2016

From 2D to 3D: On the Development of Flexible and Conformal Li-ion Batteries via Additive Manufacturing

Aaron Joseph Blake
Wright State University

Follow this and additional works at: https://corescholarlibrarieswrightedu/etd_all

Part of the Engineering Commons

Repository Citation
Blake, Aaron Joseph, "From 2D to 3D: On the Development of Flexible and Conformal Li-ion Batteries via Additive Manufacturing" (2016). Browse all Theses and Dissertations. 1654.
https://corescholarlibrarieswrightedu/etd_all/1654

This Dissertation is brought to you for free and open access by the Theses and Dissertations at CORE Scholar. It has been accepted for inclusion in Browse all Theses and Dissertations by an authorized administrator of CORE Scholar. For more information, please contact corescholar@wwwlibrarieswrightedu.
FROM 2D TO 3D: ON THE DEVELOPMENT OF FLEXIBLE AND CONFORMAL LI-ION BATTERIES VIA ADDITIVE MANUFACTURING

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

By

AARON JOSEPH BLAKE
M.S.E., Wright State University, 2013
B.S.M.E., Wright State University, 2012

2016
Wright State University
WRIGHT STATE UNIVERSITY
GRADUATE SCHOOL

December 01, 2016

I HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER MY SUPERVISION BY Aaron Joseph Blake ENTITLED From 2D to 3D: On the Development of Flexible and Conformal Li-Ion Batteries via Additive Manufacturing BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy.

________________________________
Hong Huang, Ph.D.
Dissertation Director

________________________________
Frank W. Ciarallo, Ph.D.
Director, Ph.D. in Engineering Program

________________________________
Robert E. W. Fyffe, Ph.D.
Vice President for Research and Dean of the Graduate School

Committee on Final Examination

________________________________
Hong Huang, Ph.D.

________________________________
Sharmila M. Mukhopadhyay, Ph.D.

________________________________
Henry D. Young, Ph.D.

________________________________
Christopher Muratore, Ph.D.

________________________________
Michael F. Durstock, Ph.D.
ABSTRACT

Blake, Aaron Joseph, Ph.D. in Engineering Program, Department of Mechanical and Materials Engineering, Wright State University, 2016. Title: From 2D to 3D: On the Development of Flexible and Conformal Li-Ion Batteries via Additive Manufacturing.

The future of electronic devices, such as smart skins, embedded electronics, and wearable applications, requires a disruptive innovation to the design of conventional batteries. This research was thus aimed at leveraging additive manufacturing as a means to invigorate the design of next-generation Li-ion batteries to meet the emerging requirements of flexible electronics. First, a state-of-the art approach for achieving flexible Li-ion batteries, using a robust, multi-walled carbon nanotube mat as current collector was demonstrated. A unique mechanical device was constructed to experimentally observe the correlation between mechanical fatigue and electrochemical stability. Points of failure in the conventional architecture were evaluated for improvement. Further, ink formulations were developed for printing both electrode and electrolyte membranes. Upon optimization of electrode porosity and electrical conductivity, application constraints, such as internal resistance, cycle life, and mechanical integrity, were studied to ensure maintenance of battery performance throughout the additive manufacturing process. Under similar evaluation, an electrolyte membrane fabricated using a phase inversion method with the addition of ceramic filler was revealed to impart a number of desirable performance characteristics (e.g., thermal stability, dendrite suppression) immediately upon extrusion and drying. Finally, a sequentially 3D-printed, full battery stack using these ink formulations was demonstrated
to achieve targeted capacity and energy density requirements of 1 mAh cm\(^{-2}\) and 1.8 mWh cm\(^{-2}\), respectively.
TABLE OF CONTENTS

1 Introduction & Background ........................................................................................................... 1

1.1 Flexible Batteries & Mechanical Characterizations ............................................................. 1

1.2 Printed Li-Ion Batteries to Enable Form Factor .................................................................... 3

1.3 Objectives of the Dissertation ............................................................................................... 6

1.4 Dissertation Outline................................................................................................................. 8

2 Analysis of Flexible, Robust Li-Ion Batteries Based on MWNT Current Collectors ............ 10

2.1 Introduction ............................................................................................................................ 10

2.2 Experimental Methods .......................................................................................................... 11

2.2.1 Materials ........................................................................................................................ 11

2.2.2 Sample Characterization ................................................................................................. 12

2.2.3 Electrode and Cell Fabrication ......................................................................................... 14

2.2.4 Atomic Layer Deposition ................................................................................................. 14

2.2.5 Electrochemical Characterization ................................................................................... 15

2.2.6 Fabrication and Test of Flexible Li-ion Batteries ............................................................... 15

2.3 Results and Discussion ......................................................................................................... 17

2.4 Conclusions .......................................................................................................................... 36

3 Carbon Nanofiber Composite Electrode Behavior and Optimization for 3D Printing ........ 38

3.1 Introduction ............................................................................................................................ 38

3.2 Experimental Methods ........................................................................................................ 40

3.2.1 Materials ......................................................................................................................... 40
6 All-Component 3D-Printed Li-Ion Batteries .................................................. 104
6.1 Introduction .................................................................................................. 104
6.2 Experimental Methods .............................................................................. 106
   6.2.1 Electrode and Electrolyte Ink Fabrication ............................................. 106
   6.2.2 Electrode Printing Procedure ................................................................. 107
   6.2.3 Electrolyte Printing Procedure ............................................................... 107
   6.2.4 Full Cell Printing Procedure ................................................................. 109
   6.2.5 Material Characterization ...................................................................... 109
6.3 Results and Discussion ............................................................................... 110
   6.3.1 Printed Electrode .................................................................................... 110
   6.3.2 Printed Electrode and Electrolyte Assembly .......................................... 112
   6.3.3 All-Printed Li-Ion Battery ...................................................................... 116
6.4 Conclusions ................................................................................................. 122
7 Summary and Future Work .......................................................................... 124
   7.1 Summary ................................................................................................... 124
   7.2 Future Work .............................................................................................. 126
8 Appendix ......................................................................................................... 129
9 Bibliography .................................................................................................... 132
10 Curriculum Vitae .......................................................................................... 138
LIST OF FIGURES

Figure 1.1. Schematic depiction of key research phases associated with the goals of this dissertation ................................................................. 5
Figure 2.1. Characterization of the MWNT mat ................................................. 19
Figure 2.2. Mechanical characterization on CCs with electrode coatings .............. 20
Figure 2.3. HAADF-STEM tomography on scotch tape exfoliated MWNT mat ........ 21
Figure 2.4. Comparison between metal foil and MWNT CCs and effect of CC on LiFePO_4 adhesion ........................................................................ 22
Figure 2.5. Half- and full-cell electrochemical characterization of electrodes using metal foil and MWNT CCs ........................................................................ 24
Figure 2.6. Microstructure of TiO_2 coated MWNT mat prepared by ALD ................ 27
Figure 2.7. Electrochemical performance evaluation of TiO_2 coated MWNT mat prepared by ALD ................................................................................ 28
Figure 2.8. Full-cell electrochemical characterization and mass distributions ....... 30
Figure 2.9. In situ bending of MWNT mat and metal foil full-cells ....................... 33
Figure 2.10. In situ folding of MWNT and metal foil LiFePO_4/Li_4Ti_5O_12 full-cells .... 35
Figure 2.11. Effect of folding on CC and active material coating ......................... 36
Figure 3.1. Configuration of the three-electrode split cell used for electrochemical impedance measurements ................................................................. 44
Figure 3.2. Standard equivalent circuit model (Randles circuit). ......................... 45
Figure 3.3. Photographs and scheme of the composite electrode fabrication process and rheological characterization of composite inks ........................................................................ 47
Figure 3.4. Effect of PVDF loading on shear-thickening behavior of CNF/PVDF solutions in NMP ........................................................................ 49
Figure 3.5. Effect of Li_4Ti_5O_12/CNF/PVDF ratios on composite electrode properties .... 52
Figure 3.6. Impedance spectra with model fitting (simulation) of various Li_4Ti_5O_12/CNF/PVDF composite electrodes ......................................................... 55
Figure 3.7. Lithium titanate core-shell model........................................... 55
Figure 3.8. Schematic model for lithium insertion/extraction into/from Li₄Ti₅O₁₂ electrode. [84] ................................................................. 57
Figure 3.9. Determination of effective Li⁺ diffusivity by the EIS method using Warburg impedance .............................................................. 59
Figure 3.10. Comparison of mechanical properties of selected Li₄Ti₅O₁₂/CNF/PVDF composite loadings ......................................................... 63
Figure 3.11. Characterization of sample B before and after electrochemical cycling..... 64
Figure 3.12. Ternary diagram summarizing the compositions and properties of the composite electrodes studied in this work ........................................ 65
Figure 3.13. Rheological and electrochemical properties of composites prepared using different active materials ........................................... 67
Figure 3.14. Electrochemical properties of pure CNF/PVDF composite ................ 68
Figure 4.1. Overview of the printable electrolytes prepared in this study ............... 78
Figure 4.2. SEM images and schematic representation of polymer electrolytes .......... 80
Figure 4.3. N₂ adsorption and desorption isotherms of pure Al₂O₃, a CPE-PI, a CPE, and a PE-PI .......................................................... 80
Figure 4.4. Mechanical properties of electrolyte samples ................................ 82
Figure 4.5. Electrochemical and physical properties of various electrolytes prepared in this study .......................................................... 85
Figure 4.6. Lithium metal plating/stripping from a Li|Li cell cycled at 0.15 mA cm⁻² with 1M LiPF₆-EC/DEC electrolyte in various membranes ................................. 87
Figure 4.7. Thermal properties of various electrolytes prepared in this study ........... 90
Figure 5.1. Fabrication method for the high temperature CPE-PI electrolyte ............ 96
Figure 5.2. Evaluation of thermal properties and wetting capability of the IL solution with both Celgard 2325 and CPE-PI ........................................... 100
Figure 5.3. Evaluation of the voltage hysteresis as a function of temperature for LiFePO₄//Li cells using Celgard 2325 versus CPE-PI ................................. 102
Figure 6.1. Printing of 40/40/20 active/CNF/PVDF composite electrodes .............. 110
Figure 6.2. Comparison of electrochemical properties of casted and printed composites and a conventional Li$_4$Ti$_5$O$_{12}$ electrode on copper foil .................................................. 111
Figure 6.3. First generation separator electrode assembly (SEA). (a) Photograph of a fully printed SEA ............................................................................................................. 112
Figure 6.4. Second generation printed electrode membrane architecture (PEMA) .... 114
Figure 6.5. Properties of composite electrodes prepared using phase inversion with NMP/glycerol ................................................................................................................. 116
Figure 6.6. Improvements in the performance characteristics of our printable electrode composites upon the implementation of phase inversion .......................................................... 117
Figure 6.7. All-component 3D-printed battery performance with and without phase inversion .......................................................................................................................... 119
Figure 6.8. Cross-sectional SEM of a sequentially layered Li-ion battery fabricated with the phase inversion process .................................................................................................. 120
Figure 6.9. Long-term performance of 3D printable battery components ............... 121
Figure 7.1. Overview of battery architectures and printable batteries ..................... 127
Figure 8.1. Effect of CC on electrolyte infiltration ................................................... 129
Figure 8.2. Photographs of the process of fabricating Surlyn-encapsulated flexible full-cells ................................................................................................................................. 130
Figure 8.3. Scotch tape exfoliation of a MWNT mat for TEM microscopy .............. 131
LIST OF TABLES

Table 2.1. Analysis of voltage fluctuation during in situ bending. .............................................. 33
Table 3.1. Properties of composite battery electrodes. ................................................................. 49
Table 3.2. The equivalent circuit parameters obtained from the fit of the experimental impedance spectra ................................................................................................................................. 56
Table 3.3. Parameters describing ionic transport within the composite electrodes: Warburg coefficient (A_w), effective Li^+ diffusivity (D_{Li^+}), Li^+ mobility (\mu), and Li^+ conductivity (\sigma). .................................................................................................................................................................................. 60
Table 4.1. Properties of composite battery electrolytes and Celgard 2325. ................................. 83
Table 5.1. Fitting parameters obtained by applying the VTF model to the temperature dependent conductivity data. .......................................................................................................................... 99
Table 6.1. Comparison of several key characteristics of our printed, unpackaged 3D printed Li-ion battery to reported literature ................................................................. 122
ACKNOWLEDGEMENTS

As with any large endeavor, my dissertation work would not have been possible without the support and guidance of many people.

First, I would like to sincerely thank my advisor, Professor Hong Huang, for her urging me to pursue higher education and giving me the freedom to pursue research topics I truly enjoyed. She has been instrumental in my development as a research scientist.

I would also like to thank Dr. Michael Durstock for giving me the tremendous opportunity to carry out my research efforts at the Air Force Research Laboratory. The amount of knowledge I have gained working with the flex research team during my doctoral pursuit has been truly humbling. Furthermore, I would like to thank Dr. Ryan Kohlmeyer, someone I am honored to call both a colleague and a friend. His insights as a research chemist proved beneficial to my battery research, and together we accomplished a great deal in our efforts.

I thank all of my committee members for their time and insightful inputs on my dissertation.

Finally, this Ph.D. would not have been possible without the support and the backing of my family. My wife, Meghan, especially, helped me maintain my sanity as I completed all the necessary coursework and research associated with this endeavor. I cannot thank her enough for standing by me through it all.
1 Introduction & Background

1.1 Flexible Batteries & Mechanical Characterizations

Flexible batteries have attracted significant attention in recent years owing to great progress in soft portable electronics, such as wearable sensors and devices, rollup displays, and radio-frequency identification tags. This has driven the development of energy sources capable of being embedded into flexible devices without restricting their degree of movement (e.g., during bending or folding). The realization of flexible Li-ion batteries is of particular interest because they possess higher energy density, higher operating voltage, and longer lifetime compared to alternatives such as alkaline batteries.

There have been two general approaches to creating flexible Li-ion batteries – the first is simply to make the battery thin enough for it be flexible, while the second involves growing, functionalizing or embedding active material within a flexible, conductive scaffold.\(^1\) The former approach has limited potential because by reducing the thickness of ordinary batteries one also reduces their capacity and power capability. The latter approach embodies a notion adopted by the community that the polymeric binder holding the ceramic electrode particles together does not possess the mechanical integrity to keep the electrode coating from crumbling, or bound to a dedicated current collector layer, following repeated deformation. On the contrary, the achievement of flexible batteries using alternative substrates to metal foils has been well documented in recent literature, without the need to embed the active material.\(^{1-3}\) From this dissertation research, a flexible, porous, nanocarbon-based substrate is demonstrated, which can act as a SUPERIOR replacement to metal foil current collectors while imparting unique mechanical characteristics.
To date, there have been no universal metrics to characterize and directly compare battery performances under mechanical interferences, and those that have been utilized lack in physical significance. For instance, one common demonstration is to show the flexible battery powering a light-emitting diode (LED), typically coupled with an open circuit voltage ($V_{OC}$) measurement over time, to illustrate electrochemical stability.\textsuperscript{[4-11]}

While these results may indeed be practical, inconsistencies stem from the lack of systematic and quantitative metrics for testing. The second type of test commonly applied to flexible batteries is the traditional 3-point bend test.\textsuperscript{[12,13]} However, the thin nature of many flexible LIBs (hundreds of microns) renders it less reliable, often threatening puncture of the device rather than bending. A modification of this test is to fix the battery at two ends and to adjust the end-to-end distance such that the battery bends to a particular radius.\textsuperscript{[5,7,14,15]} This works reasonably well with thicker devices, but when testing thinner devices this method becomes less accurate in defining the bend radius. Moreover, when the end-to-end distance approaches zero for a thinner device, the bend can also become localized to one area causing a non-uniform strain field. The third test focuses on folding the battery over itself, or bending over a set mandrel radius, and monitoring electrochemical characteristics in one held position.\textsuperscript{[6,10,16,17]} The concern with this test is the similarity it bears with winding metal foil electrodes around a mandrel (either cylindrical or prismatic), as with commercial 18650 cells, for example, which perform without degradation at their set winding radius. For this reason, fatigue testing during battery cycling provides a better correlation between electrochemical performance and mechanical durability.\textsuperscript{[6,18,19]}
To this end, our work in Chapter 2 reports the development of an automated flex test, which aims to better understand the correlation between mechanical and electrochemical properties of flexible batteries. Its design allows for the controlled, dynamic application of bending strains to a flexible system, which results in a more robust gauge of the system’s electrochemical performance. Although we use this test to correlate the mechanical and electrochemical performance of flexible LIBs, it could easily be extended to other flexible electronic systems.

1.2 Printed Li-Ion Batteries to Enable Form Factor

There are also challenges associated with the manufacture of energy storage devices that require unconventional or more arbitrary form factor. For example, applications in smart skins or wearable electronics necessitate an energy storage source that is able to conform to a particular shape. Because conventional batteries are limited to two primary form factors (i.e. cylindrical or prismatic), unconventional or more arbitrary shapes of emerging electronic devices cannot be met by current manufacturing processes. To work around this issue, battery manufacturers such as Apple and Nokia have adopted unique spatial arrangements of their rigid battery packs allowing them to deform their devices with minimal performance loss. However, these devices have a restricted bending range, and traditional battery designs utilizing metal foil current collectors remain susceptible to crack formation and damage to the batteries regardless of spatial arrangement.

While the spatial arrangement of battery packs offers a temporary solution, a more robust technology is still required for next generation flexible electronics. The capability to 3D-print energy storage devices poses a unique advancement to the direct manufacture
and integration of flexible electronics. Filamentary printing is a strong candidate for this process owing to its high feature resolution, enabling precise structuring of an ink onto arbitrary surfaces. Unlike most printing techniques commonly adopted for batteries, such as stencil printing,\cite{23, 24} screen printing,\cite{25, 26} ink jet printing,\cite{27-29} and spray printing,\cite{30} filamentary printing does not require masking or material removal, nor does it require the processes necessary to aerosolize or significantly reduce particle size of solids in the ink. Thus, novel 2D or 3D battery structures fabricated by filamentary printing present a means through which we could invigorate the design of next-generation electronics.

Another advantage for additive manufacturing of Li-ion batteries is that it would enable integration of the energy storage unit directly into the electronics fabrication process. This would both eliminate the need for separate battery holders that are attached post-fab and significantly reduce the weight of the electronic device. Moreover, one could print a battery directly onto a flexible substrate as opposed to a rigid one, thereby enabling designed flexibility. To facilitate such innovation, though, an ink development for the anode, cathode and electrolyte membrane materials of a Li-ion battery is required.

Regardless of the printing technique used, however, several drawbacks are commonly observed among ink formulations ranging from high processing temperatures, the incorporation of ink additives (\textit{e.g.} surfactants, viscosifiers, coagulants, or plasticizers) that potentially degrade battery performance if not removed, and timely processes required to reduce particle size enough to prevent the print head from clogging. We improve considerably upon these drawbacks with the work in this dissertation. Therein, we establish a universal method to develop 3D printable, free-standing, and current collector-embedded electrodes that are directly amenable to filamentary printing. This
simple approach utilizes brief sonication to create a well-dispersed and directly castable mixture of active material, carbon nanofibers (CNFs), and polymer binder. While the majority of ink formulations reported in literature are unique to one particular active material, we maintain excellent cyclability and rate performances throughout the manufacturing process from several Li-ion battery active materials including CNFs, lithium titanate (Li$_4$Ti$_5$O$_{12}$), lithium iron phosphate (LiFePO$_4$), and lithium cobalt oxide (LiCoO$_2$).

The above challenges are addressed in more detail throughout the remainder of this dissertation. An illustration is shown in Figure 1.1 to convey our approaches to electrochemical/mechanical characterization, ink development, and filamentary printing of our Li-ion batteries. Together, these technologies will enable the fabrication of highly customized freeform batteries given the robust design space opened up by additive manufacturing.

**Figure 1.1.** Schematic depiction of key research phases associated with the goals of this dissertation. First is the evaluation of conventionally prepared, flexible Li-ion batteries (left), second is the ink development for printable electrode composites (middle), and finally is the development of a high-performance, printable electrolyte material (right).
1.3 Objectives of the Dissertation

The objective of this dissertation research was to investigate the material integration challenges facing the fabrication of Li-ion batteries via additive manufacturing. Overcoming these challenges is key to realizing the next generation of flexible and conformal energy storage for superior device functionality and form factor. Moreover, the development of unique material combinations to fabricate 3D printable battery components will open up a new design space in which one can manufacture robust energy storage sources comprising various geometric layouts. To this end, the dissertation research was focused into five main phases, the first of which entailed background investigations into the conventional manufacturing of Li-ion batteries for flexible applications. The next three phases involved detailed investigations of 3D printable ink components for both the electrode components and battery membrane to realize a fully printed battery. An additional investigation was conducted regarding the unique thermal characteristics of the 3D printable electrolyte membrane. To summarize, the phases of this dissertation research can be described as follows:

**Background Investigation:**

1. Study the conventional manufacturing technique (i.e., doctor blade coating) to fabricate Li-ion batteries and address design limitations via an in situ mechanical/electrochemical testing protocol.
   
   a. By implementing a robust, porous multi-walled carbon nanotube mat as current collector in replacement of metal foils, we gain insight into what characteristics lead to mechanical robustness in flexible batteries.

**Detailed Investigations:**
2. Develop “substrate-free” electrode inks with a multifunctional, 3D network of carbon nanofibers to impart desirable electrochemical and mechanical properties while bolstering the necessary rheology to be filamentary printed.
   
a. In this phase, given the free-standing nature of the films, it is essential to optimize the electrode porosity and electrical conductivity in addition to meeting various application constraints, such as low internal resistance, long cycle life, and mechanical integrity.

b. In varying the ratios of the ink components for printing, it is also imperative to investigate the losses affecting cell performance and to understand influencing parameters on electrode reaction kinetics. Acquiring this knowledge is the foundation for maintaining performance through the manufacturing process.

3. Develop a ceramic polymer electrolyte material using a dry phase inversion process to control pore size formation through 3D printing, and to demonstrate its compatibility for directly printing over an electrode structure without sacrificing electrochemical performance.
   
a. Controlling the battery membrane’s microstructure without additional post-processing steps is a key breakthrough to realizing fully 3D printed batteries. This study reveals a method to produce microporous battery membranes via additive manufacturing, which to date has been a significant challenge.

4. Thermal property analysis of the ceramic polymer electrolyte membrane imbibed with an ionic liquid.
a. Moving beyond the use of organic liquid electrolytes is critical to making flexible batteries a reality because of numerous associated hazards. Ionic liquids are an attractive alternative, and once they were combined with our ceramic polymer electrolyte they were shown to exhibit exceptional thermal characteristics.

b. The goal of this investigation was thus to gain a fundamental understanding of the thermal transport properties enabling high temperature application.

5. Demonstrate a sequentially layered Li-ion battery for conformal applications via direct write printing.

   a. The goal of this investigation was to determine the feasibility of sequentially printing full battery stacks and to maintain expected performance throughout cycling.

1.4 Dissertation Outline

This dissertation is structured as seven chapters covering research efforts to-date and concluding with a summary and future work chapter. Chapter 1 reviews current trends in flexible and thin film Li-ion batteries. An emphasis is placed on 3D printing of Li-ion batteries to yield conformal, flexible energy storage devices. The issues considered in this chapter are studied in more detail in the following chapters.

