

ABSTRACT

Title of Dissertation: NANOMATERIALS FOR GARNET BASED
SOLID STATE ENERGY STORAGE

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Materials Science and Engineering

Solid state energy storage devices with solid state electrolytes (SSEs) can potentially address Li dendrite-dominated issues, enabling the application of metallic lithium anodes to achieve high energy density with improved safety. In the past several decades, many outstanding SSE materials (including conductive oxides, phosphates, hydrides, halides, sulfides, and polymer-based composites) have been developed for solid-state batteries. Among various SSEs, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is one of the most important and appealing candidates for its high ionic conductivity ($10^{-4}\sim 10^{-3}$ S/cm) at room temperature, wide voltage window (0.0-6.0V), and exceptional chemical stability against Li metal. However, its applications in current solid state energy storage devices are still facing various critical challenges. Therefore, in this quadripartite thesis I focus on developing nanomaterials and corresponding processing techniques to improve the comprehensive performance of solid state batteries from the perspectives of electrolyte design, interface engineering, cathode improvement, and full cell construction.

The first part of the thesis provides two novel designs of garnet-based SSE with outstanding performance enabled by engineered nanostructures: a 3D garnet nanofiber network and a multi-level aligned garnet nanostructure. The second part of the thesis focuses on negating the anode|electrolyte interfacial impedance. It consists of several processing techniques and a comprehensive understanding, through systematic experimental analysis, of the governing factors for the interfacial impedance in solid state batteries using metallic anodes. The third part of the thesis reports several processing techniques that can raise the working voltage of $\text{Li}_2\text{FeMn}_3\text{O}_8$ (LFMO) cathodes and enable the self-formation of a core-shell structure on the cathode to achieve higher ionic conductivity and better electrochemical stability. The development and characterization of a solid state energy storage device with a battery-capacitor hybrid design is included in the last part of the thesis.

NANOMATERIALS FOR GARNET BASED SOLID STATE ENERGY STORAGE

by

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Table of Contents

Acknowledgements.....	ii
Table of Contents.....	iv
List of Tables.....	vi
List of Figures.....	vii
List of Abbreviations.....	xiv
Chapter 1: Background.....	1
1.1. Development of Solid State Energy Storage.....	1
1.2. Ion Transport Mechanisms in Solid State Electrolytes.....	5
1.3.1. Crystallized Solids.....	5
1.3.2. Amorphous Solids.....	8
1.3.3. Composite Solids.....	9
1.3. Challenges in Developing Solid State Electrolytes.....	11
1.4. Garnet-Based Solid State Electrolytes.....	13
1.5. Emerging Opportunities for High Voltage Cathodes.....	15
1.6. Thesis Structure.....	19
Chapter 2: Nanostructured Garnet-Based Solid State Electrolytes.....	23
2.1. Three-Dimensional Garnet Nanofiber Network.....	23
2.1.1. Electrospinning-Assisted Sol-Gel Synthesis.....	24
2.1.2. Results and Discussion.....	27
2.1.3. Experimental Method.....	32
2.2. Multi-Level Aligned Garnet Nanostructure.....	32
2.2.1. Dependence of Ion Transport Properties on Tortuosity.....	32
2.2.2. Nature-Inspired Low Tortuosity Structure Design.....	35
2.2.3. Structure-Derived Template Design.....	37
2.2.4. Wood-Templated Sol-Gel Synthesis.....	43
2.2.5. Results and Discussion.....	48
2.2.6. Experimental Method.....	58
2.3. Conclusion.....	59
Chapter 3: Interface Engineering for Solid State Batteries.....	61
3.1. Negating Interfacial Impedance through Al ₂ O ₃ Coating.....	62
3.1.1. Surface Modification with Atomic Layer Deposition.....	62
3.1.2. Electrochemical Analysis on Interfaces.....	63
3.1.3. Interface Imaging and Elemental Analysis.....	67
3.1.4. Experimental Method.....	69
3.2. Critical Factors for the Garnet Li _{metal} Interfacial Impedance.....	70
3.2.1. Diffusivity and Ionic Conductivity.....	70
3.2.2. Lithiation Time.....	77
3.2.3. Lithiation Temperature.....	80
3.2.4. Lithium-Tin Alloy as Anode.....	83
3.2.5. Coating Materials and Configurations.....	88
3.2.6. Coating Thickness.....	92

3.2.7. Experimental Method.....	97
3.3. Conclusion	98
Chapter 4: High Voltage Cathode for Solid State Batteries	100
4.1. High Voltage Cathode $\text{Li}_2\text{FeMn}_3\text{O}_8$	100
4.2. Halogen Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$	102
4.2.1. Synthesis of Chlorine Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$	102
4.2.2. Synthesis of Fluorine Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$	102
4.2.3. Results and Discussion	103
4.2.4. Experimental Method.....	122
4.3. Aluminum Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$	123
4.3.1. Diffusion-Induced Self-Formation of Core-Shell Structure	124
4.3.2. Results and Discussion	126
4.3.3. Experimental Method.....	131
4.4. Conclusion	132
Chapter 5: A Solid State Energy Storage Device with a Hybrid Design	134
5.1. Battery-Supercapacitor Hybrid Devices	134
5.2. Hybrid Design of Solid State Energy Storage Device	135
5.3. Developing Solid State Gel Electrolyte	137
5.4. Results and Discussion	141
5.5. Experimental Method.....	149
5.6. Conclusion	151
Chapter 6: Conclusions and Outlook	152
6.1. Thesis Summary.....	152
6.2. Future Work	154
Appendices I. Scientific Visualizations	156
Bibliography	159

List of Tables

Table	1.1	Summary of various commonly used Li-ion SSEs.
Table	3.1	Interfacial ASR summary for various coating materials, configurations, and anode compositions
Table	4.1	Quantified content of each element and normalized chlorine concentration (x) of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ obtained from EDX.

List of Figures

Figure	1.1	Crystal structure of garnet type cubic LLZO showing its sublattice
Figure	1.2	Ion conduction mechanism in crystalline PEO polymer (Image from ref. 57).
Figure	1.3-a	Ion transport in amorphous solid polymers via (a) intrachain hopping
Figure	1.3-b	Ion transport in amorphous solid polymers via (a) intrachain hopping and (b) interchain hopping
Figure	1.4	Ion transport in composite electrolyte with inactive fillers, semi-active fillers, and active fillers.
Figure	1.5	Crystal structure of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet.
Figure	1.6	Voltage and capacity range comparison of several most popular cathode materials for lithium ion batteries.
Figure	1.7	Structural comparison of (a) layered oxides, (b) spinel oxides, and (c) poly-anion compounds.
Figure	1.8	Flow chart illustrating the overall structure and focuses of the thesis.
Figure	2.1	Experiment setup for electrospinning.
Figure	2.2	XRD pattern of garnet nanofibers matches with the XRD pattern of LLZO.
Figure	2.3	Photo of a piece of as-spun garnet nanofiber precursor network. The film is flat, flexible, and mechanically robust.
Figure	2.4	Photo of a piece of calcined garnet nanofiber network.
Figure	2.5	Schematic of the LLZO-PEO composite electrolyte membrane.
Figure	2.6	SEM images of the as-spun garnet nanofiber precursor network.
Figure	2.7	SEM images of the garnet nanofiber network after calcination.
Figure	2.8	Diameter distribution comparison of garnet precursor nanofibers and garnet nanofibers.
Figure	2.9	TEM image of garnet nanofibers showing that the fibers are multicrystalline.
Figure	2.10	TEM image magnified at the joint of two garnet nanofibers showing that the fibers are merged with each other at the points of contact. Inset shows a fast-Fourier transformation (FFT) image of the well crystalized garnet.
Figure	2.11-a	Arrhenius plot of the LLZO-PEO SCE at elevated temperatures.
Figure	2.11-b	LSV curve of the LLZO-PEO SCE showing the electrochemical stability window in the range of 0-6V.
Figure	2.11-c	Voltage profile of a long-term lithium plating/stripping cycling with a current density of 0.5 mA/cm ² at 25°C

Figure 2.12	Ion transport pathways in solid state electrolytes with different compositions.
Figure 2.13	SEM images and schematics showing the fibrous, multi-level aligned, porous structure of wood.
Figure 2.14	Schematic of multi-scale aligned mesoporous garnet $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ (LLZAO) membrane incorporated with polymer electrolyte in a lithium symmetric cell. The garnet-wood possesses multi-scale aligned mesostructure derived from natural wood, which enables the unobstructed Li ion transport along the garnet-polymer interface, through garnet, and through polymer electrolyte.
Figure 2.15	Illustrations of the wood template fabrication through compressing, and the multi-level aligned fibrous structure in the wood template.
Figure 2.16	Photo of pristine basswood.
Figure 2.17	Photo of compressed wood showing a piece of wood template fabricated from basswood through partial lignin removal and mechanical compression.
Figure 2.18	(a) Top-view and (b) Cross-sectional SEM image of pristine wood.
Figure 2.19	(a) Top-view and (b) cross-sectional SEM image of compressed wood.
Figure 2.20	SEM image of the aligned nanofiber with a diameter of around 10 nm.
Figure 2.21	Weight change of the wood template during precursor infiltration.
Figure 2.22	Photo of an as sintered aligned mesoporous garnet membrane.
Figure 2.23	Cross-sectional SEM image shows the alignment of channels at both (a) micro-scale and (b) nano-scale.
Figure 2.24	Flexibility comparison of garnet-wood to bulk garnet.
Figure 2.25	Photograph of the flexible garnet-wood consisting of aligned mesoporous garnet and PEO based polymer electrolyte.
Figure 2.26	XRD pattern of the aligned garnet matches JCPDS#90-0457, which verifies the cubic garnet structure.
Figure 2.27	Cross-sectional SEM image of the aligned garnet structure with a thickness of 18 μm .
Figure 2.28	HRTEM image of a nanoparticle broken off from the aligned garnet showing the (21 $\bar{0}$) and (021) lattice planes.
Figure 2.29	TEM image of the edge of a garnet nanoparticle showing a clear multi-crystalline structure.
Figure 2.30	EELS spectrum of the garnet surface showing the ROI, spectrum image, and relative composition map of O, C, and La, respectively.
Figure 2.31	Cross-sectional SEM image of garnet-wood with a thickness of $\sim 30 \mu\text{m}$.

Figure 2.32	SEM and its corresponding EDX images showing the complete, uniform infiltration of polymer electrolyte throughout the aligned garnet. Scale bars, 100 μm .
Figure 2.33	Nyquist plot showing the decrease in the impedance of the garnet-wood membrane with increasing temperature, the inset schematic shows the structure of the testing cell.
Figure 2.34	Comparison of the ionic conductivity of the garnet-wood and PEO based polymer electrolyte at different temperatures, the blue region indicates measurements performed within the range of room temperature (RT).
Figure 2.35	Nyquist plot of the PEO/SCN/Li-TFSI electrolyte at different temperatures.
Figure 2.36	Ionic conductivity of the PEO/SCN/Li-TFSI electrolyte at different temperatures. The blue region indicates measurements performed around room temperature (RT). Inset shows the structure of the testing cell.
Figure 2.37	Galvanostatic cycling of Li/garnet-wood/Li with a current density of 0.1 mA/cm ² at room temperature.
Figure 2.38	Galvanostatic cycling of Li/garnet wood/Li with a current density of 0.1 mA/cm ² at room temperature for over 600 hours.
Figure 3.1	Schematic, photo and cross-sectional SEM image comparison of the Li wetting behavior on treated and non-treated garnet.
Figure 3.2	EIS of the symmetric Li/ALD garnet/Li: the red curve is the EIS of ALD garnet and black curve is the EIS of bare garnet one.
Figure 3.3-a	Comparison of DC cycling for symmetric cells of Li/bare garnet/Li (black curve) and Li/ALD treated garnet/Li (red curve). The inset is the magnified curve of the ALD treated cell.
Figure 3.3-b	DC cycling of symmetric cell of Li/bare garnet/Li, showing unstable plating/stripping curve with high overpotential up to 6 V.
Figure 3.3-c	DC cycling of symmetric cell of Li/ALD treated garnet/Li, showing stable plating/stripping curve with low overpotential of 20-30 mV.
Figure 3.4	TEM sample preparation procedure using FIB.
Figure 3.5-a	Typical TEM image of the Al ₂ O ₃ /garnet interface,.
Figure 3.5-b-g	The corresponding STEM HAADF image and (c-g) EELS mappings (Al, Li, O, overlapped Al and Li, and Ti, respectively) for the sample Al ₂ O ₃ -treated garnet.
Figure 3.6-a	EELS with energy 250 – 1000 eV showing peaks of Zr M-edge, O K-edge, and La M _{4,5} -edge
Figure 3.6-b	EELS with energy 50 – 120 eV showing peaks of Li K-edge and Al L-edge.

Figure 3.7	Image of a typical testing cell with Al_2O_3 coated dense pellet sandwiched by two lithium metal electrode.
Figure 3.8	Typical EIS curve for testing cells with non-blocking lithium metal electrodes on both sides, the fitted semi-circles, and the corresponding equivalent circuit.
Figure 3.9	Nyquist plot showing the interfacial impedance decreases with the increase of heating time. The testing cells all had a 3nm Al_2O_3 coating and were heated at 200°C.
Figure 3.10	Nyquist plot showing the interfacial impedance decreases with the increase of heating time. The testing cells all had a 3nm Al_2O_3 coating and were heated at 250°C.
Figure 3.11	Nyquist plot showing the interfacial impedance decrease after being heated at 200°C for 10 minutes.
Figure 3.12	Nyquist plot showing the interfacial impedance decrease after being heated at 250°C for 10 minutes.
Figure 3.13	Nyquist plot showing the interfacial impedance decrease after being heated at 300°C for 10 minutes.
Figure 3.14	Nyquist plot comparison of testing cells after being heated at 300°C for 10 minutes and 20 minutes.
Figure 3.15	Wettability of molten Li-Sn alloys with various Sn content on alumina substrates.
Figure 3.16	Images demonstrating the fast wetting speed of Li-Sn alloy on bare garnet surface.
Figure 3.17	Cross-sectional SEM image of a garnet pellet coated with Li-Sn alloy.
Figure 3.18	SEM image focusing on the Li-Sn garnet interface.
Figure 3.19	Cross-sectional SEM image of a porous garnet structure infiltrated with Li-Sn alloy.
Figure 3.20	A close-up cross-sectional SEM image of a porous garnet structure infiltrated with Li-Sn alloy, focusing on the infiltrated Li-Sn alloy in the pores.
Figure 3.21	Nyquist plot comparison of testing cells after being heated at 250°C from 2 minutes to 15 minutes.
Figure 3.22	Nyquist plot comparison of testing cells after being heated at 220°C from 1 minutes to 15 minutes. The dense garnet in the testing cell is coated with 10nm ZnO.
Figure 3.23	Process flow chart of double coating the garnet with Al_2O_3 and ZnO.
Figure 3.24	Nyquist plot comparison of the testing cells ($\text{ZnO@Al}_2\text{O}_3\text{@garnet}$) using pure lithium anode after being heated at 220°C from 3 minutes to 15 minutes.
Figure 3.25	Nyquist plot comparison of the testing cells ($\text{ZnO@Al}_2\text{O}_3\text{@garnet}$) using Li-Sn alloy anode after being heated at 220°C from 1 minute to 6 minutes.
Figure 3.26	The experimental setup for lithium coating using hot pressing method.

