discussion

The SEM images shown in Figure 7.2 are the uncoated and two coated separators with \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \), respectively. SEM images of the separator surfaces are taken in order
to observe the coverage of the Al₂O₃ and TiO₂ coatings on the separator. The image of the uncoated separator shows a woven structure much different to that of the generally commercial used Celgard separator (see Figure A2) as they are manufactured through wet and dry processes, respectively.[179] Both coatings show a complete homogenous coverage but the Al₂O₃ coating has a smoother and denser surface than the TiO₂ one as the average particle size of Al₂O₃ (150 nm) is three times of that of TiO₂ (50 nm). This indicates that the Al₂O₃ coating would result in a coverage with less surface area as compared to the TiO₂ coating.

The separators were further analyzed by XPS to investigate the surface interaction between the coating(s) and separator. The Carbon spectra in Figure 7.3 (a) show typical two dominant peaks of a carbonaceous surface, with the C-C peak at 284.8 eV, which is also used for charge correction, and a broad peak at ~ 286 eV related to ether carbons (C-OH, C-O-C).[180] The Al₂O₃ surface shows a spectrum with a broader FWHM indicating a prominent peak at a lower binding energy (BE) of 283.8 eV suggesting C-O-Al bonds. With the fitting of the C 1s spectra, a C-O-Al peak can be fitted, to give the best fit parameters, only for Sep1 (A100) and Sep4 (A75:T25) surfaces.

The Ti₂p doublet peaks of Ti₂p1/2 and Ti₂p3/2 at 458.5 eV and 464.4 eV, respectively, are ascribed to Ti-O bonds, for the Sep2 (T100), Sep5 (A25:T75), and Sep4 (A75:T25) surfaces as shown in Figure 7.3 (b). The ΔBE between the doublet peaks, for these surfaces are 5.8 eV, indicating a Ti⁴⁺ oxidation state. The Sep3 (A50:T50) surface shows a Ti 2p peak at 458.9 with a ΔBE of 5.2 eV, which may suggest Ti-O-Al bonds. This possible bond
Figure 7.2 SEM images of separators (a) uncoated, (b) coated with $\text{Al}_2\text{O}_3$, (c) coated with $\text{TiO}_2$.

Figure 7.3 XPS spectra of (a) Carbon, (b) Titanium, (c) Aluminum, and (d) Fluorine, for all the coated separators.
“Figure 7.3 continues”
is suggested to form due to the enhancement of the interfacial chemical bond and the formation of the Ti-O-Al complex oxide from the stronger titanium oxides – Al₂O₃ interfacial interactions [181]. The Al 2p spectra in Figure 7.3 (c) shows a single peak that is attributed to Sep1, except for the Sep2 and Sep3 surfaces.[182] Obviously the TiO₂ surface does not contain any Al based compounds and thus the absence of any Al 2p peak. The surface of Sep3 shows a shift of the Al 2p peak to the lower binding energy indicating to a kind of Ti-Al bond, corresponding to the Ti 2p analysis of the same surface [183].

For the F 1s spectra the more prominent peaks are seen to be not constant, with slight shifts to the higher BE for the Sep1 (A100) and Sep4 (A75:T25) surfaces and shifts to the lower BE for the Sep2 (T100), Sep3 (A50:T50) and Sep5 (A25:T75) surfaces. These different BEs for the F-C peaks can be attributed to the density of the F on the surface, with high density F (F_{HD}-C) peaks at 687.8 eV, whereas the low density F (F_{LD}-C) peaks are found at 687.3 eV. It is observed that the Al₂O₃ rich coatings (Sep1 (A100) and Sep4 (A75:T25) surfaces) have F_{HD}-C peaks whereas the low Al content surfaces have the F_{LD}-C peaks. Additionally, the Al₂O₃ rich surfaces (Sep1 (A100), Sep3 (A50:T50) and Sep4 (A75:T25)) have spectra with peaks at 684.9 eV that can be attributed to a F-Al bond.[184] The Sep2 (T100) surface shows a prominent peak at 684.2 eV that is attributed to Ti-O-F bonds, with signs of these peaks on all the TiO₂ containing surface.[180] The F spectra indicates that the ceramic coatings interact with the binder to form additional alloyed layers, depending on the Al₂O₃ or TiO₂ content (F-Al- and Ti-O-F based alloys). The chemical bonding is expected to be beneficial and will hold the ceramic to the separator.
To further investigate the effect of the coatings on the specific surface areas of the separators with the different coatings, BET measurements were employed. Figure A4 (a) shows the N₂ physisorption isotherms of the uncoated and coated separators. All the isotherms are representative of a Type-II isotherm which are indicative of a non-porous or macroporous adsorbent.[185] Additionally, at the low relative pressures (P/P₀), although minute, there is a sharp increase in the volume adsorption that indicates the presence of micropores (< 2 nm).[186] All the measured separators are thus macroporous with a small amount of additional micropores. This corroborates the SEM micrographs where macropores are observed in the uncoated separator.