Chapter 2 covers the characterization of traditional Li-ion battery architectures using state-of-the-art methods to achieve flexibility. The advantage of using a highly robust, flexible, and porous current collector is explored. New insight is obtained regarding the
failure mechanisms of this design, and a novel mechanical characterization technique is employed to reach these conclusions.

Chapter 3 describes the ink development and optimization of material composition to achieve printable Li-ion electrodes. We investigate the desired characteristics of a printable electrode ink, and employ the use of three-electrode impedance spectroscopy to study the ionic and electronic transport properties of our \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) composite electrodes.

Chapter 4 investigates the implementation of a dry phase inversion technique to achieve the desired microstructure required of a Li-ion battery membrane through the additive manufacturing process.

Chapter 5 studies the high temperature characteristics of the ceramic polymer electrolyte material developed in Chapter 4.

Chapter 6 validates the ability to sequentially print all three necessary layers of a Li-ion battery and to achieve expected device performance.

Chapter 7 gives a succinct overview of the results of this dissertation, and includes discussion of future work enlightened by this research.
2 Analysis of Flexible, Robust Li-Ion Batteries Based on MWNT Current Collectors

2.1 Introduction

Traditional batteries, based on metal foil current collectors (CCs), fail to meet the requirements of flexible energy storage due to their rigidity and mechanical incompatibility with the electrode material. Furthermore, metal foil CCs contribute to a significant proportion of the battery’s total weight (anywhere from 15% to 80%),[31,32] and are prone to corrosion in liquid electrolyte over time,[33] which reduces overall energy density and degrades performance, respectively. These issues have led the battery research community to seek alternate CCs, such as carbon nanotubes (CNTs),[34] graphene,[4,35] textiles,[18,36] and paper,[37-42] which have led to significant advances in flexible batteries.[2] CNTs in particular, owing to their light weight, high mechanical strength, chemical stability and good electrical conductivity, have recently drawn significant interest for use in Li-ion batteries.[11,30,32,43-47] While promising progress is being made, the development of flexible, bendable, and creasable devices that can maintain their performance while being continuously exposed to these extremely harsh and dynamic mechanical conditions is still a significant challenge. In general, there is a conspicuous lack of knowledge in the community regarding how to design and fabricate mechanically flexible and highly robust batteries that can survive hundreds or even thousands of flex, bend, or crease cycles. Furthermore, previous flexible battery test methods (including LED luminescence,[4-11] 3-point bend,[12] and static folding/bending)[6,10] have lacked in establishing a quantitative comparison between cell mechanics and electrochemical characteristics.
Here, we report the development of an automated mandrel bending test designed to systematically examine the relationship between mechanical and electrochemical properties of flexible batteries. Contrary to the majority of characterization techniques used for flexible batteries, this method enables repetitive application of a known radius of curvature, and therefore a known strain, across the entire flexible device. While limited reports on mandrel bend tests are available, they lack in physical significance by either implementing a static measurement,\textsuperscript{[16,48]} or isolating the bending strain to a small area,\textsuperscript{[6]} leaving the remainder of the device unstrained. Our approach to dynamic fatigue testing addresses these issues and can also be utilized for many other devices in the growing field of flexible electronics. In the same vein, we have implemented a dynamic crease test during electrochemical cycling that subjects the flexible cell to a recurring condition of extreme mechanical strain. Together, these two \textit{in situ} mechanical tests are utilized to gain a fundamental understanding of the failure modes (\textit{e.g.} interfacial delamination, interlayer separation, and fracturing of the CC) afflicting traditional Li-ion battery architectures. We find that when a correct choice of CC is selected, traditional processing approaches can be utilized to fabricate batteries that, when exposed to continuous and severe mechanical deformation for hundreds of cycles, maintain their characteristics with negligible loss of electrochemical performance.

2.2 Experimental Methods

2.2.1 Materials

A nonwoven multiwalled carbon nanotube (MWNT) mat (Nanocomp Technologies, Inc., Merrimack, NH) was used as received. Traditional Cu (EQ-bccf-25u) or Al (EQ-bcaf-15u-280) foil current collectors (CCs) were purchased from the MTI Corporation.
Spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$) nanopowder, polyvinylidene fluoride (PVDF), and 1-methyl-2-pyrrolidone (NMP) were purchased from Sigma Aldrich. Lithium iron phosphate (LiFePO$_4$) was purchased through BASF (HED LFP-400) and graphite was purchased from Asbury Graphite Mills (HPM 850 powder). 1 M LiPF$_6$ in 1:2 ethylene carbonate:diethyl carbonate was used as received from Novolyte Technologies Inc.

### 2.2.2 Sample Characterization

Scanning electron microscopy (SEM) was performed using an FEI Sirion XL-30 FEG-SEM. Samples for cross-sectional SEM were prepared through cryo-fracturing by dipping in liquid N$_2$ followed by immediate cutting with a razor blade which cut from coating side through the CC. Transmission electron microscopy (TEM) was done on a Cs-corrected (image corrector) FEI Titan operating at 300 kV, and a 200 kV Philips CM200. High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) was used to collect a tomographic tilt series. Due to sample geometry constraints, tilt ranges varied from ±70 degrees down to ±50 degrees. After alignment using cross-correlation, Model Based Iterative Reconstruction (MBIR) was used to reconstruct the raw tilt series into a three dimensional volume. MBIR shows significantly reduced missing wedge artifacts, even down to limited tilt ranges of ±30 degrees, and so the reconstructions for the ±50 degree tilt series showed minimal artifacts. The volume was segmented and visualized in Avizo Fire 7. The low degree of noise in MBIR reconstructions allow for a simple threshold-based segmentation of the MWNT web and the iron oxide particles.

For the electrolyte wetting experiment (Figure 8.1, Appendix), samples were taped to a glass slide and 2.0 µL of liquid electrolyte was applied to the center of each sample.
with a micropipetter. Photos were taken on the top side and bottom side (photo taken through glass substrate) after letting electrolyte sit on the samples for 5 min.

Tensile test specimens were prepared according to ASTM standard E345-93 (2013) using a double-bladed cutter to form 50 x 5 mm rectangular strips. The finished specimens were examined using a Zeiss Stemi DV4 optical microscope to ensure that there were no visible flaws from cutting. Sample thicknesses were measured using a Mitutoyo digital micrometer. After cutting, the samples were mounted on paper supports to ensure alignment of the specimen and a 25.4 mm gauge length (see Figure 2.1b inset). Mechanical testing was performed using a Tinius Olsen H10K-S UTM benchtop tester with a HTE-100 N load cell at an extension rate of 0.5 mm min⁻¹.

The surface area and porosity data of the MWNT mat were calculated by Brunauer–Emmett–Teller (BET) method based on N₂ adsorption–desorption isotherms at 77 K obtained using an ASAP 2020 surface area and porosimetry analyzer (Micromeritics Instrument Corporation). The sample was degassed at 200 °C under vacuum for 12 h before running the measurement. Electrical conductivity was performed with a Lucas Labs SP4 four-point probe head controlled with a Keithley 2410 SourceMeter and a computer operated LabVIEW program. Electrical conductivity was calculated as the inverse of resistivity, which was determined by the LabVIEW program according to the following equation:

\[
\rho = \frac{\pi}{\ln(2)} t \left( \frac{V}{I} \right) = 4.532 t \left( \frac{V}{I} \right),
\]

given that the probes were centered on a very wide (lateral dimension >> spacing between probes) and very thin sample (thickness << spacing between probes).
2.2.3 Electrode and Cell Fabrication

Electrode material slurries were prepared by mixing the LiFePO$_4$ cathode or the Li$_4$Ti$_5$O$_{12}$ anode together with graphite powder and a PVDF binder solution in NMP. The mass ratio of active material:graphite:binder was 70:20:10. Both LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$ slurries were applied to MWNT mat or metal foil CCs by doctor blade (Gardco Inc.) method using a 6 mil path depth, and subsequently dried at 120 °C under vacuum for at least 12 h. Electrode samples were punched to 9.5 mm diameter discs. On average, the weights of Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$ in each electrode disc ranged from 2.0-2.5 mg on both metal foil and MWNT mat CCs corresponding to coating thicknesses between 50-60 μm.

Electrode samples were assembled in 2325 coin cell configuration under argon environment (<1 ppm H$_2$O and O$_2$). For the half-cell experiments, electrode samples on either metal foil or MWNT CCs were assembled with lithium foil as the counter and reference electrode and a porous polymer membrane (Celgard 2325) soaked in a liquid electrolyte solution of 1 M LiPF$_6$ in 1:2 ethylene carbonate:diethyl carbonate.

2.2.4 Atomic Layer Deposition

For atomic layer deposition (ALD), the surface of the MWNT mat was first stabilized by heating from 80 to 250 °C under nitrogen (99.999%) atmosphere. During ALD, The precursors tetrakis(dimethyl-amido) titanium (TDMAT, Ti(NMe$_2$)$_4$) and water were pulsed in an alternating fashion at 250 °C for 133 cycles. The reactions that occurred are described in the following equations:

\[
Ti(N(CH_3)_2)_4 + TiO_2 - OH^* \rightarrow NH(CH_3)_2 + TiO_2 - O - Ti(N(CH_3)_2)_3^* \tag{2}
\]
\[
TiO_2 - O - Ti(N(CH_3)_2)_3^* + 2H_2O \rightarrow TiO_2 - TiO_2 - OH^* + 3(NH(CH_3)_2) \tag{3}
\]
Thereafter, the ALD-TiO$_2$/MWNT was annealed at 450 °C for 3 h under argon atmosphere. The annealing process allowed desorption of water from the MWNT sample and phase transformation of any amorphous TiO$_2$ into the anatase phase.

2.2.5 Electrochemical Characterization

The coin cells were cycled using a Maccor series 4000 battery test system. LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$ were investigated for cycling stability through 100 cycles at constant a 0.2C current rate between 2.0-4.3 V vs. Li/Li$^+$ and 1.0-2.1 V vs. Li/Li$^+$, respectively. The rate studies were carried out in a similar manner, with each half-cell tested for 5 cycles at the following C-rates: 0.2C, 0.5C, 1C, 2C, 5C, and 0.2C. All C-rates were calculated with 1C being defined as 170 mA g$^{-1}$ and 175 mA g$^{-1}$ for LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$, respectively. Full-cell experiments conducted in 2325 coin cell configuration were assembled in a similar fashion to that described above, with LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$ used as cathode and anode, respectively. These cells were cycled at a constant 0.2C current rate (calculated using the active mass of the limiting electrode, Li$_4$Ti$_5$O$_{12}$) between 1.2-2.4 V, with 1C being defined as 175 mA g$^{-1}$.

2.2.6 Fabrication and Test of Flexible Li-ion Batteries

Flexible Li-ion batteries were prepared by cutting all of the battery components and encapsulating them together between two layers of 75 µm thick Surlyn (GLTE/M, Europack, Inc.). The electrodes were cut to 3 x 3 cm$^2$ with electrical lead dimensions of approximately 1 x 2 cm$^2$. The actual anode capacity/cathode capacity ratio was adjusted between 0.80-0.90 for the Li$_4$Ti$_5$O$_{12}$/LiFePO$_4$ full-cells. The Celgard 2325 separator was cut to 4 x 5 cm$^2$. Cu wires were placed in contact with the electrical leads of the electrodes with the remainder of the wire left outside of the encapsulation layers. Initially, a portion of the Cu wire leads were laminated between two sheets of 75 µm
Surlyn using a GBC 9” Personal Desktop Laminator to prevent electrolyte leakage. The perimeter of the flex-cell was sealed using a Ziploc® V151 vacuum sealer system. Sealing was performed between two non-porous Teflon sheets to prevent sticking to the heating element. Using a needle, 0.8 mL of liquid electrolyte was added to the battery in an argon glovebox, and then the excess region of the cell was sealed off using the same method as described above (Figure 8.2, Appendix). To create better contact between all of the layers, the entire battery was carefully kneaded to ensure electrolyte uptake and to remove any bubbles.

A custom-built flex tester was used for in situ analyses, in which the electrochemical performances of the flexible Li-ion batteries were assessed under repeated mechanical deformation. The instrument was composed of a linear motor and Zeta 6104 single axis drive (Parker Compumotor), which actuated the motion of two stages in either the compressive or tensile direction. Motion Planner v4.3.2 software was used to control motion of the stages. The flex tester was automated to perform 600 roll/unroll cycles, with the mandrel traveling at a linear velocity of 10 mm sec\(^{-1}\) (200 cycles at each mandrel radius). The battery under study was connected to the Maccor series 4000 battery test system and data acquisition was set to occur every 1 sec. in order to capture the real-time effect of mechanical disruption. The battery was adhered to each mandrel using double sided tape. Two 1.0 x 7.6 cm\(^2\) (400 μm thick) polydimethylsiloxane (Sylgard 184, Dow Corning) strips were placed on the stage, at each side of the flexible battery to increase the friction between the rolling mandrel and the moving stage. The flex test was performed in ambient conditions while the cell was discharged at a 0.2C current rate.
(calculated using the active mass of Li$_4$Ti$_5$O$_{12}$). Every 20 min. \( \text{i.e.,} \) 200 cycles, the mandrel was replaced with one of a smaller radius of curvature.

Bending conditions were chosen such that the strain, \( \varepsilon \), experienced by the battery ranged from 2.1% \( (r = 7.88 \text{ mm}) \) to 2.6% \( (r = 6.35 \text{ mm}) \) to 4.2% \( (r = 4.00 \text{ mm}) \) according to

\[
\varepsilon_T = -\varepsilon_C = \frac{y}{r}
\]

where \( y \) is the distance from the surface of the flex-cell to its neutral plane, and \( r \) is the mandrel radius. Given that the total thickness of the flex-cell was only \( \text{ca.} \ 335 \ \mu\text{m} \), shifting of the neutral axis could be neglected, and its location was taken to be the middle layer of the flex-cell \( \text{i.e.,} \) the separator. Therefore the tensile, \( T \), and compressive, \( C \), strains are equal in magnitude, but opposite in direction. A pure-bending set-up and linear strain field were assumed for the above calculations.

During the fold test in Figure 2.10, each battery was discharged at a 0.2C current rate and subjected to ±180° folds every 20 sec. for the duration of the test. For all of the \textit{in situ} mechanical tests using MWNT mat full-cells, it is worth mentioning that air and moisture permeability of the Surlyn encapsulant limited the duration of the test, not mechanical insult as in the case of devices fabricated with metal foil CCs.

### 2.3 Results and Discussion

Our flexible full-cell is based on the use of a nonwoven mat of multiwalled carbon nanotubes (MWNTs) that is both mechanically robust as well as highly flexible. The highly porous structure of the MWNT mat plays a critical role in establishing superior interfacial adhesion between the active material and the CC, which leads to highly robust
mechanical properties and electrochemical performance upon mechanical insult. The MWNT mat was produced by a scalable, continuous chemical vapor deposition (CVD) method yielding thin (20 µm), flexible sheets that can be produced in large areas and easily cut down to a desired size (Figure 2.1a). Scanning electron microscopy (SEM) of the MWNT mat (Figure 2.1c) shows long, interconnected MWNTs, which can reach millimeters in length according to the manufacturer’s specifications. This long nanotube network leads to mechanically robust films with high conductivity (935.5 ± 28.5 S cm⁻¹). Uniaxial tensile testing was utilized to quantify the mechanical behavior of the three CCs studied, as shown in Figure 2.1b. The MWNT mat exhibited a maximum strain at failure of 28%, which far exceeded that of Al (2%) and Cu (9%) foils. Furthermore, the ultimate tensile strength of the nanotube mat was 118 MPa compared to 153 and 133 MPa for Al and Cu, respectively. These results suggest that the MWNT mat should have sufficient tensile strength to act as a mechanical support for battery electrodes, and that the increase in maximum strain should result in improved performance under flex, bend, or crease testing. Figure 2.2 illustrates that the tensile strength of electrodes prepared by traditional doctor blade coating is indeed governed by the mechanical properties of the CCs, and the addition of the active material coating does not significantly change the force-displacement behavior. The solid traces indicate the stress calculated using the specimen width and total thickness (coating plus CC), while the dashed traces indicate the stress calculated using the specimen width and CC thickness only. The latter allows comparison to the uncoated CCs in Figure 2.1b. The stress relief observed in the plastic region of the stress-strain curves for both LiFePO₄/MWNT and Li₄Ti₅O₁₂/MWNT resulted from localized fracturing of the active material as the MWNT mat elongated.
Figure 2.1. Characterization of the MWNT mat. a) Photograph of the MWNT mat. b) Uniaxial tensile stress-strain curves for Al, Cu and MWNT CCs (inset: photograph of typical sample failure of the CCs, demonstrating the elastic behavior of the MWNT mat). c) SEM and (d), TEM images of the MWNT mat.
Figure 2.2. Mechanical characterization on CCs with electrode coatings. a,b) Uniaxial tensile stress-strain curves of (a) LiFePO$_4$ on Al and MWNT mat, and (b) Li$_4$Ti$_5$O$_{12}$ on Cu and MWNT mat.

The MWNT mat has a high porosity of 75%, which is supported by transmission electron microscopy (TEM) (Figure 2.1d) and through the film’s high specific surface area measured to be 176 m$^2$ g$^{-1}$ (porosity is calculated from the bulk density of the film, measured to be 0.52 g cm$^{-3}$, and assuming a value of 2.1 g cm$^{-3}$ for the intrinsic density of the MWNTs). TEM tomography and corresponding 3D Model-Based Iterative Reconstructions (Figure 2.3) show the highly porous and interconnected nature of the MWNT mat. It is also interesting to note that robust, free-standing layers of MWNT mat thin enough for TEM microscopy were prepared using scotch tape exfoliation, highlighting the strength of the nanotube network (Figure 8.3, Appendix). All of these factors make the MWNT mat an excellent candidate for Li-ion battery CCs.
Figure 2.3. HAADF-STEM tomography on scotch tape exfoliated MWNT mat. a) 0 degree HAADF-STEM image from the tilt series. b) MBIR reconstruction visualized in Avizo Fire with MWNTs in gold and catalyst in blue.

Schematic representations, shown in Figure 2.4a,d, of a LiFePO$_4$ slurry coated active layer on each type of CC highlight several key advantages of the porous MWNT mat over metal foils. First, the MWNT mat exhibits superior interfacial adhesion with the active material coating. This point is made clear through cross-sectional SEM (Figure 2.4e,f), revealing a very tight and continuous interface between the active material and substrate. The high porosity and better wetting of the nanotube mat gives rise to stronger binding between the active materials and CC. In contrast, cross-sectional SEM images of a LiFePO$_4$ coating on the Al foil show many gaps and portions of delamination (Figure 2.4c,d), a common problem with active material coatings on foil CCs.$^{[6,11,41,43]}$
Secondly, unlike metal foil CCs, the electrolyte can access the active material from both sides of the MWNT mat, thereby promoting homogenous wetting. Figure 8.1 (Appendix) shows the difference in liquid electrolyte wetting between the MWNT mat and a Cu foil CC. On both active material-coated and neat CCs, a 2 µL electrolyte drop quickly wicks through the MWNT mat and is visible on the bottom side of the film. On the contrary, electrolyte cannot travel through the thickness of the Cu foil. Additionally, there is a significantly lower contact angle in the neat mat vs. the neat Cu foil, indicating better wettability in the nanotube sample. This result is consistent with Wang et al. who found better wetting of droplets of active material slurry on a CNT film vs. a Cu foil.[43]
Proper wetting is a critical factor for Li-ion batteries, as insufficient or inhomogeneous electrolyte wetting has been shown to accelerate cell degradation and shorten cell life.\textsuperscript{[51]}

Half-cells composed of either LiFePO\textsubscript{4} or Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} slurries on both MWNT mat and metal foil CCs were fabricated versus lithium, and their electrochemical performance is shown in Figure 2.5. The cycling behavior of the electrodes at a constant 0.2C current rate (Figure 2.5a) is effectively the same for both the metal foil and MWNT CCs, with observed specific capacity values (based on active mass) that are expected for both LiFePO\textsubscript{4} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}. Additionally, these cells have been cycled up to 100 times with limited or no loss of performance. These results suggest that the highly porous MWNT mat is effectively acting as the CC and allows access to all of the available active material in the electrode, without itself participating in the electrochemical reaction within the specified voltage windows. Furthermore, the high porosity of the MWNT mat leads to a much lower density as compared to the metal foils (0.52, 2.56, and 8.87 g cm\textsuperscript{-3} for MWNT, Al, and Cu, respectively), and at comparable thicknesses for all three of these CCs (20, 17, and 25 µm for MWNT, Al, and Cu, respectively) there is no undesirable increase in cell volume. This in-turn leads to substantially improved total specific capacity values for electrodes using the MWNT mat as the CC. Namely, a 1.6X and 4.8X improvement were observed for LiFePO\textsubscript{4} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} electrodes, respectively, when accounting for the total electrode mass (active material, conductive additive, binder, and CC) (Figure 2.5b). Interestingly, rate studies performed on the electrodes reveal an equal or even greater performance from cells using the MWNT mat CCs (Figure 2.5c,d). In particular, the performance at high rate (5C) for LiFePO\textsubscript{4} on the MWNT mat shows a 14.7% improvement versus its Al counterpart, supporting the idea
of much better interfacial adhesion as well as better electrolyte accessibility to the active material.

![Figure 2.5](image)

**Figure 2.5.** Half- and full-cell electrochemical characterization of electrodes using metal foil and MWNT CCs. a) Cycling performances (0.2C) of LiFePO₄ and Li₄Ti₅O₁₂ on metal foil and MWNT CCs, normalized by active mass. b) Comparison of half-cell specific capacities based on total electrode mass. c,d) Rate performances of (c) LiFePO₄ on MWNT and Al, and (d) Li₄Ti₅O₁₂ on MWNT and Cu, normalized by active mass.

Another question that arises with this MWNT material is whether one can take advantage of the lithium storage characteristics of the carbon nanotubes themselves. Unfortunately, the high surface area of this material, coupled with its low reduction potential, exacerbate the formation of the solid electrolyte interface (SEI) layer, resulting in significant irreversible capacity loss. However, certain active materials can be coated
over the MWNTs that are electrochemically active in a potential window that avoids the pitfalls of the high surface area nanotubes. Atomic layer deposition (ALD) is a useful technique for the deposition of uniform thin films onto 3D networks. For batteries, in particular, the reduced dimensions achieved in ALD films significantly increase the rate of Li ingress/egress because of the short distances for Li-ion transport within particles. This behavior is explained by equation (5), which presents the diffusion coefficient (D) in dimensions of the square of diffusion length (L) divided by time. We see that the diffusion time thus decreases with the square of L, as L is decreased:

$$t = \frac{L^2}{D}.$$  

(5)

In the same manner, electron transport is enhanced because of the shortened transport distances. Finally, the high surface area of the thin films permits high contact area with the electrolyte and hence high Li-ion flux.

