

ABSTRACT

Title of Thesis: EXAMINATION OF A HIGHLY POROUS
GEL POLYMER INTERLAYER FOR
INTERFACIAL IMPROVEMENT IN SOLID
STATE LITHIUM BATTERIES

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Solid-state lithium garnet (LLZT) electrolytes display relatively high ionic conductivity, thermal stability, and compatibility with lithium metal, which makes them encouraging for the future of lithium-ion batteries. As with many other solid electrolytes, their main weakness is poor contact and high interfacial resistance with electrodes. The use of polymer gels as interlayers has been demonstrated to reduce this interface, improving cell stability and lifespan. In this study, immersion precipitation has been explored as a preparation method to create poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) polymer membranes. The resultant microstructure is highly porous and can uptake nearly 600% its weight in liquid electrolyte when forming a gel. Polymethyl methacrylate (PMMA) and lithium fluoride (LiF) are incorporated into the membranes and evaluated for their contributions to mechanical and electrochemical properties. Membranes containing LiF showed high stability up to 4.5 V vs Li/Li⁺ and were analyzed in cells of composition NMC/PVDF-HFP/LLZT/Li. Specific discharge capacities up to 174 mAh/g were

achieved during early cycling and showed promise for future exploration and application in quasi-solid-state lithium-ion batteries.

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by

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List of Abbreviations

Important Materials

IPA	Isopropyl Alcohol, Isopropanol
LiF	Lithium Fluoride
LLZT, LLZTO	Garnet-Type Solid Electrolyte
NMC	Nickel Manganese Cobalt Oxide (Typically lithiated)
PMMA	Polymethyl methacrylate
PVDF-HFP	Poly(vinylidene fluoride)-co-hexafluoropropylene
SS	Stainless Steel

Machinery and Methods

ALD	Atomic Layer Deposition
DLS	Dynamic Light Scattering
DMA	Dynamic Mechanical Analyzer
EIS	Electrochemical Impedance Spectroscopy
LSV	Linear Sweep Voltammetry
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

Other

ASR	Area Specific Resistance
ESW	Electrochemical Stability Window
GPE	Gel Polymer Electrolyte
SSE	Solid State Electrolyte

Chapter 1: Introduction

As gasoline prices continue to skyrocket and the public becomes more environmentally conscious, the adoption of electric vehicles has become a growing outlet for everyday consumers to reduce their carbon footprint ^[1]. Fully electric vehicles cut emissions by about two thirds, and hybrid vehicles by about half ^[2]. With the average American driving 13,476 miles per year, or 36.9 miles per day, individual efforts have become critical to reversing the damage done ^[3]. Many car manufacturers have also set targets to completely convert production to electric vehicles by 2030 ^[4]. Improvements in rechargeable lithium batteries have been instrumental in the rising popularity of electric vehicles, increasing consumer confidence in battery range and lifespan and resulting in a nearly twofold increase in sales from 2020 to 2021 alone ^{[5][6]}.

Today's commercial battery technology is dominated by lithium-ion systems. Like all batteries, they consist of two electrodes, a positive cathode and a negative anode, which store the lithium ions. An electrolyte carries the positive lithium ions between the anode and cathode, and a separator prevents them from coming in contact and causing a short circuit. When a battery is discharged, lithium in the anode is oxidized in a reaction that frees electrons to run through an external circuit. The, now positively charged, lithium ions are transported to the cathode as the electrons flow from the external circuit, having powered a connected device, to take part in the electrochemical reaction at the cathode. When the battery is charged, the reactions happen in reverse, with lithium ions driven back to the anode by an externally provided power source and completing one full cycle.

The current generation of lithium-ion batteries has been steadily evolving since the early 1990's. Continuous advancements have been made to increase energy and power densities, which describes the amount of electrochemical energy stored and the rate at which it can be accessed respectively, either in comparison to mass or volume. High density allows for lighter and more efficient battery packs that reduce the total weight, raise fuel efficiency, and further save the owner money^[7]. Higher voltage cathodes have been sought out to reduce current requirements for desired power output, lowering wear on the system and increasing its lifespan^[7].

Innovations in performance have been accompanied by extensive research into improved safety features for lithium-ion batteries. Liquid electrolytes, traditionally composed of a lithium salt in a flammable organic liquid solvent, have proven a major source for these issues. When exposed to high heat or irregular operation, they pose a risk of fires or explosions, which is especially dangerous in the case of vehicles with large battery arrays and high casualty potential^{[8][9][10]}. External devices such as pressure vents and thermally activated resistors have been developed to reduce these risks but have been unable to eliminate them entirely and reduce efficiency by consuming space^{[8][11]}. Solid-state electrolytes have become an active research field, making major steps in safety efforts by containing or removing the flammable liquids in lithium batteries^[12]. These rigid layers generally have high thermal and chemical stability, reducing the risk of failure to abnormal temperature swings^[12]. Unfortunately, solid electrolytes are not without their own issues, including high interfacial resistance due to difficulty in achieving good contact between the solid electrolyte and electrodes^[12].

The primary goal of this study is to reduce this interfacial resistance, thereby increasing the stability and viability of solid-state lithium batteries by introducing polymer gel interlayers synthesized via immersion precipitation. Immersion precipitation is a relatively unstudied

technique for use in quasi-solid-state electrolytes, despite resulting in highly porous structures via facile and scalable methods ^[13]. The mechanical, microstructural, and electrochemical properties have been analyzed and compared to membranes produced by more common methods from literature, as well as other fledgling studies of this process for electrochemical applications.

Chapter 2: Background

2.1 Literature Review

2.1.1 Lithium-Ion Battery History

Battery technology has been evolving for centuries since the first true battery created by Alessandro Volta in 1800, consisting of layered zinc and silver metal electrodes separated by cloth soaked in a saltwater solution ^{[7][14]}. A staple of modern electronics, lithium batteries first took hold in the 1970s as a breakthrough in high energy density that found use in military equipment, medical implants, and consumer electronics ^[7]. The improvement was dramatic, as lithium anodes have a theoretical specific capacity nearly five times higher than the previously utilized zinc. The first generations were primary batteries, unable to be recharged, and were limited by the general inability of cathodes at the time to repeatedly cycle. In 1978, the first intercalation cathodes were introduced, characterized by an open structure that could reversibly insert and release lithium ions ^[7]. Metal sulfides such as TiS_2 and MoS_2 were used as the first commercial rechargeable lithium battery cathodes around 1980 ^[7].

Multiple issues soon arose, namely fire incidents due to the reactivity of lithium metal and short circuits from its dendrite growths. Short circuits are pathways of low or negligible resistance connecting the electrodes that concentrate current flow and often cause premature cell failure. Two primary avenues were taken to suppress these issues and improve the safety and lifespan of lithium batteries; the substitution of the pure lithium anode with one less reactive, and the optimization of the electrolyte system, which is discussed further in sections 2.1.2 and 2.1.3. The most popularly adopted solution was the “rocking chair battery”, commercialized by Sony in 1991, replacing

lithium anodes and compatible cathodes with two intercalation style electrodes for increased cycling stability ^{[7][15]}. The lithium ions could insert and release between the graphite anode and lithium cobalt oxide (LCO) cathode, “rocking” back and forth and resulting in its name. The name “lithium-ion batteries” was soon adopted instead to describe these and includes many of the batteries commonly employed today in laptop computers, cellphones, and electric vehicles, among countless other applications ^[7].

In the decades that have followed, the general composition and construction of lithium-ion batteries hasn’t experienced any radical alterations. Efforts are being made to increase safety by moving away from flammable liquid electrolytes, as well as reduce the amount of rare earth metals in cathodes such as cobalt for economic and ethical reasons and explore novel new cycling mechanisms like the conversion reactions of lithium-sulfur batteries. Many studies also focus on increasing efficiency and stability, as new developments are constantly required to support the blooming market for electric vehicles ^[7].

2.1.2 Solid-State Lithium-Ion Batteries

Solid-state electrolytes have been proposed as replacements to combat the high flammability and inherent potential danger posed by traditional organic liquid electrolytes. They possess increased thermal stability, reducing the chance of catastrophic failure from unexpected temperature spikes. Additionally, the elimination of liquid electrolyte diminishes packaging requirements, increasing the cell’s energy density ^[11]. Compared to organic liquids, inorganic solid-state electrolytes generally have higher electrochemical stability, making high potential cathode materials viable without breaking down. They also are mechanically stronger, blocking the growth of dendrites between the electrodes and reducing the potential for short circuits ^{[11][16]}. Many types of inorganic solid-state electrolytes compatible with lithium-ion batteries are currently

under study, including perovskites, lithium hydrides, ceramic glasses, and garnets. In addition, polymer electrolytes (PEs) and gel polymer electrolytes (GPEs) are likewise employed for their unique benefits and are discussed further in section 2.1.3.

Despite the benefits provided by solid-state electrolytes, they are held back by brittleness and vulnerability to fracturing easily. Solid electrolytes are more proficient at stopping the growth of dendrites than liquid systems, but any small imperfections can create new pathways for them to advance ^[12]. Perhaps the largest of these issues is the high interfacial resistance between the solid electrolyte and electrodes. As two solid materials, physical contact is difficult to achieve over significant area and limits the points at which conduction can occur between the components. This creates localized points of high current flow, which increase the rate of wear and reduce cell lifespan ^{[17][18]}. On the anode side, Dr. Wachsman's lab has reduced this by using a solid-state bilayer electrolyte, with a porous network that is infiltrated with lithium metal to create a very high interfacial area ^[19]. However, this process is incompatible with most cathode materials as it requires melting and good wettability at the surface, necessitating a different solution. To reduce interfacial resistance, various interlayer materials have been explored, including atomic layer deposition (ALD) of metals and metal oxides, or flexible polymers ^{[18][20][21]}. These methods have yielded improvement, but most solid polymers require elevated operating temperatures to achieve adequate conductivity, and deposited layers are challenging and rely on flatness of the cathode for high effectiveness ^{[18][21]}. To combine a high degree of flexibility from polymers and high ionic conductivity from inorganics, gel polymers can be used as interlayers, as discussed further in the subsequent section.

2.1.3 Gel Polymer Electrolytes

Gel polymers are typically fabricated by soaking porous polymer membranes in liquid electrolyte solution and combine many of the advantages from solid and liquid electrolytes. They have similar transport mechanisms to liquid electrolytes and high ionic conductivity even at room temperature. The liquid is confined within the membrane, reducing the safety hazards despite maintaining its presence and benefits ^[22]. Gels can also still display good mechanical properties and prevent the growth of lithium dendrites, increasing cell lifespan. Some of the most widely used polymers for both solid and gel polymer electrolytes are polyethylene oxide (PEO), polyacrylonitrile (PAN), and poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP). These polymers are all semicrystalline, with their amorphous regions lending to high conductivity and the crystalline regions to high mechanical strength ^[22]. Often small additions of other materials are used to disrupt the crystallization process and further improve ionic conductivity, either via inorganic addition to form particle reinforced composites, or through copolymerization ^{[23][24]}.

Fabrication of gel polymer electrolytes is typically through facile means. Typically, polymers and desired additives are dissolved in a solution and cast, using one of several methods of phase inversion to precipitate the membrane ^{[13][24][25][26]}. These involve a nonsolvent which exchanges with the polymer solvent and leaves a porous network after drying. This nonsolvent can be included in the solution, or the cast can be subject to an immersion bath or atmosphere of vaporized nonsolvent ^[27]. The result is a porous polymer membrane which can be soaked in liquid electrolyte to form a gel. Other more complicated methods have been proven to work, such as electrospinning of highly fibrous and porous networks ^[28].