The isotherm for the separators shows the initial low P/P₀ volume adsorption and therefore indicates to micropores in the uncoated separator. With the coatings applied, a change in the BET surface areas are observed. With a 100% Al₂O₃ coating (Sep1) a decrease in the BET surface area, from 22.5 m² g⁻¹ (Uncoated) to 13.3 m² g⁻¹, is observed. This indicates to the Al₂O₃ particles penetrating into the pores and decreasing the surface area, as can be observed in the isotherm where it starts to plateau at lower P/P₀ as compared to the uncoated separator. With the 100% TiO₂ coating (Sep2) a similar BET surface area of 23.2 m² g⁻¹ is calculated as compared to the uncoated separator, and higher than that for the Al₂O₃ coated separator (Sep1) due to smaller TiO₂ particle size. The specific surface area result confirms the conclusions made from the micrographs in Figure A4 (b), following a trend of Sep1<Sep4<Sep3<Sep5<Sept2<Uncoated related to the different types of coverages between Al₂O₃ and TiO₂.
With increased interest in fast charging, thermal stability of the separator becomes more important as high temperature and temperature gradients can occur during fast charging, leading to potential safety hazards.[160] At higher temperatures, polyethylene membranes first tend to expand and then contract before final fracture due to the nature of the polymers.[187] Hence, the thermal stability of the separators is an important parameter that is characterized in terms of the thermal shrinkage, which is obtained from the change in separator diameter after exposing it to high temperature for a certain time. The thermal shrinkage is defined as,

\[
\text{Thermal shrinkage (\%)} = \frac{D_i - D_f}{D_i} \times 100\% \tag{7.1}
\]

Where \(D_i\) is the initial separator diameter before exposing to high temperature, and \(D_f\) is the final separator diameter after exposing it to high temperature.

The thermal shrinkage before and after heating at 125°C for 30 minutes is shown in Figure 7.4 (a). The uncoated polymer membrane showed the highest degree of shrinkage (~6.0%) whereas all separators with ceramic coating demonstrated improved thermal stability. Sep1 demonstrated the least shrinkage (~0.6%). The shrinkage rate follows uncoated > Sep2 (T100) > Sep5 (A25:T75) > Sep3 (A50:T50) > Sep4 (A75T25) > Sep1 (A100). A ceramic coating can dramatically reduce the shrinkage rate which could be attributed to the ceramic layer acting as heat resistant layer that forms a thermostable network to withstand the dimensional change of the polymer membrane at high temperatures [156].
Figure 7.4 Physical properties of separators (a) The thermal conductivity and thermal shrinkage of the separators with different coatings after a heat treatment of 130°C in vacuum for 30 minutes; (b) Average contact angle formed from water and electrolyte droplets on the separators with different coatings. *See SI for videos on how the electrolyte wets the coated separators within a very short time.
It is clear that the higher Al₂O₃ content in the coating layers results in decreased shrinkage and thus should be more prominent in improving thermal stability. This is due to the higher thermal conductivity of Al₂O₃ (30-40 W m⁻¹K⁻¹) [188] as compared to that of TiO₂ (2.5-5.0 W m⁻¹K⁻¹) [189,190] and denser layer with Al₂O₃ coating (Figure 7.1 and 7.2). Thermal conductivity of these separators is also measured and plotted in Figure 7.4 (a). As all the separators are highly porous the thermal conductivity is dominated by the gas phase as air has a very low thermal conductivity, which makes it impossible to differentiate the effect of the ceramic coatings on the thermal conductivity. Thus, three drops of ethanol were added to the separate to remove the gas phase which also simulates the actual condition in a LIB where the separator is soaked with electrolyte. Ethanol was used, instead of electrolyte, mainly for safety reasons. While the absolute value will be different from that of electrolyte, the trend in thermal conductivity should stand. All separators with a ceramic coating demonstrate improved thermal conductivity (>2 times) compared to the uncoated. Sep1 (A100) demonstrates the highest thermal conductivity, as expected, which is ~3.2 times than that of the uncoated separator. The thermal conductivity trend is consistent with the thermal shrinkage trend with a separator coating resulting in higher thermal conductivity also resulting in lower thermal shrinkage. Al₂O₃ coating is more favorable compared to TiO₂ for improved thermal conductivity and thermal stability. Additionally, ceramic coated separators have proven to be thermally stable than the uncoated polypropylene membranes in case of thermal runaway situation.[191,192]