In a previous work, the feasibility of using ALD to coat an active material (SnO$_2$) onto 3D networks of nickel and carbon nanotubes was demonstrated.$^{[52]}$ In light of this success, we have pursued the study of ALD coating active materials onto the MWNT mat. However, the lower voltage window of SnO$_2$ (0.02-0.9 V) corresponds to the active lithium storage region of carbon, and because high surface area materials such as MWNTs suffer from large irreversible capacities due to electrolyte decomposition and (SEI) formation in this electrochemical window, it is not an ideal candidate for the anode. Titanium dioxide (TiO$_2$), on the other hand, is electrochemically active in the 1-3V potential region, and is therefore more aptly suited for coating on carbon substrates. Hence, it was worthwhile to explore the integration of TiO$_2$ (anode) into the 3D network of our MWNT to be employed in flexible energy storage devices.
A direct comparison between the SEM micrographs of the bare MWNT sheet (Figure 2.6a,b) and the ALD-TiO$_2$/MWNT (Figure 2.6c,d) shows the presence of particle agglomerates on the surface of the MWNTs. The voltage profile for the ALD-TiO$_2$/MWNT sample (Figure 2.7b) shows a reversible capacity of 320 mAh g$^{-1}$, a value close to the theoretical capacity of TiO$_2$ (335 mAh g$^{-1}$). On the other hand, the neat MWNT sheet was cycled under the same conditions and showed to exhibit a 500 mAh g$^{-1}$ loss in capacity from the first to second discharge cycles, owing to SEI formation and irreversible lithium consumption (Figure 2.7a). The detriment of this process to full-cell behavior is shown in Figure 2.7c, where upon charge (i.e., lithiation of the MWNTs) a large irreversible capacity is observed in addition to capacity fading in the subsequent charge/discharge cycles.
Figure 2.6. Microstructure of TiO$_2$ coated MWNT mat prepared by ALD. SEM micrographs of neat MWNT sheet at (a) low and (b) high magnification, SEM micrographs of ALD-deposited TiO$_2$ on MWNT sheet at (c) low and (d) high magnification.
Figure 2.7. Electrochemical performance evaluation of TiO$_2$ coated MWNT mat prepared by ALD. a) Charge/discharge behavior of a MWNT electrode vs. Li-foil. The inset in (a) shows the voltage behavior over time for the MWNT half-cell. b) Charge/discharge behavior of a TiO$_2$/Nancomp electrode vs. Li-foil. The inset in (b) shows the cycle life and coulombic efficiency of the TiO$_2$/Nancomp half-cell. g) The electrochemical performance of a full-cell consisting of nickel-manganese-cobalt oxide (NMC) cathode and MWNT anode.

Full Li-ion cells, consisting of LiFePO$_4$ cathodes and Li$_4$Ti$_5$O$_{12}$ anodes, were assembled using MWNT CCs on both sides of the cell. Figure 2.8a shows the charge/discharge profiles of LiFePO$_4$ and Li$_4$Ti$_5$O$_{12}$ half-cells and their corresponding full-cell (calculation based on the mass of the limiting electrode) at a 0.2C current rate with all MWNT CCs. The extremely stable charge/discharge profiles for both half- and full-cells should be noted. In Figure 2.8b, the energy densities of full-cells fabricated
with all metal foil or all MWNT CCs are compared. As expected, the energy density of the full-cells when considering only the active materials was comparable for both the metal foils (105 Wh/kg) and MWNT (109 Wh/kg) CCs. When considering the total electrode mass, which accounts for over half of total battery weight in commercial Li-ion batteries, there is a 3.5X enhancement in energy density when using the MWNT mat in lieu of metal foils. A mass distribution of the primary components considered in this study is shown in Figure 7c and d to further highlight the difference of the MWNT-based battery compared to commercially available Li-ion batteries composed of metal foils. Relative to 27% of typical commercial full-cells being made up of metallic foil CCs (average taken from seven manufacturers[^31]), our MWNT mat full-cell only attributed 9.3% of its mass to the CC. Although not pursued in this study, this contribution could be further reduced to 4.8% by coating active material of both sides of the CC as is standard in industry.
Figure 2.8. Full-cell electrochemical characterization and mass distributions. a) Galvanostatic charge/discharge behavior of LiFePO₄/MWNT and Li₄Ti₅O₁₂/MWNT vs. Li (half-cells), and the corresponding LiFePO₄/Li₄Ti₅O₁₂ MWNT full-cell. b) Comparison of full-cell energy densities based on combined anode plus cathode active masses (green) and total electrode mass (orange). Mass distribution of the main components for (a) a typical commercial full-cell,[^31] and for (b,c) a MWNT-based full-cell with active material on (b) one side of the CC or (c) on both sides of the CC.

Large area, LiFePO₄/Li₄Ti₅O₁₂ full-cells were assembled as depicted in Figure 2.9a (encapsulation process is depicted in Figure 8.2, Appendix), and their behavior under continuous mechanical flex testing was compared to similar cells using metal foil CCs. An automated flex tester was developed and used to continuously roll and unroll the cells around a mandrel of three different diameters (see Figure 2.9c). This resulted in the cell being cyclically exposed to a known amount of strain ranging from 0 to 4.2% – either in tension or compression as calculated earlier in Section 2.2.6 (depicted in Figure 2.9b) – in order to explore the correlation between electrochemical performance and mechanical fatigue.
During the course of the automated flex test with the mandrel rolling at a linear velocity of 10 mm sec$^{-1}$, discharge voltage was measured for both nanotube- (black trace) and foil-based (red trace) batteries (Figure 2.9d). The center traces show 600 and 430 roll/unroll cycles for the MWNT- and metal foil-based cells, respectively (mandrels were exchanged every 20 min. during a single discharge). Throughout the discharge cycle, the strain increased from 2.1 to 2.6 to 4.2%, which corresponded to a reduction in mandrel radius from 7.88 to 6.35 to 4.00 mm. For better comparison, representative 1.5 min. increments from each mandrel cycle were selected, highlighting the amplitude of voltage fluctuation on both nanotube-based batteries (top row insets) as well as foil-based ones (bottom row insets). In the foil full-cell, cyclical voltage fluctuations were immediately apparent at 2.1% strain, with a frequency corresponding directly to the periodicity of mechanical disruption. As strain increased, larger and more random voltage fluctuations were observed until ultimately the foil-based battery shorted after only 30 roll/unroll cycles at 4.2% strain (Figure 2.9d, indicated with an “X”). We attribute this primarily to interlayer separation (as seen previously by Lee et al.$^{[18]}$) and in-plane shifting, but do not exclude minor contributions due to changes in electrolyte accessibility as the cell was deformed. In contrast, the nanotube-based cells (black traces) exhibited stable discharge characteristics as strain was increased. Even at 4.2% strain, only minor cyclic fluctuations ($< 0.005 \text{ V}$) were observed, and failure did not occur. This can be explained due to the flexibility of the MWNT mat, allowing the full-cell to readily conform to the mandrel as rolling proceeded. This in turn hindered layer-to-layer separation, giving rise to superior electromechanical stability.
Often overlooked is the fact that an ideal flexible power source should experience minimal voltage fluctuation during continuous deformation in order to maintain a steady supply voltage, a point which is especially significant for reliable microsystem performance.\textsuperscript{[53]} Therefore, the voltage fluctuation induced at each strain was analyzed using root mean square error (RMSE) as taken from each of the insets (Table 2.1). The values reported represent both the fluctuation associated with the insets of Figure 2.9d, as well as the unstrained state ($r = \infty$). Ratios between the strained and unstrained-states were used to quantify the amount of fluctuation observed at each mandrel radius. To negate the effect of voltage drift, a linear trendline was subtracted from each dataset, then the RMSE was calculated by equation (6):

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (V_i - \bar{V}_i)^2}$$  \hspace{1cm} (6)

where $n$ was the number of data points, $V_i$ was the observed voltage, and the predicted voltage ($\bar{V}_i$) was taken as the root mean square (RMS) of the unstrained data:

$$\text{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} V_i^2}$$  \hspace{1cm} (7)

Upon only increasing the strain from 2.1% to 2.6%, the metal foil-based cell exhibited a 4.4X increase in voltage fluctuation (Table 2.1), which is clearly discernable without an expanded voltage window. The mechanical instability of the metal foil full-cell translated into a nearly two order of magnitude increase ($10^{-4}$ to $10^{-2}$ V) in voltage fluctuation when increasing the level of bending strain from 0 to 4.2%. To place this into perspective, when looking at each type of battery at the largest strain tested, a 14-fold increase in voltage fluctuation was observed when using metal foils instead of MWNT mat CCs.
Figure 2.9. In situ bending of MWNT mat and metal foil full-cells. a) Schematic representation of a LiFePO4//Li4Ti5O12 MWNT flexible full-cell architecture. b) Diagram of the mechanical strains generated during bending of flexible batteries (mechanically neutral plane indicated by dashed, red line). c) Photographs of the mandrel bending test apparatus. d) In situ mandrel bending test of MWNT (black trace) and foil (red trace) full-cells during a discharge.

Table 2.1. Analysis of voltage fluctuation during in situ bending.

<table>
<thead>
<tr>
<th>r (mm)</th>
<th>RMSE_{MWNT} (V)</th>
<th>RMSE_{Foil} (V)</th>
<th>( \frac{\text{RMSE}<em>{Foil}}{\text{RMSE}</em>{MWNT}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>∞</td>
<td>2.51 x 10^{-4}</td>
<td>2.00 x 10^{-4}</td>
<td>0.97</td>
</tr>
<tr>
<td>7.88</td>
<td>4.88 x 10^{-4}</td>
<td>1.26 x 10^{-3}</td>
<td>0.61</td>
</tr>
<tr>
<td>6.35</td>
<td>5.09 x 10^{-4}</td>
<td>5.55 x 10^{-3}</td>
<td>0.75</td>
</tr>
<tr>
<td>4.00</td>
<td>8.40 x 10^{-4}</td>
<td>1.18 x 10^{-2}</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Even more importantly, our cells are highly stable to repetitive folding and creasing along a particular fold line, which corresponds to an extreme amount of mechanical stress and strain at the crease. Throughout a ±180° folding test (Figure 2.10a) the MWNT-based full-cell exhibited uncompromised performance, with the voltage fluctuation
effectively indiscernible from the background for 288 folds (Figure 2.10b), and unchanged from the beginning to the end of the test (Figure 2.10b insets). This behavior again illustrates the remarkable ability of the MWNT CC to accommodate the strains of repeated folding while maintaining excellent adhesion between both the active material/CC and interlayer interfaces. In contrast, the metal foil full-cell exhibited severe voltage instability as the number of folds increased (Figure 2.10c). We observed that this was due to accumulated damage caused by the mechanical deformation of the metal foil battery (Figure 2.10e). While the Cu electrode showed expansive buckling emanating from the fold region, the Al CC catastrophically fractured after only 94 folds (Figure 2.10c, indicated with an arrow), which caused the magnitude of voltage spikes to severely increase. This ultimately led to complete performance failure of the metal foil full-cell after 186 folds.

Failure of the metal foil electrodes resulted from either severe buckling or fracture along the fold line due to permanent plastic deformation, fatigue, and then catastrophic failure of the metal foil during testing. Although failure from tearing is easy to conceptualize, buckling is also highly detrimental to performance as it decreases compliancy and exacerbates interlayer separation, leading to severe voltage spikes and capacity degradation. On the other hand, Figure 2.10d shows that the MWNT electrodes remained intact after the fold test, exhibiting little signs of permanent deformation, crease memory, or active material delamination. We attribute this behavior to the long, intertwined MWNTs being amenable to the strains of repeated bending or folding without mechanical failure. Despite the fact that the active layer is composed of a porous assembly of particles bound together in a relatively weak framework, these results
suggest that they are remarkably robust and able to withstand extreme amounts of stress and strain when incorporated onto an appropriately flexible and robust CC.

![Figure 2.10](image)

**Figure 2.10.** *In situ* folding of MWNT and metal foil LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ full-cells. a) Schematic illustration of folding, where (+)180° or (-)180° represents one fold. Discharge plateau of (b) MWNT and (c) metal foil full-cells cycled at a 0.2C current rate during folding. Insets shown in (b) depict the voltage stability observed at both the beginning and end of test for the MWNT full-cell. Photographs of the (d) MWNT and (e) metal foil electrodes after extraction from the full-cell at the completion of the experiment.

To complement the above observations, both LiFePO$_4$/MWNT and LiFePO$_4$/Al electrodes were cryo-fractured perpendicular to the folding line for cross-sectional SEM examination (Figure 2.11). The creased region in the nanotube electrode did not appear to be significantly affected by folding, thus highlighting the excellent interfacial adhesion
between the MWNTs and active materials. The Al electrode, on the other hand, shows visible signs of delamination as well as cracking. Hence the observed folding-induced voltage fluctuations in the metal foil full-cell arise not only from layer-to-layer separation, but also from active layer detachment and/or CC damage. It is worth mentioning that the folding-induced damage on an individual electrode is an extreme case of folding. In working full-cell devices, the folding strain on each electrode is buffered by additional layers (e.g., separator, Surlyn encasing).

![Figure 2.11. Effect of folding on CC and active material coating. a) Schematic representation of an electrode with fold line A. b,c) Photograph and cross-sectional SEM image of (b) a LiFePO₄/MWNT electrode and (c) a LiFePO₄/Al electrode after being subjected to two cycles of ±180° about the same line.](image)

2.4 Conclusions

In conclusion, two dynamic mechanical testing approaches were employed for in situ characterization of flexible Li-ion batteries, with implications for analyzing a wide range of flexible devices. It was found that by replacing traditional metal foil CCs with a porous, conductive MWNT mat, high performance bendable and even creasable Li-ion batteries could be prepared. When subjected to an in situ bending test with continuous mechanical strain during discharge, a 14-fold decrease in voltage fluctuation was observed in the nanotube full-cell compared to the conventional foil full-cell at a strain of 4.2%. Along with showing superior voltage stability throughout dynamic bend testing, the MWNT mat full-cells exhibited excellent mechanical stability through 288 creases, whereas the foil full-cell exhibited continuously degraded performance with each crease.
and catastrophic fracture after only 94 folds. Improvements in mechanical performance when using MWNT CCs were explained by better active material adhesion and electrolyte wetting. The results of this work elucidate the relationship between mechanical deformation and electrochemical performance, and highlight the substantial performance enhancement that can be realized with an appropriate choice of a flexible and robust CC.
3 Carbon Nanofiber Composite Electrode Behavior and Optimization for 3D Printing

3.1 Introduction

Conventional battery electrodes, which consist of active material, conductive additive, and polymer binder doctor bladed onto a metal foil current collector (CC), cannot keep pace with evolving demands for flexibility. These foil CCs are rigid, contribute to inactive cell mass, and are prone to corrosion in liquid electrolyte over time, which can lead to degraded performance. As a result, much work has focused on developing alternative CCs or free-standing, CC-embedded electrodes leading to significant progress in the field of flexible Li-ion batteries. Of particular interest are free-standing composite electrodes that eliminate the rigid metal foil substrate by embedding the CC within the electrode material, thus reducing inactive mass. To date, multiple processing methods have been utilized to fabricate composite electrodes such as vacuum filtration, hot pressing, drop casting, doctor blading, electrospinning, or freeze-drying. While these approaches are useful for creating free-standing electrodes in a batch-type process, the processing conditions often limit deposition to only specific geometric layouts. In addition, materials fabricated by these methods are often inherently brittle, due to a lack of binder and high active material loading (often >90 wt.%), which leads to limited utility when it comes to flexible and stretchable applications.

Alternatively, direct write manufacturing techniques (e.g., filamentary, ink jet, or aerosol jet printing) are an effective means of creating complex, multifunctional structures. These template-free techniques offer an economical method for the rapid prototyping of battery electrodes and complex architectures designed to fit a specific
While recent progress in the development of printed battery electrodes reveal promising opportunities, most of these have only been demonstrated on a microbattery scale, or suffer from either time consuming or complex ink formulation procedures. Furthermore, the inclusion of printing-specific additives (e.g., surfactants, viscosifiers, coagulants, or plasticizers) is typical in these demonstrations and could have unexpected negative effects on the electrochemical performance. Therefore, a simplistic approach to direct write compatible, composite electrode inks with controllable and tunable materials properties is in high demand. The combination of composite electrode inks with additive manufacturing would offer a pathway towards mechanically compliant batteries, with a wide range of form factors, but to date this space has been unexplored. Additionally, exploiting such technology would allow printing of an electrode to be accomplished with only one ink, whereas conventional Li-ion batteries require a dedicated CC layer for charge collection and mechanical support of the electrode.

Here we describe an approach to create CC-embedded electrode inks utilizing a well-dispersed, 3D network of carbon nanofibers (CNFs) to collectively act as the conductive additive, charge collector, and porous, structural scaffold to facilitate Li$^+$ diffusion. The focus was to formulate and study a series of 3D printable electrode inks to achieve a balance between electrochemical, mechanical, and rheological properties. In order to do this, a system was developed in which the ink components (i.e., active material, CNFs, and polymer) could be independently varied to tune the ink rheology and the final electrode properties. We found that each parameter had a significant role in optimizing the overall performance of the printable electrode – CNFs promoted conductivity and the
formation of a porous microstructure for high rate performance, active material varied the
cell’s electric storage capacity, poly(vinylidene fluoride) (PVDF) governed the mechanical properties, and the combination of solvent, CNFs, and polymer all impacted the rheological properties.

3.2 Experimental Methods

3.2.1 Materials

Lithium titanate (Li$_4$Ti$_5$O$_{12}$), lithium iron phosphate (LiFePO$_4$), and lithium cobalt oxide (LiCoO$_2$) active material powders were purchased from the MTI Corporation. Carbon nanofibers (CNFs) (Pyrograf$^\text{®}$-III PR-19-HT, ≤100 µm length, 50-150 nm diameter) were supplied by Applied Sciences Inc. Graphite was purchased through Asbury Graphite Mills (HPM 850 powder) and Super P-Li carbon black was from TIMCAL Graphite & Carbon. Kynar$^\text{®}$ HSV 900 poly(vinylidene fluoride) (PVDF) was provided from Arkema Inc. Diethyl carbonate, isopropanol, and 1-methyl-2-pyrrolidone (NMP) was purchased through Sigma Aldrich.

3.2.2 Sample Characterization

SEM was performed using an FEI Quanta 600F SEM. Samples were imaged using a 5 kV accelerating voltage, and cross-sections were prepared by cryo-facturing while immersed in liquid nitrogen. Cross-sectional SEM images of the sample after electrochemical cycling were taken by disassembling the cycled coin cell and cryo-fracturing the electrode after cleaning it by dipping in diethyl carbonate and rinsing with isopropanol. All tensile tests were conducted on a TA Instruments DMA Q800 Dynamic Mechanical Analyzer in displacement control mode with a constant strain rate of 1 % min$^{-1}$ at room temperature. The composite films were cut into rectangular tensile
specimens of 20 mm length and 3-4 mm width using a razor. The finished specimens were examined using a Zeiss Stemi DV4 optical microscope to ensure that there were no visible flaws from cutting. The thickness of each specimen was determined from the average of three measurements taken along the gauge length with a Mitutoyo micrometer. Ink rheology measurements were obtained using a TA Instruments ARES-G2 Rheometer. A flow sweep method was used to observe the apparent viscosity as a function of shear rate. The experiment was conducted at ambient temperature and the shear rates were varied in a logarithmic sweep from 0.01 to 100 s$^{-1}$ with a step equilibration time of 30 s. Inks were loaded on a 25 mm diameter stainless steel plate with a constant gap of ~0.95 mm between the parallel plates for each sample. The surface area and porosity data were calculated by Brunauer–Emmett–Teller (BET) method based on N$_2$ adsorption–desorption isotherms at 77 K obtained using an ASAP 2020 surface area and porosimetry analyzer (Micromeritics Instrument Corporation). The samples were degassed at 100 °C under vacuum for 16 h. before running the measurement. Electrical conductivity was performed with a Lucas Labs SP4 four-point probe head controlled with a Keithley 2410 SourceMeter and a computer operated LabVIEW program.

3.2.3 Electrode and Cell Fabrication

Composite electrodes were prepared according to the ratios in Table 3.1. For composites consisting of active material, conductive additive, and polymer binder, each batch consisted of 100 mg of active material and 5 mL solvent (conductive additive and polymer were scaled according to the ratios in Table 3.1). The procedure for each composite consisted of first dissolving the polymer in NMP. Next, CNFs were added and probe sonicated for 1 min. at 17% amplitude using a Sonics Vibra-Cell VCX 750 Probe Sonicator with a ¼ in. microtip. Active material was then added, and the mixture was
bath sonicated for 10 min. using a Branson 2510 bath sonicator. The samples were shaken by hand several times during the sonication period for more thorough mixing. Finally, the mixtures were transferred to a 6 cm diameter PTFE dish and dried at 90 °C. Once solvent was evaporated, the samples were dried under vacuum at 120 °C overnight. Composite inks for printing and rheology were prepared using the same procedure as above, except the solids loading was doubled (200 mg active and 5 mL NMP) to increase the viscosity of the mixture. For these inks, it was also necessary to increase the probe sonication time and intensity to 2 min. at 25% amplitude to disperse CNFs. For composite anodes consisting of only CNFs and polymer, each batch consisted of 150 mg of active material and 6 mL NMP (polymer was scaled according to the ratios in Table 3.1). This mixture was probe sonicated for 2 min. at 22% amplitude, transferred to a 6 cm PTFE dish, dried at 90 °C to remove solvent, then vacuumed at 120 °C overnight.

Electrode samples were punched to 9.5 mm diameter discs. Typical weights of Li$_4$Ti$_5$O$_{12}$, LiFePO$_4$, and LiCoO$_2$ in each composite electrode disc ranged from 1.5-3.0 mg corresponding to sample thicknesses ranging between 100-200 μm, as measured by a Mitutoyo digital micrometer. Electrode samples were soaked in liquid electrolyte (1 M LiPF$_6$ in 1:1 ethylene carbonate:diethyl carbonate by wt., Novolyte Technologies) and assembled versus Li foil under argon environment (<1 ppm H$_2$O and O$_2$) in 2325 coin cell configuration. A porous polymer membrane (Celgard 2325) soaked in a liquid electrolyte solution was used as the separator.

3.2.4 Electrochemical Characterization

The cells were cycled using a Maccor series 4000 battery test system. LiFePO$_4$, LiCoO$_2$, Li$_4$Ti$_5$O$_{12}$, and CNFs were investigated for cycling stability at a constant 0.2C current rate between 2.0-4.3 V, 3.0-4.2 V, 1.0-2.1 V, and 0.01-3.0 V vs. Li/Li$^+$. 
respectively. The rate studies were carried out in a similar manner, with each half-cell tested for 5 cycles at 0.2C, 0.5C, 1C, 2C, 5C, and 0.2C for all active materials. All C rates were calculated with 1C being defined as 170 mA g\(^{-1}\), 155 mA g\(^{-1}\), 175 mA g\(^{-1}\), and 372 mA g\(^{-1}\) for LiFePO\(_4\), LiCoO\(_2\), Li\(_4\)Ti\(_5\)O\(_{12}\), and CNFs, respectively.