Phase Inversion is a common method of facilitating porosity in of polymer membranes. High porosity increases the fraction of liquid electrolyte in the gel, which typically has ionic conductivity 1-2 orders of magnitude higher than its host matrix. When referencing phase inversion, most polymer electrolyte studies are specifically referring to a method called controlled evaporation ^{[26][27]}. In this process, the desired polymer or polymers are first dissolved in a volatile solvent. A chosen miscible nonsolvent of lower volatility is added in a small weight percentage, creating a homogenous mixture. The solution is cast as a thin layer and the primary solvent quickly begins to evaporate, causing solvent exchange and polymer precipitation to occur ^{[22][26][29]}. The nonsolvent takes longer to evaporate, and may require external heating to fully remove, but the precipitate left behind is a porous polymer membrane ^{[26][29]}. If accessible, a humidity chamber can be used to finely tune the rate of evaporation and create more predictable and repeatable pore sizes ^[26].

An alternative to controlled evaporation, immersion precipitation is a secondary method of phase inversion. In this process, the selected nonsolvent is not added to create a mixture, but instead is used as a bath in which the polymer solution is immersed immediately after casting ^{[27][30]}. Polymeric coagulation and solvent exchange occur, and a porous membrane is again precipitated ^[30]. Once removed from the bath, the membrane is dried to remove any trapped residual solvent. In immersion precipitation, the choice of nonsolvent has been correlated with the degree of crystallization in the precipitated membrane (for crystalline or semicrystalline polymers) ^{[30][31]}. Utilized by Young et al, nonsolvents can be described as either “soft” or “harsh” for each polymer ^[30]. “Soft” nonsolvents facilitate slow mass transfer and give time to allow large regions of crystalline phase to form in the membrane. “Harsh” nonsolvents allow mass transfer to occur quickly, and the liquid demixing process outcompetes crystal nucleation, resulting in a primarily

amorphous structure^[30]. Both outcomes can be desirable, if high ionic conductivity or strength are more important for the application.

2.2 Material Properties

2.2.1 Poly(vinylidene fluoride)-co-hexafluoropropylene

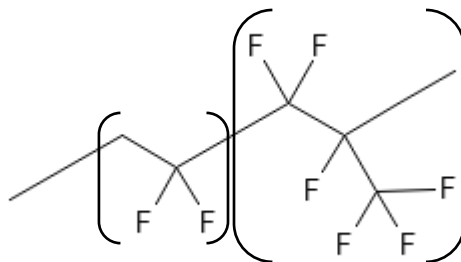


Figure 1. PVDF-HFP Molecular Structure

Illustrated above in Figure 1, PVDF-HFP is a semicrystalline polymer that has gained widespread attention for use in lithium battery electrolytes. The first monomer, PVDF primarily acts as the crystalline phase, providing mechanical strength. HFP is typically an amorphous phase, increasing flexibility and ionic conductivity^{[31][32][33]}. Much of the ionic conductivity derives from the many fluorine atoms along its carbon backbone, which have electron pairs that interact with Li^+ cations in the liquid electrolyte to form polymer-salt complexes^[33]. PVDF-HFP has a relatively high dielectric constant and low crystallinity at room temperature, further facilitating its high conductivity^[32].

In addition to its intrinsic properties, PVDF-HFP is commonly used as a polymer electrolyte because of its functionality with cutting edge electrode materials. It has a high electrochemical stability window, showing small signs of breakdown around 4.3V vs Li/Li^+ and resisting significant breakdown until 4.7V, allowing for pairing with high voltage cathodes such

as NMC and LCO ^{[20][25]}. It is also considered stable when paired with a lithium metal anode, which can supply extremely high specific capacity ^{[20][25][34]}.

2.2.2 Lithium Garnet (LLZTO)

Lithium metal has an extremely high specific capacity of 3860 mAh/g, making it extremely desirable for use as an anode material. However, it is highly reactive and can form parasitic interfaces with many common solid and liquid electrolytes ^[35]. Among those that are stable, garnet-type solid electrolytes show promise with relatively high ionic conductivity and a wide electrochemical stability window ^{[35][36]}. The base formula for garnets follows a $\text{Li}_x\text{M}_2\text{M}'_3\text{O}_{12}$ pattern, derived from the $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ orthosilicate ^{[35][37]}. Compositional classes of garnet are primarily differentiated by their lithium content, such as Li_5 , Li_6 , and Li_7 . Each increase in lithium loading corresponds to an exponential jump in ionic conductivity, peaking with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) as the current stable maximum ^[35]. Efforts to further increase stuffing have negatively observed decreases in conductivity. Additional dopants such as tantalum (LLZTO) have been used to reduce the required sintering temperature while maintaining the stability of the cubic phase ^[38]. This cubic phase is one of two that are stable in LLZO, the other being a tetragonal phase with two orders of magnitude less ionic conductivity, making it desirable to minimize the presence of tetragonal garnet ^[35].

2.2.3 Nickel Manganese Cobalt Oxide (NMC)

NMC is a type of layered oxide cathode, which have recently grown to dominate in commercial lithium-ion batteries. Layered oxides first appeared at the transition to “rocking chair” intercalation cathodes, beginning with lithium cobalt oxide, LiCoO_2 (LCO) ^{[7][39]}. LCO is polymorph with two possible crystal structures, with the more electrochemically desirable being

the layered oxide. In this phase, layers of cobalt oxide octahedrons are separated by interstitial lithium atoms ^[39]. When a specific percentage of lithium atoms are extracted during the charging process, the crystal structure is forcibly transformed, preventing much of the theoretical capacity from being realized. As an alternative, LiNiO₂ was developed but suffered from poor thermal stability and structural disorder from unconstrained lithium ions ^{[39][40]}. The substitution of half the stoichiometric nickel with manganese significantly reduced this effect and increased its viability as a cathode material ^[39].

The discovery of NMC combined the beneficial qualities of these layered metal oxides, providing high thermal stability, high operating voltages, and highly reversible capacity ^[39]. The structure is fundamentally equivalent to LCO, with the metal ion sites randomly occupied by either nickel, manganese, or cobalt. Different compositions are typically referred to by the elemental subscripts in order, such as NMC 111, 622, or 811. Despite its key role in stabilization of the layered oxide structure and performance, many efforts have been made to reduce cobalt content in cathodes due to its high price, extreme toxicity, and widespread unethical sourcing based in worker exploitation ^[41].

2.3 Previous Works

2.3.1 Polymer Interlayers

Research was done by E. Wachsman and L. Hu's groups, led by B. Liu, on the use of polymer interlayers to sandwich a solid-state garnet electrolyte ^[18]. Interfacial resistance was found to dramatically reduce between the garnet and both LiFePO₄ cathode and lithium metal anode. For

the interlayers, pure PVDF-HFP membranes were fabricated via controlled evaporation in a humidity chamber ^[18].

2.3.2 Immersion Precipitation

Immersion precipitation has been minimally applied for lithium-ion batteries. A study was published in 2021 by P. Zhang et al to create a PVDF-HFP membrane used with a LiFePO₄ cathode and lithium metal anode ^[13]. Poly(ethylene oxide) (PEO) and SiO₂ were used as additives for strength and ionic conductivity. A highly asymmetric microstructure was observed, but the processing method was successful in achieving good liquid electrolyte uptake (>500%) and relatively high ionic conductivity ^[13].

2.4 Characterization Methods

2.4.1 Electrochemical Testing

Electrochemical Impedance Spectroscopy (EIS) is used to assess the resistance of materials and assembled cells. Typically, an AC potential is applied across the cell in a sinusoidal manner. The AC current response is recorded, which should also be sinusoidal though affected by a phase shift. By varying the frequency of the applied potential and calculating both real and imaginary components of impedance, a Nyquist plot is created, characterized by one or several semicircles. Recording the impedance from various sections of these semicircles and applying an equivalent circuit model can be used to isolate the contributions of specific interfaces and bulk materials.

Chronoamperometry was utilized to determine the transference numbers of the membranes by polarization, as well as gel conductivities when paired with EIS results. For this simple technique, a constant potential is applied across the sample and the drop in current is measured over an extended time. Using symmetric steel electrodes, the general ionic transference number of

the material can be acquired via a method called DC polarization. This is the ratio of total electric current carried by ions and is ~ 1 for an electrolyte material, as any electrical conductivity can lead to an immediate short circuit. If instead symmetric lithium electrodes are employed, the specific lithium-ion transference number can be obtained via potentiostatic polarization, further distinguishing between different charge carriers. High values improve kinetics and reduce the buildup of ion concentrations, indicating better high-rate performance during cycling ^{[42][43]}.

Linear Sweep Voltammetry (LSV) gradually increases, or “sweeps”, the potential of a cell in one direction. Recording changes in current during this process reveals the electrochemical response of the cell, observed as either increases or decreases. This technique can be used to identify breakdown voltages and establish an upper potential for a safe testing zone, also known as the Electrochemical Stability Window (ESW).

Chronopotentiometry is used for more traditional cell charge and discharge cycling. A constant current is applied across the cell, and voltage increased and decreased between set cutoff values dependent on the electrode materials in use. The rate at which the cell is cycled may be increased over time, or held constant, and is reported as the “C-rate”. C is given a coefficient that describes how many half-cycles occur per hour. For example, a 0.1C rate would be fully cycled in 20 hours, 10 each for the charge and discharge. Often reported is the cells discharge capacity, which decreases with extended cycling. It is generally accompanied by the coulombic efficiency, the ratio of discharge charge capacity, measuring how much of the charge put into the cell is then recoverable for use.

2.4.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopes use a focused electron beam to produce incredibly high-resolution images up to and exceeding $10^4 \times$ magnification^[44]. It has a very high depth of field, giving images a characteristic three-dimensional appearance. This technique is extremely useful for qualitative microstructural analysis, and measurements at or below the micron scale.

2.4.3 Dynamic Mechanical Analyzer (DMA)

A Dynamic Mechanical Analyzer (DMA) can perform a multitude of mechanical property characterization. For this application, samples were stretched under a continuously ramping force until failure to obtain a stress v strain curve. Typically, the curve has a linear elastic region, in which deformation is non-permanent, and a curved plastic region, in which structural deformation does not recover. The slope of the elastic region is the elastic modulus, also known as the Young's modulus, and is comparable to the stiffness of the material. It is often reported for comparison between both ductile and brittle materials.

Chapter 3: Immersion Precipitation of Gel Polymer Interlayers

3.1 Introduction

The use of polymer gel interlayers to reduce the interfacial resistance for solid-state electrolytes has yielded promising results for increasing cell efficiency and longevity ^[18]. To improve on previous studies of gel polymers, the implementation and optimization of immersion precipitation has been utilized with aim to produce highly porous membranes for high flexibility and ionic conductivity. PMMA and LiF additives have been incorporated into the membranes, seeking to further enhance this conductivity. LiF also adds mechanical strength to counteract the inevitable loss of strength due to a highly porous microstructure. A high-voltage NMC cathode and high-capacity lithium metal anode are used to create quasi-solid-state cells with a solid lithium garnet electrolyte in tandem with the gel polymer. These cells are cycled to assess the electrochemical performance and characterized both mechanically and electrochemically to obtain comparisons to other gel membranes published in literature and commercially available.