Figure 3.27	Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses.
Figure 3.28	A zoom-in at high frequency of the Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses.
Figure 3.29	The experimental setup for lithium coating using dip-coating method.
Figure 3.30	Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses. Inset shows an image and a structure schematic of the testing cell.
Figure 3.31	Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses.
Figure 4.1	Crystal structure comparison of LFMO in (a) ideal and (b) real situation. The abundant oxygen vacancies in LFMO crystal provide sites for chlorine to occupy.
Figure 4.2	Photo of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ powder shows that the cathode color gets darker as the x increases from 0 to 1.5.
Figure 4.3	XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various chlorine concentrations.
Figure 4.4	EDX spectrum of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various chlorine concentrations.
Figure 4.5	XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations: (a) $x=0$; (b) $x=0.67$; (c) $x=1.0$; (d) $x=1.5$, inset figure shows the comparison of (440) peak location.
Figure 4.6	Lattice constant comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations: $x=0\sim 1.5$.
Figure 4.7	XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations showing a saturation dopant concentration.
Figure 4.8	Shape evolution of cuprous (Cu_2O) from cubic to octahedron reported by Xu J et al. Blue dots represent activated corners. R is defined as the growth rate ratio along the $\langle 100 \rangle$ direction over the $\langle 111 \rangle$ direction.
Figure 4.9	SEM image of undoped pristine $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=0$).
Figure 4.10	SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=0.67$).
Figure 4.11	SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=1$).
Figure 4.12	SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=1.5$).
Figure 4.13	XPS Survey spectrum of $\text{Li}_2\text{FeMn}_3\text{O}_{7.25}\text{Cl}_{1.5}$.
Figure 4.14	Detailed XPS spectrum plot showing Cl 2p.
Figure 4.15	Detailed XPS spectrum plot Mn 3s.
Figure 4.16	Detailed plot showing Mn 2p XPS spectrum, where the shoulder is marked with a short black line.
Figure 4.17	Cyclic voltammetry comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations ($0 \leq x \leq 1.5$).
Figure 4.18	Rate performance comparison (from 0.5C to 5C) of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations.

Figure 4.19	Cycling performance comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations ($0 \leq x \leq 2$).
Figure 4.20	Voltage profile comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with $x=1$ and $x=0$.
Figure 4.21	Theoretical and experimental capacity comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various Cl content.
Figure 4.22	Mechanism of the Al_2O_3 coating self-formation, and the lithiation process of the Al_2O_3 coating.
Figure 4.23	A process flow chart for synthesizing cathode particles coated with self-formed alumina layer, and their lithiation when integrated with solid state electrolytes.
Figure 4.24	TEM image of pristine LFMO particles annealed at 500°C for 1 hour.
Figure 4.25	SEM image of Al doped LFMO particles annealed at 500°C for 1 hour showing a uniform coating on the particles.
Figure 4.26	Close up SEM image of Al doped LFMO annealed at 500°C for 1 hour showing that the coating thickness is about 3 nm.
Figure 4.27	EDX spectrum of Al doped LFMO annealed at 500°C for 1 hour shows strong Al signal.
Figure 4.28	XPS results focused on Al 2p signal of Al doped LFMO annealed at 500°C for 1 hour. The binding energy for Al2p indicates that the Al is in the form of Al_2O_3 on the surface of the LFMO particles.
Figure 4.29-a	XRD pattern comparison of garnet LLZO, pristine LFMO and garnet LLZO mixture, Al-doped LFMO and garnet LLZO mixture, and Al-doped LFMO. All the samples were annealed at 500°C for 1 hour.
Figure 4.29-b	XRD pattern comparison of pristine garnet LLZO, Al-doped LFMO, and a mixture of Al-doped LFMO, garnet LLZO, and LiOH. All the samples were annealed at 700°C for 1 hour.
Figure 4.30-a	Nyquist plot comparison of 500°C annealed LFMO, 500°C annealed Al doped LFMO, and 900°C annealed Al doped LFMO;
Figure 4.30-b	A zoom-in of EIS curve at higher frequencies.
Figure 5.1	Schematic of the hybrid device consisting of LFP cathode, gel polymer electrolyte, and RGO/CNT composite anode. Zoom-in schematic shows the working mechanism of the hybrid device.
Figure 5.2	SEM image of a piece of dry PVdF-HFP co-polymer top surface.
Figure 5.3	Photo image of a piece of PVdF-HFP membrane absorbing liquid electrolyte during gelation.
Figure 5.4	CV profile of the gel electrolyte membrane composed of PVdF-HFP and organic electrolyte at the scanning rate of 1 mV/s within a potential window of 0-5 V.

Figure 5.5	Impedance comparison of the gel and liquid electrolyte shows the similar ionic conductivity of gel electrolyte with organic liquid electrolyte. (Inset plot shows their intersections with the Z' axis).
Figure 5.6-a	SEM image of the anode material shows the interconnected porous network of CNT and RGO.
Figure 5.6-b	Photograph of a piece of the RGO/CNT anode
Figure 5.6-c	Voltage profile of the RGO/CNT material in a half cell configuration against a Li metal reference electrode shows a high columbic efficiency from the second cycle
Figure 5.6-d	Capacity comparison of the RGO/CNT material at different currents densities shows the superior capacity of the anode at high rates.
Figure 5.7	SEM image of the cathode shows the 1 μm thickness of Al leaf on top of the LFP-CB-PVdF cathode.
Figure 5.8	Photograph of a piece of Al leaf supported by the stamen of a flower showing the ultra-lightweight feature of the Al leaf as a current collector.
Figure 5.9	The comparison of the charge and discharge capacities of the integrated LFP cathode at the 1st cycle, 10th cycle, and 100th cycle under a current density of 10 C shows the superior capacity and high coulombic efficiency.
Figure 5.10	Cycling performance of the integrated Al leaf/ LFP cathode at a current density of 10 C for 300 cycles without obvious capacity decay shows the outstanding stability of the integrated cathode.
Figure 5.11	Voltage profile of the hybrid cell using gel electrolyte.
Figure 5.12	EIS curve of the hybrid cell using gel electrolyte.
Figure 5.13	Cycling performance of the hybrid cell under a current density of 170 mA/g shows the great stability and high capacity of the hybrid device.
Figure 5.14	The Ragone chart shows energy density versus power density for various energy storage devices. Our hybrid devices exhibit both high energy density and power density of 180 Wh/kg and 218 W/kg, respectively.

List of Abbreviations

3D	3-dimensional
ACN	acetonitrile
ALD	atomic layer deposition
ASRs	area specific resistances
CNTs	carbon nanotubes
CV	cyclic voltammetry
DC	direct current
DEC	diethyl carbonate
DI	de-ionized
EC	ethylene carbonate
EDX	energy dispersive X-ray spectroscopy
EELS	electron energy loss spectroscopy
EIS	electrochemical impedance spectroscopy
EVs	electric vehicles
FCC	face centered cubic
FEC	fluoroethylene carbonate
FFT	fast-Fourier transformation
FIB	focused ion beam
GE	General Electric Corporation
GO	graphene oxide
HEVs	hybrid electric vehicles
HRTEM	high-resolution transmission electron microscopy
ICP-AES	inductively coupled plasma atomic emission spectroscopy
IPA	isopropanol
LATP	$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$
LFMO	$\text{Li}_2\text{FeMn}_3\text{O}_8$
LFMO-Al	aluminum doped $\text{Li}_2\text{FeMn}_3\text{O}_8$
LFMO-Cl	chlorine doped $\text{Li}_2\text{FeMn}_3\text{O}_8$, or $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$
LFMO-F	fluorine doped $\text{Li}_2\text{FeMn}_3\text{O}_8$, or $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{F}_x$
LFP	LiFePO_4
LIBs	lithium-ion batteries
LIPON	lithium phosphorus oxynitride
LiTFSI	bis(trifluoromethane)sulfonimide lithium salt
LLCZN	$\text{Li}_7\text{La}_{2.75}\text{Ca}_{0.25}\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$
LLTO	$\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$
LLZAO	$\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LSV	linear sweep voltammetry

MD	molecular dynamics
NiMH	nickel-metal hydride
NMP	n-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
PAN	poly(acrylonitrile)
PE	polyethylene
PEO	polyethylene oxide
PMMA	poly(methyl methacrylate)
PVdF	poly(vinylidene fluoride)
PVdF-HFP	poly(vinylidene fluoride-hexafluoropropylene)
PVP	polyvinylpyrrolidone
RGO	reduced graphene oxide
ROI	region of interest
RT	room temperature
SCEs	solid composite electrolytes
SCN	succinonitrile
SEI	solid-electrolyte-interface
SEM	scanning electron microscopy
SPEs	solid polymer electrolytes
SSEs	solid state electrolytes
SSLiBs	solid state Li-ion batteries
TEM	transmission electron microscopy
TMA	trimethyl alumina
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSZ	Y ₂ O ₃ -doped ZrO ₂
ZEBRA	Zeolite Battery Research Africa

Chapter 1: Background

1.1. Development of Solid State Energy Storage

Since its invention in 1970s, rechargeable lithium-ion batteries (LIBs) have attracted much attention for their high energy and power density, great reliability, and reasonable cost.^{1,2} Enabled by intense scientific research, advances in battery technology have greatly expanded the applications of LIBs. Nowadays, from large scale energy storage needs including vehicles and airplanes to small scale power supply for handheld gadgets like cellphones and watches, LIBs can be found in almost every aspect of life. In addition to continue empowering numerous existing industries, the advances of battery technology have also greatly promoted the growth of new industries like electric vehicles (EVs).³ Though invented more than 100 years ago, EVs did not reveal their promising future until the beginning of the 21st century when nickel-metal hydride battery (NiMH) technology was introduced to the automobile market.^{4,5} Recent advances in LIBs have greatly reduced battery costs while improving power, energy and cycling performance, further accelerating the development of EVs.

Despite the tremendous efforts devoted to battery research from both academia and industry communities, current LIBs are yet to achieve their full potential due to intrinsic material limitations of typical battery components. Conventional secondary batteries (rechargeable batteries) consist of two electrodes (anode and cathode) of different electrochemical potentials. Connecting them is the electrolyte, a material which is electrically insulating but ionically conductive. During discharging, ions migrate through the electrolyte from the anode to the cathode, where they reunite with electrons that have

simultaneously traveled through the energy-consuming devices via an external circuit. This basic configuration of secondary batteries has rarely been changed since its first invention.⁶

One of the greatest challenges facing LIBs today lies in the electrolytes. Most modern commercial LIBs utilize liquid electrolytes due to their high ionic conductivity and outstanding wettability to electrodes. However, with the demand for higher power and energy density, and simultaneously better stability, the liquid electrolytes quickly become inadequate. Their electrochemical and thermal stability, nonflammability, and mechanical strength can no longer meet the needs of today's consumers.⁷

Another challenge facing LIBs is the application of lithium metal anodes. Considered as the "Holy Grail" of LIBs, metallic lithium anode can provide the lowest electrochemical potential and highest energy density.^{8,9} Its application however is greatly hindered by its nearly infinite volume change during cycling and the dendrite growth caused by uneven lithium stripping and plating. Especially in conventional LIBs using liquid electrolytes, lithium dendrites will eventually penetrate through the separator and short circuit the cell. Therefore, it is crucial to address these issues in electrolytes in order to fully unleash the potential of LIBs.

Replacing the liquid electrolytes with solid state electrolytes (SSEs) will not only meet the above-mentioned challenges, but also enable the practical application of lithium metal anodes to achieve higher energy densities.^{10,11} SSEs are fast ion conductors in solid form that contains highly mobile ions. Common SSEs can be categorized into inorganic solids and organic solid polymers.

The development of SSEs has a long history. The beginning of the inorganic SSE research is marked with the discovery of the Ag_2S and PbF_2 by Michael Faraday in the

early 19th century.¹² Later in the 1960s, another milestone was set by the discovery of the fast sodium-ion-transport phenomenon in β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$), which later enabled the invention and development of high temperature solid state Na-S batteries.^{13,14} The following successes of Ag_3SI , RbAg_4I_5 , and β -alumina in the early 1970s greatly accelerated research on inorganic SSEs.¹⁵⁻¹⁸ In the 1980s, the ZEBRA (Zeolite Battery Research Africa) battery system was invented based on the high temperature β -alumina electrolyte, and is currently being further developed by the General Electric Corporation (GE) in the United States.^{19,20} In the early 1990s, the discovery of the thin film lithium phosphorus oxynitride (LIPON) marks the beginning of SSEs being employed in LIBs.²¹ Until today, numerous inorganic SSE material types have been reported, including garnets,²²⁻²⁶ perovskites,²⁷ sulfides,^{28,29} and hydrides.³⁰⁻³²

The development of organic solid polymer electrolytes (SPEs) started much later. It was not until the 1980s when the ionic transport property of polyethylene oxide (PEO) based polymer electrolyte was discovered did the SPEs attract much attention.³³ Since then, various solid polymers and polymeric composite systems with high Li-ion conductivity have been developed as SSEs or quasi-solid gel polymer electrolytes, such as poly(vinylidene fluoride) (PVdF),³⁴ poly(acrylonitrile) (PAN),³⁵ poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP),^{36,37} and poly(methyl methacrylate) (PMMA).³⁸ Recently, solid composite electrolytes (SCEs), a combination of inorganic ion conductors with organic solid polymers, are becoming popular due to high ionic conductivity and great versatility. Many state-of-the-art SCEs also contain an engineered 3-dimensional (3D) conductive framework, which not only reinforces the mechanical strength of the electrolyte but also greatly improves ionic conductivity.³⁹⁻⁴¹

Decades of continuous research and advances in SSEs have pushed this promising material family to the center of the research spotlight like never before. Nowadays, in addition to the persistent explorations for superionic conductors, the research focus of SSEs has expanded to understanding the fundamental ion transport mechanisms through computational modeling and advanced characterizations, innovative structure and configuration design, and improving electrochemical performance in full cells. Current top-notch SSEs for LIBs exhibit high Li-ion conductivity, outstanding chemical stability at high operating voltages and against metallic lithium anodes, and robust mechanical strengths. Table 1.1-1 summarizes several common SSEs for solid state Li-ion batteries (SSLiBs).

Table 1.1. Summary of various commonly used Li-ion SSEs.