### 3.2.5 Three-Electrode Electrochemical Impedance Spectroscopy and Equivalent Circuit Modeling

Electrochemical impedance spectroscopy (EIS) experiments were conducted in a three-electrode split cell (MTI Corp.) with Li foil as the counter and reference electrodes (Figure 3.1). The area of the working electrodes (i.e., Li\(_4\)Ti\(_5\)O\(_{12}\) composites) was 1.6 cm\(^2\). The liquid electrolyte used was the same as for the cycling experiments. Measurements were performed with a Gamry Reference 600 Potentiosat/Galvanostat/ZRA at open circuit potential by applying an AC-amplitude of 10 mV over a frequency range from 50 mHz to 300 kHz at room temperature. Prior to performing the EIS measurements, the cells were subjected to one discharge/charge cycle at 0.2C between 1.0 and 2.1 V in order to activate the electrode/electrolyte interface, followed by a discharge cycle to 50\% depth-of-discharge. The electrode was then allowed to equilibrate for 2 h. before the EIS measurements were taken in order to minimize the drift in open circuit voltage. A stable open circuit voltage was typically attained at 1.58 V.
Because of the existence of an electrical double layer within Li-ion batteries, the resistance of a battery cannot be simply treated as a pure resistor. While there are many equivalent circuit models for Li-ion batteries, a typical one is shown in Figure 3.2. In this model, $R_s$ is the electrolyte resistance, $C_{dl}$ is the double-layer capacitance at the electrode/electrolyte interface, $R_{ct}$ is the faradaic (charge transfer) resistance at the electrode/electrolyte interface, and $Z_w$ is the Warburg impedance which models the diffusion of lithium ions in the electrode. When an AC signal $I = I_0 \sin(\omega t)$ is applied to the cell under study, the response is given by $V = V_0 \sin(\omega t - \varphi)$, where $I_0$ and $V_0$ are signal amplitude, $\omega = 2\pi f$ (f is frequency, Hz), and $\varphi$ is the phase angle. The mathematical expression of the complex impedance is not given here because it depends entirely on the equivalent circuit model chosen. Given the complexity of the equivalent
circuit model used in this study, further discussion is held off until later to provide better context for each circuit element.

![Circuit Model](image)

**Figure 3.2.** Standard equivalent circuit model (Randles circuit).

### 3.4 Results and Discussion

The process to develop our electrode inks is shown in Figure 3.3a-c, and first involved sonication of the active material and CNFs in a polymer solution. Next, the mixture was cast onto a PTFE dish, yielding a free-standing and flexible battery electrode. The advantage of casting is that it more closely mimics filamentary printing of solvent-based inks (solution-cast direct write) unlike other common approaches to prepare composite electrodes, such as filtration or hot pressing. Moreover, casting allows us to gain a fundamental understanding of the intrinsic properties of the electrodes before having to optimize printing conditions. In this pursuit, a stable and well understood Li-ion battery anode, lithium titanate (Li$_4$Ti$_5$O$_{12}$), was used throughout the course study. CNFs were selected because of their high conductivity and large aspect ratio.$^{[74]}$ Further, these CNFs have a stacked-cup architecture$^{[74]}$ composed of many graphitic edges, which explains the observed ease in dispersibility, processability, and ink homogeneity. These attributes resulted in a highly conductive, percolative network throughout the composite, which allowed for the fabrication of CC-embedded electrodes. Finally, high molecular weight PVDF was utilized to govern the mechanical stability of the free-standing and flexible
electrodes, while solvent (N-methyl-2-pyrrolidone, NMP) aided in uniform dispersion and stability yielding inks that could be printed over a period of months.

Over the course of optimization, it was important to document several key characteristics of the electrodes to understand what led to a favorable balance between electrochemical performance and flexibility. Table 3.1 shows the apparent density, electronic conductivity, tensile strength at failure, and electrochemical capacity as each of the three electrode components were varied (sample codes from this table are used throughout the discussion for clarity). In general, the conductivity increased as a function of CNF loading, while the tensile strength at break and high rate capacity were dictated by polymer loading, which will be discussed in further detail later in the discussion. Indeed the combination of these materials also impacted the ink’s rheological properties, therefore the apparent viscosity as a function of shear rate of four distinct Li$_4$Ti$_5$O$_{12}$/CNF/PVDF electrode inks was studied (Figure 3.3d). Each of these inks displayed a three-regime flow curve, consisting of two non-Newtonian shear-thinning regions separated by a shear-thickening region. The presence of a shear-thinning region allows us to apply the power law (Oswald-de Waele relationship) to describe the flow behavior of each ink. According to the power law equation (8), the viscosity is given by:

$$\eta = K\dot{\gamma}^{n-1},$$

(8)

where K is the flow consistency index ($\eta$ at $\dot{\gamma} = 1$ s$^{-1}$), $\dot{\gamma}$ is the shear rate, and n is the flow behavior index. Overall, the viscosity level increased with increasing concentration of CNF and polymer. Samples B and F exhibited shear-thickening flow at high shear rate that was consistent with previous reports on CNF suspensions, which attributed this behavior to the alignment of CNFs in strong shear fields.$^{75,76}$ Notably, the shear-
thickening peak occurred at lower shear rate for samples A and D, which both possessed a high concentration of PVDF. It is probable that the PVDF was acting a lubricant, fast tracking the alignment of the CNFs at lower shear rate as the polymer chains began to orient in the flow direction.

![Figure 3.3](image)

**Figure 3.3.** Photographs and scheme of the composite electrode fabrication process and rheological characterization of composite inks. a) Photographs of Li$_4$Ti$_5$O$_{12}$ active material (top), CNFs (middle) and PVDF (bottom). b) Photograph of a 40/40/20 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite ink. c) Photograph and schematic representation of a flexible composite prepared by casting the mixture shown in (b) in a 6 cm diameter PTFE dish. d) Apparent viscosity as a function of shear rate of four types of Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites. Active material concentration was held constant at 40 mg mL$^{-1}$ for all inks.
Figure 3.4a supports that the shear-thickening peak shifted to lower shear rate as the PVDF loading was increased. In the two extreme cases, it was observed that the shear-thickening region shifted to the highest shear rate (20 s\(^{-1}\)) when no PVDF was included (red curve), while the shear-thickening region was entirely absent from the pure PVDF/NMP solution (black curve). In fact, the shear-thinning behavior of the latter appears almost Newtonian relative to the CNF suspensions. Such behavior corroborates with the aforementioned hypothesis because the PVDF chains clearly disentangle and align with less shear force than required for the CNFs, given the modest slope of the black curve. A hypothetical flow curve of the alignment of PVDF chains is shown in Figure 3.4b, and the data suggest that this occurs more readily than the alignment of the CNFs. So as more of the polymer “lubricant” is added to the suspension, the shear-thickening region occurs at increasingly lower shear rate, reaching 1 s\(^{-1}\) at 3.7 wt\% (3 vol. %) PVDF. Hence, as we add higher concentrations of polymer to the suspension, the more likely it is for the PVDF chains to interact with the CNFs and aid in their alignment or aggregation, manifesting itself in the observed shear-induced transition.
Figure 3.4. Effect of PVDF loading on shear-thickening behavior of CNF/PVDF solutions in NMP.  a) Flow curves of CNF/PVDF solutions with various PVDF loading.  All samples were prepared in 5 mL of NMP.  b) Typical viscosity curve of a polymer solution showing an idealized view of the effect of shear on the entanglements of concentrated polymer solutions.[77]

Table 3.1. Properties of composite battery electrodes.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition</th>
<th>Ratio</th>
<th>ρ   [g cm⁻³]</th>
<th>σₑ[⁰] [S cm⁻¹]</th>
<th>TS[⁰] [MPa]</th>
<th>0.2C Capacity [mAh g⁻¹]</th>
<th>5C Capacity [mAh g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>25 / 25 / 50</td>
<td>0.97</td>
<td>10.50</td>
<td>12.7</td>
<td>141</td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>40 / 40 / 20</td>
<td>0.61</td>
<td>10.13</td>
<td>2.5</td>
<td>150</td>
<td>77</td>
</tr>
<tr>
<td>C</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>40 / 30 / 30</td>
<td>0.75</td>
<td>8.32</td>
<td>2.5</td>
<td>130</td>
<td>77</td>
</tr>
<tr>
<td>D</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>40 / 20 / 40</td>
<td>0.80</td>
<td>7.17</td>
<td>5.8</td>
<td>139</td>
<td>37</td>
</tr>
<tr>
<td>E</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>50 / 25 / 25</td>
<td>0.76</td>
<td>6.25</td>
<td>2.2</td>
<td>125</td>
<td>73</td>
</tr>
<tr>
<td>F</td>
<td>Li₄Ti₅O₁₂ / CNF / PVDF</td>
<td>67 / 17 / 17</td>
<td>0.88</td>
<td>3.82</td>
<td>1.1</td>
<td>129</td>
<td>73</td>
</tr>
<tr>
<td>G</td>
<td>Li₄Ti₅O₁₂ / Graphite / PVDF</td>
<td>40 / 40 / 20</td>
<td>1.01</td>
<td>1.34</td>
<td>4.3</td>
<td>123</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>Li₄Ti₅O₁₂ / CB[⁰] / PVDF</td>
<td>40 / 40 / 20</td>
<td>0.82</td>
<td>Brittle[⁰]</td>
<td>Brittle[⁰]</td>
<td>170</td>
<td>64</td>
</tr>
<tr>
<td>I</td>
<td>LiCoO₂ / CNF / PVDF</td>
<td>40 / 40 / 20</td>
<td>0.73</td>
<td>10.43</td>
<td>2.1</td>
<td>137</td>
<td>80</td>
</tr>
<tr>
<td>J</td>
<td>LiFePO₄ / CNF / PVDF</td>
<td>40 / 40 / 20</td>
<td>0.66</td>
<td>10.68</td>
<td>2.3</td>
<td>156</td>
<td>106</td>
</tr>
<tr>
<td>K</td>
<td>CNF / PVDF</td>
<td>50 / 50</td>
<td>0.94</td>
<td>12.40</td>
<td>14.8</td>
<td>115</td>
<td>-</td>
</tr>
<tr>
<td>L</td>
<td>CNF / PVDF</td>
<td>67 / 33</td>
<td>0.55</td>
<td>14.28</td>
<td>4.7</td>
<td>250</td>
<td>-</td>
</tr>
</tbody>
</table>

[⁰] Sample ratios by wt%; [⁰] Four-point probe electrical conductivity; [⁰] Tensile strength at failure; [⁰] Carbon black; [⁰] The sample is too brittle to measure electrical conductivity or mechanical properties.

Figure 3.5 concerns the optimization of electrochemical performance based on composite ratios. The rate performances of four distinct Li₄Ti₅O₁₂/CNF/PVDF
compositions were studied in Figure 3.5a. Here, it is useful to define the parameter “theoretical utilization,” which we use to define the percentage of the theoretical capacity we are accessing for a given active material at a certain current rate. It is given by equation (9):

\[
\text{Theoretical Utilization (\%)} = \frac{i_{\text{dis}} \times t \times m \times M_w \times n \times e}{\text{Observed discharge capacity} \times \text{Theoretical capacity}}
\]  

(9)

where \(i_{\text{dis}}\) is the discharge current, \(t\) is the time to discharge, \(m\) is the mass of the active material, \(M_w\) is the molecular weight of the active material, \(n\) is the total number of electrons transferred, and \(e\) is the elementary charge. All of the composites in Figure 3.5a exhibited reasonable theoretical utilization of active material (>74%) at low rate (0.2C), but there was a sharp drop off in high rate performance as polymer loading increased. Namely, samples A and D (50 and 40% polymer, respectively) showed decaying cycle performance at high rate when compared to samples B and F (20% polymer or less). The effect of polymer loading was even more evident when comparing the charge/discharge profiles at various rates (Figure 3.5b). While sample A achieved just over 80% theoretical utilization at 0.2C, the high polymer content impeded electrochemical performance at higher rates (e.g., 5% theoretical utilization at 5C). The corresponding charge/discharge plateaus were not flat at any of the current rates tested for this sample, indicating significant Ohmic polarization and poor reaction kinetics with increasing current rate (Figure 3.5b, top). Sample B, on the other hand, displayed stable and flat charge/discharge profiles with excellent theoretical utilization of 86% and 51% at 0.2C and 5C, respectively (Figure 3.5b, bottom).

Because the polymer loading correlated with degraded performance, it was clear that one of the biggest factors dictating high rate capacity was polymer loading. An intuitive
explanation could be that high polymer loading lead to decreased electrical conductivity that in turn hindered performance, but this conclusion is not supported. All of the Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites displayed in Table 3.1 indeed possessed good electrical conductivities between 3 and 10 S cm$^{-1}$. This was expected because the CNF loading was well above the percolation threshold (< 1 wt.% when using CNFs imbedded in a polymer matrix$^{[78]}$). This range of conductivity has also previously been shown to be sufficient in Li-ion batteries without dedicated metal foil CCs.$^{[6,10,79]}$ For this reason the relationship between polymer density and rate capability was analyzed (Figure 3.5c). At low rate, >70% theoretical utilization was achieved for all types of Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites tested. Conversely, at high rate, there was a negative correlation between electrochemical performance and increased polymer density. To further understand this correlation, Brunauer–Emmett–Teller specific surface area analysis was performed on samples A and B as well as on pure CNFs (Figure 3.5d). The surface area decreased from 40 m$^2$ g$^{-1}$ for pure CNFs to 14 m$^2$ g$^{-1}$ and 4 m$^2$ g$^{-1}$ in the composites with 20% and 50% polymer loading, respectively. This suggested that increased polymer loading resulted in the reduction of void space and limited access to the CNFs/active material. However, further study was necessary to pinpoint the exact causes of polarization losses and performance degradation.
Figure 3.5. Effect of Li$_4$Ti$_5$O$_{12}$/CNF/PVDF ratios on composite electrode properties. a) Rate performances of four types of Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites. b) Representative charge/discharge profiles of samples A and B taken at various current rates. c) 0.2C and 5C capacity as a function of composite PVDF density for all of the Li$_4$Ti$_5$O$_{12}$/CNF/PVDF compositions from Table 3.1. d) N$_2$ adsorption and desorption isotherms of pure CNFs, a 40/40/20 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite (sample B), and a 25/25/50 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite (sample A).

Electrochemical impedance spectroscopy (EIS) was studied in Figure 3.6 and Table 3.2 in order to adequately understand the polarization losses effecting cell performance. EIS is a powerful analytical technique used to investigate electrochemical processes that occur at charge transfer interfaces. It has frequently been applied to the study of lithium storage materials, such as Li$_4$Ti$_5$O$_{12}$, but previous works have focused primarily on changes in the charge transfer resistance based on the interpretation of one or two
semicircles and an inclined line.\textsuperscript{[80-83]} These studies typically employ a two electrode cell, whose results are difficult to interpret because the responses generated by such a setup are characteristic not of one charge transfer interface, but of every reaction interface within the cell. Thus, when the charge transfer resistance is interpreted from such data, it actually represents a summation of the responses from both the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/electrolyte interface and the Li/electrolyte interface. For this reason, a three-electrode configuration is preferred because it allows one to isolate the response of an individual reaction interface by the addition of a reference electrode. However, studies using a three-electrode configuration on the Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} system remain limited.\textsuperscript{[84,85]}

Here, we utilized three-electrode impedance spectroscopy to study the electronic and ionic transport properties of our Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} electrode composites. The impedance spectra were fitted to the equivalent circuit shown in Table 3.2, where the true capacitance has been replaced with a constant phase element (CPE) to better represent the non-homogenous nature of the porous composite electrode. Put another way, the semi-circles in all of the impedance spectra were slightly depressed, making it necessary to correct for the deviations from an ideal capacitor behavior in an RC-element with the complex impedance of a CPE:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^\alpha},$$

(10)

where Q is the admittance, j is the square root of -1, \(\omega\) is angular frequency, and \(\alpha\) is a value between 0 and 1 that describes the AC response of the reaction interface (\textit{i.e.,} the electrical double layer). Note that a CPE has also replaced the common Warburg element in the model in order to more accurately represent the finite diffusion process.
Each curve in Figure 3.6 shows several characteristic features beginning with a high frequency intercept ($R_s$), located near the origin because the solution resistance between the working and reference electrodes is compensated by the three-electrode set-up. Thereafter, there are three depressed semicircles observed throughout the frequency regime for each composite. For the sake of clarity, the following comparisons between the remaining frequency responses are drawn solely between samples A and B (black and blue spectra, respectively).

The first semicircle ($R_h$) at 15 kHz represents a Schottky barrier at the CNF/active material interface,$^{[84]}$ which originates from the semiconducting Li$_4$Ti$_5$O$_{12}$ (in its 50% lithiated state) being brought into contact with conductive CNFs. The second semicircle ($R_m$) at 252 Hz represents the contact impedance between the stainless steel testing platform and the composite electrode.$^{[81,86]}$ A three-fold increase in resistance was observed in sample A over sample B for both $R_h$ (3.06 vs. 0.99 $\Omega$ cm$^2$) and $R_m$ (16.67 vs. 5.18 $\Omega$ cm$^2$), which indicated sluggish electron transfer reactions at the surface of the electrode and poor electronic conductivity during Li$^+$ insertion, respectively. The increased impedance values in sample A vs. sample B are consistent with the electrochemical data in Figure 3.5b. The third semicircle ($R_l$) at ca. 12 Hz represents the charge transfer process as Li$^+$ migrates into the active material through the rock-salt shell and ultimately into the spinel core structure.$^{[82,83]}$ Because this reflects an intrinsic property of Li$_4$Ti$_5$O$_{12}$, this response was held constant (~18 $\Omega$ cm$^2$) for all of the composites. Finally, the combination of a semicircle and straight line in the lowest frequency region represents the phase transformation from Li$_4$Ti$_5$O$_{12}$ (spinel) into Li$_7$Ti$_5$O$_{12}$ (rock-salt)$^{[83,84]}$ (see Figure 3.7) and the solid-phase diffusion of Li$^+$ within the
bulk of the electrode material,\textsuperscript{[87]} respectively. Overall, the impedance curves of sample B suggest comparable electronic transport properties relative to similar works performed with Li$_4$Ti$_5$O$_{12}$ coatings on Cu foil,\textsuperscript{[81,84]} which indicate that the embedded CNFs act as a sufficient alternative to dedicated metal foil CCs.

Figure 3.6. Impedance spectra with model fitting (simulation) of various Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite electrodes. Spectra were shifted along the y-axis for better visual comparison.

Figure 3.7. Lithium titanate core-shell model. The voltage profile at left depicts the progression of the LTO-rock-salt shell formation during lithium insertion, and of the LTO-spinel shell formation during lithium extraction.\textsuperscript{[88]} The various phases of lithium titanate achieved throughout lithium insertion/extraction are shown at right.
Table 3.2. The equivalent circuit parameters obtained from the fit of the experimental impedance spectra. The resistance values have been normalized to areal resistances.

<table>
<thead>
<tr>
<th>Component</th>
<th>Representation</th>
<th>A (25/25/50)</th>
<th>D (40/20/40)</th>
<th>B (40/40/20)</th>
<th>F (67/17/17)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s (\Omega \text{ cm}^2) )</td>
<td>Ohmic resistance of liquid electrolyte</td>
<td>0.41 ± 0.01</td>
<td>0.45 ± 0.02</td>
<td>0.63 ± 0.02</td>
<td>0.24 ± 0.01</td>
</tr>
<tr>
<td>( R_h (\Omega \text{ cm}^2) )</td>
<td>Shotky barrier resistance (CNF/LTO interface)</td>
<td>3.06 ± 0.43 (8.2 ± 1.3) x 10^{-7}</td>
<td>2.41 ± 0.37 (6.7 ± 0.3) x 10^{-6}</td>
<td>0.99 ± 0.15 (1.4 ± 0.5) x 10^{-3}</td>
<td>2.10 ± 0.26 (3.3 ± 0.7) x 10^{-3}</td>
</tr>
<tr>
<td>( \alpha_h )</td>
<td>Contact resistance between SS and electrode</td>
<td>0.90 ± 0.06</td>
<td>0.95 ± 0.05</td>
<td>0.98 ± 0.02</td>
<td>0.97 ± 0.03</td>
</tr>
<tr>
<td>( R_m (\Omega \text{ cm}^2) )</td>
<td>Contact resistance between SS and electrode</td>
<td>16.67 ± 1.06 (6.6 ± 1.9) x 10^{-6}</td>
<td>9.14 ± 1.20 (6.3 ± 0.4) x 10^{-4}</td>
<td>5.18 ± 0.58 (4.2 ± 0.3) x 10^{-5}</td>
<td>7.84 ± 0.87 (5.8 ± 0.8) x 10^{-5}</td>
</tr>
<tr>
<td>( \alpha_m )</td>
<td>Contact resistance between SS and electrode</td>
<td>0.97 ± 0.03</td>
<td>0.75 ± 0.09</td>
<td>0.94 ± 0.03</td>
<td>0.78 ± 0.06</td>
</tr>
<tr>
<td>( R_l (\Omega \text{ cm}^2) )</td>
<td>Transfer across the phase boundary (spinel/rock-salt)</td>
<td>18.72 ± 2.79 (1.0 ± 0.4) x 10^{-5}</td>
<td>17.79 ± 2.53 (2.9 ± 0.5) x 10^{-3}</td>
<td>17.99 ± 2.96 (6.9 ± 0.4) x 10^{-3}</td>
<td>18.28 ± 2.66 (1.2 ± 0.5) x 10^{-3}</td>
</tr>
<tr>
<td>( \alpha_l )</td>
<td>Transfer across the phase boundary (spinel/rock-salt)</td>
<td>0.87 ± 0.11</td>
<td>0.84 ± 0.06</td>
<td>0.98 ± 0.02</td>
<td>0.88 ± 0.08</td>
</tr>
</tbody>
</table>

Figure 3.8 depicts a proposed model to explain the impedance responses observed for the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) composite electrodes. Note that the responses analyzed in this work correspond to the “single particle lithiation” state. At high frequency (\( R_h, \sim 15 \text{ kHz} \)), electronic conduction occurs in which electrons are transported via the conductive additive (CNFs) to the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) active material (i.e., the Schottky barrier). At mid-frequency (\( R_m, \sim 250 \text{ Hz} \)), the observed response stems from a contact impedance between the electrode itself and the stainless steel platform upon which it sits within the three-electrode split cell. If the electron transfer is impeded at this point, electrical neutrality of the particles becomes difficult to maintain and the conduction of ionic charges through the electrolyte and onto the surface of the active material becomes
hindered. This is the most significant parameter affecting the performance of the electrodes because we require high electronic conductivity at this interface to promote electrical neutrality for facile Li$^+$ insertion/extraction. Finally at low frequency ($R_l$, ~12 Hz), the charge transfer process occurs at the electrode-electrolyte interface, which as described earlier is an intrinsic property to the Li$_4$Ti$_5$O$_{12}$ material used. The de-lithiation process follows these steps in reverse order with the addition of a H$_2$ gassing step, as described by Wu et al.$^{[84]}$

Figure 3.8. Schematic model for lithium insertion/extraction into/from Li$_4$Ti$_5$O$_{12}$ electrode.$^{[84]}$

In addition to understanding the electronic properties of the composite electrodes, it was imperative to analyze the fundamental ionic transport properties. The effective Li-ion diffusivity of each electrode was thus evaluated by the EIS method using Warburg impedance.$^{[89,90]}$ The Warburg coefficient ($A_w$) for chemically reversible multi-electron mechanisms can be calculated according to equation (11):$^{[91]}$
\[ A_w = \frac{RT}{n^2F^2A\sqrt{2}} \left( \frac{1}{c_i^0D_i^{1/2}} \right) \]  

(11)

where \( R \) = ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)),

\( T \) = absolute temperature (K),

\( n \) = total number of electrons transferred

\( F \) = Faraday constant (96,485 C mol\(^{-1}\)),

\( A \) = area of the electrode (cm\(^2\)),

\( c_i \) = molar concentration (mol cm\(^{-3}\)) of species \( i \),

\( D_i \) = diffusion coefficient (cm\(^2\) s\(^{-1}\)) of species \( i \).