3.2 Experimental

3.2.1 Materials

To produce the polymer membranes, poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP; $M_w \sim 40,000$, $M_n \sim 130,000$) was obtained from Sigma Aldrich, and both poly(methyl methacrylate) (PMMA; MW $\sim 120,000$, 600 micron) and lithium fluoride (LiF; 99.85%) from Alfa Aesar. Solvents ethanol (100%, anhydrous) and isopropanol (99%) were obtained from Pharmco, and acetone from VWR Chemicals.

To produce garnet bilayers, lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$; >98%) was obtained from Alfa, lanthanum oxide (La_2O_3 ; 99.99%) and lithium carbonate (Li_2CO_3 ; 99.99%) from GFS, zirconium oxide (ZrO_2 ; 99.9%) from Inframat, and tantalum (IV) oxide (TaO_2 ; 99.99%) from Thermo Scientific. Menhaden fish oil, polyalkylene glycol (PAG), polyvinyl butyral (PVB), and butyl benzyl phthalate (BBP) were all obtained from Tape Casting Specialists. Cross-linked PMMA was used from Kowa Chemicals of the MX-150 (1.5 μm) and MX-1500H (15 μm) varieties.

Lithium metal foil (99.9%) was obtained from MTI. Commercial Nanomyte BE-54E (NMC 622) cathodes came from NEI. Liquid electrolyte solution used was 1M lithium hexafluorophosphate (LiPF_6) in ethylene carbonate (EC)/diethyl carbonate (DEC) of equal volume fractions from Sigma Aldrich.

3.2.2 Synthesis of Gel Polymer Interlayers

To prepare polymer membranes, polymer pellets were dissolved in acetone at 18 wt% and mechanically stirred overnight at 40°C. As shown in Table 1, pure PVDF-HFP was used for Membranes 1 and 3. For Membranes 2 and 4, the polymer composition was a 7:3 ratio of PVDF-HFP to PMMA. This ratio was chosen and maintained to make the effects of PMMA incorporation easily identifiable and to be comparable with referenced literature^[25]. Additionally, 4 wt% lithium fluoride was added to Membranes 3 and 4. Mixtures containing LiF were heated to 50°C. The solutions were cast onto aluminum foil at 400 μm using a doctor blade, then quickly immersed in an isopropanol bath, where they were left for 1-2 minutes under gentle agitation of the bath. The solidified membranes were carefully removed from the isopropanol and left to dry at room temperature, where they slowly increased in opacity until fully white in color.

Table 1. Polymer membrane solution compositions by weight percentage

	PVDF-HFP	PMMA	LiF
Membrane 1	18%	0%	0%
Membrane 2	12.6%	5.4%	0%
Membrane 3	18%	0%	4%
Membrane 4	12.6%	5.4%	4%

The membranes were cut to approximately 1 cm² and dried under vacuum at 55°C for ten hours. Fully dried membranes were soaked in standard liquid electrolyte solution of 1M LiPF₆ in 50:50 EC:DEC for up to 5 minutes before application in pouch cells. Once swollen with liquid electrolyte, the membrane opacity reverted from opaque to transparent.

3.2.3 Synthesis of Garnet Bilayer Electrolytes

Garnet powder was synthesized using a solid-state reaction previously utilized by our lab group^{[21][45][46]}. Lithium hydroxide monohydrate, lanthanum oxide, zirconium oxide, and tantalum oxide were milled together in isopropanol with yttria-stabilized zirconia (YSZ) media in stoichiometric amounts to achieve a composition of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂. To account for inevitable lithium loss during sintering, approximately 8 mol% excess lithium was incorporated into the recipe. The mixture was dried, compacted into pellets with a hydraulic press, and calcined at 950°C for 10 hours. XRD was performed on the calcined powder to confirm a cubic garnet structure. The pellets were then ground and milled once again in isopropanol until a particle size of approximately 500 nm was achieved, measured via dynamic light scattering (DLS) on a Malvern Zetasizer Nano Z590. The mixture was again dried, ground, and stored. Some powders underwent additional milling in smaller YSZ media to reduce the particle size to approximately 300 nm.

These prepared garnet powders were used for tape casting to produce thin, flexible ceramic sheets, utilizing established techniques ^[21]. Two tape types were desired, a porous and a dense layer. For the dense tape, the 300 μm garnet powder was dispersed in ethanol with fish oil. This was repeated for the porous tape with the 500 μm powder, and the addition of lithium carbonate, lanthanum oxide, zirconium oxide, and tantalum oxide. A prepared solution of binders and plasticizers in ethanol (polyvinyl butyral, polyalkylene glycol, and butyl benzyl phthalate) were combined with the garnet mixture and centrifugally mixed to create a slurry. To the porous slurry, PMMA was added to act as a pore former. Both slurries were degassed, and excess solvent driven off to achieve an optimal viscosity. Tapes were cast onto Mylar through a 254 μm gap for the porous tape and 152 μm for the dense tape and dried to evaporate the solvent. To create bilayers, dense and porous layers were laminated together and briefly hot-pressed to improve adherence. Laminated bilayers were sandwiched between sacrificial tapes of compatible composition and sintered in a tube furnace at 1100°C for three hours on a bed of mother powder ($\sim 1.3 \text{ g/cm}^2$) to mitigate lithium loss. Densification and lamination success were confirmed qualitatively via SEM.

The bilayers were heated to 850°C for three hours in argon atmosphere to remove surface impurities, then transferred directly to an argon glovebox. Atomic Layer Deposition (ALD) was performed to coat the porous layer with a nanoscale coating of either aluminum oxide (Al_2O_3) or zinc oxide (ZnO) ^{[21][45]}.

3.2.4 Pouch Cell Construction

For electrochemical testing, pouch cells were chosen to test the materials of interest. As compared to other devices like coin cells, they have less empty space and higher energy density, as well as faster production and easier recycling after use ^[47]. To begin constructing the anodes in an argon atmosphere glovebox, lithium metal was melted on a hot plate and surface polished, then

wetted onto strips of nickel foil which served as the negative current collectors. The porous side of the garnet bilayer was placed on the liquified lithium and allowed time for to infiltration of the structure to occur. Once completed, the heat source was turned off and the lithium allowed to cool and solidify.

Strips of the commercial NMC 622 cathode were cut to approximately 0.36 cm^2 of active material, with a portion of the electrode coating removed to expose the underlying aluminum foil to act as the positive current collector. These were then dried and brought into the glovebox. A spot welder was used to attach aluminum tabs to the positive current collectors, and nickel tabs to the negative current collectors, which would be accessible outside the pouches for electrochemical testing.

The anode and connected garnet electrolyte were secured in the pouch using polyimide Kapton tape on the nickel tab. Meanwhile, both the NMC cathode and polymer membrane were soaked in liquid electrolyte as noted previously for up to five minutes. The membranes, now gels, were placed over the garnet electrolyte and then carefully topped with the cathode, secured with more Kapton tape. A pouch cell sealer was used to vacuum seal the pouches and prevent contamination or leakage of the contents.

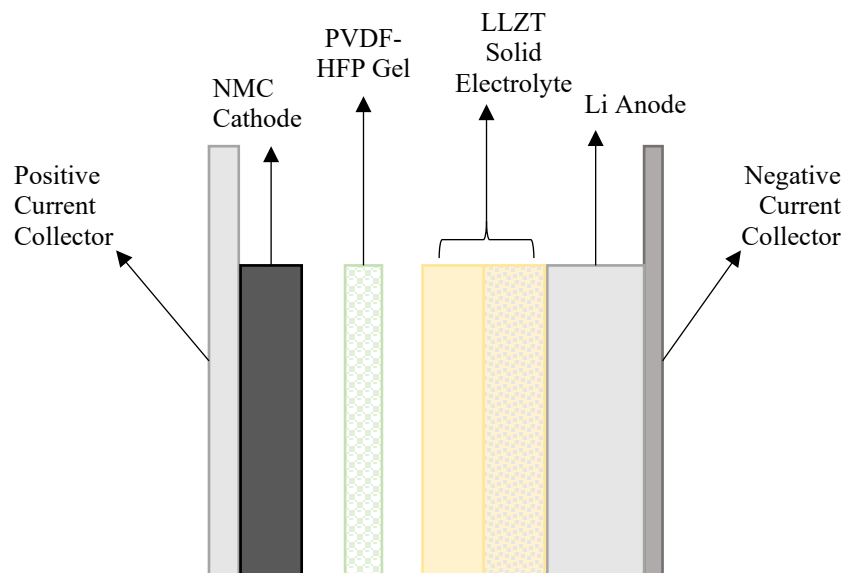


Figure 2. Schematic of quasi-solid-state cell assemblage

3.2.5 Measurements and Characterization Methods

Scanning electron microscopy (SEM) was done with a TESCAN XEIA3 machine by P. Jaschin and T. Hamann. Imaging was performed at 5 kV. Polymer membranes were immersed in liquid nitrogen and freeze-fractured before cross-sectional imaging. Carbon sputter was applied to the surface to prevent charging and image distortion.

Tensile testing was performed by M. Erdi on a TA Instruments DMA Q800 using the procedure outlined in his 2022 study^[48]. Five samples were cut from each dry polymer membrane and measured immediately before testing. They were stretched individually from 0 to 5 N at a constant 0.01 N/min at room temperature to establish stress v strain curves^[48]. The failure stress was recorded at the point of sample failure, and the elastic modulus was calculated as the slope of the curve's linear region.

X-Ray Diffraction (XRD) was performed with a Bruker D8 Advance Bragg-Brentano Diffractometer in the range of $2\theta = 10 - 70^\circ$. This was performed by W. Schubert. A mounting

putty was used to secure membrane samples which contained CaCO_3 and TiO_2 . The characteristic peaks of these materials were recorded and marked to be overlooked in the acquired spectra.

Electrochemical characterization was performed on a BioLogic instrument with functions including a potentiostat, galvanostat, and impedance analysis. Linear sweep voltammetry (LSV) was employed to measure the electrochemical stability window (ESW) of the prepared polymer gel layers. The gel was sandwiched between one aluminum and one lithium electrode. First, voltage was increased at a rate of 0.5 mV/s to 2.5V vs open-circuit voltage (OCV; $\sim 3.2 - 5.7\text{V}$ vs Li/Li^+). Next, voltage was decreased at the same constant rate of 0.5 mV/s to -2V vs OCV ($\sim 3.2 - 1.2\text{V}$ vs Li/Li^+). The two curves were plotted together to analyze the ESW. The utilized liquid electrolyte solution of LiPF_6 in EC:DEC has been reported to begin showing instability around 4.5V [49].