Materials	Conductivity RT (S/cm)	Major Advantages	Major Disadvantages
$\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$, $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}\text{P}_3\text{O}_{12}$ ²⁷ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ^{22,42} and $\text{Li}_{7.06}\text{M}_3\text{Y}_{0.06}\text{Zr}_{1.94}\text{O}_{12}$ (M = La, Nb or Ta) ^{23,25,26} $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (M = Al, Cr, Ga, Fe, Sc, In, Lu, Y or La) ⁴³⁻⁴⁵ $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ ⁴⁶⁻⁴⁸	$10^{-5} \sim 10^{-3}$	• High ionic conductivity • High mechanical strength • Wide stable voltage window	• Unstable with lithium metal • Non-flexible • Brittle, hard to handle in large-scale fabrication • Moisture/ water sensitive
LiPON ^{49,50}	10^{-6}	• Stable with lithium metal	• Expensive thin film fabrication • Difficult to control chemical composition
$\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ ^{28,29}	$10^{-7} \sim 10^{-3}$	• High ionic conductivity • Good mechanical strength and flexibility • Low grain boundary resistance	• Moisture sensitive • Narrow stable voltage window • Oxygen sensitive • Reactive with various cathode materials

PEO, ⁵¹⁻⁵³ PAN, ³⁵ PMMA, ³⁸ and PVdF based composite polymer electrolyte ³⁴	$10^{-5} \sim 10^{-4}$	•Stable with lithium metal •Good flexibility •Low cost, easy for large-scale fabrication	•Narrow temperature window for mechanical strength •Limited ionic conductivity
$\text{Li}(\text{BH}_4)_{1-x}(\text{NH}_2)_x$ ³⁰⁻³²	$10^{-4} \sim 10^{-3}$	•Stable with lithium metal •High ionic conductivity	•Moisture sensitive •Reactive with various cathode materials
$\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ ⁵⁴⁻⁵⁶	$10^{-7} \sim 10^{-6}$	•Good manufacturing reproducibility and simple processing	•Low ionic conductivity

1.2. Ion Transport Mechanisms in Solid State Electrolytes

1.3.1. Crystallized Solids

As introduced in previous sections, solid state electrolytes can be generally categorized into three families: inorganic solids, organic solids, and composite solids. Inorganic solids are usually crystalline materials with well-defined crystal structure. Some of the organic solids, like polymer electrolytes at low temperature, are also crystalline materials or have crystalline zones in them. Crystallinity is one of the determining factors on the ion transport behavior in the solid state electrolytes. Different from the ion diffusion mechanism in liquid electrolytes, ion transport in crystalline materials relies on ion hopping among vacant lattice sites. The hopping mechanism dominates not only in inorganic solids, but also in the crystallized zones in organic solids.

For the clarity of explanation, we take cubic phase $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) as an example to understand the ion transport mechanism in inorganic solids. Figure 1.1 shows the crystal structure of a cubic garnet LLZO. Immobile ions La, Zr, and O form a crystalline framework and mobile Li ions form a sublattice. The Li ion sites are interconnected through

face and edge sharing, forming a 3D ion transport network. It is vital that the number of equivalent (or nearly equivalent) sites in the crystal is much larger than the number of the mobile species for the crystal to be conductive. In addition, the migration energy barriers between adjacent available sites should be low enough for ion hopping. High energy barriers requires high activation energy, which usually leads to low ionic conductivity. Besides, the vacant sites for ion hopping must be connected to form a continuous diffusion pathway to enable sufficient ion transport throughout the crystal. Since the ion conduction relies on the ion hopping through vacant sites, the ionic conductivity in crystallized inorganic solids can be greatly influenced by the crystal structure or phase changes. For example, cubic phase LLZO usually exhibits higher conductivity than tetragonal phase LLZO. One of the reasons for this conductivity increase lies in the shortened transport distance due to the structure change. In tetragonal phase LLZO, the distances between Li sites is much longer than that in cubic phase, due to the anisotropic crystal structures in the (001) and (100) planes.²²

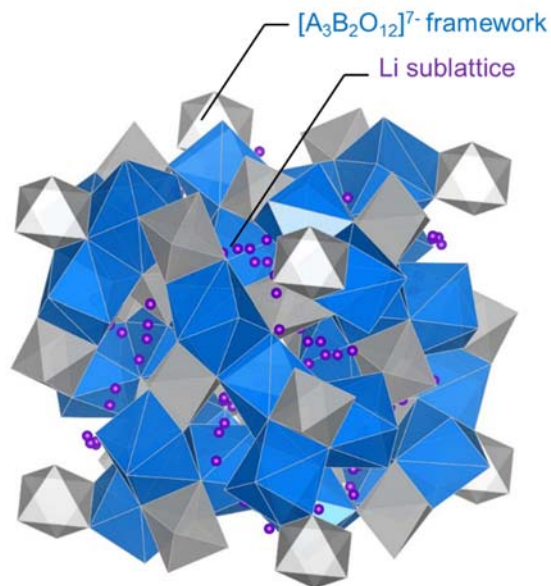


Figure 1.1. Crystal structure of garnet type cubic LLZO showing its sublattice.

The transport mechanism in the crystallized zones in organic solids is very similar to that in inorganic crystals (figure 1.2). Taking PEO as an example, figure X b shows the crystalline zone in the polymer electrolyte with the addition of LiXF_6 ($\text{X} = \text{P}, \text{As}, \text{Sb}$). In the crystalline zone, two PEO chains forms the surface of a cylinder within which the Li ions are confined. Each Li ion is coordinated by five ether oxygens, three from one PEO chain and two from the other. In other words, the crystal “sites” for mobile species in the crystalline PEO is formed by five oxygens. Anions, XF_6^- ($\text{X} = \text{P}, \text{As}, \text{Sb}$) in this case, is excluded from the PEO chain cylinder and forms rows in the inter-chain space.

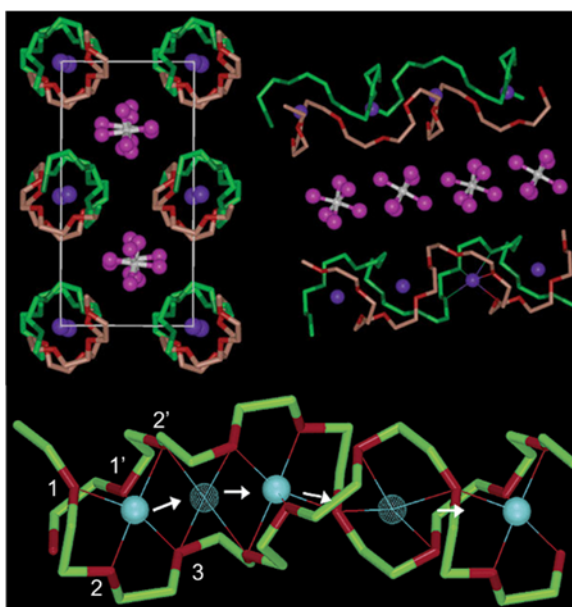


Figure 1.2. Ion conduction mechanism in crystalline PEO polymer (image from ref. 57).

Similar to that in inorganic solids, ion transport in crystalline polymer relies on ion hopping through vacant “sites”. In this case where the site is formed of five ether oxygens, Li ion has to pass the barrier of two ether oxygens to get to an intermediate site formed by 4 ether oxygens from two chains, then pass another bottleneck of two oxygen, then eventually reach the next stable site coordinated by 5 ether oxygens. The migration of Li

ion is hindered by a series of “bottlenecks” which lead to high energy barriers for hopping. Thus explains why the ionic conductivity of crystalline polymers is usually very low.⁵⁷

1.3.2. Amorphous Solids

Similar to that in a crystalline system, ion transport in amorphous solid electrolytes relies on ion hopping along the polymer chain and between several different chains.⁵⁸ In amorphous solids, amorphous zones in PEO as an example, the polymer chains usually have much higher flexibility than those in a crystalline polymer. Instead of forming hollow cylinders where ions are confined in rigid, well defined ether oxygen coordinated sites, polymer chains in amorphous zones are usually expanded and entangled. Contrast to the ion transport in liquid electrolytes where the solvated ions migrate through the electrolyte together with the solvent molecules, ion transport in polymer electrolytes usually does not involve the physical transport of solvent molecules (polymer chains) because the polymer chains are usually entangled. However, in the amorphous zone of the polymer electrolyte (or above glass transition temperature), the chain segmental motion is significant enough that ions solvate-desolvate from the ether oxygen coordinated spots along the chains. Thus, the intrachain ion transport is enabled (figure 1.3-a). At locations where the anion sites on one chain is substituted by the adjacent anion sites on an additional neighboring ligand, the mobile species are transferred from one chain to another, which enables the interchain transport (figure 1.3-b).

The chain entanglement gives the polymer electrolyte its solid form, while the microscopic environment where the chain segmental motion is significant, ions can be effectively transported as if they were in liquid electrolyte (even though solvated anions or polymer chains are not as mobile as those in a liquid electrolyte). The transport mechanism

in amorphous polymer electrolytes determines that the ion conductivity heavily depends on the local segmental motion of the polymer, which is a determining factor for the polymer's mechanical strength. In other words, higher amorphousness is beneficial to ion transport but harmful to mechanical strength. The dilemma between the ionic conductivity and mechanical strength has long been a focus of polymer electrolyte researches.⁵⁹

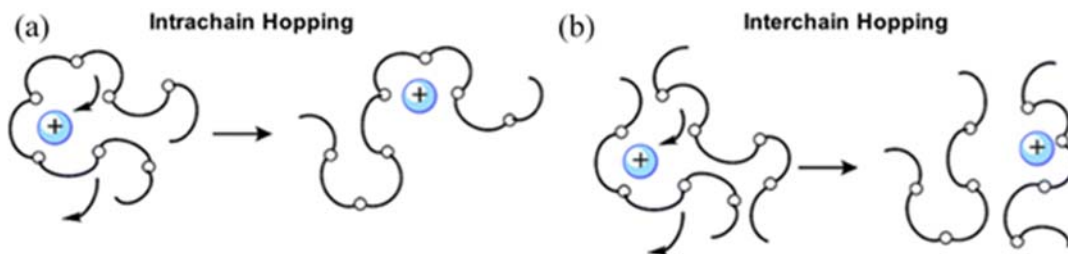


Figure 1.3. Ion transport in amorphous solid polymers via (a) intrachain hopping and (b) interchain hopping (image from ref. 58).

1.3.3. Composite Solids

Composite solid state electrolytes are usually consisted of conductive polymer matrix, fillers, and plasticizers. As introduced in previous sections, the ionic conductivity of polymer electrolytes depends on the amorphousness. The more amorphous the polymer is, the higher mobility the ions have, and therefore the higher the ionic conductivity can be. The addition of fillers and plasticizers improves the ionic conductivity of the polymer by decreasing the crystallinity. Plasticizers are short-chained polymers. When mixed with the polymer matrix, the plasticizer chains interfere the local polymer chain alignment, generating a small amorphous zone around the plasticizer chain. Similarly, fillers can introduce a thin amorphous layer at the filler-polymer interface in the polymer matrix, too.

Ions transport is promoted at the interface (surface of the filler). Therefore the addition of fillers and plasticizers can effectively promote ionic conductivity.

The ion transport mechanism in composite electrolyte can be a combination of multiple mechanisms depending on the properties of the fillers. For example, the preferred ionic transport pathway in composite electrolyte depends on the concentration of the fillers. With very low filler content, the composite electrolyte behave as a polymer electrolyte. When the concentration of the fillers approaches percolation, the composite electrolyte behaves like a polymer electrolyte with much lower ion conductivity due to the insufficient contact of the fillers and fillers blocking the ion transport through the polymer matrix.⁶⁰ In addition to polymer concentration, the fillers' conductivity can also influence the ion transport behaviors in the composite electrolytes.

Based on their ionic conductivity, the fillers can be categorized as inactive fillers, semi-active fillers, and active fillers (figure 1.4). Inactive fillers are ion insulators to the mobile cations in the composite electrolyte, including SiO_2 , Al_2O_3 , and TiO_2 particles. Semi-active fillers are not conductive to the mobile cation, but they are anion conductors that have abundant positive-charged vacancies on the surface (Y_2O_3 -doped ZrO_2 , YSZ for example). Active fillers are ion conductors that is highly conductive to the same mobile cations in the polymer electrolyte matrix (LLZO for example). In composite electrolyte with inactive fillers, ions are effectively transported along the amorphous zone at the interface of the fillers and polymer matrix, in addition to transporting directly through the polymer matrix. In composite electrolyte with semi-active fillers, this transport along the surface is further promoted. The positive-charged vacancies on the surface will couple with the anions in the composite electrolyte, which enables mobile cations to decouple with

localized anions. As a results, the ion mobility is much higher at the surface of the semi-active fillers. In composite electrolyte with active fillers, in addition to all the transport pathways in composite electrolytes with inactive and semi-active fillers, mobile ions can also transport through the conductive fillers. In this case, every part of the composite electrolyte is conductive and the ion transport is no longer blocked by ionic insulators.

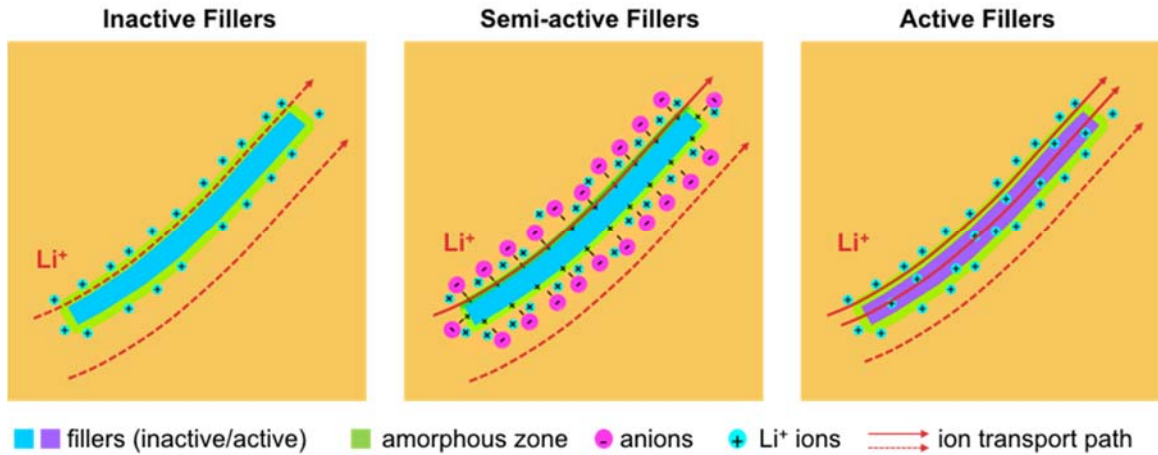


Figure 1.4. Ion transport in composite electrolyte with inactive fillers, semi-active fillers, and active fillers.

1.3. Challenges in Developing Solid State Electrolytes

For inorganic SSEs, there are two major challenges: (1) maximizing the intrinsic ionic conductivity of the electrolyte and (2) minimizing the interfacial impedance between the electrolytes and electrodes.¹¹ Intense research focused on meeting the first challenge has discovered many promising SSE materials with high ionic conductivity. However, the second challenge is still limiting the application of these materials. Due to insufficient solid-solid contacts between inorganic SSEs and solid electrodes, the interfacial impedance in current state-of-the-art SSLiBs is $\sim 1000 \text{ } \Omega/\text{cm}^2$, which is 100-1000 times higher than Li^+ batteries with organic electrolytes. Such high interfacial impedance not only limits the

initial rate performance of SSLiBs, but also increases dramatically over long-term cycling, greatly impacting the battery life. SSLiB interfaces are typically planar, resulting in high impedance due to low specific surface area. Attempts to make 3D high surface area interfaces can also result in high impedance due to poor contact (e.g. pores) at the electrode-electrolyte interface that hinder ion transport or degrade due to expansion and contraction with voltage cycling. Thus, grand challenges exist at the SSE-electrode interface, specifically: large interfacial impedance for charge transfer and transport; and mechanical degradation of interface with electrochemical charge/discharge cycles.