However, for this study thermal runaway experiments have not been performed due to lack
of available facilities. The effect of the ceramic coatings on electrolyte wettability was characterized with contact angle measurements using two solvents, deionized (DI) water and electrolyte. All separators demonstrated a hydrophobic nature towards the DI water, evidenced by the high contact angle (>100°) as shown in Figure 7.4 (b). The contact angle was even higher with the ceramic coatings. Since the separator is polyethylene with a surface energy of 30 mJ m⁻² [179] and the surface energy of Al₂O₃ and TiO₂ is above 60 mJ m⁻² [193], the ceramic coating is supposed to be more hydrophilic, thus it is assumed that the higher contact angle with ceramic coatings is most likely attributed to the surface coverage of PVDF-HFP, which has a low surface energy.[194]

For measuring the contact angle of the electrolyte with the separators, a static contact angle was only recorded for the uncoated separator, in contrast to the ceramic coated separators where the electrolyte was quickly absorbed into the separator. Just for comparison purpose, a dynamic contact angles from all the coated separators are obtained from a single frame in each video as shown in Figure A6. A smaller contact angle (~15°) is observed for all the coated separators. This is due to the improved electrolyte wettability, especially in the in-plane direction resulting from both the ceramic coatings (Al₂O₃ and TiO₂) on separator membrane. [195] Similar contact angles are expected with other common electrolyte formulation [196], and thus, shows the improved electrolyte wettability compared to the uncoated one.

The apparent contact angle can also be affected by the surface roughness where the particle size and slurry rheological properties can play a role in it. As shown in Figure 7.2,
the TiO$_2$ coating showed a higher surface roughness albeit smaller particle size than Al$_2$O$_3$. This is attributed to the much larger surface area, which is much more challenging to disperse. The viscosity of TiO$_2$ and Al$_2$O$_3$ dispersion is shown in Figure A5. Both exhibited a shear thinning behavior while the TiO$_2$ one demonstrated higher viscosity. Besides surface roughness, the coating porosity can also affect the contact angle and electrolyte absorption.[150] More detailed characterization on the microstructure of the coating is needed to fully understand their underlying relation with electrolyte absorption.

Figure 7.5 shows a bar chart with the impedance measurements of the separators and the inset figure represents the Nyquist plot for the separators. The impedance was normalized to the separator thickness for better comparison as the separator thickness was different. As shown in the Nyquist plot, the resistance per unit thickness is lower for all the coated separators than the uncoated separators. While, Celgard 2325 shows the highest resistance, probably due to lower porosity (39% vs 55% for uncoated separator).[48,195] In case of coated separators, the membranes with higher Al$_2$O$_3$ (Sep1 and Sep4) content in the coating shows slightly less resistance than coatings with higher TiO$_2$ content (Sep2 and Sep5) indicating Al$_2$O$_3$ coating is more beneficial to achieve low impedance.