DC polarization was also performed on the Biologic. The gel was sandwiched between symmetric stainless-steel electrodes and subject to a constant 10 mV. The test was intended to be run for 1 hour but was shortened due to high noise from the equipment. An L-shaped curve was obtained, seen in Figure 3.14. Equation 1 below was used to calculate the total ionic transference number where I_{total} was the total current, measured at the onset of the test, and I_e was the electronic current, measured at the very end of the test.

$$\textbf{Equation 1. } t_{\text{ion}} = \frac{I_{\text{total}} - I_e}{I_{\text{total}}}$$

Potentiostatic polarization was performed similarly, with the substitution of stainless steel for symmetric lithium electrodes. Electrochemical impedance spectroscopy (EIS) was performed before polarization in the range of 1 Hz – 1 MHz. Chronoamperometry was conducted at a constant 50 mV for 5 hours, after which EIS was performed a second time. Equation 2, the Bruce-Vincent Equation, was used to calculate the lithium-ion transference number from the three combined

graphs. The ΔV is the applied potential i.e., 50 mV. I_0 and I_{ss} are the initial and “steady-state” currents respectively, with the initial measured at the onset of testing and the “steady-state” once the current had stabilized. R_0 is the resistance before polarization, and R_{ss} from after, both obtained from their respective EIS Nyquist plots.

$$\textbf{Equation 2. } t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$

All EIS studies were performed on the BioLogic in the frequency range of 1 Hz – 1 MHz. To determine conductivity values, stainless steel symmetric cells were assembled with a gel electrolyte. EIS measurements were conducted in the range above to generate Nyquist plots, from which the bulk resistance of the gels was obtained. Equation 3 was used with this value as well as the gel thickness (l) and area specific resistance (ASR) to calculate the total conductivity. Equations 3 and 4 can be combined to calculate lithium-ion conductivity.

$$\textbf{Equation 3. } \sigma_{total} = \frac{l}{ASR}$$

$$\textbf{Equation 4. } \sigma_{Li^+} = t_{Li^+} \times \sigma_{total}$$

Chronopotentiometry was used for cell charge-discharge cycling on an Arbin Instruments battery analyzer. Cells were cycled between 3 and 4.3V as recommended by the cathode manufacturers. The current rates used were 0.05C, 0.1C, and 0.2C, all tested at room temperature.

3.3 Results and Discussion

3.3.1 Fabrication and Optimization of Gel Polymer Interlayers

Polymer gel membranes were prepared using the immersion precipitation method, a type of phase inversion. As mentioned previously, this method was chosen for its ability to facilitate high porosity and to expand its limited previous evaluation for electrochemical applications. This

method is also facile and highly scalable ^[27]. The polymer solution is cast at a fixed height using a doctor blade onto a moving belt, then carried through a coagulation bath in which phase inversion occurs ^[27]. The general setup mirrors tape casting, which is performed extensively by members of our lab group. It does however lack the unique and crucial coagulation bath component, requiring a unique small-scale process to be designed.

The qualifications for the nonsolvent choice were miscibility with acetone, higher density/lower vapor pressure than acetone, and the inability to dissolve PVDF-HFP and PMMA at room temperature. Isopropanol (IPA) met all these requirements and was in ample supply in the research space. Initially, deionized water was used as the nonsolvent bath, however IPA was found to result in opaque membranes more consistently, correlating strongly to good porosity and an ideal microstructure. T. Young et al reported that the final microstructure was highly dependent on the diffusion kinetics of the system and sequence of phase-separating events, which is beyond the scope of this study but supports the importance of nonsolvent selection ^[30]. Acetone was selected over other common solvents for PVDF-HFP such as dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP). Acetone is significantly easier to remove during the drying process due to its low boiling point and is safer for use, as both alternatives pose toxicity and carcinogenic dangers.

The PVDF-HFP solution was cast onto cut squares of aluminum foil, using a spray of alcohol underneath to create a flat, uniform surface. A Mylar film was placed under the path of the doctor blade for steady casting and uniformity, and its thickness was factored into cast height. Once cast and dried, membrane thicknesses were measured via SEM and included below in Table 2. Expected shrinkage was above 90% from the volume of polymer in solution, but the porosity of the membranes resulted in expanded thickness.

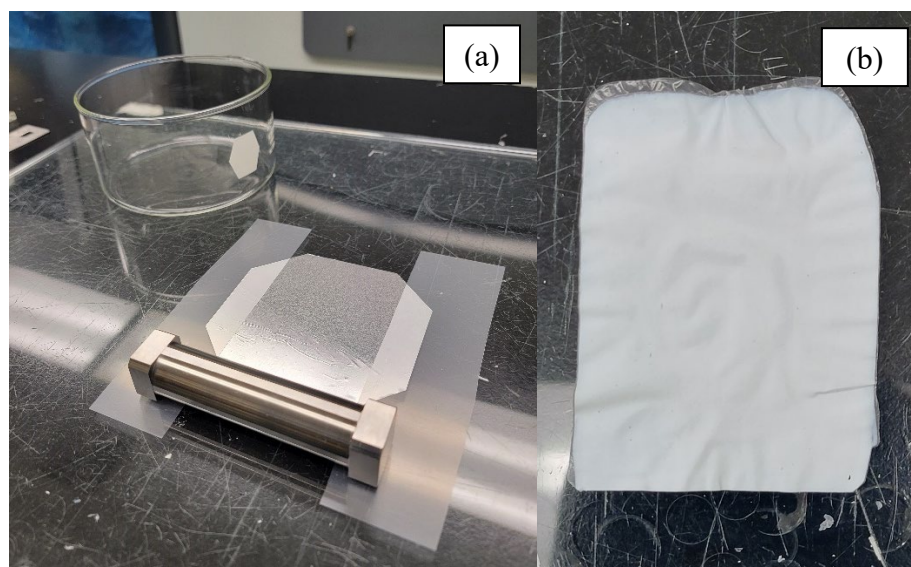


Figure 3. (a) Small-scale immersion precipitation setup and (b) dried polymer membrane

Table 2. Membrane shrinkage after air drying

	Solution Cast Thickness (μm)	Membrane Thickness (μm)	Shrinkage (%)
PVDF-HFP	400	90	77.5
PVDF-HFP + PMMA	400	140	65
PVDF-HFP + LiF	400	80	80
PVDF-HFP + PMMA + LiF	400	95	76

The thickness of membranes produced was increased throughout this study. Short circuits observed during cycling and characterization were attributed to pinholes through which the opposing electrodes were able to touch. With a low thickness and high porosity, this idea seemed plausible, because of horizontal expansion from liquid electrolyte swelling and vertical compression during pouch cell sealing. This effect should theoretically be negated by the insulating garnet electrolyte protecting the anode in full cells; however, issues may arise with dendrite growth and electrically conductive impurity formation. The elimination of these is beyond

this study, though a continuous area of research. Increasing the thickness of the membranes saw a significant increase in performance and ability to evaluate constructed cells more successfully.

In an optimal system, disregarding any processing abnormalities or inherent material challenges, an extremely thin interlayer would be desirable for the maximization of energy density and minimization of resistance. Dried casts were produced as thin as 15 μm , shown below in Figure 4, and could theoretically be produced thinner with a lower vapor pressure solvent than acetone. The high rate of evaporation necessitates a minimum cast thickness for acetone, lest it completely dry before immersion and prevent phase inversion from occurring.

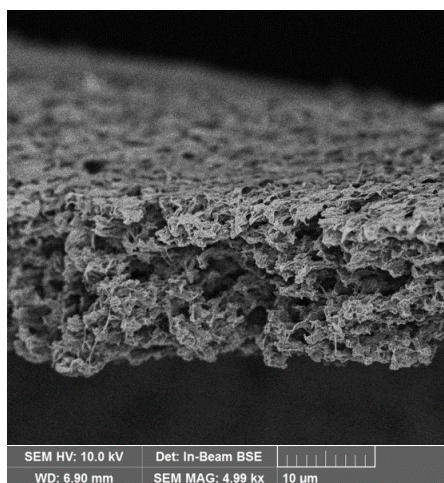


Figure 4. SEM image of thin PVDF-HFP membrane cross-section

3.3.2 Microstructural Evaluation

SEM was used to qualitatively evaluate the microstructure of the produced membranes. Often, freeze fracturing of the membranes was performed with liquid nitrogen to preserve microstructure for cross-sectional images. Samples that required slicing by razorblade show dense compacted regions near the surface. Both membranes containing lithium fluoride retained flexibility and had to be cut to obtain cross-sectional images. All samples were coated with conductive carbon via sputtering to mitigate surface charging and image distortion.

The resultant microstructure of all membranes created in this study is extremely porous as desired, comprised of a fibrous network. This is believed to be unique among gel electrolytes, which are typically sponge-like and subsequently denser. An example with pure PVDF-HFP is shown in Figure 5 from the surface and cross-sectional view. No distinctions were noted between the top and bottom surfaces. While immersed, one surface is adhered to the aluminum foil and one in full contact with the IPA, and previous immersion precipitation studies had yielded asymmetric membranes ^[13]. Fortunately, this issue was avoided, though the surface fibers appeared thicker and more tightly packed than those in the center. These membranes also lack the dense surface skin observed in comparable literature works which may hamper liquid electrolyte pickup ^[13] ^[24].

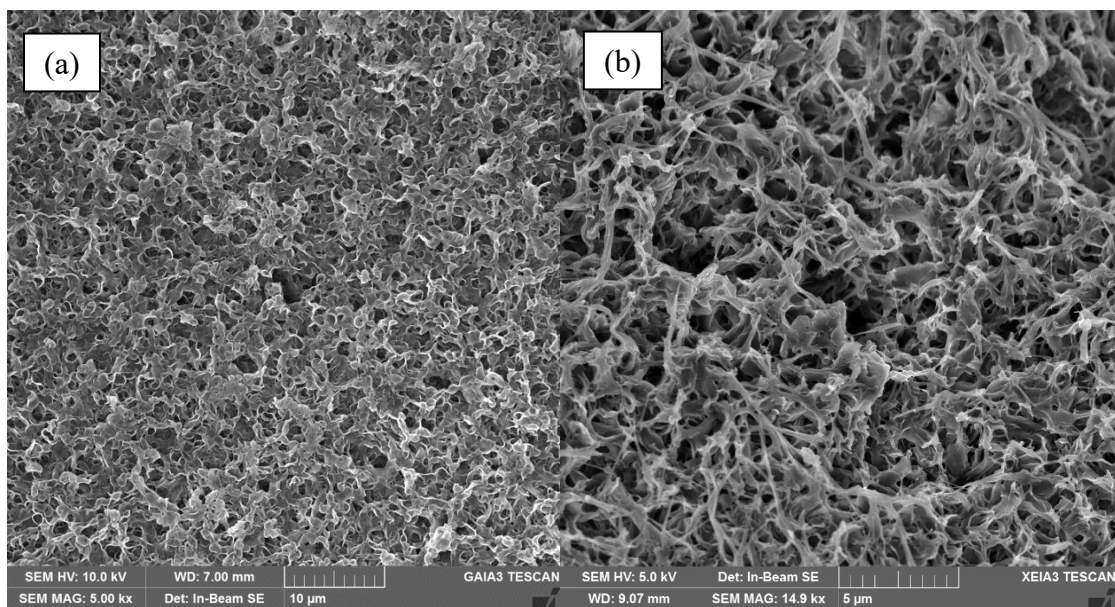


Figure 5. (a) Surface and (b) cross-sectional images of PVDF-HFP membrane

The microstructure of membranes containing PMMA was similar in morphology, but showed a slight visible increase in porosity, which is pictured below in Figure 6 and highlighted by the high magnification image of Figure 7. The exact cause of this phenomena is unknown but was consistently observed. Membranes containing PMMA were qualitatively observed as most regularly turning opaque during membrane drying, found to correspond with highly porous

structures. This persisted even in challenging environmental conditions as described in Section 3.3.1, suggesting that small amounts of PMMA may ease processing conditions and be beneficial to reproducibility.