For organic SPEs, the challenges major challenge lies in achieving high ionic conductivity at room temperature. However, attempting to increase ionic conductivity often lead to a decrease in mechanical strength.⁶¹⁻⁶⁴ Efforts aimed at understanding the ion conduction mechanisms in SPEs have pointed out a direct link between the SPEs' ionic conductivity and amorphicity/crystallinity. Intense research has been focused on decreasing the crystallinity (decreasing the glass transition temperature) of SPEs through various methods including the addition of plasticizer and fillers. However, as SPEs become more ionically conductive through reducing their crystallinity (due to the decrease in glass transition temperatures), they inevitably start to lose solid form as well. Highly amorphous SPEs suffer from poor mechanical strength which greatly increases the difficulty in handling and hinders its application in SSLiBs. This dilemma between increasing ionic conductivity and maintaining mechanical strength is another challenge facing SPEs.

1.4. Garnet-Based Solid State Electrolytes

Towards the development of high energy density batteries, the metallic lithium (Li) anode is one of the most promising alternatives to replace conventional anode materials, due to its highest gravimetric energy density (3860 mAh/g) and lowest electrochemical potential (~ 3.04 V against the standard hydrogen electrode).⁶⁵⁻⁶⁷ However, its application in conventional cell configurations is greatly hindered by safety concerns, including liquid electrolyte decomposition and the high combustibility of organic electrolyte, as well as solid-electrolyte-interface (SEI) formation.^{7,56,68-70} In particular, Li dendrite growth and propagation can penetrate through the polymer separator in conventional full cell configurations and cause catastrophic short circuits. Therefore extensive studies have focused on SSEs with great ionic conductivity and good mechanical strength that can address Li dendrite-dominated challenges^{8,71}.

In the past several decades, many outstanding solid electrolyte materials, including conductive oxides^{23,72-76}, phosphates, hydrides, halides, sulfides⁷⁷⁻⁷⁹, and polymer based composites^{57,80-82}, have been developed for solid-state batteries.¹⁰ Among various inorganic solid electrolytes, Li-garnet-type metal oxides have attracted much attention for its high ionic conductivity and outstanding electrochemical stability. Garnet is a kind of orthosilicates with a general formula of $A_3B_2(SiO_4)_3$. In a typical garnet structure, A and B occupies the eight- and six-coordinated cation sites in a face centered cubic (FCC) with a $Ia\bar{3}d$ space group, respectively. The BO_6 octahedrons and BO_4 tetrahedrons for a stable framework through edge and face sharing.⁸³ For example, the $Ca_3Al_2Si_3O_{12}$ garnet is consisted of a framework of CaO_8 with Al and Si on the interstitial sites (figure 1.5). The Si in the general garnet formula can be substituted by other elements to achieve improved

properties. Therefore, the general formula for garnet can be written as $A_3B_5O_{12}$ ($A = \text{La, Mg, Y,}$ and $B = \text{Al, Ga, Mn, and Ni}$). Li-type-garnet is obtained by substituting Si with Li to achieve a general formula of $A_3B_2(\text{LiO}_4)_3$. This structure can be further modified to achieve better properties through cation substitution on A and B sites, and doping (with Al, Ca, Nb, etc.).

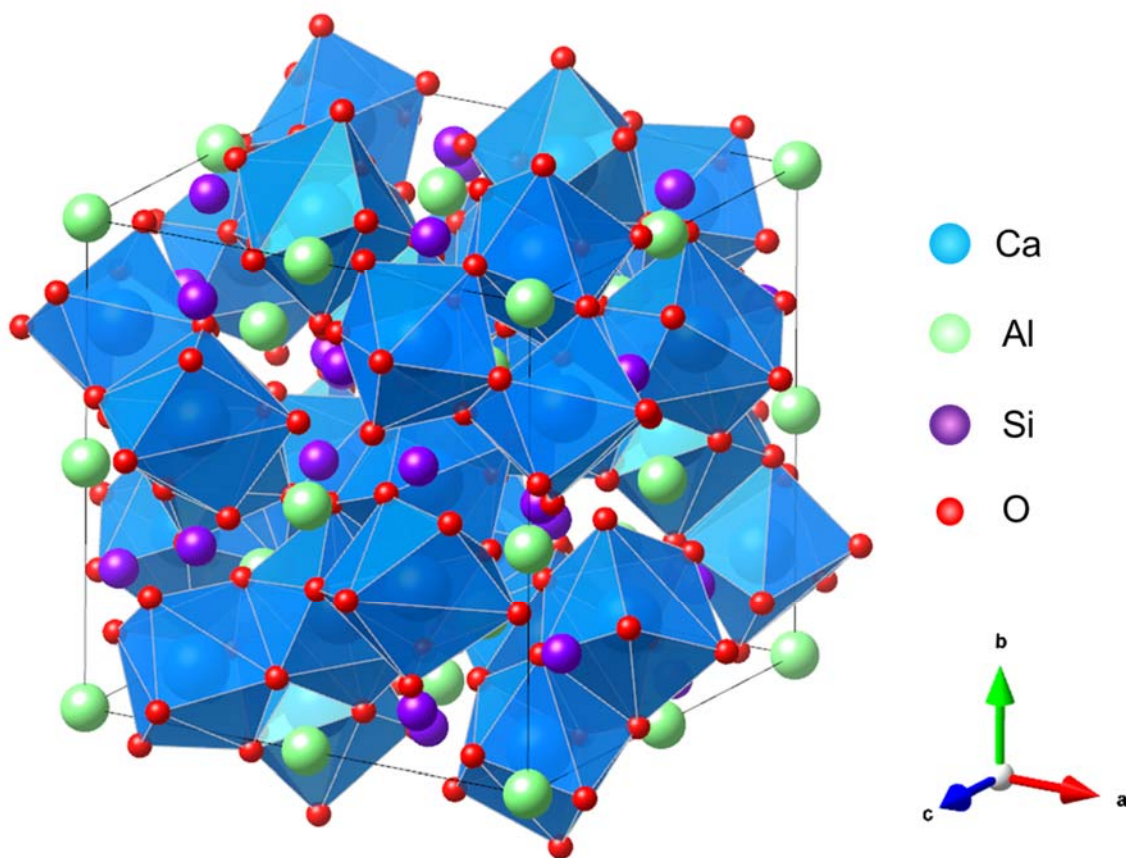


Figure 1.5. Crystal structure of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnet.

Among various lithium garnets, $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Nb, Ta}$) have attracted much attention for its outstanding ionic conductivity.²³ Especially, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is one of the most important and appealing candidates for its high ionic

conductivity (10^{-4} ~ 10^{-3} S/cm) at room temperature,⁷⁴ wide voltage window (0.0-6.0V),^{26,84} and exceptional chemical stability against Li metal.⁸⁵ Since its discovery, the conductivity of the garnet type SSEs has continued to improve by judicious doping to increase the Li content of the garnet structure. These Li-stuffed garnets exhibit the most promising physical and chemical properties for SSEs including:

- The highest known RT bulk conductivity ($\sim 10^{-3}$ S/cm obtained by Thangadurai with cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$).^{42,86}
- High electrochemical stability for high voltage cathodes (up to 6 V), about 2 V higher than current organic electrolytes and about 1 V higher than the more popular LiPON;
- Excellent chemical stability in contact with elemental and molten Li anodes up to 400 °C;
- Li^+ transference number is close to the maximum of 1.00, which is critical to battery cycle efficiency, while typical polymer electrolytes are only ~ 0.35 ;
- Wide operating temperature capability, electrical conductivity increases with increasing temperature reaching 0.1 Scm^{-1} at 300 °C, and maintains appreciable conductivity below 0 °C. In contrast, polymer electrolytes are flammable at high temperature;
- Synthesizable through simple solid combustion reactions in air, hence easy to scale up for bulk synthesis and creation of low-cost supply chain.

1.5. Emerging Opportunities for High Voltage Cathodes

Since the very beginning of LIBs research, the quest for higher energy and power densities has never changed. Fast-growing industries like electric vehicles and portable

electronic devices are demanding faster advances in battery technologies than ever. In the basic configuration of a conventional LIB, the output voltage of the cell is determined by the electrochemical potential difference of the two electrodes, and the energy density is the product of the output voltage multiplying cell capacity. Thus, to achieve high energy density, it is of great importance to design and improve the cathode material with high electrochemical potential to yield a higher output voltage.^{87,88} However, compared to the numerous advances in developing high-capacity anode materials, the progress in investigating high voltage cathode materials has largely lagged behind. In fact, one of the key bottlenecks constraining energy and power density of the current state-of-the-art LIBs lies in the capacity and voltage of the cathode materials. Before the advances in SSEs in recent decades, the research and application of high voltage cathodes was majorly limited by the low decomposition voltage of traditional liquid electrolytes⁸⁹⁻⁹¹. Figure 1.6 compares the voltage and capacity ranges of several most popular cathode materials for lithium ion batteries.⁹² Recent advances in solid state electrolytes⁴² and high voltage electrolytes⁹³⁻⁹⁵ have brought new opportunities for the development of high voltage cathodes, and granted hope to improving energy density by increasing cell voltage.

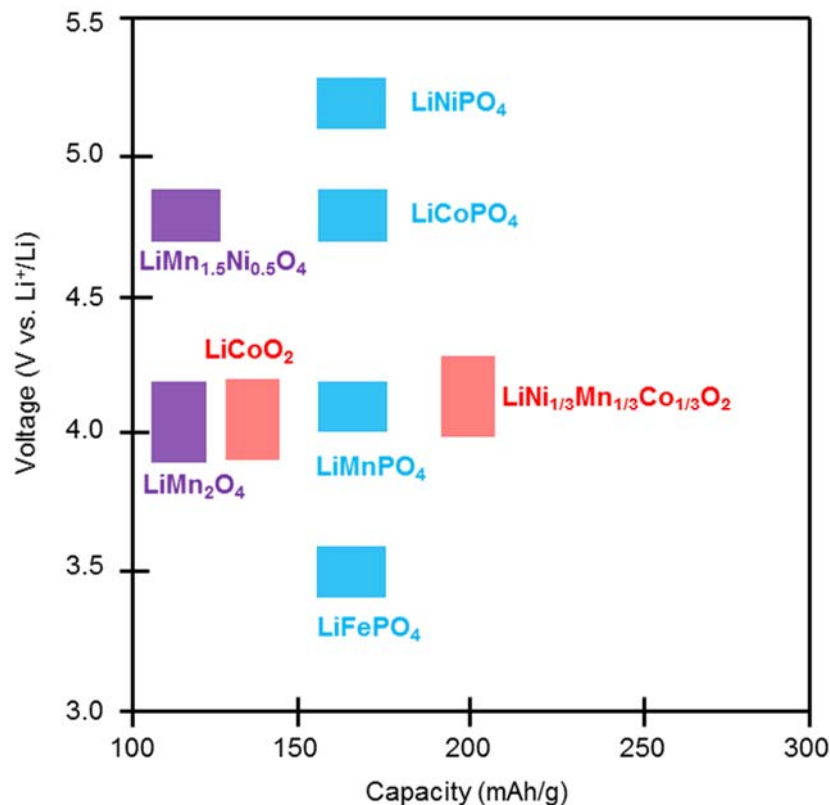


Figure 1.6. Voltage and capacity range comparison of several most popular cathode materials for lithium ion batteries.

Several families of promising high voltage cathode materials include layered oxides with the α -NaFeO₂-type structure (LiMO₂, M = Co, Ni, Mn), spinel oxides (LiMMn_{2-x}O₄, M = Ni, Cr, Fe, Cu, *etc.*), and poly-anionic compounds (phosphates, sulfates, silicates, *etc.*).⁹⁶ Figure 1.7 compares the crystal structure of these three types of high voltage cathodes.

The layered oxides usually have a distorted rock-salt structure (figure 1.7-a). With a general formula of LiMO₂ (M = Co, Ni, Mn), the crystal consists of alternating layers of edge-sharing MO₆ octahedra and Li⁺ ions. During charging (or discharging), the Li⁺ ions deintercalate (or intercalate) from the planar space between two layers of MO₆ octahedra via diffusion to vacant octahedral sites through the adjacent tetrahedral sites. Though the

layered structure of the MO_6 remains unchanged at even full lithium extraction, the lattice parameter shrinks dramatically. Many reported high voltage cathodes including $LiCoO_2$ and $LiMnO_2$ suffer from the substantial volume changes caused by the lattice shrinkage and expansion during cycling. The volume change of cathodes in layered oxides family greatly degrade the mechanical stability and reliability of the cathodes during long-term cycling.

The spinel oxides structure is usually a 3D framework constructed of M_2O_4 ($M = Ni, Cr, Fe, Cu, etc.$) octahedrals with Li^+ ion occupying the tetrahedral positions of a cubic close packed O^{2-} lattice (figure 1.7-b). The interstitial space of the spinel structure is a series of edge-sharing octahedral sites that also share faces with the adjacent tetrahedral sites. These tetrahedral sites form a 3D pathways throughout the whole spinel framework for fast lithium diffusion during charging and discharging. Many spinel structured oxides have been reported as high voltage cathodes for LIBs, for example, $Li_2NiMn_3O_8$ (4.7 V)^{97,98}, $Li_2CrMn_3O_8$ (4.8V)⁹⁹, $Li_{2.02}Cu_{0.64}Mn_{3.34}O_8$ (4.9V)¹⁰⁰, $Li_2FeMn_3O_8$ (4.8V)^{101,102}, and $LiCoMnO_4$ (5.1V)⁸⁸. The spinel oxides have been considered as promising candidates for high voltage cathodes for their stable M_2O_4 ($M = Ni, Cr, Fe, Cu, etc.$) framework and 3D fast ion pathways. However, many spinel oxides still face critical challenges including transition metal cation loss during cycling, phase transformations upon Li^+ ion extractions, and relatively low voltage compared with other high voltage cathodes.

Similarly, the poly-anion compounds also have 3D interconnected frameworks for Li^+ ion diffusion in terms of the crystal structure (figure 1.7-c). The poly-anion compound materials have been intensely studied over the past several decades for their appealing cyclability, safety, and high voltage. For example, the olivine structured $LiCoPO_4$ has a

discharge plateau of 4.8V and $\text{LiMn}_{1/3}\text{Fe}_{1/3}\text{Co}_{1/3}\text{PO}_4$ is reported to have a discharge plateau at 4.9V.¹⁰³⁻¹⁰⁵ Some Ni-based poly-anion compounds have discharging plateaus over 5V, such as LiNiPO_4 (5V), LiNiPO_4F (5.3V), and $\text{LiNiO}(\text{PO}_4)$ (5.27V). Though the poly-anion compounds is highly competitive in terms of plateau voltages, their electronic and ionic conductivity is usually very low. Thus their electrochemical performance is greatly limited.