However, it is common to empirically determine the value of \( A_w \) from the slope of the real impedance (\( Z' \)) versus the reciprocal of the square root of the angular frequency (\( \omega^{-1/2} \)) (Figure 3.9a). Because mass transport does not manifest itself as an influencing parameter at high frequency, this portion of the graph could be neglected and only the linear portion at low frequency was analyzed (Figure 3.9b).\(^{[91]} \) The effective Li-ion diffusivity (\( D_{Li^+} \)) can then be determined via a modification of equation (11):

\[ D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4c^2A_w^2} \]  

(12)

Here, the total number of electrons transferred was determined from the electrochemical reaction of spinel lithium titanate:

\[ \text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- \leftrightarrow \text{Li}_7\text{Ti}_5\text{O}_{12} \]  

(13)

where we see that the value of total electrons transferred is 3. The molar concentration was obtained from equation (14):

\[ C = \frac{(\chi/3)}{459.09 \text{ g mol}^{-1}} \times 3.43 \text{ g cm}^{-3} \]  

(14)
where $x/3$ is the molar ratio of lithium to spinel lithium titanate in $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$, 459.09 g mol$^{-1}$ is the molar mass of lithium titanate, and 3.43 g cm$^{-3}$ is the density of lithium titanate. The composition $x$ was taken to be 1.5 (i.e., 50% depth of discharge, DOD), based on the experimental EIS set-up in which the electrode was lithiated to 50% DOD prior to the measurement. Based on the evaluation of these parameters in Figure 3.9b, it was evident that the trend in value for $D_{Li^+}$ between samples was consistent with their respective rate performances in Figure 3.5a. As suggested earlier, it was likely that in composites with high PVDF loading, the network of interconnected spaces between particles was occupied by polymer rather than electrolyte. As a result, many of the Li$^+$ diffusion pathways were blocked yielding low $D_{Li^+}$ values of $1.5 \times 10^{-13}$ and $2.0 \times 10^{-12}$ cm$^2$ s$^{-1}$ for samples A and D, respectively. On the other hand, the more porous nature of samples B and F promoted higher $D_{Li^+}$ values of $1.4 \times 10^{-12}$ and $1.1 \times 10^{-12}$ cm$^2$ s$^{-1}$, respectively which are within range of typical Li$^+$ diffusivities in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($10^{-9} – 10^{-13}$ cm$^2$ s$^{-1}$).[92,93]

Figure 3.9 Determination of effective Li$^+$ diffusivity by the EIS method using Warburg impedance. a) Example of the dependence of the real impedance ($Z'$) on frequency ($\omega^{-1/2}$) plotted over the entire frequency range. b) $Z'$-$\omega^{-1/2}$ plot at low frequency for determination of the Warburg coefficient.
In order to fully describe ionic motion and to understand the ease with which ions pass through the electrode under a concentration gradient or external electric field, it was necessary to derive both the effective mobility and ionic conductivity in addition to the effective diffusivity. The ionic mobility $\mu$ is related to the diffusivity by the Nernst-Einstein equation:

$$\mu = \frac{zeD_{Li^+}}{k_BT} \quad (15)$$

where $z$ is the ion valence, $e$ is the elementary charge, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. The motion of Li$^+$ is then defined by the ionic conductivity, which can be calculated according to equation (16):

$$\sigma_i = n \cdot z \cdot e \cdot \mu \quad (16)$$

where $n$ is the molar concentration of lithium ($C$) multiplied by Avagadro’s number ($6.022 \times 10^{23}$ atom mol$^{-1}$). Combined with diffusivity, these parameters fully define the ionic transport properties of the electrode material. The corresponding values for each composite electrode are displayed in Table 3.3. It was observed that sample B exhibited the highest ionic transport properties relative to the other composites, which was consistent with its superior rate performance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_w$ ((\Omega) s$^{-1/2}$)</th>
<th>$D_{Li^+}$ (cm$^2$ s$^{-1}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$s$^{-1}$)</th>
<th>$\sigma_i$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (25/25/50)</td>
<td>8.95</td>
<td>1.48 x 10$^{-13}$</td>
<td>5.85 x 10$^{-12}$</td>
<td>2.11 x 10$^{-9}$</td>
</tr>
<tr>
<td>D (40/20/40)</td>
<td>7.65</td>
<td>2.03 x 10$^{-13}$</td>
<td>8.00 x 10$^{-12}$</td>
<td>2.88 x 10$^{-9}$</td>
</tr>
<tr>
<td>B (40/40/20)</td>
<td>2.93</td>
<td>1.38 x 10$^{-12}$</td>
<td>5.46 x 10$^{-11}$</td>
<td>1.97 x 10$^{-8}$</td>
</tr>
<tr>
<td>F (67/17/17)</td>
<td>3.35</td>
<td>1.06 x 10$^{-12}$</td>
<td>4.17 x 10$^{-11}$</td>
<td>1.50 x 10$^{-8}$</td>
</tr>
</tbody>
</table>
Figure 3.10a shows the stress-strain curves for the same four composite loadings discussed previously. From these curves and analyses of mean mechanical properties (Figure 3.10f,g), a positive correlation between both tensile strength and strain to failure with increased polymer loading was clearly observed. Sample B, which exhibited excellent electrochemical performance, possessed moderate mechanical properties (TS and $\varepsilon_f$ of 2.5 MPa and 1.8%, respectively). Such properties are improved or comparable to other current state-of-the-art free-standing composites.[58,64,66] Although tensile strength could be improved up to 12.7 MPa at 50 wt% PVDF, our former results indicated that polymer loading beyond 20 wt% detriments high rate performance (see Table 3.1).

In order to better understand what leads to improved mechanical strength and electrochemical performance, cross-sectional scanning electron microscopy (SEM) was used to characterize two distinct Li$_4$Ti$_5$O$_{12}$/CNF/PVDF samples (Figure 3.10b-e). Both samples appeared homogeneous through thickness, which is important for proper electrode function. Sample A with 50% polymer (Figure 3.10b,c) had very limited visible pores. The high polymer content and limited pore structure explains the excellent mechanical properties, which come at the cost of high rate performance due to the lack of diffusion pathways. Conversely, sample B with only 20% polymer appeared to be composed of more pores (Figure 3.10d,e), which supports the findings of the surface area experiment (Figure 3.5d). Such porosity is desired for superior electrochemical performance, but not surprisingly, some mechanical properties were sacrificed. That being said, the electrochemical and mechanical properties of this composition provided the best trade-off for overall performance. Moreover, the structural integrity of sample B
was maintained between the beginning and end of the electrochemical rate study (Figure 3.11). Cross-sectional SEM showed nearly identical morphology before and after cycling, highlighting the robust nature of the composite electrodes.

Further, the 40% loading of active material in these composites is comparable to commercial Li-ion battery electrodes, which typically consist of ~30-35% active materials when considering active material, conductive additive, binder, and metal foil CC.[31] It is worth mention that other more common conductive additives for Li-ion batteries, such as graphite or carbon black, were also fabricated at the optimum loading found for the Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites (samples G and H). However, both presented undesirable issues during casting, such as inhomogeneous settling in the case of graphite or cracking and curling in the case of carbon black, which solidified our decision to utilize CNFs as the conductive element.

The main goal of this work has been to develop a simple approach to high performance, all-printed Li-ion batteries. As we tailored our composite mixtures towards printing, it was necessary to examine the macroscopic film properties after drying. The inset photographs in Figure 3.10b show composite samples A and B, respectively, after casting in a PTFE dish. Sample B retained its casting shape without shrinkage, a desirable trait for a printable ink, whereas sample A exhibited significant shrinkage and out-of-plane buckling around the edges during the casting process. Any shrinkage or out-of-plane deformation would severely complicate printing, particularly for building up sequential layers in the z-direction. Indeed, the 40/40/20 ratio of active/CNF/PVDF gave a good balance between electrochemical performance, mechanical integrity, and shape retention while drying, making it a strong candidate for the filamentary printing process.
Figure 3.10. Comparison of mechanical properties of selected Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite loadings. a) Representative uniaxial tensile stress-strain curves of four types of Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composites. b,c) Photograph and cross-sectional SEM images of a 25/25/50 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite (sample A) casted in a 6 cm diameter PTFE dish. The SEM image in (c) was taken at the dashed white box in (b). d,e) Photograph and cross-sectional SEM images of a 40/40/20 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite (sample B) casted in a 6 cm diameter PTFE dish. The SEM image in (e) was taken at the dashed white box in (d). The mean (f) tensile strength and (g) strain at failure were calculated from five or more samples at each loading. Error bars are included which display the 95% confidence interval for each sample.
Figure 3.11. Characterization of sample B before and after electrochemical cycling. (a,b) Cross-sectional SEM images before cycling. The SEM image in (b) was taken at the dashed white box in (a). The inset in (a) is photograph of a 9.5 mm diameter sample B disc before cycling. (c,d) Cross-sectional SEM images after cycling. The SEM image in (d) was taken at the dashed white box in (c). The inset in (c) is photograph of the same 9.5 mm diameter disc from the inset in (a) after cycling.

A ternary diagram is presented in Figure 3.12 to summarize the above findings. Three boundaries are marked within the diagram representing regions of desirable versus undesirable properties. The first boundary marks the divide in mechanical integrity between the composites, wherein sample F falls to the right of this boundary implying that it is too brittle to be used appropriately. The second boundary represents the high-rate utilization (5C discharge capacity / 0.2 C discharge capacity), below which we see that samples A and D exhibit insufficient utilization of the active material. The third boundary marks the difference in absolute capacity in mAh \((i.e., \text{not corrected by active mass})\) between each composite. Given the low active material loading in sample A, it
does not meet the requirement for acceptable absolute capacity. To place this metric into perspective, commercial Li-ion battery electrodes only possess about 30-40% active material when accounting for all components (active and inactive) of the electrode, which diminishes their absolute capacity and therefore their specific energy density. With an absolute capacity of only 35 mAh, sample A falls below the acceptable 48 mAh value of standard electrodes. The intersection of each of these boundaries marks a region (highlighted in green) of acceptable balance between the several important properties. Samples B, C, and E fall within this region and exhibit acceptable properties for a free-standing, printable electrode. While sample B exhibited the best tradeoff in properties, we do not rule out that there is room between compositions of samples B, C, and E to adjust the ratio of each electrode component to further optimize overall performance.

Figure 3.12. Ternary diagram summarizing the compositions and properties of the composite electrodes studied in this work.
To emphasize the versatility of our approach to the fabrication of high performance electrodes, lithium iron phosphate (LiFePO₄, sample J) and lithium cobalt oxide (LiCoO₂, sample I) cathode composites were prepared using the optimized ratios for Li₄Ti₅O₁₂ (Figure 3.13). Notably, substituting active material had minimal effect on the rheological properties of the ink (Figure 3.13a), which means that the proposed ink development process can be directly applied for other active materials with little to no modification. Figure 3.13b,c shows the rate performances and cycling performances of all three of these electrodes, which displayed excellent theoretical utilizations of >85 and >50% at low and high rates, respectively. Additionally, these compositions displayed consistent performance over 100 cycles, as well as extremely stable charge/discharge profiles (Figure 3.13c and d). It is worth mentioning that within the electrochemical windows studied for LiFePO₄, LiCoO₂, and Li₄Ti₅O₁₂, the CNFs acted only as a conductive additive since only minor contributions (~1% or less) to active material specific capacity were observed.
Figure 3.13. Rheological and electrochemical properties of composites prepared using different active materials. a) Apparent viscosity as a function of shear rate of 40/40/20 active/CNF/PVDF composite inks. b) Rate performances and (c) cycling performances (0.2C) of 40/40/20 active/CNF/PVDF composites prepared using Li$_4$Ti$_5$O$_{12}$ (blue), LiFePO$_4$ (black), or LiCoO$_2$ (red). d) Representative charge/discharge profiles (0.2C) of each type of active material composite.

It is also worthy to note that the graphitic stacked-cup CNFs closely resemble graphite electrochemically,\textsuperscript{94} thus providing another viable anode composite (Figure 3.14). Composites consisting of only CNFs and PVDF were prepared with CNF/PVDF ratios of 50/50 (sample K) and 67/33 (sample L). Both of these composite ratios formed free-standing, flexible films, but there was a tradeoff between electrochemical performance and mechanical strength. Although both samples showed excellent 0.2C cyclability over 50 cycles, sample K with 50% CNFs was only able to achieve a
reversible capacity of 115 mAh g\(^{-1}\), whereas sample L with 67% CNFs showed a 250 mAh g\(^{-1}\) CNF-specific capacity (Figure 3.14). This decreased electrochemical performance can be attributed to increased polymer loading, which fills the voids within the composite and blocks potential diffusion pathways, but leads to a nearly 3X enhancement in tensile strength (Table 3.1).

**Figure 3.14.** Electrochemical properties of pure CNF/PVDF composite. a) Cycling performances (0.2C) and (b) representative charge/discharge profiles (0.2C) of 67/33 (sample L, blue) and 50/50 (sample K, black) CNF/PVDF composites.

### 3.5 Conclusions

In conclusion, an approach to create 3D printable, free-standing, and CC-embedded composite electrodes was developed. This simple approach utilized a well-dispersed and directly castable mixture of active material, CNFs, and polymer to make printable electrode inks with a balance between electrochemical performance and mechanical integrity. We found that each component had a significant role in optimizing the overall performance of the printed electrode – CNFs promoted conductivity and the formation of a porous microstructure for high rate performance, active material varied the cell’s electric storage capacity, PVDF governed the mechanical properties, and the combination
of solvent, CNFs, and polymer all impacted the rheological properties. Free-standing electrodes of three common Li-ion battery active materials (Li$_4$Ti$_5$O$_{12}$, LiFePO$_4$, and LiCoO$_2$) were prepared, each demonstrating excellent cyclability and rate capability.
Ceramic Polymer Electrolyte Prepared by One-Step Dry Phase Inversion Method

4.1 Introduction

The realization of flexible Li-ion batteries is of particular interest because they possess higher energy density, higher operating voltage, and longer lifetime compared to alternatives such as alkaline batteries.\cite{ref1,ref2} Confounding this development, however, is a challenge stemming from the conventional manufacture of energy storage devices, resulting in the rigid form factors we are familiar with today (cylindrical, prismatic). Printed batteries present a means through which we could overcome this challenge, and would enable integration of the battery directly into the electronics fabrication process.\cite{ref48} This would both eliminate the need for separate battery holders that are attached post-fab, and significantly reduce the weight of the electronic device. Moreover, one could print onto a flexible substrate as opposed to a rigid one, thereby enabling enhanced design flexibility.

Filamentary printing is a strong candidate for this process owing to limited rheological restrictions (e.g., viscosity, particle size, etc.). There have been two reports on fabricating Li-ion batteries via this technique;\cite{ref68,ref73} however, they avoided the challenges associated with printing sequential, compositionally unique layers on top of one another by utilizing interdigitated architectures. Additionally, these works required high temperature annealing (600 °C) for adequate electrode function, prohibiting direct printing onto most flexible devices. It is well known that for all-printed batteries, coating the separator/electrolyte layer has been the most problematic.\cite{ref20} The printed battery membrane must meet all of its functional requirements (e.g., physically separate the electrodes, promote Li\textsuperscript{+} diffusion) without compromising the performance of the
underlying active layer during the printing process. There have been only limited reports that print both the separator/electrolyte and electrode layers,[23,25,27,30,73,95] and the demonstration of high rate performance out of such printed systems has not yet been established.

One of the biggest obstacles in achieving a high performance, printable membrane is a matter of controlling the porosity. The necessity for a methodology to print porous materials without additional processing steps has never been more evident. Battery membranes need to be microporous and as thin as possible, while maintaining good tensile strength, thermal stability, uniform pore-size distribution, and electrochemical stability.[96] This work represents a unique advancement in the fabrication of high performance, flexible, and printable ceramic polymer electrolytes. Such membranes were used directly after drying without additional post-processing steps, such as stretching, etching, or dipping in a coagulation bath, to impart desirable porosity. This material can also be printed directly over an electrode layer without sacrificing performance in either layer. One key advantage of this approach is that sequential printing gives rise to a tight and continuous interface between both layers, which is a desired trait for discharge voltage stability in a flexible energy storage device under mechanical abuse.

4.2 Experimental Methods

4.2.1 Electrode, Electrolyte, and Cell Fabrication

Lithium titanate (Li$_4$Ti$_5$O$_{12}$) and lithium iron phosphate (LiFePO$_4$) were purchased from the MTI Corporation. Carbon nanofibers (CNFs) (Pyrograf®-III PR-19-HT) were supplied by Applied Sciences Inc. Kynar® HSV 900 poly(vinylidene fluoride) (PVDF)
was provided from Arkema Inc. Nanodur® nano alumina powder (40-50 nm average particle size, 99.5% purity) was purchased through Alfa Aesar. 1-methyl-2-pyrrolidone (NMP) and glycerol were purchased from Sigma Aldrich.

Nanocomposite electrolytes were prepared by dissolving 0.1726 g PVDF in 3 mL NMP (or NMP/glycerol 95/5 w/w for samples made with the phase inversion process). For electrolyte membranes containing ceramic filler, 0.4030 g Al₂O₃ (70/30 Al₂O₃/PVDF w/w) was added and bath sonicated for 3 h. using a Branson 2510 bath sonicator. At this point the mixture is suitable for casting or printing (more details for printing are described in Chapter 6). For casting, the mixtures were transferred to a 6 cm diameter PTFE dish and dried at 90 °C. Once NMP was evaporated, the samples were placed under vacuum at 120 °C overnight to remove glycerol and any other remaining solvent.

The procedure for each composite electrode consisted of first dissolving PVDF in 5 mL NMP (or NMP/glycerol 95/5 w/w). Next, the CNFs were added and probe sonicated for 1 min. at 17% amplitude using a Sonics Vibra-Cell VCX 750 Probe Sonicator with a ¼ in. microtip. 100 mg active material was then added (CNF and PVDF loading was determined using the composite wt. ratios listed in the text and figure captions), and the mixture was bath sonicated for 10 min. The samples were shaken by hand several times during the sonication period for more thorough mixing. Finally, the mixtures were transferred to a 6 cm diameter PTFE dish and dried at 90 °C. Once NMP was evaporated, the samples were dried under vacuum at 120 °C overnight. Composite inks for printing were prepared using the same procedure as above, except the solids loading was doubled to increase the viscosity of the mixture and sonication intensity was increased to 21% for 2 min.
Casted electrolyte membranes were punched to 19.0 mm discs and composite electrode samples were punched to 9.5 mm diameter discs. Typical thicknesses of electrolytes used in this study were ~100 µm, although similar performance was observed in thicknesses as low as 30 µm. Typical weights of Li₄Ti₅O₁₂ and LiFePO₄ in each composite electrode disc ranged from 1.5-3.0 mg corresponding to sample thicknesses ranging between 100-200 µm, as measured by a Mitutoyo digital micrometer. Electrode samples were assembled versus Li foil under argon environment (<1 ppm H₂O and O₂) in 2325 coin cell configuration. Our polymer electrolytes, or Celgard 2325, were soaked in a liquid electrolyte solution (1 M LiPF₆ in 1:1 ethylene carbonate: diethyl carbonate by wt. (Novolyte Technologies)) and used as the separator.

4.2.2 Sample Characterization

Cross-sectional scanning electron microscopy (SEM) was performed using a FEI Quanta 600F SEM after cryo-fracturing samples while immersed in liquid nitrogen. Conductive electrode samples were imaged at a 5kV accelerating voltage without coating. Electrolyte samples were coated with a conductive 10 nm iridium coating to avoid charging artifacts and imaged using a 5 kV accelerating voltage. Ink rheology measurements were obtained using a TA Instruments ARES-G2 Rheometer. A flow sweep method was used to observe the apparent viscosity as a function of shear rate. The experiment was conducted at ambient temperature and the shear rates were varied in a logarithmic sweep from 0.1 to 100 s⁻¹ with a step equilibration time of 30 s. Inks were loaded on a 25 mm stainless steel plate with a constant gap of ~0.95 mm for each sample. All mechanical tensile tests were conducted on a TA Instruments DMA Q800 Dynamic Mechanical Analyzer in strain control mode with a constant strain rate of 5 % min⁻¹ at room temperature (ASTM D882). A preload force of 0.01 N was applied to compensate
for any take-up of slack. The composite films were cut into rectangular tensile specimens of 10-12 mm length and 3-4 mm width using a razor. The finished specimens were examined using a Zeiss Stemi DV4 optical microscope to ensure that there were no visible flaws from cutting. The thickness of each specimen was determined from the average of three measurements taken along the gauge length with a Mitutoyo micrometer. The surface area and porosity data were calculated by Brunauer–Emmett–Teller (BET) method based on N₂ adsorption–desorption isotherms at 77 K obtained using an ASAP 2020 surface area and porosimetry analyzer (Micromeritics Instrument Corporation). The samples were degassed at 120 °C under vacuum for 16 h. before running the measurement. For the wettability experiment, a 10 µL drop of liquid electrolyte was placed on the membrane and the time for the sample to fully wet was measured. Porosity was measured by completely immersing samples in liquid electrolyte overnight and massing after gently wiping excess electrolyte from the surface of membranes with a paper towel. Samples were massed before and after soaking and porosity was calculated as the volume of the absorbed liquid over the volume of the dry membrane. The volume of the liquid was calculated with the mass of the absorbed liquid and a density of 1.22 g cm⁻³ for liquid electrolyte.

Thermal stability was studied by placing both our nanocomposite membrane and Celgard 2325 on a hotplate for 5 min. at increasing temperatures. The exact temperatures used are displayed in Figure 4 and were determined using a non-contact IR thermometer. Shrinkage was monitored by taking photos after each treatment temperature and by measuring the dimensions of each sample.
4.2.3 Electrochemical Characterization

Cells were cycled using a Maccor series 4000 battery test system. LiFePO₄ and Li₄Ti₅O₁₂ were investigated for cycling stability at a constant 0.2C current rate between 2.0-4.3 V and 1.0-2.1 V vs. Li/Li⁺, respectively. The rate studies were carried out in a similar manner, with each half-cell tested for 5 cycles at each rate, i.e. 0.2C, 0.5C, 1C, 2C, 5C, and 0.2C. All C rates were calculated with 1C being defined as 170 mA g⁻¹ and 175 mA g⁻¹ for LiFePO₄ and Li₄Ti₅O₁₂, respectively.