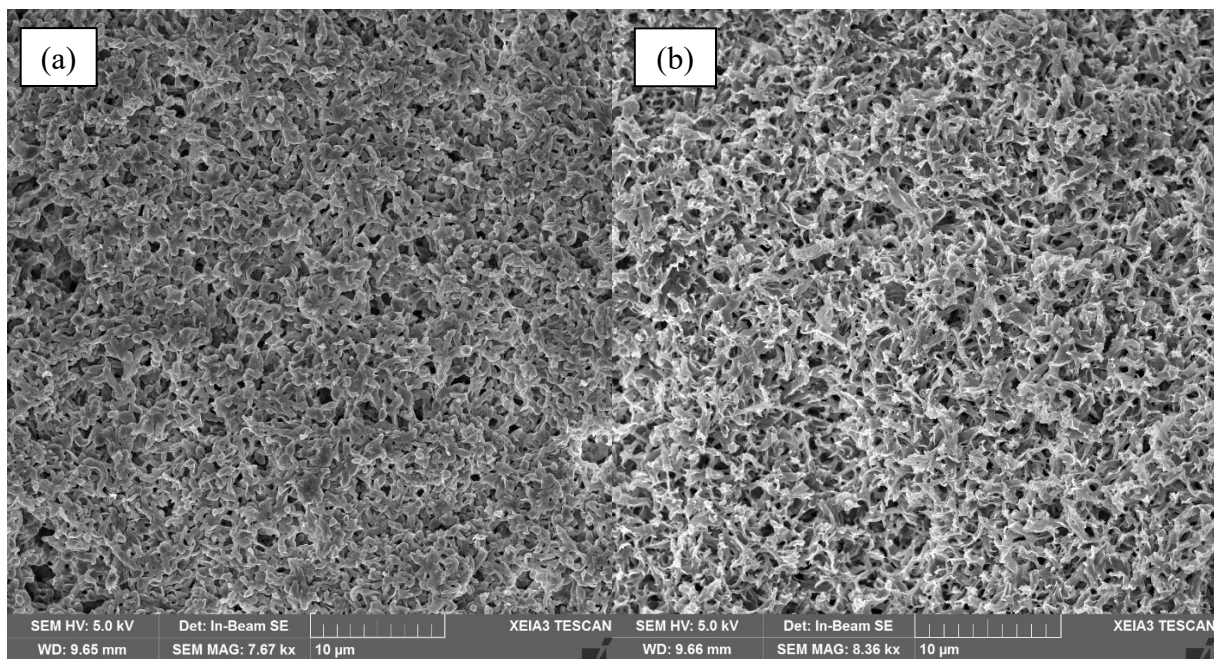


Figure 6. Surface (a) and cross-sectional (b) images of membranes containing PMMA

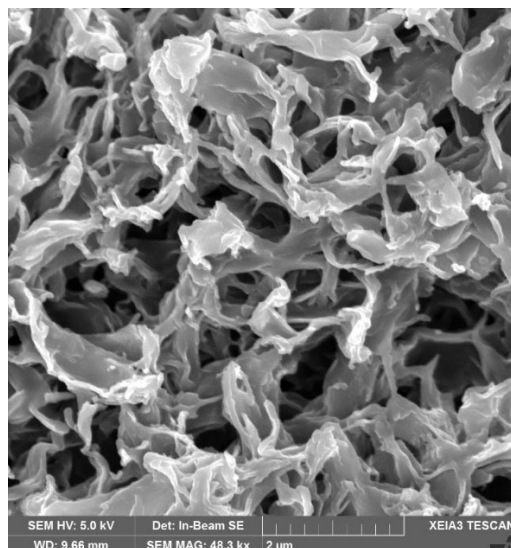


Figure 7. High magnification image of cross-section showcasing high porosity and fibrous microstructure in membrane containing PMMA

Membranes containing lithium fluoride again showed similar overall morphology, though with visible inclusions of cube-shaped lithium fluoride crystals shown in Figure 8b. Crystals were observed to have even dispersion throughout the membrane except for the surfaces. The highly fibrous structure limited the amount of contact between polymer and LiF, restricting the extent of the beneficial properties expected from its inclusion. The microstructure of membranes containing both PMMA and LiF was nearly indistinguishable from that of just LiF and did not warrant its own discussion.

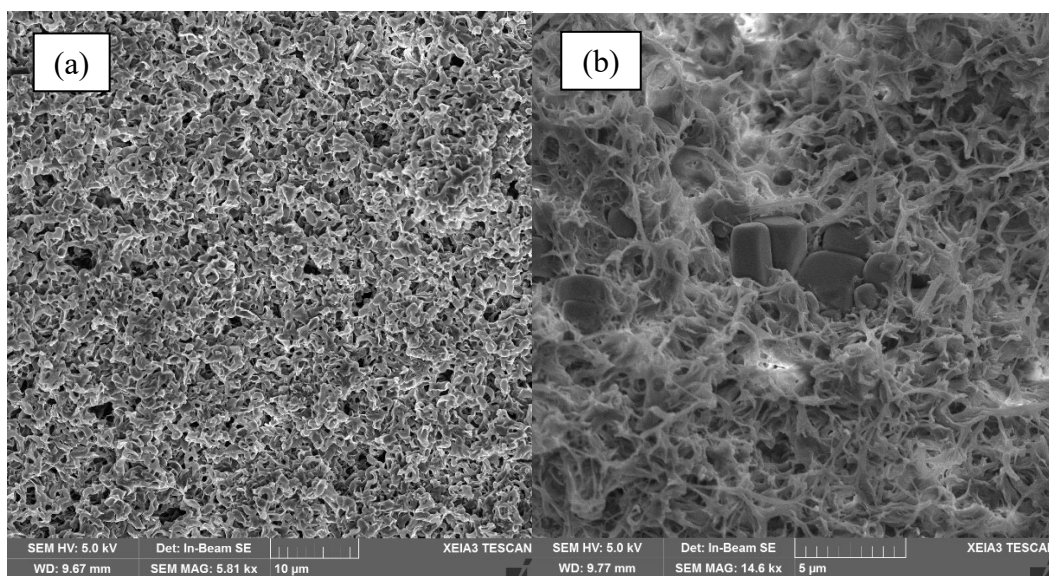


Figure 8. Surface (a) and cross-sectional (b) images of membrane containing LiF.

SEM of garnet electrolytes was performed to qualitatively assess the success of sintering densification and bilayer lamination. Gold sputtering was applied to avoid charging and image distortion. Failure of the garnet to densify can result in pinholes and facilitate dendrite penetration. The gel structure is intentionally highly porous and consequently less proficient at blocking dendritic growth, relying on dense garnet for fortification. Analyzing SEM before using bilayers to construct cells can identify potential issues that are not visible without high magnification.

Figure 9. shows a successfully sintered bilayer, which is planar and has clear distinction between the porous and dense layers.

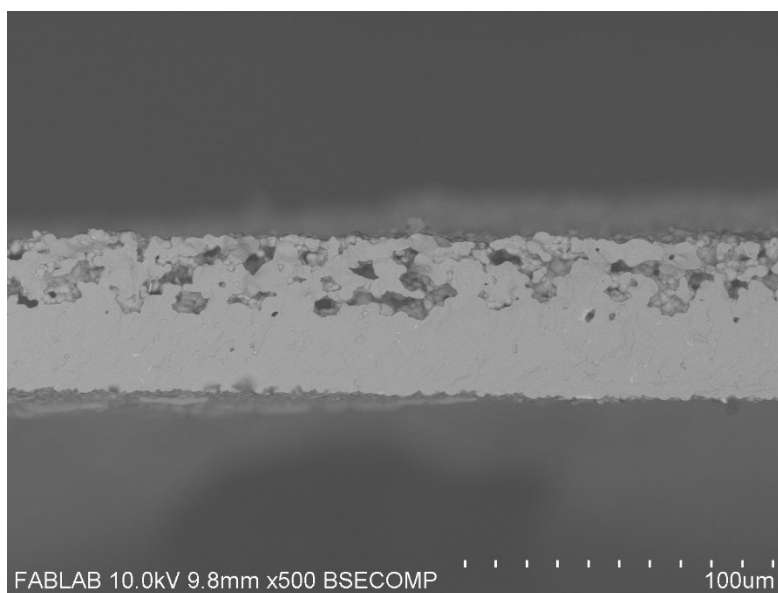


Figure 9. Backscatter SEM image of LLZT bilayer showing good densification and no delamination

As the fibrous microstructure of these membranes makes the accurate estimation of porosity difficult, liquid electrolyte uptake was measured during cell assembly by weighing membranes before and after soaking in liquid electrolyte solution for one or five minutes. Compiled below in Figure 10, despite small observed differences in microstructure there were no large correlations between composition and liquid uptake. This was surprising, as the membrane containing PMMA was visually the most porous network and had the highest measured thickness, suggesting high uptake potential. It was however evident that longer soak times allowed for more pickup, up to a 200% increase. After this confirmation, all membranes used in cells were soaked for approximately 5 minutes.

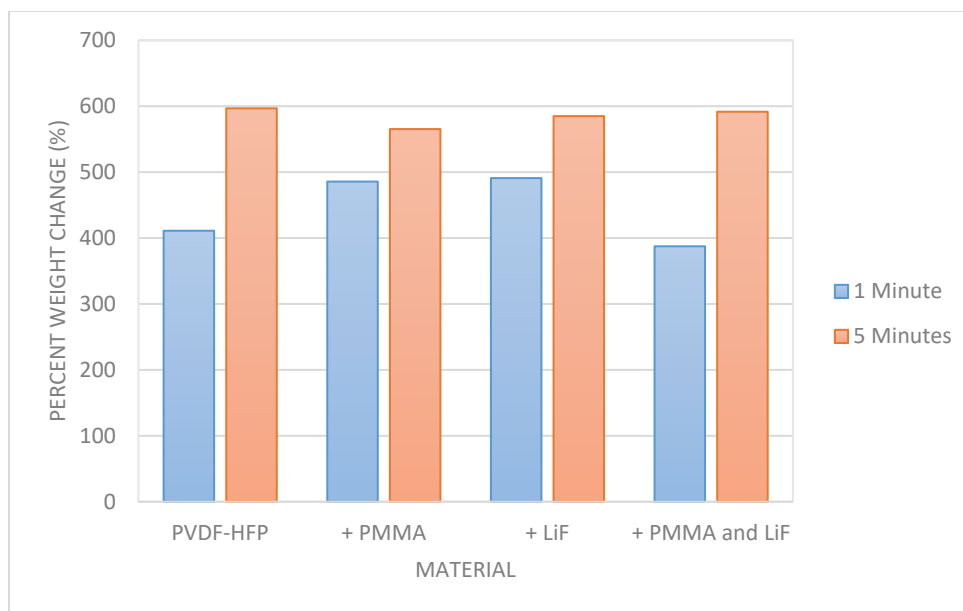


Figure 10. Uptake of Liquid Electrolyte by Porous Membranes

The average liquid electrolyte pickup after five minutes was 585%, which is very high and attributed to the immersion precipitation method of membrane preparation. This indicates strong potential for high ionic conductivity. By comparison, high porosity membranes also produced by immersion precipitation from P. Zhang et al were reported at less than 200% liquid electrolyte uptake, despite also being comprised of pure PVDF-HFP [13]. When supplemented with organic and inorganic additives, more comparable numbers were achieved, though this is still nearly 50% below the average in this study even after soaking for 2 hours. For comparison, commercial polypropylene/polyethylene Celgard separators were found to have only 126% liquid electrolyte uptake by Zhang et al [13].