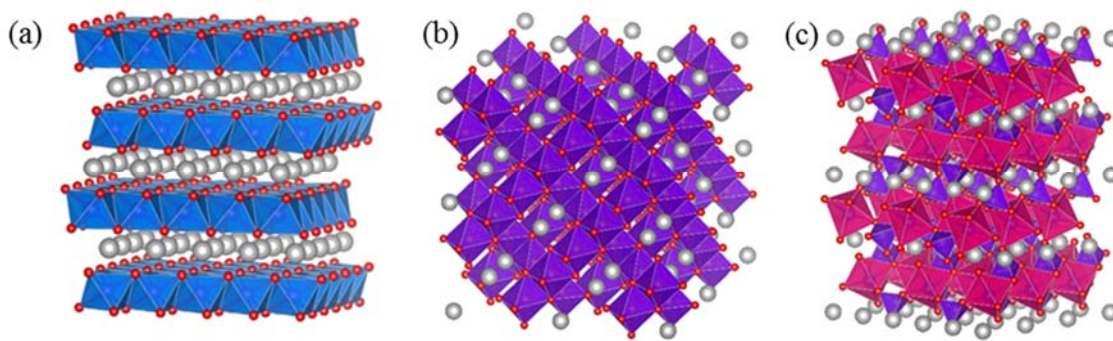


Figure 1.7. Structural comparison of (a) layered oxides, (b) spinel oxides, and (c) poly-anion compounds.

1.6. Thesis Structure

This quadripartite thesis focuses on developing nanomaterials and corresponding processing techniques to improve the comprehensive performance of solid state batteries from the perspectives of electrolyte design (including structure design and interface engineering), cathode improvement (including structure design and voltage elevation), metallic anode modification (mainly on Li-Sn alloy), and full cell construction (solid state battery-supercapacitor hybrid device). The overall structure and focuses of the thesis is shown in figure 1.8.

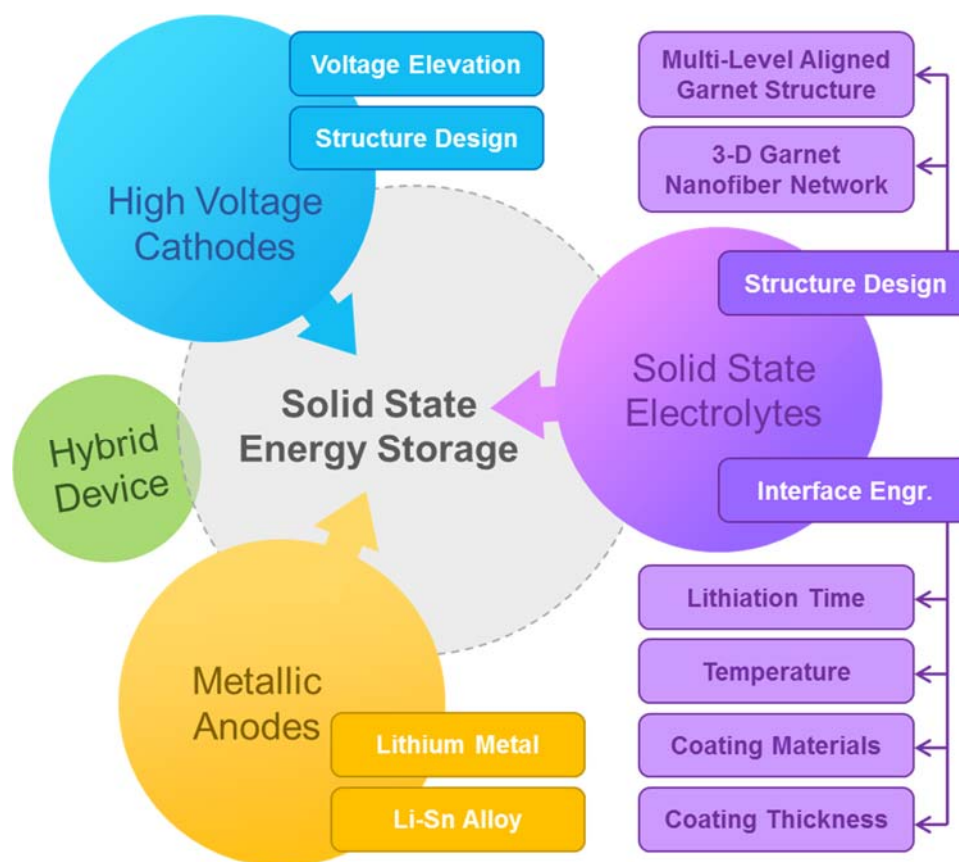


Figure 1.8. Flow chart illustrating the overall structure and focuses of the thesis.

In Chapter 1, we review a brief history of the development of solid state energy storage technologies. We then look in to the ion transport mechanism in various solid state electrolytes. The transport mechanism in crystalline solids, amorphous solids, and composite solids is introduced and compared. This chapter also points out the major challenges in developing solid state electrolytes. Later in Chapter 1, we introduce an outstanding solid state electrolyte candidate, garnet type LLZO. Its electrochemical properties and ion transport mechanism is also discussed. At last, we review the high voltage cathode materials, whose promising future in solid state batteries is recently enabled by the development of solid state electrolytes.

In Chapter 2, we focus on improving the ionic conductivity of solid state electrolyte through nanostructure designing. Two novel garnet structures are developed to achieve outstanding ionic conductivity, superior flexibility, and high electrochemical stability. The first design is a 3D garnet nanofiber network. This structure consists of continuous, interconnected garnet nanofibers, along which Li ions can be effectively transported without being impeded by gaps, cracks, or defects in the electrolyte. The second design is a multi-level aligned garnet nanostructure. This structure has aligned pores sized from nanometer scale to submicron scale. The electrolyte matrix (or pores) are aligned along the direction of ion conduction, and the tortuosity of the structure is approaching to 1. The low tortuosity design exhibits superior ion conductivity and great flexibility.

In Chapter 3, we focus on negating the anode|electrolyte interfacial impedance. It consists of several processing techniques and a comprehensive understanding, through systematic experimental analysis, of the governing factors for the interfacial impedance in solid state batteries using metallic anodes. We report an atomic layer deposition assisted Al_2O_3 coating technique which can greatly reduce the interfacial resistance between metallic lithium anode and garnet electrolyte. Based on the technique, we then investigate the lithiation process of the Al_2O_3 coating layer. Furthermore, we explore other possible critical factors that can influence interfacial resistance, including time, temperature, anode composition, coating composition, coating configuration, and coating thickness. The alloying for metallic lithium anode is also include in this chapter.

In Chapter 4, we report several processing techniques that can raise the working voltage of $\text{Li}_2\text{FeMn}_3\text{O}_8$ (LFMO) cathodes and enable the self-formation of a core-shell structure on the cathode to achieve higher ionic conductivity and better electrochemical

stability. The first technique utilizes halogen elements to dope LFMO. The resulting doped cathode exhibits better electrochemical stability and higher working voltage. The mechanism of voltage elevation and other related doping effects are included in this chapter as well. We then introduce a novel cathode material that can automatically form a core-shell structure during annealing. The lithiated Al_2O_3 shell protects the cathode from decomposition and undesired side reactions. In addition, it can also improve the ionic conductivity of the cathode. Thorough characterizations and electrochemical tests are discussed at the end of the chapter.

In Chapter 5, we present a solid state energy storage device with a battery-supercapacitor hybrid design. The design utilizes gel based solid electrolyte, featuring high rate battery cathode and high capacity supercapacitor anode, to achieve a high power, high energy density performance. Though it seems less closely related with the solid state systems introduced in previous chapters, it deserves a place in the thesis because it is my very first research during my PhD studies. The study on this quasi-solid system has provided many inspirations for researches in all solid state systems.

Chapter 2: Nanostructured Garnet-Based Solid State Electrolytes

2.1. Three-Dimensional Garnet Nanofiber Network

Since the invention of lithium ion batteries (LIBs), the quest for higher energy density, better safety, and longer lifespan has never changed. To meet the demands from the fast-growing battery market, modern battery technology is seeking new opportunities in metallic lithium anodes. Considered as the “Holy Grail” of LIBs, lithium metal anodes have the highest specific capacity (3860 mAh/g) and the lowest negative electrochemical potential ($\sim 3.04\text{V}$ vs. the standard hydrogen electrode). These unique properties can maximize the capacity and voltage window for a maximized energy density in LIBs. Unfortunately, the application of lithium metal anodes in conventional LIBs using liquid electrolyte is problematic. Current challenges facing the lithium metal anodes include side reactions with electrolyte and electrode materials, dendrite growth, and SEI formation.

A popular strategy to solve the above mentioned problems is to replace the conventional liquid electrolyte with solid state electrolytes (SSEs). SSEs are fast ion conductors in solid form that contains highly mobile ions. Among common SSEs, solid composite electrolytes (SCEs) are very attractive due to their high ionic conductivity and great flexibility. Common SCEs consist of solid polymer electrolytes (SPEs) and fillers. The fillers can be either active or inactive, depending on whether they participate ion transport process or not. State-of-the-art SCEs utilize active fillers that are made of ion conductive materials including $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLTO),¹⁰⁶ tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO),¹⁰⁷ and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP).⁶⁴ The addition of these fillers can not only improve the ionic conductivity of the polymer matrix by expanding local amorphous

regions, but also improve the electrochemical stability and mechanical strength of the SCEs. However, SCEs using powdered fillers all facing the particle agglomeration problem. This challenge greatly increases the difficulty of synthesis and quality control. Therefore, creating an ion conductive framework with interconnected long-range ion transport pathways is critical to a successful design of SCEs.

2.1.1. Electrospinning-Assisted Sol-Gel Synthesis

The LLZO garnet electrolyte was synthesized *via* an electrospinning-assisted sol-gel method. The starting materials were $\text{La}(\text{NO}_3)_3$ (99.9%, Alfa Aesar), $\text{ZrO}(\text{NO}_3)_2$ (99.9%, Alfa Aesar), and LiNO_3 (99%, Alfa Aesar). Stoichiometric amounts of chemicals were dissolved in de-ionized water and 10% excess LiNO_3 was added to compensate for lithium volatilization during high temperature synthesis. Citric acid and ethylene glycol in the mole ratio of 1:1 were consequently added into the solution. The solution was then mixed with polyvinylpyrrolidone (PVP) polymer under stirring for 1 hour at room temperature. The mixture was then transferred into a syringe for electrospinning.

Figure 2.1 shows the experiment setup of electrospinning. The whole setup was in a closed box where the humidity was adjusted to control the evaporation speed of the solvent in precursor. The loaded syringe was placed on an air pump to control the feeding speed of precursor. During electrospinning, a high voltage was applied between the syringe needle and the rolling collecting drum which is covered by a thin Al foil. The precursor shot out of the syringe and formed a non-woven fabric film on the rolling collecting drum. At last, the collected nanofiber precursor film was calcined at 800 °C in air for 2 h, resulting in a garnet nanofiber network consisted of well crystallized LLZO (figure 2.2). The

morphology of the as-spun garnet nanofiber precursor network and the calcined garnet nanofiber network is compared in figure 2.3 and figure 2.4. After calcination, the fiber shrunk due to the burn off of organic components in precursor. However, the fibrous micro-structure was preserved.

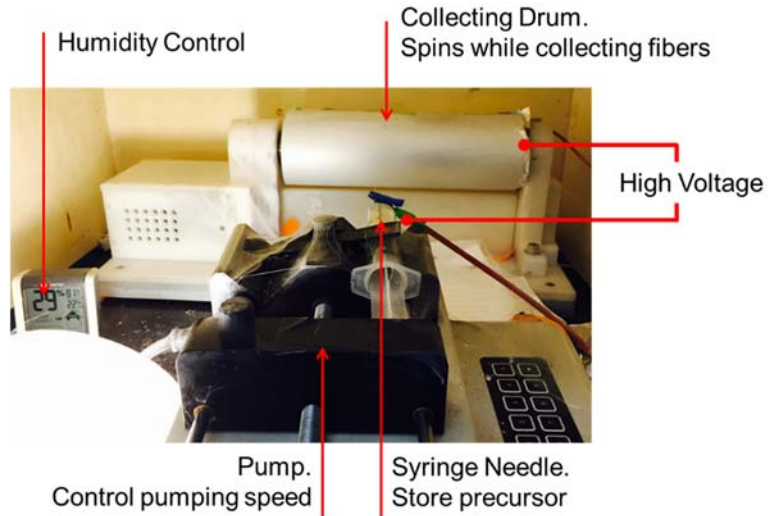


Figure 2.1. Experiment equipment setup for electrospinning.

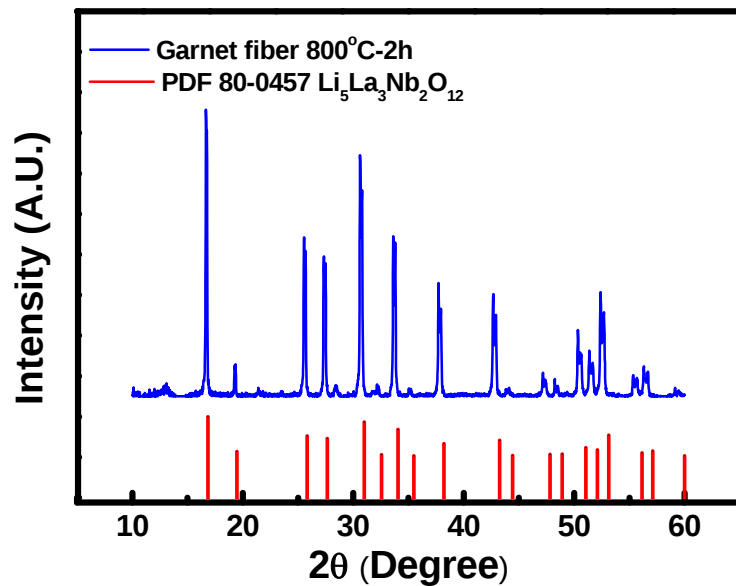


Figure 2.2. XRD pattern of garnet nanofibers matches with the XRD pattern of LLZO.