This is consistent with literature that the interaction of Li with Al$_2$O$_3$ could facilitate lithium ion diffusion.[156,197] The electrochemical rate performance of the surface-modified separators is evaluated with NMC cathodes using half cells between 3.0 to 4.3 V. Figure 7.6 a-d show the voltage profiles at different currents and Figure 4.6e shows the cycling performance for the charge-discharge cycles. All the cells demonstrated excellent
Figure 7.5 Impedance normalized with respect to the separator thickness ($\Omega \mu m^{-1}$), the inset shows the Nyquist plot of the impedance ($\Omega \mu m^{-1}$) of these separators.
rate performance at low current. A negligible difference in the discharge capacities is observed for all the cells at low current (C/10) as shown in Figure 6a. At C/2 a slight drop in the discharge capacity is observed for the coated separators, probably due to higher separator thickness with the ceramic coating. Similar behavior is observed at higher rate (1C and 2C) as shown in Figure 7.6c and 7.6d, where a significant drop in the specific discharge capacity is observed for all coated separators. The impedance spectra in Figure 7.5 show low resistance for coated separators when normalized to separator thickness, even though the ceramic layer was coated on the uncoated separator. Their higher thickness (twice as much as the uncoated membrane) leads to increased resistance and more significant voltage drop across the membrane at higher current densities.

If the ceramic layer is coated on a thinner uncoated separator and the total thickness is maintained constant, the rate performance with the coated separator can be improved. The charge-discharge rate capability profiles in Figure 4.6e shows excellent capacity retention for both uncoated and coated separators at C/10 rate. The cells with higher TiO$_2$ content on the separators (Sep2, Sep3 and Sep5) show significant degradation at 2C rate. While cells with higher Al$_2$O$_3$ (Sep1 and Sep4) coating show better rate capability than the TiO$_2$ coated separators. It is also observed that Sep1 (100% Al$_2$O$_3$) shows better cycling stability than the uncoated separator with an excellent capacity retention ratio of ~92% at 2C rate.
Figure 7.6 Rate performance of the uncoated and coated separators at different rates (a) C/10, (b) C/2, (c) 1C, (d) 2C, and (e) cycling performance
“Figure 7.6 continued”
Figure 7.7 shows the time-dependent self-discharge of the cells with the uncoated and coated separators. Minimizing self-discharge is important in LIBs as it may contribute to overall capacity loss. Some of the major factors contributing to the battery self-discharge are, (a) internal electron leakage happening through the electrolyte via a separator membrane; (b) side reactions such as anode corrosion and cathode reduction at electrode-electrolyte interface; and (c) external electron leakage due to poor isolation or external resistance between the connectors.

To understand the self-discharge behavior, half cells are assembled using different separators while the cathode and electrolyte were kept the same. The cells are charged at C/2 constant current (CC) until it reached a cut-off voltage of 4.3 V, and then the cells are allowed to rest for 350 hours as the open circuit voltage is monitored. All the cells show a similar exponential voltage drop of 20 mV in the first ~12 hours of the rest period after which the self-discharge rate starts deviating to a more linear decay. After 350 hours, the cells with coated separators exhibit a lower voltage drop, with Sep1 (Al$_2$O$_3$) demonstrating a voltage decay of <50 mV while the uncoated separator showed a decay of up to 70 mV after 350 hours. Although, the trend of self-discharge and ceramic coating compositions might not be entirely clear, we observe a reduction in self-discharge with Al$_2$O$_3$ (Sep1, Sep3, and Sep4) coated separators. This could be attributed to the reduction in average pore size with the coated separators that assist in restraining the micro-shorting. While this improvement might not be significant at a cell level, in a practical EV battery pack, this
Figure 7.7 Self discharge curve of the cells after being charged to 4.3 V and monitoring open circuit voltage for 350 hours
could translate into significant decrement in the irreversible capacity loss during a self-discharge process.[198–200]

7.4 Conclusion

In this work, we report a roll-to-roll process of ceramic coating on separators that demonstrate robust mechanical strength, good cycling performance and enhanced safety for high performance lithium-ion batteries. Ceramic slurries with various combinations of Al₂O₃ and TiO₂ were prepared and coated on the separator. Electrochemical impedance spectroscopy was carried out to understand the resistive behavior of separators with coatings. It can thus be concluded that:

- All the ceramic coated separators exhibit excellent electrolyte wettability, which is crucial for the electrolyte filling process during battery assembly.
- Ceramic coated separators improved the thermal conductivity, which is crucial for effective heat dissipation and thermal management of batteries. The thermal conductivity is enhanced as the TiO₂ content decreased and the Al₂O₃ content increased in the ceramic mixture. Sep1 (Al₂O₃) showed 3.2 times higher thermal conductivity than the uncoated separator (0.6 vs 0.18 W m⁻¹K⁻¹). The coated separators also demonstrated robust thermal stability, with Sep1 showing extremely low shrinkage at 130°C.
- The electrochemical impedance spectra reveal that Sep1 has the least resistance among all the separators. This translated to superior rate performance for Sep1 with 92% capacity retention at high current (2C).
• The time-dependent self-discharge was significantly reduced with ceramic coatings that is important for irreversible capacity loss. Sep1 shows a voltage drop of only 40 mV after 350 hours vs 70 mV for the uncoated separator.

• Compared to TiO₂, coating with Al₂O₃ demonstrated better performance including higher thermal conductivity and stability, lower resistance, and less self-discharge.

These results provide insights on a scalable coating process on separators that enhances the thermal, mechanical, and electrochemical properties of a separator for practical application.
CHAPTER 8

CONCLUDING REMARKS
In this dissertation, various lithium ion battery components (anode, cathode, and separator) are investigated from materials, design, and architecture perspective to understand their impact on electrochemical rate performance and establish ways of improving the energy density under extreme fast charging conditions. One of the major drawback of graphite based chemistries in LIBs is lithium plating and dendrite formation. To better understand the lithium nucleation and dendrite morphology evolution, a unique setup was designed to carry out operando video microscopy studies. It was observed that the porosity of the graphite electrode plays a part in governing the morphology of the dendritic structures. Low porosity electrodes (25%) showed mossy dendrites, while the high porosity electrodes (50%) showed needle-like dendrites. The mossy structure is attributed to the high local current densities at the electrode surface, which lead to fracturing of SEI layer that is formed on the nucleated lithium. This would in turn create fresher surface for lithium to deposit, allowing the formation of mossy structure via root-growth mechanism. In case of high porosity electrodes, needle-like dendrites are observed mainly because of the low local current densities, that allows the SEI layer to evolve with the nucleated lithium metal and accommodate the expansion of the lithium filament. While changing the porosity had an impact on lithium dendrite morphology, varying the mass loading had no impact, suggesting dendrite formation is a surface phenomenon, and is mainly controlled by the current densities at the surface that govern the mass transport and charge transfer kinetics. In order to address the issue of lithium plating under fast charging condition, it is critical to understand the impact of each battery components on the rate
performance and energy density of LIBs under extreme fast charging conditions. The influence of separator membrane properties and their impact on the electrochemical performance is discussed in chapter 4. Two widely used Celgard separator membranes, Celgard 2325 and 2500, with varying porosity (39% and 50%) and structures (tri-layer vs single layer) are used for this study. The higher porosity membrane, Celgard 2500, demonstrates better electrolyte wetting and higher electrolyte uptake, as well as showing excellent rate performance with high specific charge and discharge capacities at fast charging conditions. The charge-discharge voltages and the voltage drop profiles revealed that there is higher polarization with Celgard 2325 membrane. Further, the discharge voltages were also lower in case of Celgard 2325, while it were higher for Celgard 2500 resulting into higher energy density with the high porosity membrane (Celgard 2500). The rate performance was backed with electrochemical impedance spectroscopy characterization, which revealed that the tortuosity of the Celgard 2500 is lower by a factor of one in comparison to Celgard 2325, providing shorter pathways for lithium ion diffusion. The caveat with the high porosity single layer separator membrane (Celgard 2500) is its poor thermal stability and higher self-discharge.