3.3.3 XRD Analysis

PVDF-HFP is a semicrystalline polymer, of which the crystalline phase is valued for strength and the amorphous phase for its ionic conductivity. For this application, dendrite suppression is ideally performed entirely by the solid garnet electrolyte, so low crystallinity is

prioritized. Characteristic peaks for PVDF-HFP occur at angles $2\theta = 18.5^\circ$, 20.2° , 27.2° , and 39.1° [24]. Lithium fluoride is highly crystalline and presents its own peaks, marked in green in Figure 11c. The CaCO_3 and TiO_2 peaks marked on each spectrum were present in the adhesive putty used to mount samples and should be ignored for all purposes of this work.

Broadening and reduced intensity of the characteristic peaks are indicative of decreased crystallinity. The change is slight, but noticeable from both PMMA and LiF additives as compared to the pure PVDF-HFP in Figure 11a. PMMA is highly amorphous and substituting it for semicrystalline PVDF-HFP was expected to reduce the number of crystalline regions. Lithium fluoride accomplishes this goal by different means, as the crystals locally disrupt the crystallization process. As briefly discussed earlier and visible in Figure 8b, the fibrous microstructure limits the interfacial contact of polymer and LiF crystals and dampens this effect.

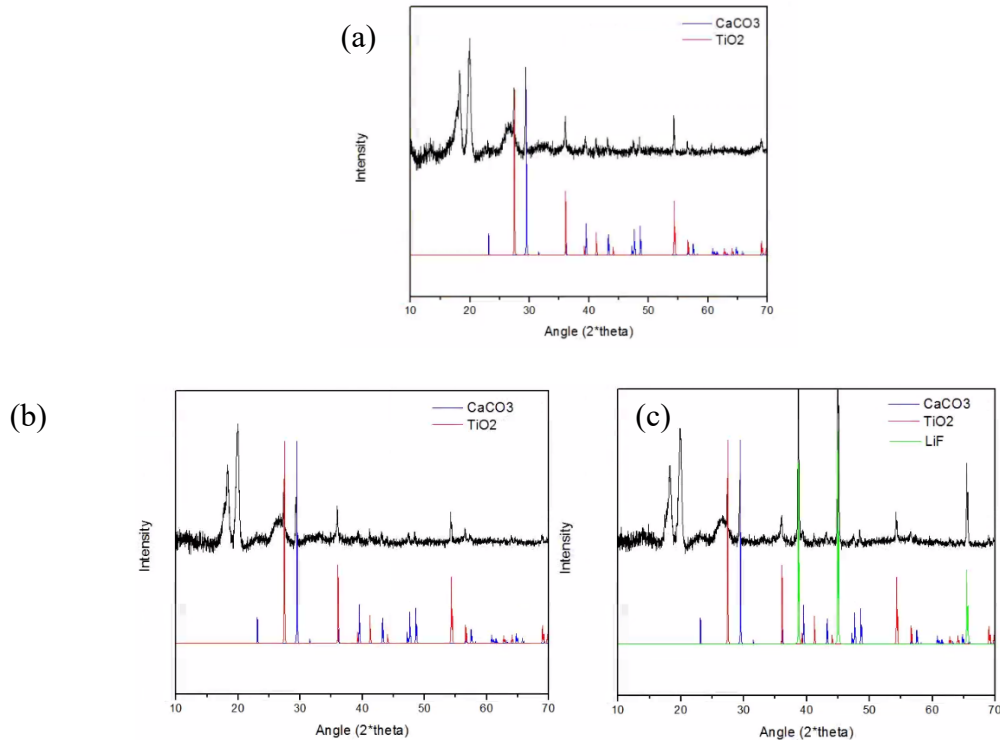


Figure 11. XRD spectra of (a) PVDF-HFP membrane (b) with PMMA and (c) with LiF

3.3.4 Mechanical Testing

Data obtained from analysis of tensile testing is displayed below in Figure 12 and Figure 13. The pure PVDF-HFP porous membrane had an elastic modulus of 161 MPa. Using a 7:3 composition of PVDF-HFP to PMMA significantly reduced the elastic modulus to 98 MPa. This may be in part due to the slightly larger pore sizes observed in membranes containing PMMA, its amorphous nature, or the two polymer chains not well entangling and strengthening each other. Similar trends were observed in other studies of polymer electrolytes utilizing a PMMA blend, with a sacrifice in strength made willingly to gain an increase in flexibility and liquid electrolyte compatibility ^{[25][50]}.

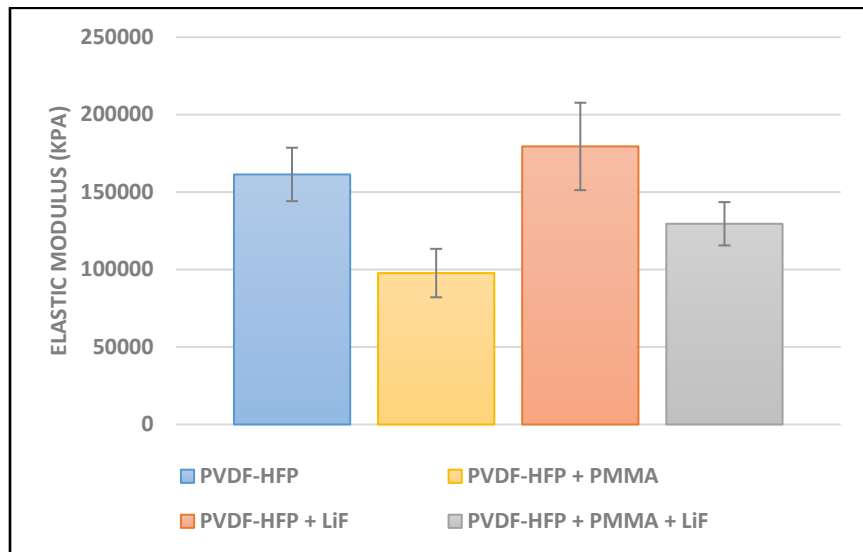


Figure 12. Elastic modulus data obtained from tensile testing

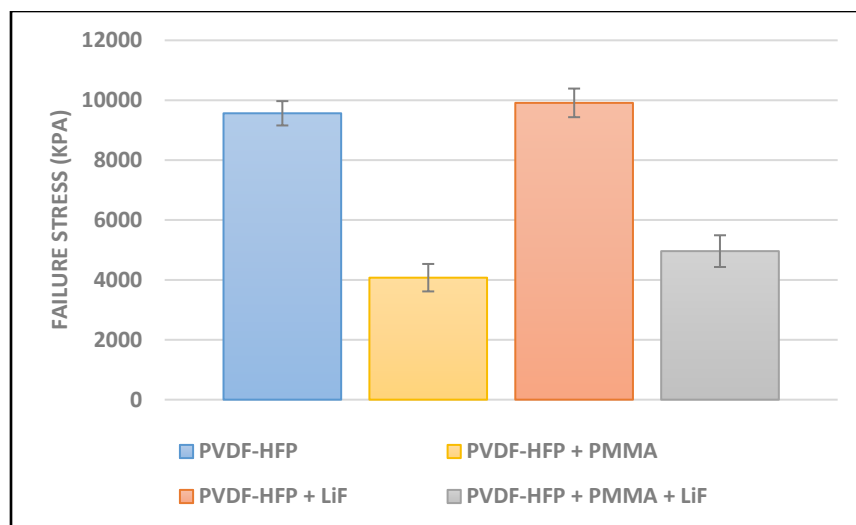


Figure 13. Failure stress data obtained from tensile testing

Membranes with lithium fluoride reinforcement saw a small increase in elastic modulus to 179 MPa. L. Yang et al saw a nearly threefold increase in elastic modulus with the incorporation of LiF, however the membranes of that study were notably less dense and fibrous because of preparation via controlled evaporation, increasing the interfacial contact between polymer and LiF [24]. When both additives were used together, PMMA was found to have a larger negative effect on strength than the positive impact of LiF. The resultant elastic modulus was 130 MPa, intermediate between pure PVDF-HFP and that containing PMMA. As noted with the LiF membrane, the highly porous and fibrous structure likely reduces the effectiveness of a particle reinforcement. The trends for failure stress in each membrane followed the same patterns as those for elastic modulus, and do not require further discussion.

On average, these membranes were recorded to have an elastic modulus about one magnitude lower than those reported by studies focused on controlled evaporation-produced membranes [24][25]. This was expected, with a tradeoff of higher porosity for reduced strength. Against more comparable immersion precipitated membranes produced by P. Zhang et al, both Membranes 1 and 3 showed about 1.5 times higher failure stress [13]. The membranes produced by

Zhang showed a high degree of asymmetry that may have concentrated stresses and caused membranes to fail sooner ^[13]. Their pure PVDF-HFP membranes produced without SiO₂ reinforcement were reported to be weaker, but by an unspecified amount.

3.3.5 Electrochemical Testing

The electrochemical stability of the gel membranes was evaluated by linear sweep voltammetry (LSV). PVDF-HFP gels were sandwiched between one stainless steel (SS) and one lithium electrode. Lithium acts as both the quasi-reference and counter electrode, and SS as the working electrode. The first sweep began at the open-circuit voltage (OCV; ~3.2V vs Li/Li⁺). A second sweep was performed down from OCV, to fully cover the manufacturer-recommended voltage range of the commercial NMC 622 cathodes, 3 - 4.3V.

The first notable increase in current occurs around 4.5V in Figure 14 due to anodic current from the oxidation of some material in the electrolyte system ^[51]. This is likely representative of simultaneous solid polymer and liquid electrolyte breakdown and matches expected values from literature ^{[13][25][49]}. After 4.5V, the slope quickly increases, and the gel would likely show signs of breakdown. From this data, the polymer gel is stable up to 4.5V, which well encompasses the desired testing window.

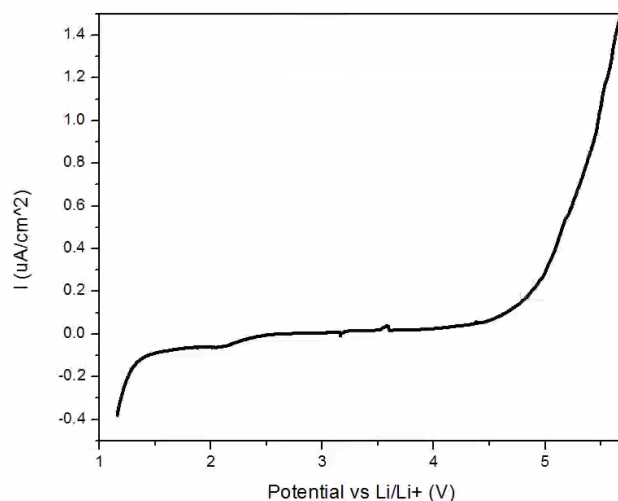


Figure 14. Electrochemical Stability Window of PVDF-HFP gel

The transference number is the ratio of species that carry electronic current during cell cycling. For electrolyte materials, generally the total ionic transference number is reported, and expected to ideally be ~ 1 , as any measurable electronic conductivity can result in short circuits and cell failure. To measure the total ionic transference number by DC polarization, gels are inserted between stainless steel electrodes and a low potential is applied. At the onset of testing, current is facilitated by both electronic and ionic conductivity. As the test proceeds, ionic species are driven to and blocked by the SS electrode, leaving the remaining value of current attributed to the electronic conduction. In Figure 15, the initial region of this curve is shown to highlight the sharp drop in current and subsequent levelling during only the first 10 seconds. Some noise was observed in the “steady-state” current value, so an average value was recorded for calculations. This noise is likely due to the resolution provided by the BioLogic, which was not rated for measurements at such a low current. The total ionic transference number was calculated using Equation 1 and was approximately 0.98. The observed noise and rate of data collection for initial points are possible sources of error that may artificially decrease this value, and the gel is assumed to be wholly ionically conductive.