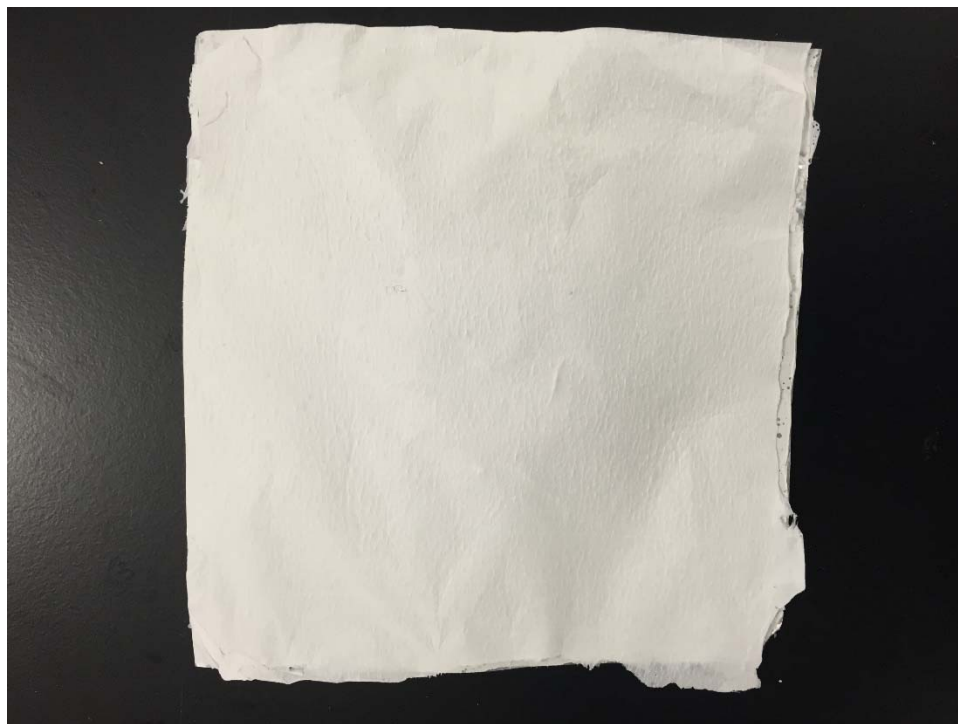


Figure 2.3. Photo of a piece of as-spun garnet nanofiber precursor network. The film is flat, flexible, and mechanically robust.

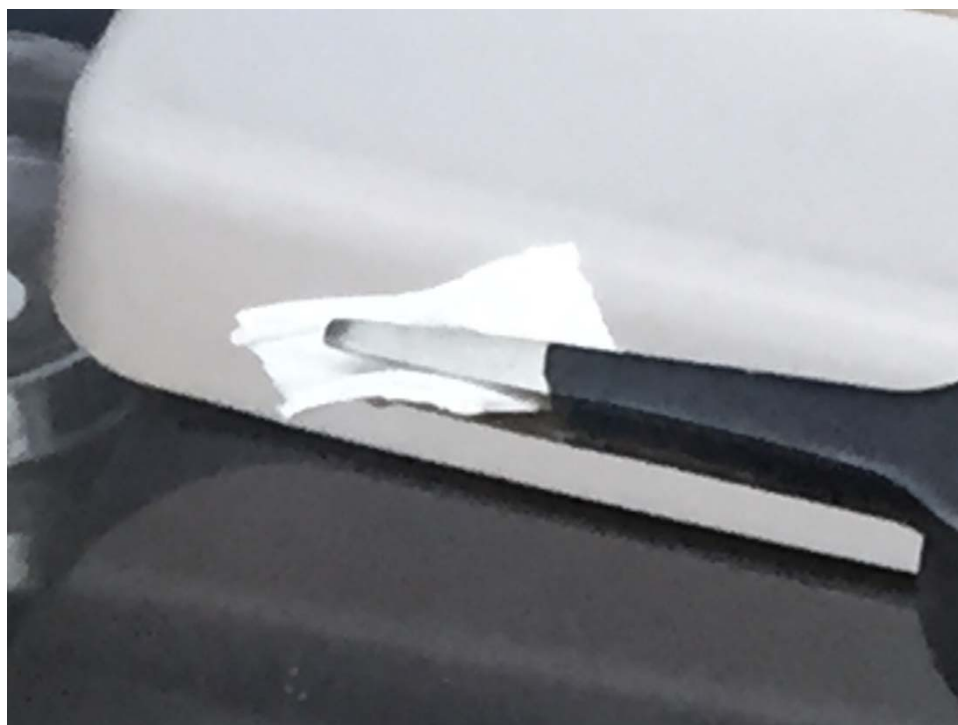


Figure 2.4. Photo of a piece of calcined garnet nanofiber network.

2.1.2. Results and Discussion

Figure 2.5 shows the structure of the 3D LLZO-PEO membrane. A zoom-in view of the membrane (top right) shows the detailed structure of the garnet framework in the membrane. The highly porous LLZO structure consists of randomly distributed and interconnected nanofibers, forming a continuous Li^+ ion transport “highway” network. The PEO based SPE was infiltrated into the framework, filling up all the empty space between garnet nanofibers. This preparation method effectively avoids the problematic filler-mixing process commonly required in conventional SCE preparations. Figure 2.6 shows the morphology of an as-spun garnet nanofiber precursor network before sintering and figure 2.7 shows the morphology of a garnet nanofiber network before the infiltration of SPEs. The average diameter of the nanofibers are about 138 nm (figure 2.8). TEM analysis in figure 2.9 and figure 2.10 reveals that the garnet fibers are multicrystalline, and the intersection of two contacting nanofibers is merged together, which ensures the sufficient contact between nanofibers.

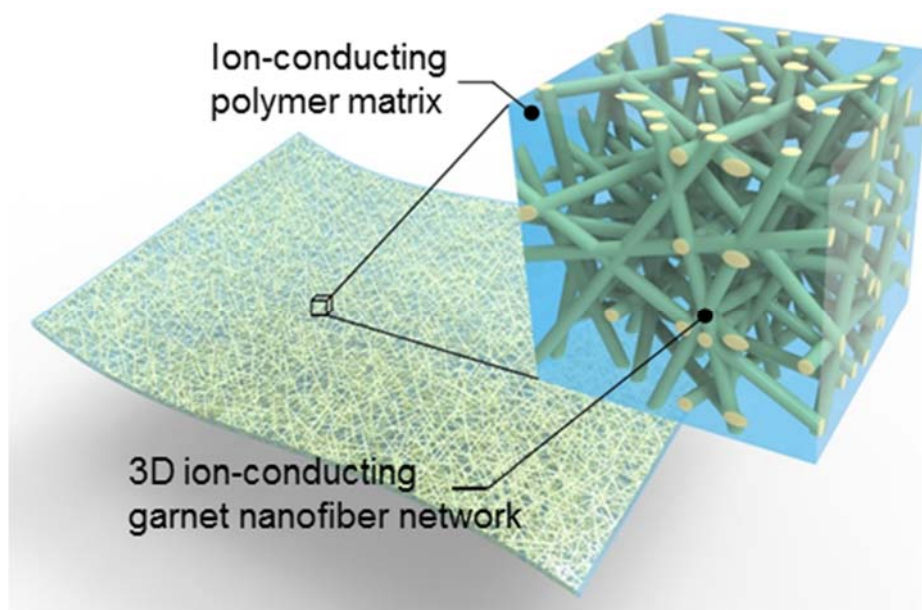


Figure 2.5. Schematic of the LLZO-PEO composite electrolyte membrane.

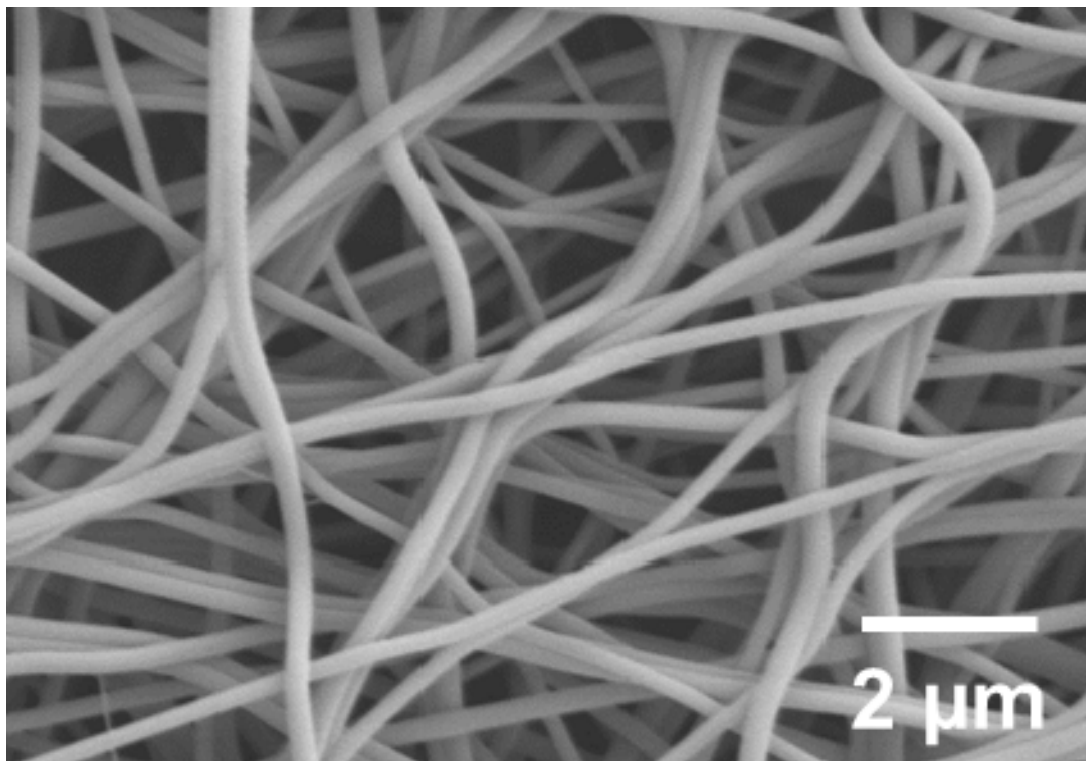


Figure 2.6. SEM images of the as-spun garnet nanofiber precursor network.

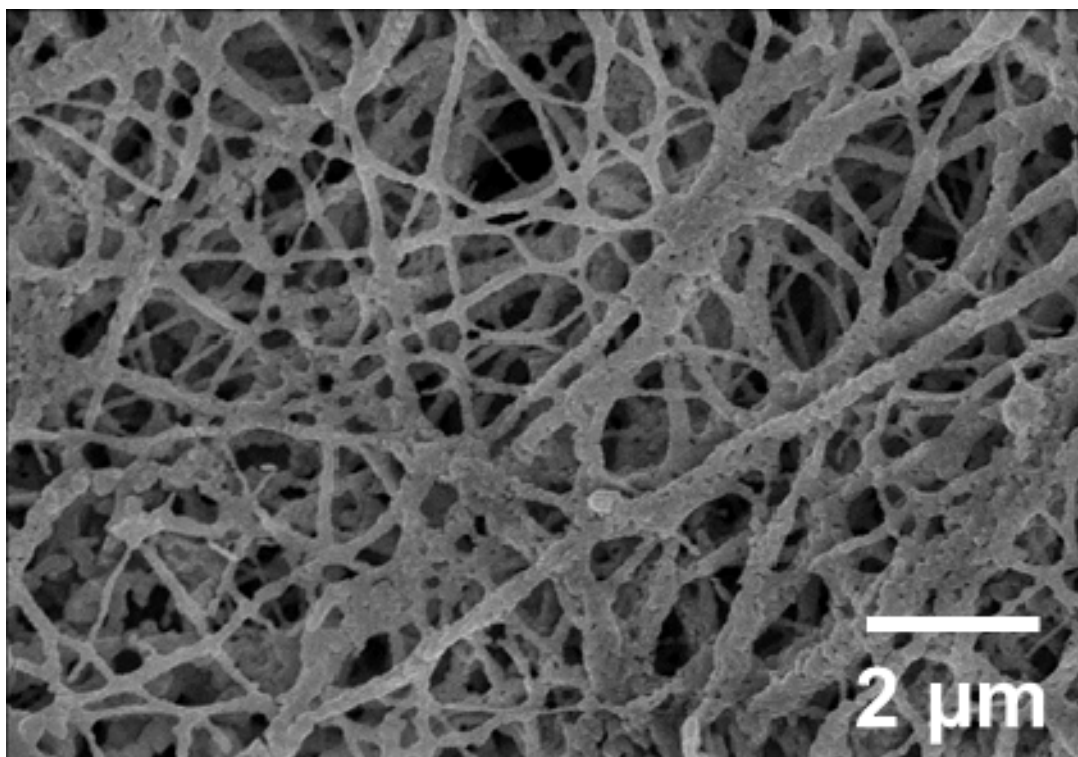


Figure 2.7. SEM images of the garnet nanofiber network after calcination.

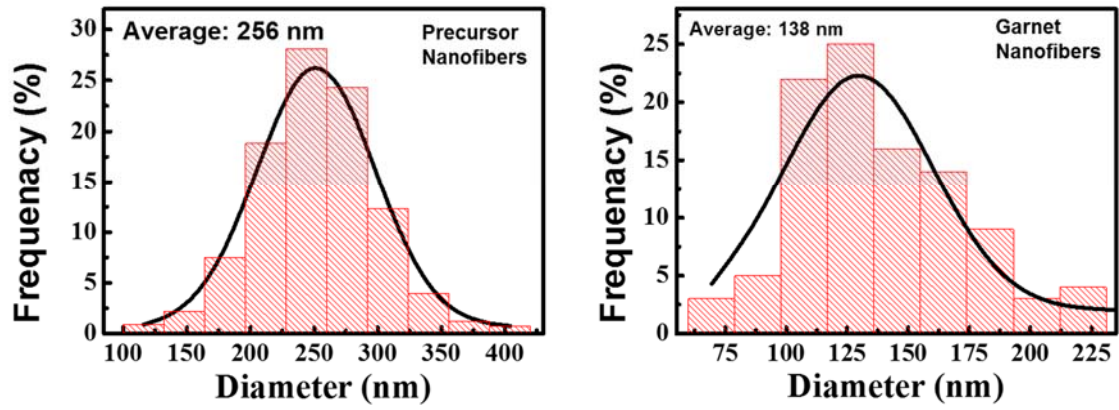


Figure 2.8. Diameter distribution comparison of as-spun garnet precursor nanofibers and calcined garnet nanofibers.