To tackle the issues with thermal stability and self-discharge through separator membrane, ceramic coatings are applied on one side of single layer membranes as discussed in chapter 5. A unique approach is used by developing binary ceramic systems to slurry-coat the separators via roll-to-roll process. The ceramic coated separators demonstrate excellent electrolyte wettability, high thermal conductivity, and low thermal
shrinkage. The 100% Al₂O₃ coated separator shows the best rate performance among all the other separators. This was attributed to the lower impedance per unit thickness with the 100% Al₂O₃ coating. It is hypothesized that the lower impedance with the Al₂O₃ coating is because Al₂O₃ facilitates in faster lithium ion diffusion. It was also observed that the Al₂O₃ coating improves the self-discharge of the cell.

After addressing the separator membrane, the influence of cathode design (porosity, tortuosity, and mass loading) on the rate performance under extreme fast charging conditions will be discussed in chapter 6. Sixteen different scenarios are tested under XFC conditions by varying the electrode porosity and mass loading. Impedance spectroscopy is used to correlate the influence of tortuosity and diffusion lengths with the rate performance of these cathodes. Symmetric cells are tested to confirm the diffusion limitation and the polarization behavior of the cathode half cells. The best scenario is identified as 11.5 mg cm⁻² with 35% porosity and 5C constant current constant voltage charge, and 11.5 mg cm⁻² or 15.0 mg cm⁻² with 25% porosity and 5C constant current and constant voltage charge for gravimetric and volumetric energy density, respectively. Increasing the electrode mass loading resulted to higher energy density at low currents (0.2C), but no significant improvement is observed in specific capacity and energy density under XFC conditions mainly due to the mass transport limitation resulting in underutilization of the cathode. Lowering the cathode porosity improved the specific discharge capacity and energy density for low mass loading (i.e., 11.5 mg cm⁻²) and the effect is negligible for high mass loading (i.e., 25 mg cm⁻²) conditions. For example, the specific discharge capacity and energy
density were increased by 13% and 9%, respectively, when reducing the cathode porosity from 50% to 35%. The superior rate performance from the symmetric cells at high currents densities clearly indicated that Li metal plating in half cells is a significant factor for poor rate performance. These results provide significant details on cathode design for extremely fast charging application and reveal information regarding the practical limitations from the cathode side.

One of the major issues during fast charging is the mass transport limitation in the electrolyte phase, which leads to lithium plating and result into capacity degradation over long term cycling. To address this from the anode perspective, a novel anode architecture and a new material are explored for high rate capability application in chapter 7. With regards to the anode architecture, freeze tape casting (FTC) via roll-to-roll process is deployed in order to reduce the electrode tortuosity by directionally aligning the solid particles. FTC assists in improving the lithium ion diffusivity by shortening the lithium pathways. Rate performance of different graphite electrodes is evaluated under various extreme fast charging testing protocols with different anode architectures - conventional coating, single layer freeze tape cast coating, and dual-layer hybrid freeze tape cast coating. The rate performance of these electrodes is tested with symmetric cells (50% SOC) under XFC conditions. It is demonstrated that, the best possible way of developing a low tortuosity electrode with high structural stability is via hybrid freeze tape casting. The hybrid FTC electrode has dual layers, a thin bottom layer via conventional coating (calendared to ~35% porosity), and a top layer developed via freeze tape casting. The
hybrid FTC shows excellent rate performance under XFC conditions, with ~20% improvement in the specific charge capacity at 5C. Hybrid FTC not only provides the benefit of high energy density, but the calendared bottom layer also enhances the power density. Meanwhile, the single layer freeze cast shows good structural integrity with thin coatings, but at the cost of low areal loading that would not be suitable for EV application. The single layer FTC also demonstrate some delamination after cycling.