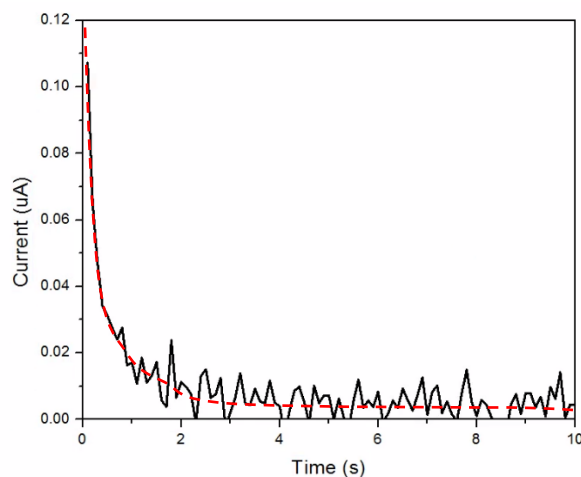


Figure 15. DC polarization curve of PVDF-HFP gel

The total ionic transference number can further be subdivided into conductivity afforded by lithium (Li^+) cations, hexafluorophosphate (PF_6^-) anions, and other small contributors. Potentiostatic polarization was performed on cells with two symmetric lithium electrodes separated by a polymer gel. Before polarization, EIS was used to determine the initial total resistances from the extrapolated x-intercepts of the observed semicircle on the Nyquist plots shown in Figure 16a-c. For the polarization process, a small potential of 50 mV is applied across the cell and held for an extended time. In theory, with the use of non-blocking lithium electrodes, the initial current will be fully ionic. If the PF_6^- anions expectedly not participate in redox reactions, their conductivity contributions will fade over time and the “steady-state” current will be comprised only of lithium cation contributions ^[42]. Total resistance after polarization is again analyzed via EIS after polarization. Equation 2, the Bruce-Vincent Equation, is used to calculate the lithium-ion transference numbers of pure PVDF-HFP gels, and those with added PMMA and LiF. It follows a similar structure to Equation 1 for total ionic conductivity, but the change in total resistance before and after polarization is incorporated to account for formation of a passivating

solid electrolyte interphase (SEI) layer on the lithium electrode which leads to an increase in total resistance [42].

Potentiostatic polarization curves are shown below in Figure 17a-c. As with DC polarization, the minimum current resolution of the BioLogic instrument resulted in noise and fluctuation of the recorded current value. To accommodate for this, values in the “steady-state” region were averaged to obtain an I_{ss} value for calculations. The gels containing PMMA and LiF both experienced apparent dendritic growth and short circuits after multiple hours of polarization, where a sharp increase was seen in the current. Measurements were taken from the stable region before this occurred. Unfortunately, the short circuits made post-polarization EIS impossible. The missing R_{ss} values were approximated by repeating the 10% decrease in bulk resistance observed in the pure PVDF-HFP cell.

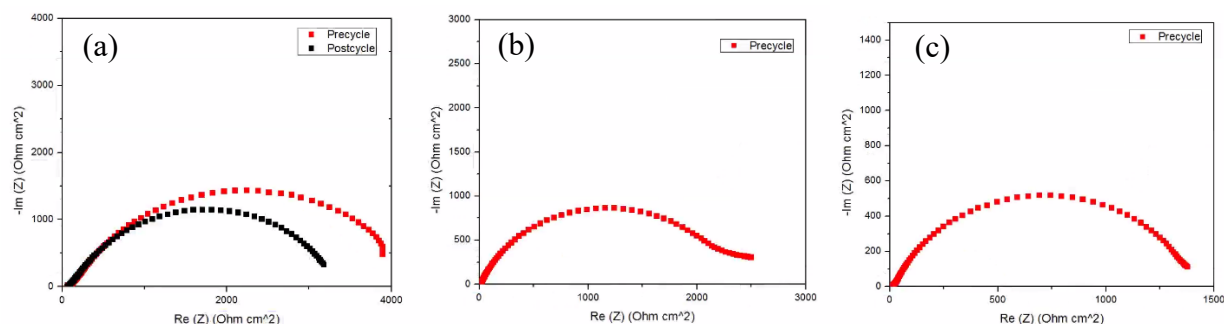


Figure 16. EIS generated Nyquist plots of pre and post-potentiostatic polarization of (a) PVDF-HFP gel (b) with PMMA and (c) with LiF

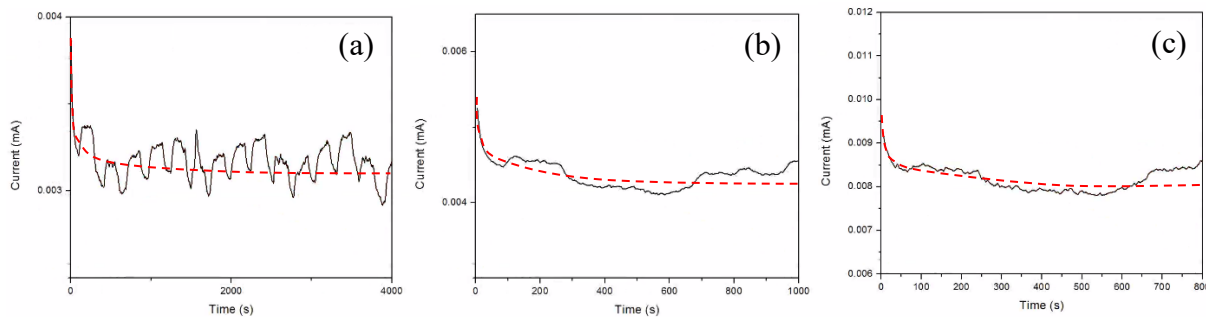


Figure 17. Potentiostatic polarization curves of (a) PVDF-HFP gel (b) with PMMA and (c) with LiF

Using the equations and error estimations discussed above, pure PVDF-HFP was found to have a lithium transference number of ~ 0.33 . This would indicate that $1/3$ of ionic conduction is carried out by lithium ions, which is slightly below values reported in literature for other PVDF-HFP gels produced through various means ^{[13][24]}. Gels containing PMMA showed better performance, with a calculated transference number of ~ 0.56 . PMMA was observed to reduce crystallinity and increase porosity of the membranes, which improves ionic transport and may explain this result. Gels with LiF also showed notable improvement, with a transference number of ~ 0.51 . Lithium fluoride has been shown to facilitate ionic conductivity, which is directly related to the transference number ^[24].

Ionic conductivity is a critical property of electrolyte materials and determines how quickly and steadily cells can be cycled. Cells were constructed with symmetric stainless steel blocking electrodes and PVDF-HFP gels containing LiF. EIS was performed to obtain total resistance, and the obtained Nyquist plot is pictured below in Figure 18. For this graph, no classical semicircle is present, only an x-intercept and a Warburg tail. This is indicative of a “flooded” cell, in which the amount of liquid electrolyte is so high that it is near-solely responsible for conduction, however the membrane was produced using the standardized process of soaking for ~ 5 minutes before cell assembly with no excess liquid applied. The $0.8 \Omega \cdot \text{cm}^2$ resistance was used in Equations 3 and 4 to calculate ionic conductivities of the gel, with gel thickness estimated from dry measured

thickness via SEM and liquid electrolyte uptake to account for swelling. The high compressibility of the gels makes physical measurement impractical. The devised Equation 5 for approximate thickness is displayed below.

$$\text{Equation 5. } l_{gel} = \frac{(l_{dry} * A) + (\frac{m_{LE}}{\rho_{LE}})}{A} = \frac{V_{dry} + V_{LE}}{A}$$

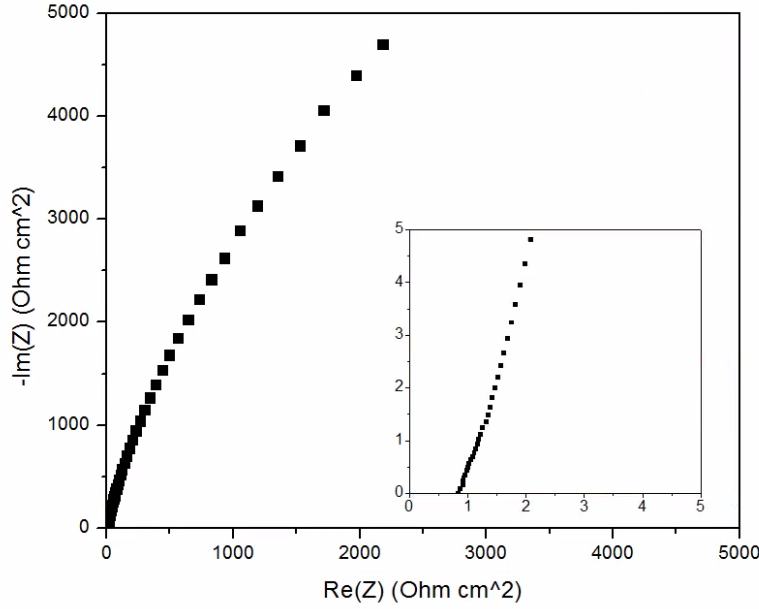


Figure 18. Nyquist plot obtained from EIS of PVDF-HFP gel containing LiF additive with stainless steel electrodes

The total conductivity of the PVDF-HFP and LiF gel was calculated as $7.93 \times 10^{-3} \text{ S/cm}^2$. Using Equation 4, that translates to a lithium conductivity of $4.44 \times 10^{-3} \text{ mS/cm}^2$. These values are relatively high, comparable to those reported by commercial liquid electrolytes of the same composition as used in this study. This indicates that conduction occurs near-exclusively through the liquid electrolyte in this cell, the ideal case for a gel electrolyte with high porosity. “Flooded” cells are not uncommon, but typically are created by adding excess liquid to the gelling membrane, and the observed values can likely be attributed to the high rate and scale of liquid electrolyte uptake. These values should be taken as a maximum, as the approximation of gel thickness in Equation 5 does rely on multiple assumptions.

Charge-discharge behavior was evaluated using chronopotentiometry, also known as galvanostatic cycling. Cutoff voltages for the testing window were defined as 3 – 4.3V, in accordance with recommended cathode material specifications. Pouch cells of construction shown in Figure 3.1 were evaluated at various rates, beginning with C/20 and increasing to C/10 and C/5 if stable cycling was observed. Cycling rates were symmetric for charge and discharge. All testing was performed at room temperature.

The most common method of failure observed was indicative of dendritic growth and resulting in partial short circuits. Typically, high instability would be observed in the recorded potential and current within the first 2-3 cycles, accompanied by very low coulombic efficiencies. This was drastically reduced by incorporating LiF into polymer gels, which have been observed to suppress the growth of lithium dendrites mechanically and chemically ^{[24][52]}. Dendrite growth from the anode should theoretically be blocked by the dense garnet electrolyte but can advance through any small imperfections in the structure.