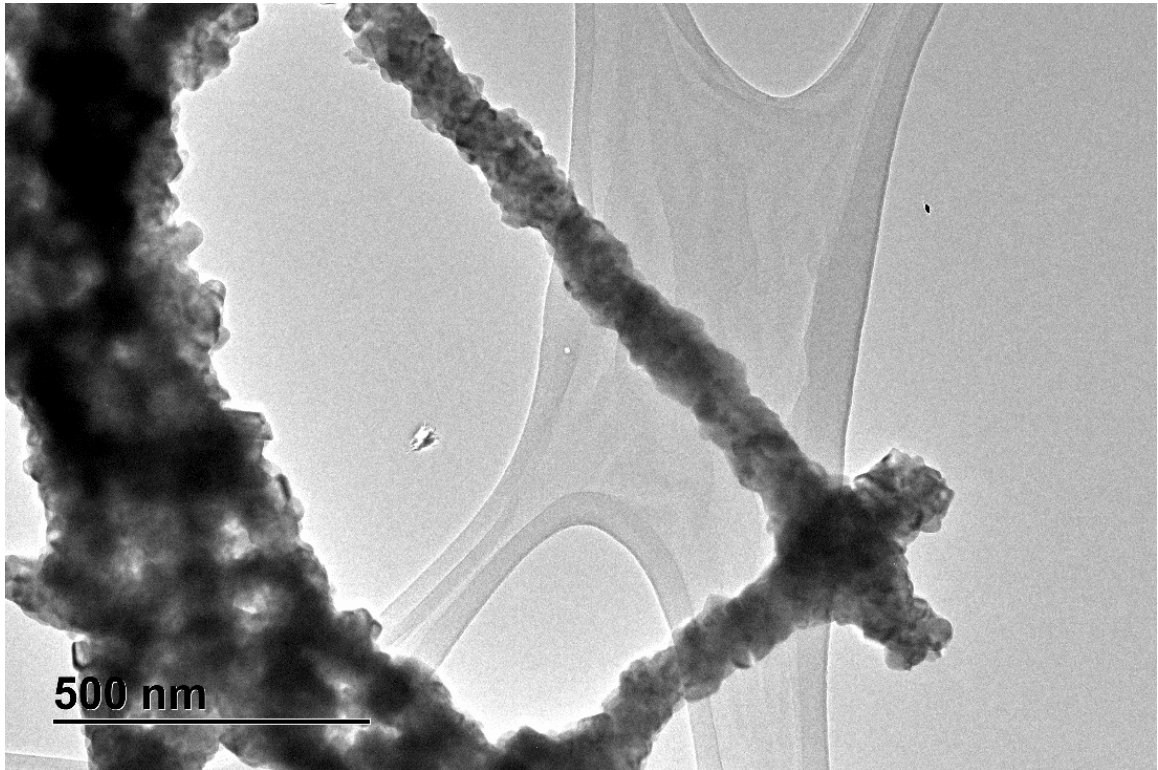


Figure 2.9. TEM image of garnet nanofibers showing that the fibers are multicrystalline.

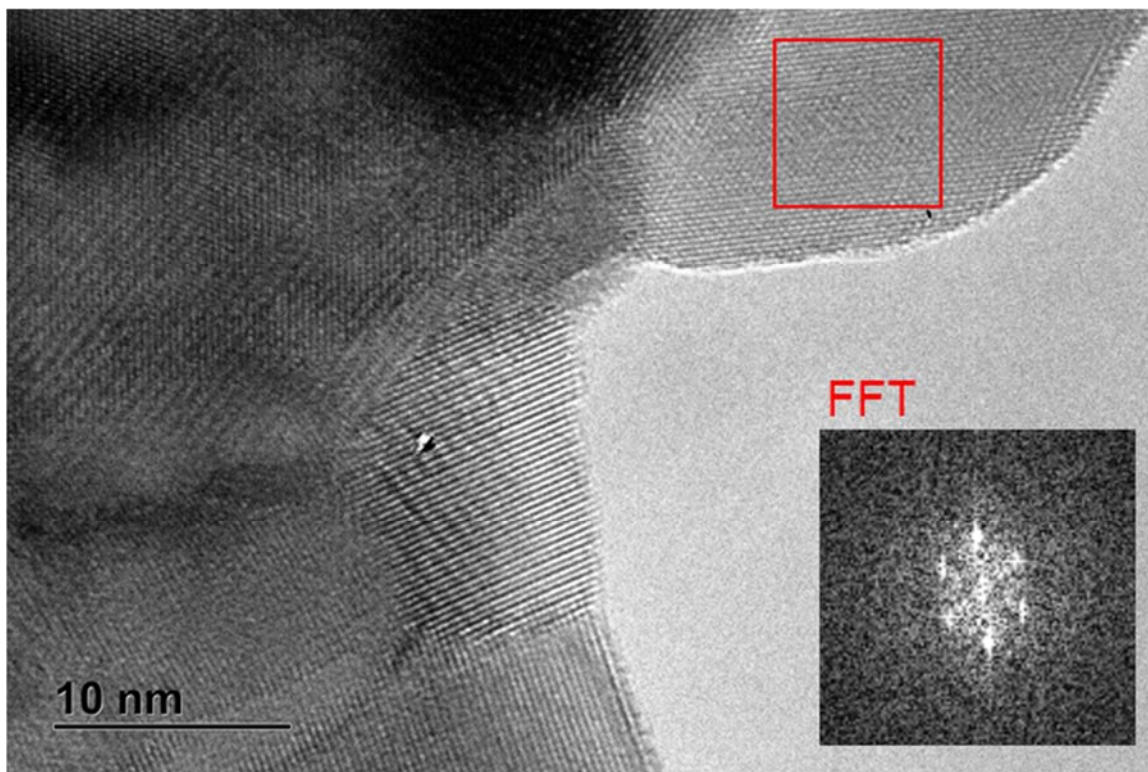


Figure 2.10. TEM image magnified at the joint of two garnet nanofibers showing that the fibers are merged with each other at the points of contact. Inset shows a fast-Fourier transformation (FFT) image of the well-crystallized garnet.

Electrochemical impedance spectroscopy (EIS) tests were performed to investigate the ionic conductivity of the LLZO-PEO membrane. The electrolyte membrane was tested in coin cell with stainless steel on both sides as blocking electrodes. The frequency range was from 1 Hz to 1MHz with an amplitude of 50mV. Figure 2.11-a shows the temperature dependence of the membrane's ionic conductivity. The LLZO-PEO membrane exhibited a high ionic conductivity of 2.5×10^{-4} S/cm at room temperature, which is much higher than that of conventional PEO based SPEs (in the range of 10^{-6} ~ 10^{-9} S/cm) and very close to the bulk conductivity of LLZO (10^{-3} S/cm). Figure 2.11-b shows the electrochemical stability test results obtained through the linear sweep voltammetry (LSV) techniques. The

test membrane was assembled in to a coin cell with stainless steel as the working electrode and lithium metal as the counter and reference electrode. The LLZO-PEO membrane exhibits a wide stable voltage window up to 6V vs. Li/Li⁺. Lithium plating/stripping cycling test was performed on a Li/LLZO-PEO/Li symmetric cell to further investigate the electrolyte's electrochemical stability. Figure 2.11-c shows the voltage profile of a long-term lithium plating/stripping cycling with a current density of 0.5 mA/cm² at 25°C. The test cell remained stable for over 1000 hours of cycling without any shorting. The outstanding electrochemical stability of the LLZO-PEO membrane is highly desirable for applications in high voltage LIBs.

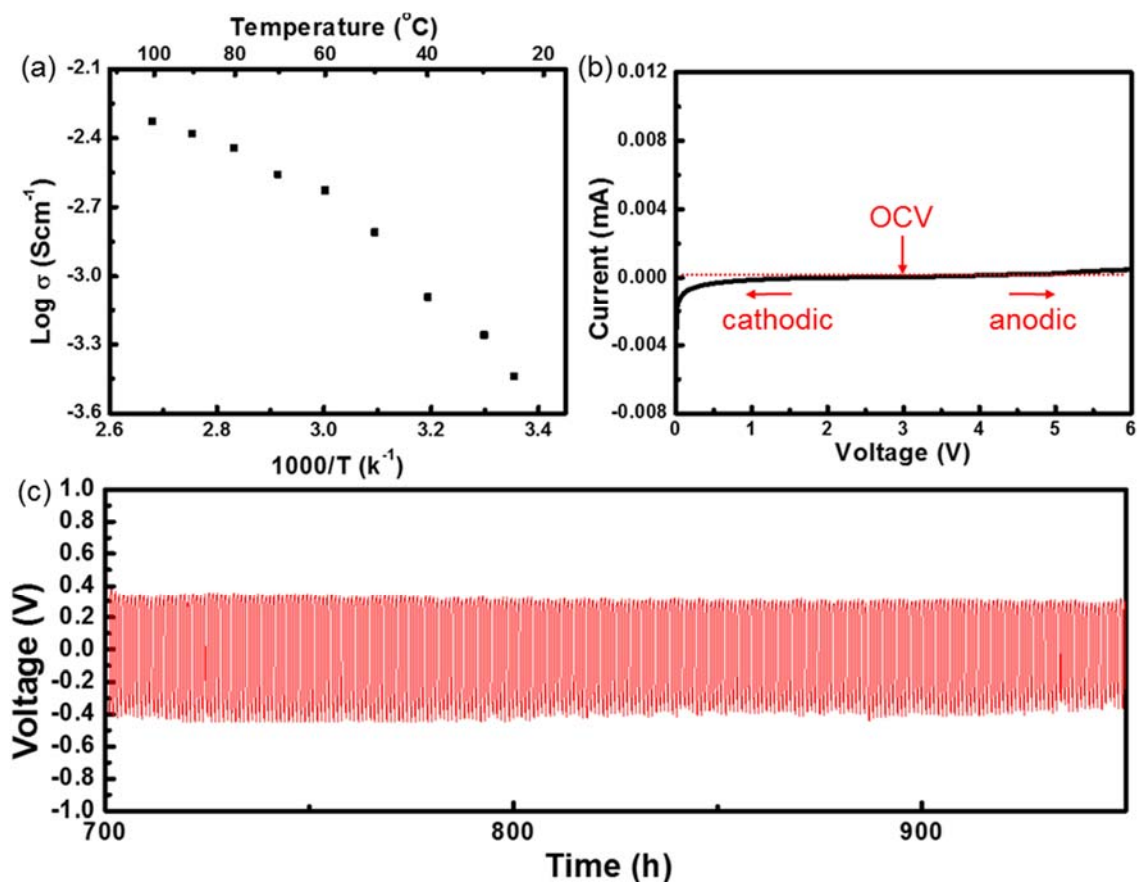


Figure 2.11. (a) Arrhenius plot of the LLZO-PEO SCE at elevated temperatures. (b) LSV curve of the LLZO-PEO SCE showing the electrochemical stability window in the range

of 0-6V. (c) Voltage profile of a long-term lithium plating/stripping cycling with a current density of 0.5 mA/cm² at 25°C.

2.1.3. Experimental Method

Materials Preparation. The garnet precursor solution was prepared by dissolving stoichiometric LiNO₃ (≥99.0%, Aldrich), La(NO₃)₃ (≥99.9%, Aldrich), Al(NO₃)₃·9H₂O (≥98.0%, Aldrich), ZrO(NO₃)₂·xH₂O (99.9%, Aldrich), and acetic acid (≥99.7%, Aldrich) in ethanol (≥99.8%, Aldrich) at room temperature under magnetic stirring. The total cation concentration of the precursor solution was 2 mol/L. 15% excess lithium nitrate was added to compensate for lithium loss at high calcination temperature.

Materials Characterization. Scanning electron microscopy (SEM) was performed with a Hitachi SU-70 analytical scanning electron microscope. The electrochemical impedance (EIS) and symmetric cell cycling tests were performed using a BioLogic battery testing system at room temperature. The EIS was performed over a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude.

2.2. Multi-Level Aligned Garnet Nanostructure

2.2.1. Dependence of Ion Transport Properties on Tortuosity

As introduced in previous chapters, improving the bulk ionic conductivity of both inorganic and organic solid state electrolytes has long been a focus in the research field. In addition, recent developments also suggest that solid composite electrolytes (SCEs) with engineered nanostructures can give rise to further improvements in ionic conductivity,^{108,109} electrochemical stability,¹¹⁰ and mechanical strength.¹¹¹ For example, a

solid state SCE proposed by Cui *et al.* consisting of polyacrylonitrile (PAN)-LiClO₄ with Li_{0.33}La_{0.557}TiO₃ (LTO) nanowires exhibited outstanding ionic conductivity at room temperature and good electrochemical stability.¹⁰⁶ Another PEO based solid state SEC with an enhanced 3D flexible Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ (LLZAO) network was also reported to exhibit high ionic conductivity at room temperature and good mechanical strength.³⁹

Most of the previously reported structure-engineered composite electrolytes can be categorized into several groups based on the morphology of the ceramic fillers (figure 2.12). For structures with random pores, the ionic conductivity heavily depends on the porosity of the structure. The higher porosity the structure is, the harder it is to achieve high ionic conductivity due to the increased resistance at gaps and boundaries. For structures using particles, nanorods, and nanowires as conductive fillers, one key factor in achieving high conductivity is percolation degree. The ion transport promoting effect of the conductive fillers is only visible when the fillers percolate the whole composite electrolyte. Recent studies suggest that at a low filler concentration, the fillers are isolated in the matrix, blocking ion conduction instead of promoting.⁶⁰ Replacing nanoparticles with nanorods and nanowires increases the surface area, where the polymer matrix has a lower crystallinity and higher ion conductivity. The nanorods and nanowires enable the continuous ion transport along the surface and reduced the critical concentration for fillers to percolate the composite electrolyte. However, the nanorods and nanowires still suffer from the same agglomeration problem that is typical for nanoparticles. As introduced in the previous chapter, the 3D garnet nanofiber network is free of agglomeration issue and greatly promotes the ion transport by providing fast, continuous ion transport pathway. Comparing the ionic conductivity and tortuosity of the previously reported structures of

previously reported composite electrolytes, it can be found that the inorganic components in these SECs are either isolated particles or random fibrils with a high tortuosity that increases the transport distance of ions. In other words, the composite electrolyte exhibits higher ionic conductivity when the ion transport pathway is shorter. The shortest pathway possible in a composite electrolyte should be a straight connection bridging two sides of the electrolyte. Therefore, it is reasonable to expect a maximized ionic conduction in composite electrolyte with fillers aligning along the ion conducting direction.

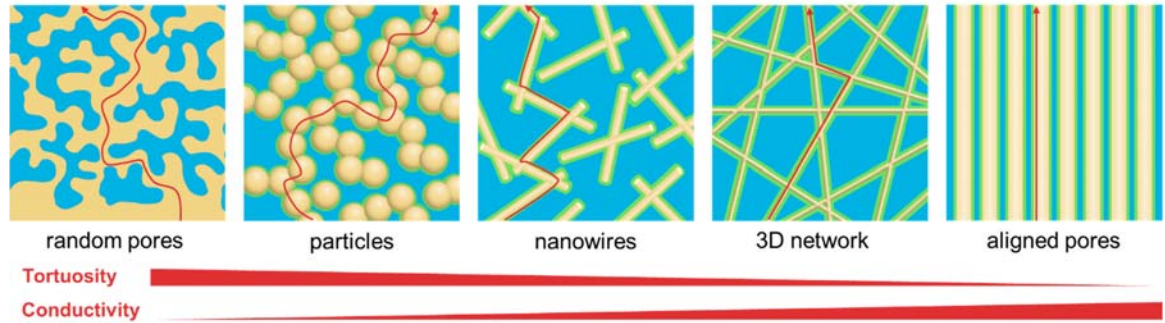


Figure 2.12. Ion transport pathways in solid state electrolytes with different compositions.

In composite electrolytes, the effective transport properties are usually influenced by the morphology of the conductive phases. This dependence of transport properties on the mass transport in the complex conductive phases can be simplified to the dependence of transport properties on one effective geometric parameter: tortuosity τ . In general, the relationship between tortuosity and transport properties can be defined as,

$$\kappa_{eff} = \kappa_0 \epsilon / \tau \quad (\text{E } 2.1)$$

where κ_0 and κ_{eff} are the intrinsic and the effective transport properties of the conducting phase respectively, ϵ is the volume fraction of the conductive phase. Due to the morphological complexity of the conductive phase, the tortuosity is often a function τ of ϵ .