The conductivity cells consisted of two parallel, stainless steel blocking electrodes (A = 1.89 cm²) and a membrane soaked with liquid electrolyte. Cells were allowed to age for at least 8 h in order to activate the membrane before measurements were recorded. Temperature was controlled by a Tenney environmental chamber and recorded with a k-type thermocouple. The ionic conductivity was measured every 10 °C from 20 to 60 °C. The cells were allowed to equilibrate for 1 h at each temperature before the next measurement was recorded. Measurements were performed with a Gamry Reference 3000 at open circuit potential by applying an AC-amplitude of 5 mV over a frequency range from 1 Hz to 1 MHz. The ionic conductivity was calculated according to equation (17):

\[ \sigma = \frac{l}{R_b \times A}, \]

where \( l \), \( R_b \), and \( A \) are the thickness of the membrane (cm), bulk resistance (Ω), and area of the electrode (cm²), respectively. Symmetric Li/electrolyte/Li cells for dendritic failure testing were prepared in 2325 coin cells. Liquid electrolyte saturated membranes (12.7 mm diameter) were placed between 10.0 mm diameter Li foil discs. After aging for 8 h., cells were subjected to an alternating ±0.15 mA cm⁻² current density (~0.2C rate) for 4.5 h. with a 30 min. rest between.
4.5 Results and Discussion

Our approach involved the combination of phase inversion and high ceramic loading to develop high performance and printable Li-ion battery electrolytes. The dry phase inversion method used a mixture of NMP (a good solvent) to dissolve PVDF and glycerol to act as a weak non-solvent. This dual solvent system yielded high porosity after drying owing to phase separation into a solid-like polymer rich phase and a liquid-like polymer lean phase due to the higher boiling point of the non-solvent, glycerol. Phase inversion has been used to achieve highly porous battery membranes,\textsuperscript{[97-101]} however, the resulting pore structure typically exhibits a large cellular- or finger-like morphology that is not ideal for high rate performance or safety because it does not inhibit dendritic lithium growth. To overcome this issue, a high loading (70 wt.%) of Al\textsubscript{2}O\textsubscript{3} nanoparticles (40-50 nm) was incorporated into a PVDF matrix to help reduce pore size as well as aid in lithium dendrite suppression, thermal stability, and electrolyte wetting. Although there have been several reports that combined phase inversion with ceramic fillers using either coagulation baths\textsuperscript{[102-105]} or non-solvent incorporated (“dry”) methods,\textsuperscript{[106-110]} there are still many opportunities for improvement, especially in the field of additive manufacturing.

Figure 4.1a-d qualitatively illustrates the effect of phase inversion and Al\textsubscript{2}O\textsubscript{3} addition on electrolyte films prepared via casting, which closely mimics filamentary printing of solvent-based inks. Inks containing only PVDF (PE and PE-PI) (Figure 4.1a,b) led to undesirable shrinkage and out-of-plane buckling. Interestingly, when NMP alone was used to prepare an Al\textsubscript{2}O\textsubscript{3}/PVDF ceramic polymer electrolyte (CPE), the color turned from white to orange/brown during heated drying (Figure 4.1c). This color change can
be explained by an Al₂O₃-catalyzed dehydrofluorination reaction in PVDF to form conjugated double bonds along the main chain and crosslinking between polymer chains.\textsuperscript{[111,112]} When both phase inversion and Al₂O₃ were used together (CPE-PI) large area, flexible composite films that maintained their casting shape without degradation could easily be obtained (Figure 4.1d,e). These properties were attributed to the interaction between glycerol and Al₂O₃, which protected PVDF from dehydrofluorination. Glycerol has been shown to interact strongly with Al₂O₃ by forming a bridging alkoxy bond with one of the primary alcohols and a hydrogen bond with the secondary alcohol group.\textsuperscript{[113]}

Figure 4.1f shows apparent viscosity as a function of shear rate of the electrolyte inks prepared in this study. PE and PE-PI displayed nearly identical rheological properties, suggesting that glycerol did not affect the polymer component. Not surprisingly, adding 70 wt.% Al₂O₃ to an ink containing PVDF and NMP caused a substantial increase in apparent viscosity at all shear rates tested (e.g. ~14x increase at 1 s\(^{-1}\)), likely due to a flocculated Al₂O₃ suspension.\textsuperscript{[114]} Surprisingly, adding glycerol to the CPE ink (CPE-PI) reduced the apparent viscosity to levels consistent with the PE or PE-PI inks containing only PVDF and solvent. The strong interaction between glycerol and Al₂O₃ created a solvation layer around the nanoparticles that aided in a more uniform dispersion and deflocculation of Al₂O₃ throughout the electrolyte ink.
Figure 4.1. Overview of the printable electrolytes prepared in this study. a-d) Schematic illustration of the electrolyte ink compositions and corresponding dried films after casting ink in a 6 cm PTFE dish. e) Photograph of a flexible CPE-PI membrane (6 cm diameter). f) Apparent viscosity as a function of shear rate of all electrolyte inks prepared in this study.

Scanning electron microscopy (SEM) was used to characterize the cross-sections of three different electrolyte films, PE-PI, CPE, and CPE-PI (Figure 4.2), which showed vastly different morphologies. PE-PI (Figure 4.2a-c) was dominated by large voids (ca. 5 µm) over the majority of the film with the walls of these voids being comprised of many smaller, cellular pores (Figure 4.2b). In contrast, the morphology appeared denser in CPE because the phase inversion agent was not used to generate a porous structure (Figure 4.2d-f). SEM showed Al₂O₃ was clearly present, but PVDF appeared to fill in
potential voids around the ceramic. Finally, in the case of CPE-PI, a favorable microstructure was achieved containing many submicron pores (Figure 4.2g-i). The formation of such microstructure can be explained by the drying mechanism of the phase inversion process and the strong interaction between Al₂O₃ and glycerol.¹¹³ Due to the slower evaporation of the weak non-solvent (glycerol), a solid-like PVDF phase and a liquid-like glycerol phase were formed as the good solvent (NMP) evaporated. As this occurred, many ceramic particles preferentially occupied the glycerol phase. Since PVDF is insoluble in this phase, the resultant film was left with small voids between Al₂O₃ particles after complete drying. This hypothesized model is directly supported by Brunauer–Emmett–Teller specific surface area (S\textsubscript{BET}), which was run on all of the samples discussed above, as well as pure Al₂O₃ (Figure 4.3). Al₂O₃ and PVDF displayed a S\textsubscript{BET} of 33 and 3 m\textsuperscript{2} g\textsuperscript{-1}, respectively. CPE exhibited a S\textsubscript{BET} of only 4 m\textsuperscript{2} g\textsuperscript{-1}, suggesting that PVDF coated the majority of the Al₂O₃. On the other hand, CPE-PI exhibited a S\textsubscript{BET} of 17 m\textsuperscript{2} g\textsuperscript{-1} (roughly 50% of neat Al₂O₃) indicating the retention of void space between nanoparticles, which can potentially act as Li⁺ transport pathways.
Figure 4.2. SEM images and schematic representation of polymer electrolytes. a,b) Cross-sectional SEM images and c) schematic representation of PE-PI. d,e) Cross-sectional SEM images and f) schematic representation of CPE. g,h) Cross-sectional SEM images and i) schematic representation of CPE-PI.

Figure 4.3. N\textsubscript{2} adsorption and desorption isotherms of pure Al\textsubscript{2}O\textsubscript{3}, a CPE-PI, a CPE, and a PE-PI.
Mechanical properties of electrolytes used in this study are displayed in Figure 4.4. CPE and PE-PI displayed poor ultimate strain values of 1.3 and 3.9%, respectively. The low strain to failure observed for PE-PI can be explained by the resultant microstructure, composed primarily of large, void-like pores (Figure 4.2a). In the case of CPE, the low ultimate strain likely stemmed from covalent crosslinking of neighboring PVDF chains due to Al2O3-catalyzed dehydrofluorination, rather than an unfavorable pore structure. The resulting embrittlement of this film was reflected in its high modulus relative to the other samples (Figure 4.4b). Both PE and CPE-PI, on the other hand, exhibited an ultimate strain of ~28%, but the tensile strength of the latter decreased by 6x owing to increased porosity. However, the high strain to failure achieved by CPE-PI makes it suitable for flexible battery applications because this characteristic is closely related to strain tolerance.115
Figure 4.4. Mechanical properties of electrolyte samples. a) Representative stress-strain curves. The mean (b) modulus, (c) tensile strength, and (d) strain at failure were calculated from five or more samples at each loading. Error bars are included which display the 95% confidence interval for each sample.

A summary of various physical properties of the membranes prepared in this study, along with ionic conductivities of said membranes soaked with electrolyte, can be found in Table 4.1. As expected, PE showed limited porosity (21%), and the addition of ceramic in CPE had an insignificant effect on this value (25%). Both of the electrolytes prepared with phase inversion using glycerol, however, displayed high porosities (>50%) exceeding that of Celgard 2325 (38%). The ionic conductivity of each membrane infiltrated with electrolyte was observed to correlate with both the materials used and the solvents present. The use of phase inversion resulted in a two order of magnitude increase in conductivity when applied to similar material compositions. For example,
CPE exhibited a low conductivity of 0.0080 mS cm\(^{-1}\) compared to 0.82 mS cm\(^{-1}\) for CPE-PI. Interestingly, while the porosity was comparable for both CPE-PI and PE-PI, the ionic conductivity was 4x less in the latter. Even though the majority of its morphology consisted of large, open pores, the smaller, cellular pores in PE-PI likely reduced the ionic conductance of this film. In contrast, CPE-PI had uniform porosity throughout its entire thickness, resulting in the highest observed conductivity among the electrolytes prepared in this study and was on par with Clegard 2325 (0.64 mS cm\(^{-1}\)).

Table 4.1. Properties of composite battery electrolytes and Celgard 2325.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Composition</th>
<th>Ratio(^a)</th>
<th>Solvent</th>
<th>Porosity(^b) [%]</th>
<th>(\sigma_i) ([\text{mS cm}^{-1}])</th>
<th>(E_a) ([\text{kJ mol}^{-1}])</th>
<th>TS(^c) [MPa]</th>
<th>(\varepsilon_f) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE-PI</td>
<td>PVDF / Al(_2)O(_3)</td>
<td>30 / 70</td>
<td>NMP / Glycerol</td>
<td>51</td>
<td>0.82</td>
<td>10.6</td>
<td>5.4 ± 0.3</td>
<td>28.2 ± 1.7</td>
</tr>
<tr>
<td>CPE</td>
<td>PVDF / Al(_2)O(_3)</td>
<td>30 / 70</td>
<td>NMP</td>
<td>25</td>
<td>0.0080</td>
<td>43.6</td>
<td>14.2 ± 0.7</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>PE-PI</td>
<td>PVDF</td>
<td>100</td>
<td>NMP / Glycerol</td>
<td>53</td>
<td>0.20</td>
<td>18.4</td>
<td>3.5 ± 0.2</td>
<td>3.9 ± 0.5</td>
</tr>
<tr>
<td>PE</td>
<td>PVDF</td>
<td>100</td>
<td>NMP</td>
<td>21</td>
<td>0.0017</td>
<td>52.9</td>
<td>32.9 ± 0.6</td>
<td>28.0 ± 2.5</td>
</tr>
<tr>
<td>Celgard 2325</td>
<td>PE/PP(^g)</td>
<td>--</td>
<td>--</td>
<td>38</td>
<td>0.64</td>
<td>10.8</td>
<td>70.7 ± 9.9(^a)</td>
<td>94.7 ± 7.8(^h)</td>
</tr>
</tbody>
</table>

\(^a\) Sample ratios by wt.\%; \(^b\) Porosity: calculated as the volume of the absorbed liquid electrolyte over the volume of the dry membrane; \(^c\) Room temperature ionic conductivity; \(^d\) Activation energy; \(^e\) Tensile strength; \(^f\) Strain to failure; \(^g\) Polyethylene / Polypropylene; \(^h\) Celgard properties in the machine direction (MD).

Figure 4.5 compares the electrochemical performances of cells consisting of CPE, CPE-PI, or Celgard 2325 electrolyte membranes. Cells were fabricated in the half-cell configuration using a current collector-embedded, 40/40/20 lithium iron phosphate (LiFePO\(_4\))/carbon nanofiber (CNF)/PVDF composite electrode. The rate performances and corresponding voltage profiles (Figure 4.5a,b) suggest that CPE-PI promotes Li\(^+\) diffusion kinetics to the same extent as commercial Celgard 2325. Both displayed very stable capacities and flat voltage profiles at each C-rate (\(e.g., 156\) and 102 mAh g\(^{-1}\) at 0.2C and 5C, respectively for CPE-PI). This excellent performance directly supported
the hypothesis that Li\textsuperscript{+} diffusion could readily occur through the voids between neighboring Al\textsubscript{2}O\textsubscript{3} particles. In contrast, CPE exhibited severely limited rate performance and, in fact, zero capacity at 2C and 5C. This shortfall in rate performance was attributed to PVDF occupying void space and coating the Al\textsubscript{2}O\textsubscript{3} particles, therefore inhibiting transport.

Next, CPE-PI was tested for 100 cycles at a 0.2C current rate (Figure 4.5c). This electrolyte maintained comparable performance to the commercial separator throughout the duration of the test, highlighting its excellent stability as a potential high performance printable electrolyte. Figure 4.5d compares the electrolyte wettability of CPE-PI and a commercial separator by applying the same amount of liquid electrolyte to the center of each sample. Our composite electrolyte showed near complete wet-out within 30 min., whereas the commercial material did not wet beyond the initial application site. From a commercial point-of-view, good wettability can shorten the electrolyte filling step during assembly and extend the battery’s lifetime, whereas poor wettability can do the exact opposite by increasing the internal ionic resistance.\textsuperscript{[116]}
It is worth mentioning that PE-PI did not function properly as a battery electrolyte. Although highly porous, this material often failed as a result of electrical shorting, likely due to dendritic lithium growth through the large pores. To better assess the risk of dendrite formation through each of the electrolytes prepared in this study, symmetric Li/electrolyte/Li cells were prepared and subjected to an alternating ±0.15 mA cm\(^{-2}\) current (~0.2C rate, Figure 4.6). During this test, PVDF films (PE and PE-PI) failed...
within 85 h. As expected, the addition of Al\textsubscript{2}O\textsubscript{3} impeded dendritic failure in both CPE and CPE-PI, but the former failed at 500 h., whereas the latter functioned without failure throughout the duration of the test (>4000 h.). One potential explanation for the better dendrite suppression and safety of CPE-PI over CPE is due to enhanced Al\textsubscript{2}O\textsubscript{3} dispersion leading to better tortuosity and more uniform current flow. For comparison, Celgard 2325 exhibited failure after ~3400 h.
Figure 4.6. Lithium metal plating/stripping from a Li|Li cell cycled at 0.15 mA cm\(^{-2}\) with 1M LiPF_6-EC/DEC electrolyte in various membranes.  

a) Schematic representation of the cell configuration.  
b-f) Voltage as a function of time for symmetric cells that were subjected to an alternating ±0.15 mA cm\(^{-2}\) current density (~0.2C rate). Here, current was sourced until a precipitous change in voltage was observed, signaling failure due to dendritic penetration through the electrolyte.
The thermal properties of the electrolytes prepared in this study are shown in Figure 4.7. Celgard showed 3% dimensional shrinkage at 105 °C and 34% shrinkage at 140 °C. This material continued to shrink until catastrophic failure occurred due to melting of its constituent polyethylene and polypropylene layers, which occurs at 133 and 158 °C, respectively. The large shrinkage before reaching the melting points of both polymers can be explained by shape recovery behavior resulting from the stretching process used to induce adequate porosity during manufacturing. In contrast, during the same test, CPE-PI displayed excellent thermal stability due to the high ceramic loading, showing complete shape retention until 190-200 °C, where only 3-5% dimensional shrinkage was observed. This characteristic satisfies the US Advanced Battery Consortium’s (USABC) goal for thermal shrinkage of battery separators (<5% at 200 °C).

Figure 4.7c shows the temperature-dependence of ionic conductivity for the composite electrolyte samples and Celgard 2325. Each sample showed Arrhenius behavior within the temperature range studied, and thus invoked application of the Arrhenius equation (18):

\[
\sigma_i = \sigma_0 \exp\left(-\frac{E_a}{RT}\right),
\]

where \(\sigma_i\) is the ionic conductivity, \(\sigma_0\) is a pre-exponential factor, \(E_a\) is the activation energy, \(R\) is the gas constant, and \(T\) is the absolute temperature. In order to easily fit the data to this Arrhenius relationship, equation (18) can be manipulated by taking the natural log of both sides and re-arranging:

\[
\ln(\sigma_i) = \left(-\frac{E_a}{R}\right) \frac{1}{T} + \ln(\sigma_0),
\]
and the activation energy can be easily obtained from the slope of the gradient multiplied by the gas constant. The activation energy for CPE-PI was similar to that of Celgard 2325 (10.6 vs. 10.8 kJ mol$^{-1}$, respectively), which corroborated with how well these two materials performed over the range of C-rates tested (Figure 4.5a). This suggests that the mechanism of ionic conduction - involving the diffusion of solvated ions in the liquid electrolyte - was the same for these two materials. PE and CPE showed the highest activation energies (52.9 and 43.7 kJ mol$^{-1}$, respectively) and lowest ionic conductivity, likely attributed to an ionic conduction mechanism in which ions migrate via the structural relaxation of polymer chains. Finally, the activation energy achieved by PE-PI fell between the aforementioned materials (18.4 kJ mol$^{-1}$). Given the bimodal pore structure of this material, consisting of both large and small, cellular pores (Figure 4.2b), it is probable that both ionic conduction mechanisms were invoked. Within the large pores, ionic conduction occurred via the diffusion of lithium ions in the liquid electrolyte, while within the small, non-connected pore region the ions migrated by the structural relaxation of the polymer chains. However, the presence of the large pores ultimately caused PE-PI to microshort when enacted as a battery membrane (see Figure 4.6f).
Figure 4.7. Thermal properties of various electrolytes prepared in this study. a,b) Thermal shrinkage comparison between CPE-PI and Celgard 2325. Photographs were taken of each sample after heating on a hotplate for 5 min. at each temperature. The dashed line in b) shows the goal for acceptable thermal shrinkage for separators (<5% at 200 °C).[116] c) Temperature-dependence of ionic conductivity.

4.6 Conclusions

We have demonstrated a dry phase inversion technique geared toward printable and controlled porosity in Li-ion battery electrolytes with high temperature and high rate performances. Our approach utilized a unique NMP/glycerol solvent system to generate porosity within a polymer matrix. When used in combination with a nanoceramic Al₂O₃ filler, a desirable pore structure was obtained throughout the membrane. These
electrolytes offered electrochemical performance on par with commercial separator films even at current rates as high as 5C, with better thermal stability and electrolyte wetting. This technology is an enabling step toward direct integration of flexible power in confined areas or on non-planar device surfaces through filamentary printing.
5 Poly(vinylidene fluoride)–Alumina Nanocomposite as an Ionic Liquid Host for Enhanced Safety, Ion Transport and Thermal Stability

5.1 Introduction

During the development of our 3D printable electrolyte ink in Chapter 4, it was realized that this material possessed the necessary attributes for utilization in Li-ion batteries requiring high temperature operation. In contrast to Celgard 2325, the ceramic polymer electrolyte developed by phase inversion (CPE-PI) withstood temperatures up to 180 °C without shrinkage (see Figure 4.7). There is, indeed, a great demand for energy storage devices capable of operating in high temperature environments (80-300 °C) for applications in automotive, aviation, aerospace, and defense.\textsuperscript{118} For example, power sources are needed for high temperature electronics around engines where temperatures can easily reach 150 °C. Unfortunately, traditional Li-ion batteries using organic electrolytes are often limited to temperatures not exceeding 60-80 °C due to the nature of the decomposition reaction between solvents (\textit{e.g.}, EC, DEC, DMC, EMC, PC) and lithium hexafluorophosphate.\textsuperscript{119} Further, commercial polyolefin separators (\textit{e.g.}, Celgard 2325) are thermally limited by an intrinsic shutdown temperature (130 °C in the case of polyethylene), whose purpose is to prevent thermal runaway in the event of a short circuit. Thus, both the organic electrolyte and separator materials would need to be replaced to achieve a Li-ion battery capable of high temperature operation.

Ionic liquids (ILs), which are molten salts at room temperature, are gaining much attention as battery electrolytes because of their high thermal stability, low volatility, and low flammability. Moreover, unlike other alternatives to liquid electrolytes, such as solid ceramic electrolytes, ILs still possess wetting properties with the electrode that facilitate electrolyte diffusion while reducing the risk of electrolyte leakage. These
properties make ILs an excellent choice for special applications requiring power sources to operate in high temperature conditions. Among the known ILs, those containing imidazolium based cations have found the most success for Li-ion battery application owing to acceptable ionic conductivities. In general, the ionic conductivity of an IL is inversely proportionally to its viscosity (typically, one to two orders of magnitude higher than that of organic electrolytes), as described by the Walden rule:\(^{[120]}\)

\[
\Lambda = k \frac{k}{\eta_v}, \text{ where } \Lambda = \Sigma \lambda_i
\]

where \(\Lambda\) is the molar conductivity, \(\eta_v\) is the viscosity, \(k\) is a temperature dependent constant, and \(\lambda_i\) is the ionic conductivity of ion species \(i\).

In this chapter, IL-based electrolytes are fabricated in the form of free-standing films by immersing membranes into a solution of lithium bis(trifluoromethanesulfonamide)/1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (\([\text{BMIM}][\text{TFSI}]\)). We study the thermal transport properties of the IL solution in both CPE-PI and commercial Celgard 2325 and find enhancements in ionic conductivity and electrochemical performance for CPE-PI, which likely stem from enhanced wettability of the material with the IL.

5.2 Experimental Methods

5.2.1 Materials and Cell Fabrication

NMP, glycerol, and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) were purchased from Sigma Aldrich, and \([\text{BMIM}][\text{TFSI}]\) was purchased from EMD Millipore.

Nanocomposite electrolytes were fabricated as described in section 4.2.1. A 0.6 M LiTFSI-[BMIM][TFSI] solution was prepared in a nitrogen glovebox by dissolving 0.1 g LiTFSI in 0.7 g [BMIM][TFSI] in an 8 mL vial. The IL solution was then stirred in the
sealed vial overnight at 50 °C under inert atmosphere. The procedure for the fabrication of composite LiFePO₄ electrodes is described in section 3.2.3.

Casted electrolyte membranes were punched to 19.0 mm discs and composite electrode samples were punched to 9.5 mm diameter discs. Typical thicknesses of electrolytes used in this study were ~150 µm.

5.2.2 Material Characterization

Contact angle measurements were taken with an Attension contact angle meter (Biolin Scientific). Thermal cells (LiFePO₄//Li) were cycled using a Maccor series 4000 battery test system, with battery holders extended with copper wiring into an oven (Memmert Beschickung loading model 100-800). The ionic conductivity cells consisted of two parallel, stainless steel blocking electrodes (A = 1.89 cm²) and a membrane soaked with IL solution. Cells were allowed to age for at least 2 h in order to activate the membrane before measurements were recorded. In the case of the IL solution, conductivity measurements were taken using a 0.0433 cm thick polypropylene (PP) disc with a 0.635 cm diameter cut-out removed from its center. Excess IL solution was used to fill the electrolyte well formed by the PP disc laid into a 2325 coin cell. The ionic conductivity was measured every 20 °C from 30 to 150 °C. Cells were allowed to equilibrate for 1 h. at each temperature before the next measurement was recorded. Measurements were performed with a Gamry Reference 3000 at open circuit potential by applying an AC-amplitude of 10 mV over a frequency range from 1 Hz to 1 MHz. The ionic conductivity was calculated according to equation (17). Lithium ion transference numbers (T_{Li⁺}) were measured using symmetric Li/electrolyte/Li cells prepared in 2325 coin cells. Experimental details for T_{Li⁺} calculation are provided in the discussion.
5.3 Results and Discussion

The process to fabricate our high temperature electrolyte is illustrated in Figure 5.1a, and first involved preparing CPE-PI by casting or printing, as described in Chapter 4. Electrolyte membranes were then imbibed with 0.6 M LiTFSI-[BMIM][TFSI], which is similar to concentrations of IL-based electrolytes prepared in other works.[121-123] Large area sheets of CPE-PI could be prepared by blade coating (Figure 5.1b) for lower temperature testing (< 100 °C, where thicknesses of ca. 60 µm were acceptable to prevent dendrite puncture), otherwise casting was necessary to prepare films of ca. 150 µm thickness for high temperature testing. These films were highly flexible, as illustrated by Figure 5.1c, but more importantly, the favorable microstructure of the CPE-PI films was maintained up to thicknesses of ca. 150 µm (Figure 5.1d).
Figure 5.1. Fabrication method for the high temperature CPE-PI electrolyte. (a) Schematic of the fabrication process with the incorporation of the IL solution. (b,c) Blade coated films (dry) depicting the flexible nature of the composite. (d) Cross-sectional SEM micrograph showing the electrolyte microstructure.