The reported current density of commercial NMC 622 cathode was 2 mAh/cm², or 181.5 mAh/g. During cell assembly, cathodes were photographed and sized using ImageJ software to calculate cell capacities and appropriate current for desired cycling rates ^[53]. Initial cycling began at 0.1 mAh/cm² (C/20) with high observed discharge capacities up to 172 mAh/g and coulombic efficiency up to 95%. The rate was increased to 0.2 mAh/cm² (C/10) with high capacity retention and less instability of coulombic efficiency than the initial cycles as seen in Figure 3.20, reaching 171 mAh/g and 98% efficiency. The initial cycle at 0.4 mAh/g (C/5) had a 24% drop in discharge capacity to 133 mAh/g and began to show instability visible in Figure 19. Subsequent cycles continued to drop in capacity and showed high indications of partial short circuits. The cell was returned to cycling at a C/10 rate, but permanent damage had already occurred, and it continued

to operate at less than 100 mAh/g. These cycles are not included in Figure 3.20 as they do not add any meaningful data. Figure 20 shows that the Nyquist plots for this cell. The black curve was obtained before any cycling was performed, and the red was after the loss of performance occurred. An increase of $\sim 60 \Omega \cdot \text{cm}^2$ was observed, possibly due to breakdown of the electrolyte materials after many partial short circuits.

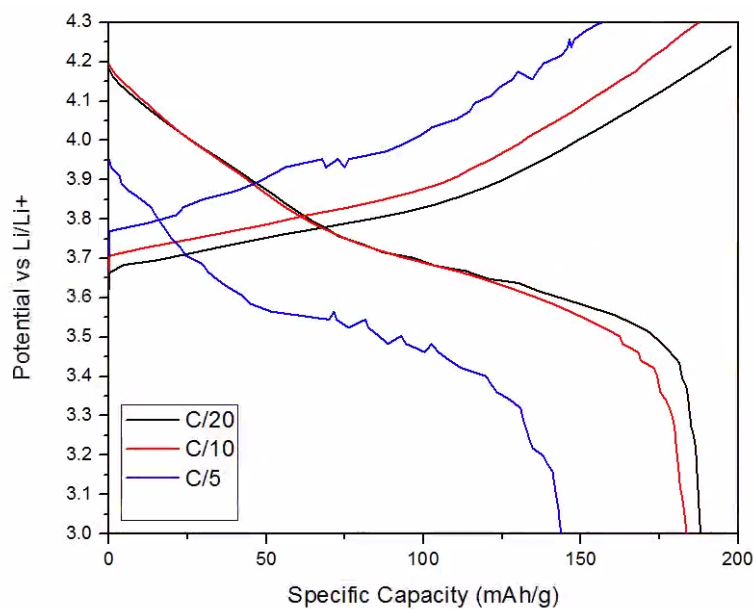


Figure 19. Galvanostatic charge-discharge curves at different cycling rates of cell containing LiF-supported gels

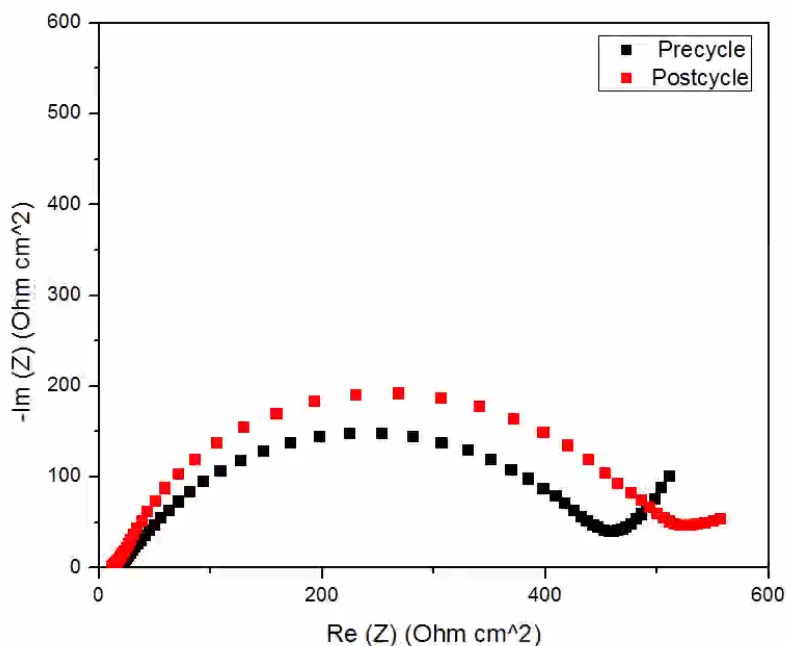


Figure 20. EIS produced Nyquist plots of cell containing LiF supported membrane before and after cycling

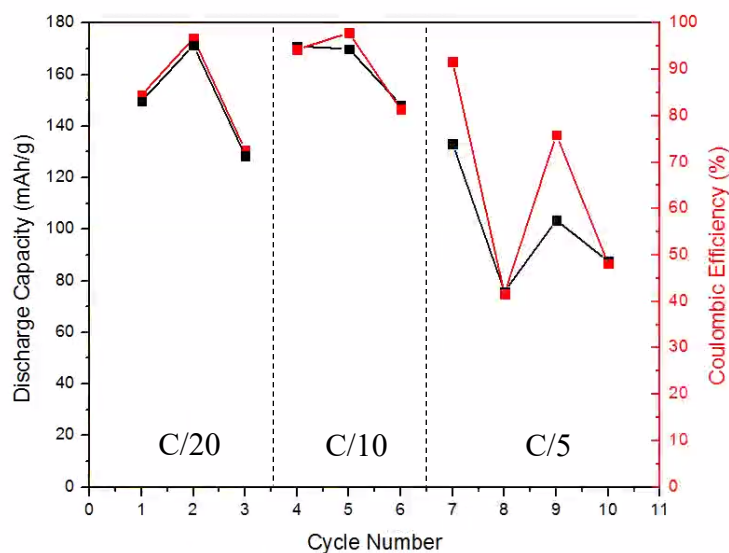


Figure 21. Coulombic efficiency and specific discharge capacity over first 10 cycles of PVDF-HFP + LiF gel

Apart from dendrite growth as a failure mechanism, difficulty cycling at higher rates may be in part attributed to relatively low ionic conductivity of polymer and gel electrolytes at room temperature ^[22]. While the reported value for total conductivity was 7.93×10^{-3} S/cm, other samples recorded lower values dependent on processing, likely showing more contributions to

resistance from the polymer membrane. Room temperature operation is ideal, as the need for an external heat source significantly restricts the versatility of cell application. The increased thickness of gel also increases the ohmic resistance of the cell. Thinner membranes were produced, shown in Figure 4, but were not able to be cycled successfully. If these could be incorporated and successfully protected, it may also improve the efficiency and rate capability of future cells.

3.4 Conclusions

Utilizing the immersion precipitation method can produce polymer membranes with very high porosity and fibrous microstructure. This porosity enabled nearly 600% average liquid electrolyte uptake while maintaining appreciable mechanical strength. Ionic conductivity was comparable in magnitude to the liquid electrolyte at 7.93×10^{-3} S/cm, mirroring “flooding” behavior due to the high porosity and liquid uptake. During cycling, high electrochemical stability enabled charge up to 4.3V vs Li/Li⁺ and discharge capacities up to 172 mAh/g, though coulombic efficiency showed high variability. The mechanical and material properties suggest that these gels could have a promising future for lithium-ion battery technology, but future work will need to be done to improve their stability and resistance to dendrite penetration. Continued advancements in the repeatable processing of solid garnet electrolytes by groups such as Dr. Wachsman’s will also contribute by removing this primary failure mechanism.

Chapter 4: Conclusions and Recommendations

4.1 Conclusions

Through experimental exploration of the immersion precipitation process for polymer interlayer fabrication and use in electrochemical applications, we have reached the following conclusions.

- (1) Immersion precipitation can consistently produce high porosity membranes from PVDF-HFP polymer with a unique fibrous microstructure. Liquid electrolyte uptake was recorded at nearly 600% for all membrane compositions evaluated. The choice of nonsolvent for immersion impacts the final microstructure and ease of processing, with isopropanol observed to produce uniform morphology more regularly than water.
- (2) The addition of PMMA to PVDF-HFP membranes facilitates higher porosity and decreases crystallinity but lowers the elastic modulus by over half. Gels containing PMMA have a relatively high measured lithium transference number and are more likely than those without to develop ideal microstructure after casting.
- (3) Inclusion of LiF increases the mechanical strength of PVDF-HFP membranes and reduces the frequency of cell failure which suggest dendrite growth. It also decreases membrane crystallinity and affords a relatively high lithium transference number of 0.51. The ionic conductivity of PVDF-HFP gels containing LiF is relatively high, and believed to be predominately carried by the liquid electrolyte due to their high porosity.
- (4) Polymer gels containing LiF show good electrochemical stability up to 4.5V vs Li/Li⁺, allowing compatibility with a high voltage NMC 622 cathode. During cycling, discharge

capacities up to 188 mAh/g were measured, though high fluctuations in capacity and coulombic efficiency were observed.

- (5) Gels designed as interlayers with intentional high porosity present challenges for characterization and cycling. When sandwiched between a cathode and ideal dense garnet electrolyte, pinholes would not present issues, however when attempting to study symmetric cells or when garnet bilayer structure contains imperfections, they often experience partial or complete short circuits. Increasing the thickness of polymer membranes and use of lithium fluoride both reduce the prevalence of this issue but do not eliminate it.

4.2 Recommendations for Future Work

Immersion precipitation remains unconventional for electrochemical applications. From the observations and results of this study, numerous research avenues have presented which may improve the materials studied or implement this method for novel purposes.

- (1) The microstructure of produced PVDF-HFP was extensively studied while dry, but it is unknown how it may have changed after soaking in liquid electrolyte or while in use as an interlayer. Due to the very high liquid uptake, it is assumed that there would be significant expansion. It would also be beneficial to observe the compression of the gel after vacuum sealing during pouch cell assembly. The gels are very flexible, and it is unclear how much the porous microstructure would be compacted, which may increase cell resistance and explain the below-expected conductivity measurements.
- (2) Reduction of membrane thickness was done easily, with membranes measured as thin as 15 μm . Replacement or partial substitution of acetone with a lower volatility solvent could allow

for even thinner casts. This was the original design for the study and would be interesting to explore if short circuits could more readily be prevented.

- (3) The density and cast microstructure of produced membranes was inconsistent at times and believed to be affected by relative humidity. During humid weather, cast membranes showed less opacity after drying and less porosity on SEM imaging. No data was collected on this possibility, so it was excluded from this study, but more understanding may improve future processing consistency and performance.
- (4) Both PMMA and LiF were found to contribute unique benefits in PVDF-HFP membranes, however little optimization was done on the weight percent of each included. LiF improved cell stability to a level that cycling could be consistently evaluated and better understood, despite other chronic problems. It is unknown if additional LiF would further improve performance. PMMA incorporation showed benefits for liquid uptake and transference number, but a heavy penalty of elastic modulus and failure stress. Using a lower fraction of PMMA could maintain these benefits and strengthen the membranes.
- (5) Gel cathodes were produced via immersion precipitation, using NMC 622 powder with PVDF-HFP binder and carbon nanotubes. A porous microstructure was observed qualitatively via SEM, and over 300% liquid electrolyte uptake was recorded. This porosity was higher than ideal and resulted in low loading of $\sim 0.83 \text{ mAh/cm}^2$ but could be optimized with more time. Liquid cells were cycled with very high efficiency but low capacity and merit further investigation.

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