With regards to exploring a new material, titanium niobium oxide (TiNb$_2$O$_7$ - TNO) is a promising material for high rate capability applications. It’s high redox potential (1.5 V) and high theoretical capacity (387 mAh g$^{-1}$) that makes it suitable for extreme fast charging application, especially due to its ability to avoid lithium plating. In this study, TNO-NMC622 2 Ah pouch cells are built and tested for XFC (10 minutes total charging time). Excellent charge-discharge capacities are observed at 6C, 6.5C and 7C with capacity retention of greater than 83% at high currents. Long-term cycling revealed dramatic capacity degradation after 300 cycles and severe gas evolution at the end of 400 cycles at charge rate of 5C, 6C, 6.5C and 7C with a constant discharge at 0.33C. To address the gassing behavior during the cycling of TNO based anodes, half-cell and full-cell configurations are investigated via operando mass spectrometry analysis. The main gases generated during the cycling process are C$_2$H$_4$, O$_2$, and CO$_2$. During the low current cycle (0.1C), formation of a reversible SEI film on TNO surface was observed during the lithium insertion process. A protective surface coating is applied on the TNO particles that significantly reduced the gas evolution. The rate of CO$_2$ and C$_2$H$_4$ evolution is lowered by
almost 2 and 5 times respectively, at 0.1C in half-cell configuration, while the mitigation of gases is more pronounced in full-cell configuration at both low and high currents.
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APPENDIX

Figure A1 TPS 2500S thermal conductivity analyzer with Kapton sensor for thermal conductivity measurements

Figure A2 SEM image of the Celgard 2325 separator membrane
Figure A3 The C1s spectra with C-O-Al peak for coated separators
Figure A4 (a) $N_2$ physisorption isotherms of the Uncoated and the differently coated separators with their corresponding BET surface areas, and (b) their pore size distribution as calculated from the desorption data.
Figure A5 Viscosity of ceramic slurries (100% Al<sub>2</sub>O<sub>3</sub> and 100% TiO<sub>2</sub>) at different shear stress
Figure A6 Video frame of contact angle measurements on coated separators using electrolyte
Figure A7 3D plot showing the (a) specific charge capacity, (b) charge gravimetric energy density and (c) charge volumetric energy density for varying porosity and mass loading conditions.
Figure A8 Voltage profile and the corresponding background-corrected mass signals m/z = 44 ($^{12}$CO$_2$), 32 (O$_2$), and 27 (C$_2$H$_4$) for (a) TiNb$_2$O$_7$-Li metal pouch cell cycled in the voltage range of 3.2-1.0 V, (b) NMC622-Li metal pouch cell cycled in the voltage range of 4.4-3.0 V, at higher currents (1C, 3C and 5C).
Figure A9 TEM images of TNO electrode (a) after complete lithium insertion during first cycle at 1V cutoff, (b) after complete lithium insertion after two cycles at 1V cutoff.

Figure A10 TEM images of coated TNO electrode (a) after compete lithium insertion during first cycle at 1V cutoff, (b) compete lithium insertion after two cycles at 1V cutoff.
Figure A11 Voltage profile and the corresponding background-corrected mass signals m/z = 44 ($^{12}$CO$_2$), 32 (O$_2$), and 27 (C$_2$H$_4$) for coated TNO-NMC full cell (a) First charge cycle and its corresponding voltage relaxation period, (b) First discharge cycle and its corresponding voltage relaxation period
VITA

Dhrupad Parikh was born on January 24th, 1990 and grew up in Mwanza, Tanzania (East-Africa). He then moved to Gujarat, India for his high school and undergraduate studies where he obtained bachelor’s degree in Mechanical Engineering from Charotar University of Science and Technology, Ahmedabad. After graduation, Dhrupad worked as a research engineer for two years at Indian Institute of Technology (IIT), Gandhinagar. His work mainly comprised of different research-based and industrial projects. He then moved to United States for further studies, where he received his thesis-based master’s degree in Mechanical Engineering (Thermal Fluid and Energy Systems) from Colorado School of Mines under the guidance of Dr. Nils Tilton. At Mines, Dhrupad was awarded a continuance fellowship by the University and a travel award from ASHRAE society to present at a conference. After finishing his master’s, Dhrupad got admitted to Bredesen Center for Interdisciplinary Research and Graduate education at the University of Tennessee to pursue his doctoral studies and joined Dr. Jianlin Li of Energy Storage and Conversion Manufacturing Group at Oakridge National Laboratory. Dhrupad’s research focuses on 1) improving the energy density and extreme fast charging capabilities of LIBs; 2) exploring novel materials for fast charging application; 3) gassing behavior in LIBs under fast charging conditions; 4) all-solid state batteries. He has been a member of Electrochemical Society since 2018 and has presented at various conferences throughout his doctoral studies.