Figure 5.2a shows the temperature dependence of ionic conductivity of both the neat IL solution and when it was absorbed into either CPE-PI or Celgard 2325. At room temperature, the ionic conductivity of the neat IL solution, and CPE-PI and Celgard imbibed with the IL were 1.4, 0.21, and 0.023 mS cm\(^{-1}\), respectively. While it was expected for the ionic conductivity to drop when implementing either membrane material, the interaction between the IL and Celgard was observed to reduce overall ionic mobility to the greatest extent. More importantly, at temperatures exceeding 110 °C, the polyethylene component of Celgard began to melt and close up the pore structure of the membrane, thus severely inhibiting ionic motion. The DSC thermograms in Figure 5.2b
indicated that the polyethylene melting point occurred at 132 °C for Celgard, whereas the melting point was increased to 166 °C in CPE-PI owing to its PVDF component. Regardless, the ionic conductivity dependence on temperature for the IL solution in both materials followed a Vogel-Tamman-Fulcher (VTF) behavior, as described by equation (20):\(^{124-126}\)

\[
\sigma(T) = AT^{-1/2}\exp\left(\frac{-B}{T-T_0}\right),
\]

(20)

where \(A\) = pre-exponential factor (S cm\(^{-1}\) K\(^{-1/2}\)),

\(T\) = absolute temperature (K),

\(B\) = psuedoactivation energy (K), \(E_a/R\)

\(T_0\) = ideal glass transition (K).

In accordance with its definition, the value of \(T_0\) was taken to be 50° below the glass transition,\(^{127}\) and was thus assumed to be 131 K for [BMIM][TFSI]. The fitted parameters of the VTF equation are presented in Table 5.1. It is interesting to note that the pre-exponential factor \(A\), which is proportional to the number of charge carriers, was three times larger for CPE-PI than for Celgard. A slight decrease in activation energy was also observed for CPE-PI (9.4 versus 10.9 kJ mol\(^{-1}\)), although both membranes exhibited a higher activation energy relative to the neat 0.6 M LiTFSI-[BMIM][TFSI] solution (8.2 kJ mol\(^{-1}\)). It is probable that the nature of the ceramic within CPE-PI promoted the absorption of a higher amount of the ionic liquid throughout the material, thus impacting the ion distribution and the effective free volume.\(^{123}\)

To corroborate this point, the contact angle of an IL solution droplet was monitored as a function of time for both materials (Figure 5.2c). The polyolefin separator exhibited a contact angle of 58° after 10 sec., which was about three times larger than that of CPE-
PI at 20 °C. This suggested that the IL solution could readily infiltrate the free volume of CPE-PI owing to a preferential interaction between the IL and polymer matrix, yielding an order of magnitude higher effective ionic conductivity in CPE-PI vs. Celgard. It is reasonable to assume that the lower porosity (38 vs. 51% for Celgard and CPE-PI, respectively) and hydrophobic nature of the polyolefin film led to poor surface affinity with the IL and in turn hindered ionic mobility.\cite{128,129}

While Figure 5.2a depicts the overall ionic motion for the IL solution hosted by either Celgard or CPE-PI, it does not uniquely represent the Li-ion contribution to the movement of charge, which is a more significant metric dictating battery performance. The unique nature of the IL entails the existence of several charged species in addition to Li-ions, which imposes two issues. The first is that the overall ionic motion is often misleading for ILs given that it represents the motion of both the cation and anion included in the IL, as well as the incorporated Li-salt. The second issue is that unless properly balanced, a low contribution of the Li-ion to the total current in the IL leads to an increase in concentration overpotential, which degrades device operation.

To gauge this contribution, it is necessary to measure the Li-ion transference number ($T_{Li^+}$). This was done using a DC polarization technique first proposed by Bruce, Evans and Vincent,\cite{130} wherein an electric field is applied to a symmetric Li cell (Li/electrolyte/Li). The nature of this cell is such that the two Li electrodes are non-blocking only to the migration of Li-ions under the electric field. Thus, the final, steady-state current associated with the flux of Li-ions can be separated from the initial current associated with the total ionic movement. $T_{Li^+}$ can then be calculated according to equation 21:

98
\[ T_{Li^+} = \frac{I_{SS}(\Delta V - I_0 \cdot R_0)}{I_0(\Delta V - I_{SS} \cdot R_{SS})} \]  

(21)

where \( I_{0/ss} \) = initial/steady-state current,

\( R_{0/ss} \) = initial/steady-state interfacial resistance,

\( \Delta V \) = applied voltage (30 mV).

Figure 5.2d shows the evolution of \( T_{Li^+} \) for both Celgard and CPE-PI. Generally, the values showed to be equivalent between the two materials at temperatures exceeding 30 °C, indicating that with the addition of thermal energy the solvation of Li-ions in the IL became constant regardless of the host material. However, at room temperature there was indeed a statistically significant difference between \( T_{Li^+} \) values observed for Celgard versus CPE-PI. One potential reason for this difference at room temperature could stem from better IL wetting on CPE-PI, as discussed previously. With increasing temperature, however, the reduced viscosity of the IL made mobility of the Li-ion comparable regardless of host material.

**Table 5.1.** Fitting parameters obtained by applying the VTF model to the temperature dependent conductivity data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Representation</th>
<th>VTF Fitting Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[K cm(^{-1}) cm(^2) mol(^{-1})]</td>
<td>Celgard 2325</td>
</tr>
<tr>
<td>A</td>
<td>Pre-exponential factor proportional to the number of charge carriers</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>Psuedoactivation Energy</td>
<td>1316</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>Second-order thermo-dynamic transition related to a state of zero conformational entropy</td>
<td>131</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>Coefficient of determination</td>
<td>0.995</td>
</tr>
<tr>
<td>( E_a )</td>
<td>Activation Energy</td>
<td>10.9</td>
</tr>
</tbody>
</table>
Figure 5.2. Evaluation of thermal properties and wetting capability of the IL solution with both Celgard 2325 and CPE-PI. (a) Temperature dependence of ionic conductivity. (b) DSC thermograms. (c) Contact angles of the IL solution measured on Celgard 2325 and CPE-PI films as a function of time. Inset photographs show the equilibrated contact angle of the IL solution on Celgard 2325 (top) and CPE-PI (bottom). (d) Evolution of $T_{Li^+}$ with temperature.

The effect of temperature on electrochemical performance was evaluated using half-cells with LiFePO$_4$ as the working electrode (Figure 5.3). The cell implementing Celgard was barely functional at 20 °C, yielding only very low capacity and a large voltage hysteresis of 1.5 V (Figure 5.3a). We attribute this behavior primarily to the poor wetting of the polyolefin film with the IL solution, therefore leading to increased ionic resistance. While a significant improvement of this cell’s performance was observed at 50 °C (Figure 5.3b), the voltage hysteresis still showed to be larger than that observed for the
CPE-PI thermal cell (0.23 V vs. 0.17 V). By 130 °C, the Celgard cell was unable to complete a delithiation cycle, and the voltage started to behave erratically and tend toward zero (Figure 5.3f). In contrast, it was observed for CPE-PI that the increasing temperature created a progressively lower voltage hysteresis between the lithiation/delithiation curves (Figure 5.3d-f). While a reasonable capacity of 130 mAh g⁻¹ was indeed achieved at 20 °C, the overpotential was too large (0.49 V) to afford viable long-term performance; this concern was mitigated once the temperature was elevated to 50 °C, where the device reached full capacity (160 mAh g⁻¹) with minimal hysteresis (0.17 V). Finally, we were able to achieve high temperature Li-ion performance at 130 °C using CPE-PI. We observed that the cell’s voltage hysteresis was even further reduced and full capacity was maintained when using CPE-PI as a IL host matrix. Both the superior wetting capability and enhanced ionic transport promoted by the CPE-PI host matrix afforded this improved performance. Further, the refractory nature of the ceramic component aided in the achievement of high temperature stability.
Figure 5.3. Evaluation of the voltage hysteresis as a function of temperature for LiFePO$_4$/Li cells using Celgard 2325 versus CPE-PI. Voltage hysteresis observed for representative galvanostatic charge/discharge curves (0.1C rate) for Celgard 2325 (a-c) and CPE-PI (d-f). Delithiation and lithiation refer to Li$^+$ leaving or entering the working electrode.
5.4 Conclusions

We have demonstrated an IL-based electrolyte using our CPE-PI membrane as a host matrix, which exhibited superior performance relative to Celgard 2325 over a large temperature range from 20 to 130 °C. The effect of temperature on ionic conduction was evaluated for the IL in CPE-PI, and it was shown that the interaction between the two materials favored enhanced ion mobility and electrochemical performance versus the Celgard control. Finally, with the implementation of CPE-PI as an IL host, we were able to demonstrate a working Li-ion cell at 130 °C, which is a significant step to enable specialty applications for DoD, aerospace, and/or automotive.
6 All-Component 3D-Printed Li-Ion Batteries

6.1 Introduction

One of the biggest obstacles to enable sequentially printed batteries via additive manufacturing (AM) has been the unfavorable interaction between each component layer (current collector, electrode, and electrolyte) during deposition. For example, it is commonly observed that coating a solution on top of a porous electrode structure results in penetration of the two materials, and thus severely limited cell performance. To circumvent this issue, others have adopted electrode configurations that do not require sequential stacking, such as side-by-side architectures.\textsuperscript{68,73} A significant advantage of 3D printing each layer over top of one another, however, is the good interfacial adhesion expected to result. For instance, while conventional batteries are susceptible to component shifting during assembly – which can lead to shorting, thermal runaway, and voltage instability – sequential printing of each Li-ion battery component would mitigate this issue. Unfortunately, while a few reports have explored the ability to sequentially 3D-print Li-ion batteries, several issues remain apparent.

In two separate works employing screen-printing to fabricate Li-ion batteries, a gel polymer electrolyte was used where a lithium salt-based liquid electrolyte was incorporated into a polymer ink.\textsuperscript{23,25} Unfortunately, these types of gel electrolytes often lack the mechanical integrity necessary to physically separate the anode and cathode, leading to electrical shorting. Additionally, such electrolytes utilize moisture sensitive lithium salts and carbonate mixtures that can decompose and drastically limit long term battery stability. Working in inert environments (e.g., Ar glovebox) or dry rooms can alleviate these challenges, but ease of scalability for these printable batteries is restricted. In another report, ink-jet printing was used to deposit an ionogel electrolyte;\textsuperscript{27} still, its
lack of mechanical integrity yielded the use of a fiberglass membrane necessary to maintain physical separation between the electrodes.

Singh et al.’s paintable battery was the first study to demonstrate a successfully printed separator layer without the need for an additional support layer. Their separator solution was composed of poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP), poly(methyl methacrylate) (PMMA) and silica (SiO₂) dispersed in acetone. However, where they were able to exploit the fast evaporation of acetone as a processing advantage in their airbrush printing method, we will in fact find this aspect to be disadvantageous to filamentary printing. The fast evaporation of acetone coupled with the manner in which the ink is dispensed in filamentary printing results in both nozzle clogging and non-uniform drying kinetics which drastically alter the final film porosity. Interestingly, the only other studies to use filamentary printing to fabricate a Li-ion battery avoided the separator layer all together, instead using a predefined distance between electrodes that was later filled with liquid electrolyte or a dense, ceramic polymer electrolyte that severely limited high rate performance. This approach may be viable for microbatteries, but as the size of the battery is scaled up (especially in the z-direction), the risk of the electrodes collapsing and causing a short is more likely to occur. Therefore, a more reliable method of fabricating Li-ion batteries for novel 2D and 3D designs is required.

In this chapter, we explore the use of additive manufacturing to fabricate each battery component, ultimately leading to the demonstration of a fully printed Li-ion battery. To facilitate this goal, we demonstrate that the incorporation of the “dry” phase inversion technique utilized to fabricate our ceramic polymer electrolyte (see Chapter 4) proved
beneficial when used with our electrode formulation. Specifically, the dual solvent system allowed for the achievement of two goals: first, it bolstered active material loading to increase cell capacity due to higher porosity; second, it allowed for all three main battery components to be printed sequentially without significant interlayer mixing or performance loss owing to decreased solvent strength with the incorporation of a non-solvent. The interfacial properties of the all-component 3D-printed Li-ion battery are assessed using scanning electron microscopy, and the electrochemical performances are evaluated through cycling tests. We demonstrate that sequentially printed Li-ion batteries can be fabricated via an AM process using our ink formulations, while meeting the performance specifications of wearables and sensors.

6.2 Experimental Methods

6.2.1 Electrode and Electrolyte Ink Fabrication

Lithium titanate (Li$_4$Ti$_5$O$_{12}$) and lithium iron phosphate (LiFePO$_4$) composite electrodes were fabricated in a similar fashion to that described in section 3.2.3; however, the component ratios were modified to 50/20/30 (active/CNF/PVDF) in order to increase active mass loading and areal capacity. Further, the dual solvent system utilized for the fabrication of the nanocomposite electrolytes was adopted here for the fabrication of the composite electrodes by phase inversion. Specifically, 0.45 g PVDF was dissolved in 15 mL NMP, followed by the addition of 0.81 g glycerol (95/5 weight ratio, NMP/glycerol). Next, 0.3 g CNFs were added and probe sonicated four times in 30 sec. increments at 25% amplitude using a Sonics Vibra-Cell VCX 750 Probe Sonicator with a ¼ in. microtip. The sample was shaken by hand in between each 30 sec. sonication treatment for more uniform ink dispersion. 0.75 g active material was then added and the
mixture was bath sonicated for 30 min. Nanocomposite electrolyte inks were fabricated as described in section 4.2.1. A conventional Li$_4$Ti$_5$O$_{12}$ electrode on copper foil was prepared at a mass ratio of 70:20:10 Li$_4$Ti$_5$O$_{12}$: graphite: PVDF in NMP. The slurry was applied to a copper foil current collector (MTI Corp.) by doctor blade (Gardco Inc.) method using a 6 mil path depth, and subsequently dried at 120 °C under vacuum overnight.

6.2.2 Electrode Printing Procedure

Filamentary printing was performed by extrusion from a syringe mounted on a custom Aerotech 3D-motion gantry (Pittsburgh, PA). Typical motion speeds were 5 to 20 mm s$^{-1}$. Extrusion was controlled using an Ultimus V pressure pump system from Nordson EFD (East Providence, RI) at pressures ranging from 0.5 to 5 psi and 5 to 25 psi for the electrode and electrolyte inks, respectively. The stainless steel syringe tips, also from Nordson EFD, were 18 to 25 gauge and ¼ to ½ in. in length. Needle geometry, pressure, and print speed were tuned to maximize print reliability and fidelity (reliable extrusion and wetting of ink). Inks were deposited onto glass substrates that were scrubbed with acetone and blown dry with compressed air. Tool paths were developed in the AeroBasic scripting language.

Individual printed electrodes were deposited in a single layer pass, yielding thicknesses of 100-200 μm. Printed electrodes were initially dried on a hot plate set to 110 °C for 10-15 min., then dried under vacuum at 120 °C overnight before use.

6.2.3 Electrolyte Printing Procedure

Printed separator electrode assembly (SEA) films, using PVDF-HFP (Kynar® Flex 2801, provided from Arkema Inc.) as a separator, had nominal diameters of 20 mm with a
center electrode of nominally 10 mm. These films were produced in a layer-by-layer manner with the electrode being deposited first followed by a "collar" of separator material (20 wt.% PVDF-HFP in NMP) going from the outer edge of the SEA to the edge of the electrode. A layer of separator ink was then printed atop the electrode and collar layer. Heat treatments followed each material deposition. The electrode ink was dried on a hot plate set to 110 °C for 10-15 min. until dry in appearance. The heat treatments following each layer of separator ink required partial drying by covering with a glass dish and heating to 90 °C for 10-20 min. The dispense-tip-to-substrate height was set to accommodate the highest point of the dried electrode layer. Before electrochemical performance evaluation, printed SEAs were initially dried on a hot plate set to 110 °C for 10-15 min., then placed under vacuum at 80 °C for 2-3 h.

Multilayer electrolyte prints using CPE-PI as the membrane layer required specific drying conditions to prevent the existing printed structure from swelling as the next layer was dispensed atop it. Between printing each layer, the sample was partially dried by covering with a glass dish and heating to 90 °C for 10-20 min. depending on the amount of ink dispensed. The next layer of ink was then dispensed atop this partially dried ink. Fully printed electrode membrane assemblies (PEMAs) were made by first depositing the electrode then surrounding it with a collar of electrolyte material and finally covering it with one or two layers of electrolyte. Challenges in PEMA fabrication arose from the inherent roughness of the dried electrode ink, which had a surface roughness of over 10 µm. This required that the separator ink be dispensed above the highest feature causing an uneven surface-to-nozzle distance. However, the higher boiling point solvent and the
moderate viscosity of the electrolyte ink allowed leveling prior to drying. Printed electrolytes and PEMAs were fully dried under vacuum at 120 °C overnight before use.

Both printed SEAs and PEMAs were soaked in liquid electrolyte and assembled versus Li foil. After fabrication, the cells were allowed to age at least 8 h. before electrochemical cycling in order to allow for homogeneous electrolyte wetting.

6.2.4 Full Cell Printing Procedure

Printed full-cells were fabricated with a CPE-PI membrane of 20 mm nominal diameter and a center electrode of nominally 7 mm. Full-cells were produced in a layer-by-layer manner with the cathode (LiFePO₄) first being deposited on glass at 120 °C followed by a "collar" of CPE-PI material going from the outer edge of the SEA to the edge of the electrode. A layer of CPE-PI ink was then printed atop the electrode and collar layer with the temperature set to 110 °C. Once sufficiently dried, the anode material (Li₄Ti₅O₁₂) was deposited having a nominal diameter of 7 mm. Before electrochemical performance evaluation, printed full cells were dried under vacuum at 90 °C for 2-3 h.

6.2.5 Material Characterization

Cross-sectional scanning electron microscopy (SEM) was performed using an FEI Quanta 600F SEM after cryo-fracturing samples while immersed in liquid nitrogen. Cells were cycled using a Maccor series 4000 battery test system. LiFePO₄/Li₄Ti₅O₁₂ full cells were investigated for cycling stability at a constant current rate (determined by the area of the smallest electrode) between 1.2-2.4 V vs. Li/Li⁺, respectively.
6.3 Results and Discussion

6.3.1 Printed Electrode

A schematic illustration of the pressure-driven printing process to print an electrode disc is shown in Figure 6.1a. A printed Li$_4$Ti$_5$O$_{12}$ disc (40/40/20 composition) was electrochemically cycled in a half-cell configuration and its rate performance was shown to be on par with both the same composition prepared via casting and a conventional slurry coated electrode (Figure 6.1b). To emphasize the capability in freeform design of our inks, a LiFePO$_4$ cathode composed of the same ratios was used to print a complex pattern (Figure 6.1c) which could easily be flexed or deformed while on a PET sheet without any visible cracking or delamination. This highlights the feasibility of printing complex patterns for targeted form factors, or those which yield higher flexibility or stretchability (e.g., serpentine, crossed).

![Figure 6.1](image)

**Figure 6.1.** Printing of 40/40/20 active/CNF/PVDF composite electrodes. a) Schematic illustration of the filamentary printing process. b) Rate performance of a printed and casted composite and a conventional Li$_4$Ti$_5$O$_{12}$ electrode on copper. c) Photograph of a complex filamentary printed design prepared using LiFePO$_4$ cathode ink on transparency paper.

For perspective, the areal and volumetric performances of three different electrode samples are shown in Figure 6.2. The small areal footprint of our printed electrode gave it a slight advantage over the conventionally prepared electrode in terms of both areal
capacity and areal energy/power density. On the other hand, volumetric properties of the printed electrode fell below that of the conventional electrode. This was to be expected, however, because of the high porosity of the printed electrode (about 60-70%) versus that of the conventional electrode (about 35%). This aspect could be further optimized, but the areal properties of the electrode are in fact more important for the targeted application space. Given the small dimensions of wearables and sensors, it is the areal footprint of the energy storage device that is of most concern. Thus, the properties exhibited by our printed electrodes are a promising achievement in realizing fully printed Li-ion batteries for portable applications.

**Figure 6.2.** Comparison of electrochemical properties of casted and printed composites and a conventional Li$_4$Ti$_5$O$_{12}$ electrode on copper foil (70:20:10 Li$_4$Ti$_5$O$_{12}$:graphite:PVDF). All three samples contain between 3.0-3.5 mg cm$^{-2}$ active loading.
6.3.2 Printed Electrode and Electrolyte Assembly

Figure 6.3 shows a first attempt to fabricate a printed separator electrode assembly (SEA) using our electrode inks. A PVDF-HFP separator was successfully printed directly on top of a printed LiFePO$_4$ composite electrode, which demonstrated expected half-cell electrochemical performance at a 0.05C current rate. Although this result showed great promise, the corresponding charge/discharge profiles indicated ohmic polarization losses arising from the separator layer. In other words, even at a slow current rate of 0.05C, the SEA could not accommodate the reaction time associated with the mass transport/diffusion of lithium due to the dense nature of the polymer layer. Additionally, coating the PVDF-HFP solution layer over the electrode led to infiltration into the underlying porous structure, causing further hindrance in performance.

![First generation separator electrode assembly (SEA).](image)

**Figure 6.3.** First generation separator electrode assembly (SEA). (a) Photograph of a fully printed SEA. (b) Cycle performance and charge/discharge profile (0.05C) of a printed SEA.

Improving upon the pitfalls observed with our initial printed SEA, a second-generation, printed electrode membrane architecture (PEMA) was prepared by depositing
our ceramic polymer electrolyte (CPE-PI) directly over a LiFePO$_4$ composite cathode (Figure 6.4a,b). From SEM, it was clear that sequential printing of this porous membrane material onto the electrode gave rise to a tight and continuous interface (Figure 6.4c,d). The dual solvent system (NMP and glycerol) permitted only a limited amount of the electrolyte ink to diffuse into the porous composite electrode leading to excellent interfacial adhesion without severe penetration of the two materials. This finding was highly desirable, since we have already reported that interlayer contact is the key for performance stability under mechanical abuse, such as bending or creasing.$^{[131]}$

It should be stressed that the utilization of phase inversion within the electrolyte ink was imperative to achieving high performance in the PEMA. Owing to the reduced solubility of PVDF in the dual solvent system (NMP/glycerol), the porosity of the underlying layer was maintained when the electrolyte was deposited onto the porous electrode and the electrochemical performance (Figure 6.4e,f) compared favorably to when each layer was stacked separately (Figure 4.5b,c). In contrast, Figure 6.3b revealed that when the pure PVDF-HFP electrolyte was printed directly over the same composite electrode in our first generation SEA, the cell only reached expected capacity at very low current rates (0.05C)$^{[95]}$. This result emphasizes the benefit of the phase inversion process in promoting facile reaction kinetics for Li-ion battery operation.
Figure 6.4. Second generation printed electrode membrane architecture (PEMA). a) Schematic illustration of the filamentary printing process. b) Photograph and c,d) cross-sectional SEM images of a fully printed PEMA. The SEM image in d) is a zoomed in region from c). Rate performance (e) and cycling performance (f) of the PEMA configuration shown in a-d).

The dry phase inversion approach used to prepare high performance electrolytes was also directly amenable to our printable electrode inks because they utilized the same polymer and solvent. Figure 6.5 shows the effect of glycerol addition on the properties of a Li$_4$Ti$_5$O$_{12}$ composite electrode. When only NMP was used, a 40/20/40 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite electrode displayed a sharp drop off in both 2C and 5C performance. The addition of 5 wt.% glycerol led to increased capacity at all of the C rates tested and significantly improved high rate performance (Figure 6.5a).
Additionally, the phase inversion process had a significant impact on mechanical properties (Figure 6.5b). The composite prepared from NMP only was relatively stiff with a low strain to failure. In contrast, the Li$_4$Ti$_5$O$_{12}$ composite prepared using the phase inversion process displayed a decrease in tensile strength, but exhibited a 3x increase in ductility over its NMP only counterpart. The increased ductility for these samples afforded a higher degree of flexibility without failure making them more suitable for application in flexible electronics. The observation of both improved electrochemical performance and enhanced ductility can be explained by the increased porosity afforded by the phase inversion process (Figure 6.5c,d). When using only good solvent, a dense cross-section with limited visible pores was observed (Figure 6.5c). This dense morphology blocked active material sites and potential Li$^+$ diffusion pathways, which explains the poor high rate performance that was observed. On the contrary, when the same composite included 5 wt.% glycerol, noticeable voids formed throughout that facilitated Li$^+$ diffusion and allowed better access to the active material (Figure 6.5d).
Figure 6.5. Properties of composite electrodes prepared using phase inversion with NMP/glycerol. a) Electrochemical rate performances and b) uniaxial tensile stress-strain curves of 40/20/40 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite electrodes prepared with and without glycerol. c,d) Cross-sectional SEM images of a 40/20/40 Li$_4$Ti$_5$O$_{12}$/CNF/PVDF composite electrode prepared with d) and with c) without glycerol.

6.3.3 All-Printed Li-Ion Battery

In order to meet the needs of our projected application space (e.g., wearables, packaging logistics, RFID tags, etc.), and to compete with other reports on printed batteries, it was still necessary to increase the active mass loading of our electrodes. An areal capacity of 1 mAh cm$^{-2}$ is generally accepted to meet the aforementioned requirements.\cite{132} Figure 6.6 assesses the performance characteristics of the best composite ratios yet tested. In the case of maintaining 40 wt.% active material in the composites, the areal capacity fell short of 1 mAh cm$^{-2}$ regardless of our ability to
increase the active loading from 2.9 to 4.2 mg cm$^{-2}$ (Figure 6.6a). However, because of the large porosity afforded by the phase inversion method, it was feasible to further increase the active material content to 50 wt.% and correspondingly reduce the polymer content to 30 wt.. Upon doing so, reliable performance was achieved at 1 mAh cm$^{-2}$ with an active mass loading of 7.2 mg cm$^{-2}$. Interestingly, the Ragone plot in Figure 6.6b indicated that our printable composite electrodes (both 40/40/20 and 50/20/30) compared favorably against other reports on printed electrodes in half-cell configuration.$^{133-135}$ Indeed, the composite with higher active mass loading presented an improvement in energy and power density. Hence, the phase inversion method coupled with increased active mass loading promoted a small areal footprint and facile reaction kinetics while boosting the energy and power capability, respectively.

![Figure 6.6](image)

**Figure 6.6.** Improvements in the performance characteristics of our printable electrode composites upon the implementation of phase inversion. (a) Cycle life plot at 0.2C rate showing an increase in both active mass loading and areal capacity. (b) Ragone plot comparing the areal energy and power densities of our 40/40/20 and 50/20/30 Li$_4$Ti$_5$O$_{12}$ composite electrodes to reported literature values for printed half cells.

Figure 6.7a shows an illustration of the 3D-printed full cell encapsulated within a 2325 coin cell. While the dimensions and rigidity of this encapsulation were not well-
suited for the targeted application space, it did provide the necessary hermeticity for battery testing. Figure 6.7b demonstrates the cycle life of the 3D-printed battery using either 40/40/20 (active / CNF / PVDF) composite electrodes from NMP only, or 50/20/30 composite electrodes from NMP/glycerol (phase inversion). The printed full cell incorporating phase inversion electrodes exhibited more stable performance with less than 6% capacity fade over 10 cycles. Comparatively, the full cell utilizing electrodes printed from NMP only exhibited 9.2% less capacity by the 10th cycle, or about 15% fade overall. Moreover, the areal capacity of the 3D-printed full cell with phase inversion was shown to reach 1.0 mAh cm⁻² (1.8 mWh cm⁻² areal energy density) with minimal voltage hysteresis (Figure 6.7b). This contrasted strongly with the poor performance observed with the electrodes printed from NMP only, whose areal capacity was only ca. 0.3 mAh cm⁻². We attribute the enhanced performance of the former cell to the dual solvent system utilized throughout the process having mitigated the dissolution of the underlying layer as each new wet layer was applied. When using only NMP as solvent, each new wet layer partially dissolved the underlying layer leading to densification of the composite, which inhibited access to active material sites.
Figure 6.7. All-component 3D-printed battery performance with and without phase inversion. (a) Illustration of the 3D-printed battery comprised of Li$_4$Ti$_5$O$_{12}$ and LiFePO$_4$ sequentially layered with the CPE-PI electrolyte layer. (b) Battery capacity as a function of cycle number. Charge/discharge profile of the 3D-printed battery with (c) and without (d) electrodes fabricated by the phase inversion process.

Figure 6.8a shows a cross-sectional SEM image of a sequentially layered Li-ion battery. At high magnification, we examined the interface between each electrode and the electrolyte (Figure 6.8b,c) and found no indication of penetration of the active material or other components into the electrolyte or vice versa. This point was further supported by the minimal hysteresis and stability of the all-printed battery’s charge/discharge profile (Figure 6.7b). Thus, the sequential coating of each layer was not shown to reduce accessibility to active sites within the electrodes. Moreover, the tight
and continuous interface observed between each component is expected to promote performance stability for flexible applications, as suggested by our previous work.\textsuperscript{[131]}

Figure 6.8. Cross-sectional SEM of a sequentially layered Li-ion battery fabricated with the phase inversion process. (a) Low magnification micrograph of all three battery components after sequential deposition. High magnification micrographs highlighting the interface achieved between the anode and electrolyte (b) and the cathode and electrolyte (c).

Given the sensitivity of device performance to processing conditions, it was challenging to maintain the desired level of performance throughout cycling tests for the printed full cells. For example, adjusting the heated stage to the right temperature during printing was crucial to promoting desirable drying kinetics when each layer was deposited. Unfortunately, this became more difficult to control as each new wet layer was deposited. Further optimization of the 3D printing process is currently under investigation to mitigate this issue. Nevertheless, both the printable electrode and electrolyte components could be stacked individually to monitor cycling performance
over a longer duration. Such a cell exhibited minimum decay in capacity over 50 cycles, and maintained a stable areal capacity of ca. 1 mAh cm$^{-2}$.

**Figure 6.9.** Long-term performance of 3D printable battery components. (a) Schematic of the individually stacked full cell components. Cycle life (b) and charge/discharge profile (c) of an individually stacked full cell (0.2C rate, based on Li$_4$Ti$_5$O$_{12}$ loading).

Table 6.1 summarizes the cell specifications and performance metrics of our all-printed Li-ion battery compared to reported literature. Comparisons are intentionally focused on secondary battery technology, with the exception of Table 6.1d, which is a primary chemistry (non-rechargeable) that has been transitioned into a commercial technology by Imprint Energy (Alameda, CA). Overall, our battery meets the standards set forth by these works, achieving an areal capacity and energy density of 1.0 mAh cm$^{-2}$ and 1.8 mWh cm$^{-2}$, respectively. It should be acknowledged that these values could be further improved by increasing the active material loading, optimizing composite density, and selecting alternative active materials with higher voltage electrochemical couples.
Table 6.1. Comparison of several key characteristics of our printed, unpackaged 3D printed Li-ion battery to reported literature.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Fabrication Technique</th>
<th>Cell Chemistry</th>
<th>Nominal Voltage</th>
<th>Dimensions (w x h x t)</th>
<th>Areal Capacity</th>
<th>Areal Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Filamentary Printing</td>
<td>Li$_2$Ti$_3$O$_7$/LiFePO$_4$</td>
<td>1.8 V</td>
<td>0.3 cm$^2$ *disc sample for coin cell</td>
<td>1.0 mAh cm$^{-2}$</td>
<td>1.8 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>a</td>
<td>Transfer Printing</td>
<td>Li/LiCoO$_2$</td>
<td>3.4 V</td>
<td>2.5 x 2.5 x 0.2 cm$^3$</td>
<td>0.1 mAh cm$^{-2}$</td>
<td>0.4 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>b</td>
<td>Ink Jet</td>
<td>Li$_2$Ti$_3$O$_7$/LiFePO$_4$</td>
<td>1.8 V</td>
<td>*dimensions not reported</td>
<td>0.3 mAh cm$^{-2}$</td>
<td>0.5 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>c</td>
<td>Stencil Printing</td>
<td>Carbon-Zinc MnO$_2$ (Primary)</td>
<td>1.3 V</td>
<td>0.5 x 0.5 x 0.01 cm$^3$</td>
<td>1.0 mAh cm$^{-2}$</td>
<td>1.3 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>d</td>
<td>Airbrush Printing</td>
<td>Li$_2$Ti$_3$O$_7$/LiCoO$_2$</td>
<td>2.3 V</td>
<td>5.0 x 5.0 x -- cm$^3$ *thickness not reported</td>
<td>1.2 mAh cm$^{-2}$</td>
<td>2.8 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>e</td>
<td>Filamentary Printing</td>
<td>Li$_2$Ti$_3$O$_7$/LiFePO$_4$</td>
<td>1.8 V</td>
<td>0.1 x 0.08 x 0.06 cm$^3$</td>
<td>1.2 mAh cm$^{-2}$</td>
<td>2.2 mWh cm$^{-2}$</td>
</tr>
<tr>
<td>f</td>
<td>Filamentary Printing</td>
<td>Li$_2$Ti$_3$O$_7$/LiFePO$_4$</td>
<td>1.8 V</td>
<td>0.7 x 0.3 x -- cm$^3$ *thickness not reported</td>
<td>1.9 mAh cm$^{-2}$</td>
<td>3.4 mWh cm$^{-2}$</td>
</tr>
</tbody>
</table>

6.4 Conclusions

We have explored the process of filamentary printing each battery component, starting with the electrode and then the electrode/electrolyte, and finally demonstrating an all-component 3D printed Li-ion battery. In this pursuit, the phase inversion process previously used for our electrolyte material was found to be applicable to our composite electrode inks, which led to electrodes with increased electrochemical performance and
better mechanical characteristics over those prepared with good solvent alone. The phase inversion method was also determined to enable sequential printing of full-cell battery assemblies through the solubility difference afforded by the dual solvent in each layer during printing and drying. Ultimately, we have demonstrated the ability to sequentially print each component of a Li-ion battery to meet the emerging requirements of wearable, flexible and embedded technology.
7 Summary and Future Work

7.1 Summary

This dissertation work has investigated the development of flexible and conformal Li-ion batteries and related fundamental aspects observed within each component as well as the interface. Limited by a deficiency of innovation in current manufacturing processes, a conspicuous lack of knowledge has persisted within the community regarding how to fabricate mechanically robust, compliant batteries. Initial background investigations thus sought to improve upon the shortcomings of traditional Li-ion battery fabrication with aims to enable flexible applications. Utilizing a state-of-the-art approach to achieve device flexibility, active material slurries were blade coated onto a highly robust, multi-walled carbon nanotube (MWNT) mats. Through the implementation of dynamic bend and crease performance testing, our research experimentally elaborated on the fundamental limitations of traditional Li-ion battery design using metal foils. It was revealed that the interfacial properties imbued by the porous MWNT mat gave rise to superior adhesion between the active material layer and current collector, leading to unprecedented performance under mechanical strains. Utilizing this knowledge, a unique advancement toward the additive manufacture of printable batteries was developed for the design of compliant energy sources from the perspective of each 2D component.

First, a well-dispersed and directly castable mixture of active material, carbon nanofibers (CNFs), and polymer was fabricated to yield high-performance, printable electrode inks. The unique properties of this composite were mainly attributed to the formation of a 3D CNF network that acted collectively as the conductive additive, embedded charge collector, and porous, structural scaffold to facilitate Li\(^+\) diffusion. Systematic evaluations were applied to ensure sufficient electrode porosity and electrical
conductivity in addition to meeting various application constraints, such as low internal resistance, cycle life, and mechanical integrity. Meeting such metrics was imperative to maintaining battery performance through the additive manufacturing process.

Second, a ceramic polymer electrolyte material was developed via a phase inversion approach, which possessed all the necessary properties to enable high performance operation. Specifically, the addition of a nano-ceramic filler simultaneously implemented with a unique solvent/weak non-solvent system promoted the formation of submicron pores throughout the porous, polymeric membrane matrix. The resulting 3D printable electrolyte ink required no coagulation bath or additional processing steps to generate a favorable hierarchical pore structure and surface to facilitate rapid \( \text{Li}^+ \) diffusion, great liquid wettability, and outstanding thermal/mechanical behaviors.

To supplement the material development performed for the 3D printable electrolyte, a thorough investigation was conducted on our ceramic polymer electrolyte membrane imbibed with an ionic liquid to take advantage of its thermal stability. It was revealed that the favorable interaction between the ionic liquid solution and ceramic polymer electrolyte promoted enhanced ionic transport properties and enabled high temperature device operation up to 130 °C.

The electrode and electrolyte ink formulations developed through this research were further applied to demonstrate an all-component 3D-printed Li-ion battery. The sequentially printed battery demonstrated a stable areal capacity and energy density of 1 mAh cm\(^{-2}\) and 1.8 mW cm\(^{-2}\), which satisfied the requirements of the proposed application space and compared favorably against similar works on printed Li-ion batteries. Such a breakthrough is anticipated to enable the direct integration of a power source into an
electronic device through the ability to deposit batteries on non-planar surfaces, or in confined areas by additive manufacturing.

7.2 Future Work

This dissertation work has established a strong foundation for the pursuit of several exciting research topics. First, given the complexity of the ink formulations and the difficulty encountered in sequentially printing each component without interlayer mixing, experimentation with novel 2D and 3D architectures could not be explored in the given time frame. Architecture is one crucial research front in the pursuit of stretchable devices, and has also been shown to impact capacity retention and cell cycle lifetime in batteries. As stressed throughout this dissertation, additive manufacturing technologies are anticipated to enable rapid prototyping and exploration of a broad array of novel battery architectures, which could not easily be explored by traditional battery fabrication methods. Therefore, the utilization of additive manufacturing would allow one to probe an array of battery architectures including serpentine, interdigitated, and crossed patterns (Figure 7.1A-D), which have varying degrees of intrinsic flexibility/stretchability.

Beyond the enhanced mechanical effects of such macroscale patterns, micropatterning of electrodes was recently shown to significantly increase capacity retention and cell cycle lifetime by improving electrolyte wetting. This phenomenon could be exploited using additive manufacturing by creating hierarchical structures within the battery electrodes that have architectures geared towards macroscale flexibility/stretchability, and that are decorated with printed capillary microstructure for improved battery performance.
A second topic of research should be the development of a flexible encapsulant that is impermeable to both moisture and air. For flexible application, the only current choice for an encapsulant is the aluminum-polymer pouch typically used in industry. They come in a variety of thicknesses, but even the thinnest pouch available is susceptible to significant crease memory. Moreover, once these cells are vacuum sealed to ensure tight contact between all the battery components, the overall rigidity prevents them from being bent or folded at all. One possible route to achieving a truly flexible encapsulant for Li-ion batteries could be to ALD coat the Surlyn material used in Chapter 2 with a thin layer of material to act as a moisture/air barrier.
Finally, it was observed during the thermal studies presented in Chapter 6 that there was potential for even higher temperature performance than what was demonstrated. If performance at temperatures exceeding 150 °C could be shown, this work would be a first of its kind for rechargeable Li-ion batteries. Unfortunately, the coin cell architecture we implemented used polypropylene gaskets to ensure a hermetic seal, but they were not able to withstand temperatures beyond 130 °C for any extended period of time. In addition, there was indication of performance irregularity during electrochemical cycling if the voltage window was not appropriately adjusted at elevated temperature. There are several possible causes believed to be behind this issue: (1) crystal structure breakdown of the LiFePO₄ electrode at elevated temperature, (2) degradation of the imidazolium IL, (3) formation of LiF during the dehydrofluorination of the CPE-PI membrane, or (4) unstable solid-electrolyte interphase formation on the Li metal anode. It would be worthwhile to study these causes and to pinpoint any major issues. For instance, one could monitor the crystal structure of the electrode when cycled at elevated temperatures.
Figure 8.1. Effect of CC on electrolyte infiltration. White arrows in the photograph of the bottom side indicate the edge of the electrolyte spot. Scale bars: 0.5 cm.
Figure 8.2. Photographs of the process of fabricating Surlyn-encapsulated flexible full-cells. a) LiFePO$_4$/MWNT (left) and Li$_4$Ti$_5$O$_{12}$/MWNT (right) electrodes and separator membrane (center) (b) Wire leads thermally laminated between two pieces of 75 µm Surlyn. c) 75 µm Surlyn pouch thermally sealed on three edges containing the electrodes, separator, and wire leads. A needle cap is contained in the opposite side of the pouch. d) Pouch after thermally sealing the final edge after folding. An additional seal was placed at the nanotube electrode leads. e) Pouch after addition of 0.8 mL liquid electrolyte (punctured pouch at the needle cap). Bubbles were kneaded away from the battery and sealed (middle of the pouch). A final seal was done closer to the
battery to remove new bubbles after the first charge. f) Sealed flexible battery used for *in situ* mechanical testing after cutting away the excess Surlyn. g) Metal foil full-cell in a Surlyn pouch made using the same procedure shown in (a-f). Scale bars: 1.0 cm

**Figure 8.3.** Scotch tape exfoliation of a MWNT mat for TEM microscopy.
9 Bibliography


[65] Z. Cao, B. Wei, ACS Nano 2014, 8, 3049.
10 Curriculum Vitae

EDUCATION

Doctor of Philosophy
Institution: Wright State University, Dayton, Ohio, USA
Major: Materials & Nanotechnology
Date: December, 2016
Dissertation: From 2D to 3D: On the Development of Flexible and Conformal Li-Ion Batteries via Additive Manufacturing
Advisor: Prof. Dr. Hong Huang

Master of Science
Institution: Wright State University, Dayton, Ohio, USA
Major: Renewable Energy Engineering
Date: December, 2013
Thesis: Synthesis and Characterization of Graphene Oxide/Sulfur Nanocomposite for Li-ion Batteries
Advisor: Prof. Dr. Hong Huang

Bachelor of Science
Institution: Wright State University, Dayton, Ohio, USA
Major: Mechanical Engineering
Date: June, 2012
Research: Wind Turbine Model Design
Transparent Battery Design/Anode Materials for Li-ion Batteries

RESEARCH PUBLICATIONS


CONFERENCE PAPERS


PATENTS


AWARDS & HONORS

- AFRL RXAwesome Light Bulb Award, 2015
- Graduate Student Excellence Award in Renewable Energy Engineering, 2014
- Wright State University College of Engineering Assistantship, 2013-14
- National Science Foundation Graduate Research Fellowship, 2012-14
- Tau Beta Pi National Honor Society, 2012 – Present
- Choose Ohio First Scholar, 2010-2015
- Wright State University Dean’s List, 2010-2012
RESEARCH & PROFESSIONAL EXPERIENCE

Research Assistant – Flexible Materials & Devices
AFRL/Wright State University, Dayton, OH May 2014 – Present
- Developed Li-ion battery component inks for 3D printing of conformal designs.
- Assisted in the design and construction of flexible Li-ion cells for electrochemical and mechanical evaluation.
- Employed the use of various electrochemical testing equipment (e.g., EIS, CV, etc.) for electrode/battery characterization.
- Reported project progress to team leaders.
- Participated in SBIR write-ups, contract proposals, etc. in pursuit of the development and commercialization of AFRL developed technology.

Graduate Research Assistant
Wright State University, Dayton, OH June 2012 – April 2014
- Synthesized reduced graphene oxide nanosheets (rGO) for use in electrode nanocomposites, while developing improvements and alternatives to the process.
- Prepared liquid electrolytes solutions to optimize reaction kinetics of the sulfur electrode.
- Reviewed/analyzed electrochemical performance data from rGO/sulfur experiments and implemented changes based on results to optimize cathode for battery specifications.
- Applied X-ray diffraction techniques, qualitative microscopy, and other material characterization methods to study the structure and morphology of the rGO/sulfur nanocomposites.

Engineering Intern
Wright-Patterson AFB, WPAFB, OH December 2011 – June 2012
- Worked with a team of three engineers developing spectral methods to remotely analyze highly reactive volatile organic compounds (HRVOCs).
- Designed and created mechanical devices to assist with spectroradiometric measurements.
- Completed purchase orders for items needed by the Engineering Physics Department.
Sales/Turnkey Engineering Intern
Gosiger, Inc., Dayton, OH June 2011 – September 2011

- Generated time studies for turnkey processes.
- Responsible for developing sales materials for proposals.
- Created solid models of tools and machined parts using Solidworks.
- Reviewed customer supplied prints and created gage plans.
- Responsible for documentation of the turnkey.
- Operated CMM (Coordinate Measuring Machine) and performed manual gauging during runoffs.

SKILLS
Laboratory: Carbon nanomaterials, energy materials, battery cycling, cyclic voltammetry, AC impedance spectroscopy, X-ray diffraction, mechanical testing, differential scanning calorimetry, thermo-gravimetric analysis, scanning electron microscopy, BET, FT-IR, glovebox operation, rheology.


Personal: Strong written and oral presentation skills, hardworking and passionate, high energy level, able to communicate technical information to non-technical audience, self-starter, exercise enthusiast, recreational musician.

PROFESSIONAL ASSOCIATIONS
- Tau Beta Pi Engineering Honor Society; Member
- Materials Science and Engineering Society (MSES); Treasurer 2012-14
- Materials Advantage; Member
- Order of the Engineer (OOE); Member