In composite electrolytes, the relationship of effective ionic conductivity can be predicted using the Bruggeman relationship:

$$\sigma_{eff} = \sigma_0 \epsilon^\alpha \quad (\text{E } 2.2)$$

or equivalently,

$$\tau = \epsilon^{1-\alpha} \quad (\text{E } 2.3)$$

where σ_0 and σ_{eff} are the intrinsic and the effective transport properties of the conducting phase respectively, and α is the Bruggeman exponent.^{112,113} For tortuous ion transport pathways, $\tau > 1$ and the effective conductivity is always lower than the intrinsic conductivity. When transport pathways are straight lines parallel to the direction of ion conduction, $\tau = 1$ and the conductivity of the composite electrolyte reaches its maximum, which is equal to the intrinsic conductivity of the major conductive phase (the one that is more conductive if two or more conductive phases exist in the system). The ion transport behavior, and therefore the ionic conductivity, can be significantly influenced by the tortuosity of the electrode and electrolyte materials, especially when the electrodes and/or electrolytes are thick.¹¹⁴ Recent developments on ultra-thick electrodes demonstrated that the ionic conductivity and electrochemical performances of the cell was greatly enhanced due to the faster ion transport imparted by straight pores with low tortuosity.^{115,116} In this context, constructing SSE nanostructures with low tortuosity is highly desirable to achieve a high ionic conductivity.

2.2.2. Nature-Inspired Low Tortuosity Structure Design

Inspired by the aligned structure of natural wood (figure 2.13), a highly ionically conductive garnet network with well-aligned mesostructures through templated synthesis

was designed. Wood was adopted as a sacrificial template resulting in multi-scale aligned porosity, low tortuosity, and high specific surface area of garnet mesostructures. Due to its high ionic conductivity, good chemical stability with Li anode, and wide electrochemical window, garnet-type LLZO was chosen as the model system to fabricate a low tortuosity and aligned solid-state electrolyte.

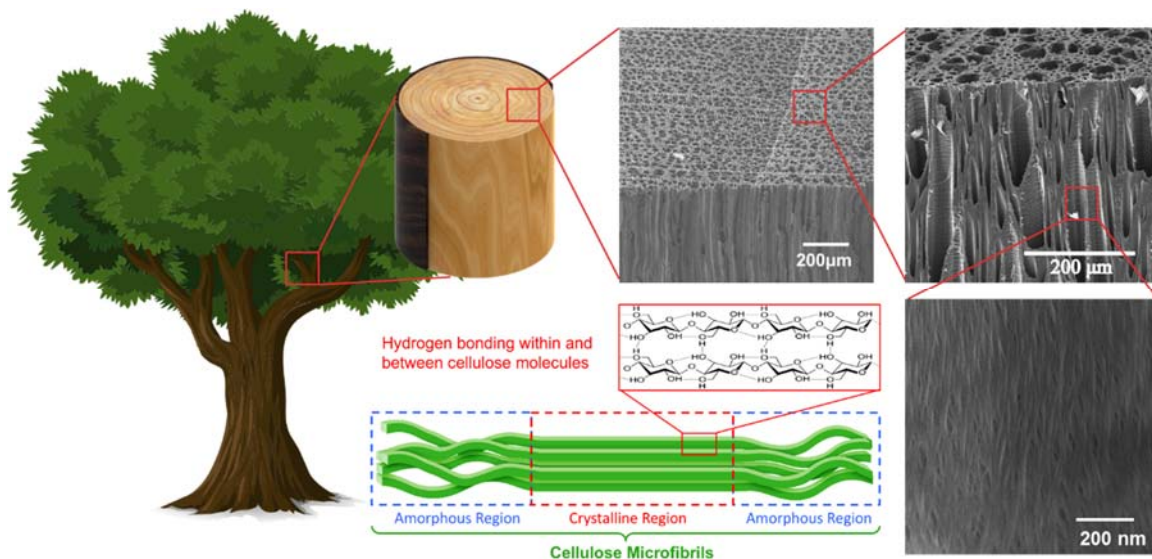


Figure 2.13. SEM images and schematics showing the fibrous, multi-level aligned, porous structure of wood.

Among various organic solid electrolytes, plasticized polyethylene oxide (PEO) enhanced with inorganic oxide fillers is widely used due to its ionically conductive properties in an amorphous state, scalability, electrochemical stability against Li metal, and reasonable mechanical strength.^{117,118} Therefore, PEO based polymer electrolyte was used to develop a composite electrolyte called garnet-wood (Figure 2.14), where PEO polymer electrolyte was infiltrated into the aligned garnet templated by wood. The polymer electrolyte provides additional transport pathways and also reinforces the mechanical

strength of the composite structure. Li-ion can effectively transport through garnet, polymer, and along garnet-polymer interfaces. Based on this concept, the design principle and fabrication process for aligned garnet-wood electrolyte can be extended to other types of solid-state electrolytes.

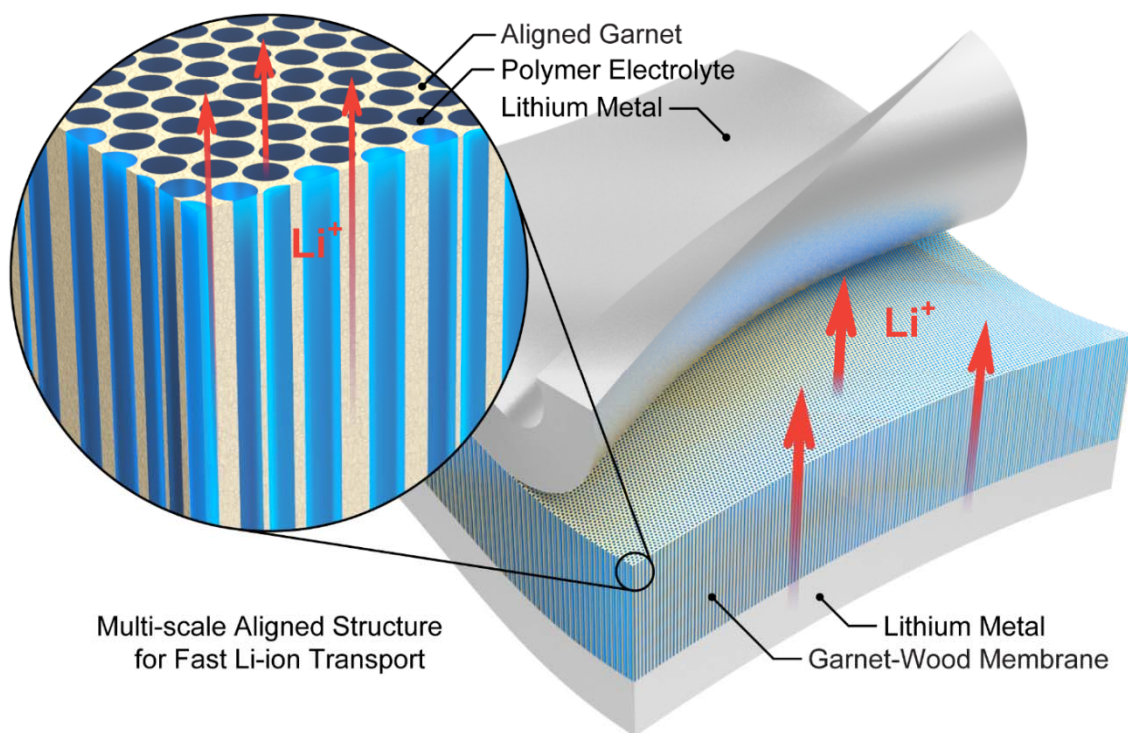


Figure 2.14. Schematic of multi-scale aligned mesoporous garnet $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ (LLZAO) membrane incorporated with polymer electrolyte in a lithium symmetric cell. The garnet-wood possesses multi-scale aligned mesostructure derived from natural wood, which enables the unobstructed Li ion transport along the garnet-polymer interface, through garnet, and through polymer electrolyte.

2.2.3. Structure-Derived Template Design

There are two major requirements for the template design using wood. First, the wood template needs to possess a multi-level aligned structure that can be replicated by

garnet. Second, the wood template needs to be able to absorb large amount of garnet precursor. Therefore, basswood was chosen as a template to develop the aligned garnet solid-state electrolyte framework due to its high growth rate, low cost, and high porosity. The wood template was obtained after partially removing lignin from a piece of natural basswood by chemical treatment, followed by compressing and slicing perpendicular to the longitudinal direction (natural growth direction) of the wood (figure 2.15). Mechanical pressing was used to densify the wood. Additional hydrogen bonds formed between adjacent cellulose fibers during densification, which maintains the dense structure of the framework. Figure 2.16 and figure 2.17 shows the appearance of wood template before and after compressing, respectively. The compressed wood template shows a darker color.

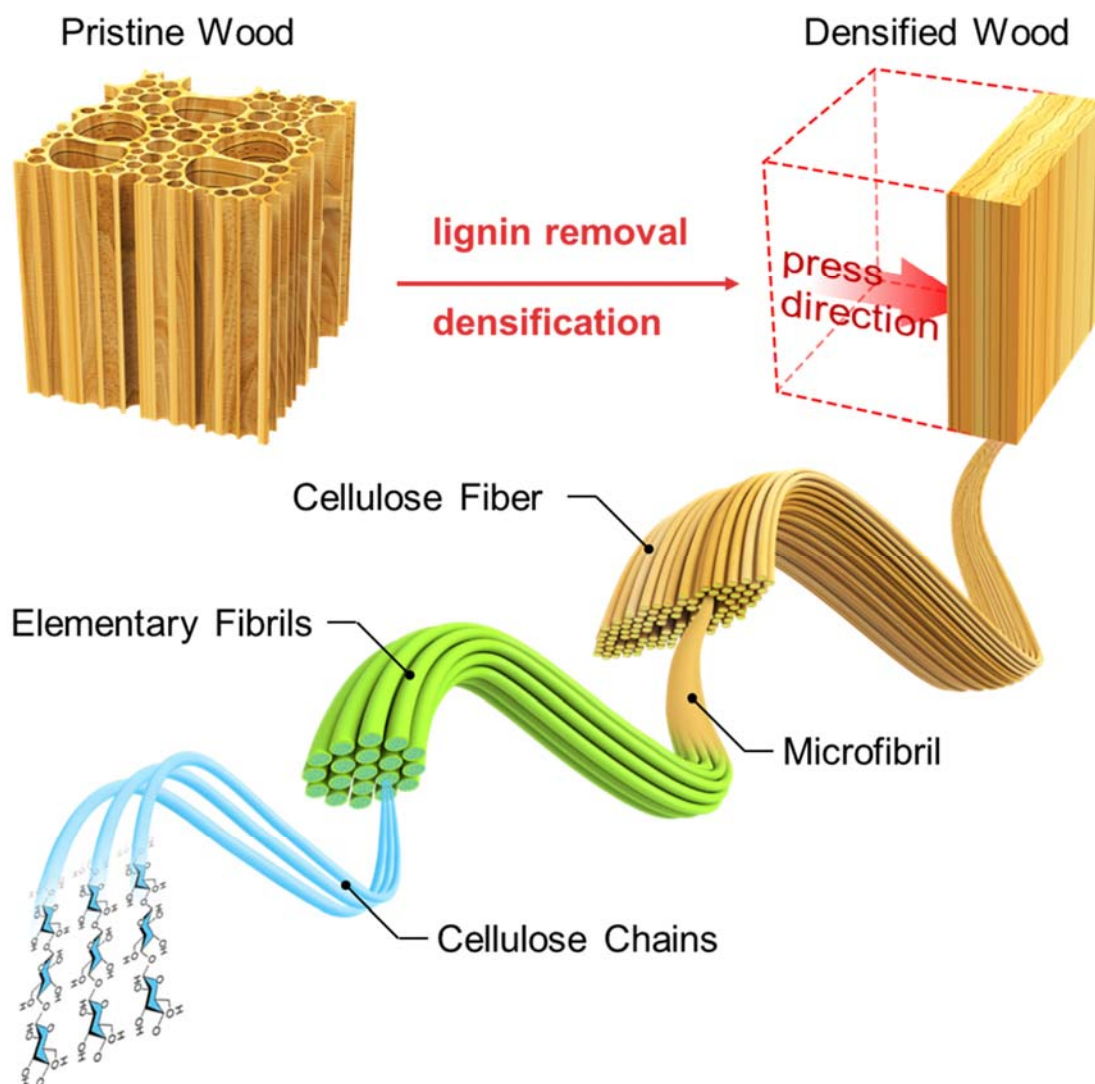


Figure 2.15. Illustrations of the wood template fabrication through compressing, and the multi-level aligned fibrous structure in the wood template.

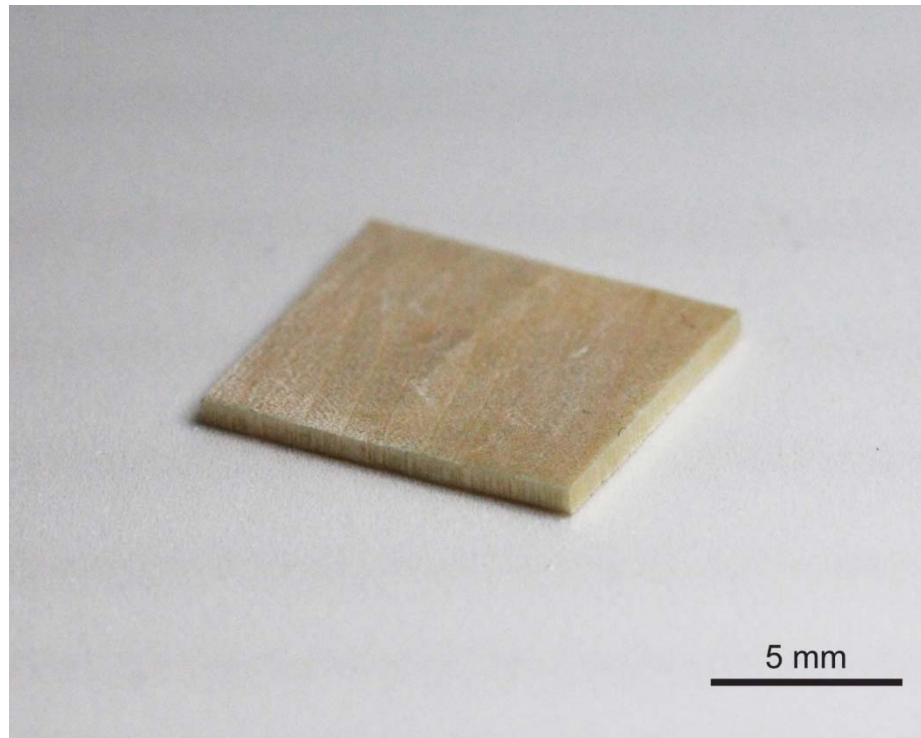


Figure 2.16. Photo of pristine basswood.

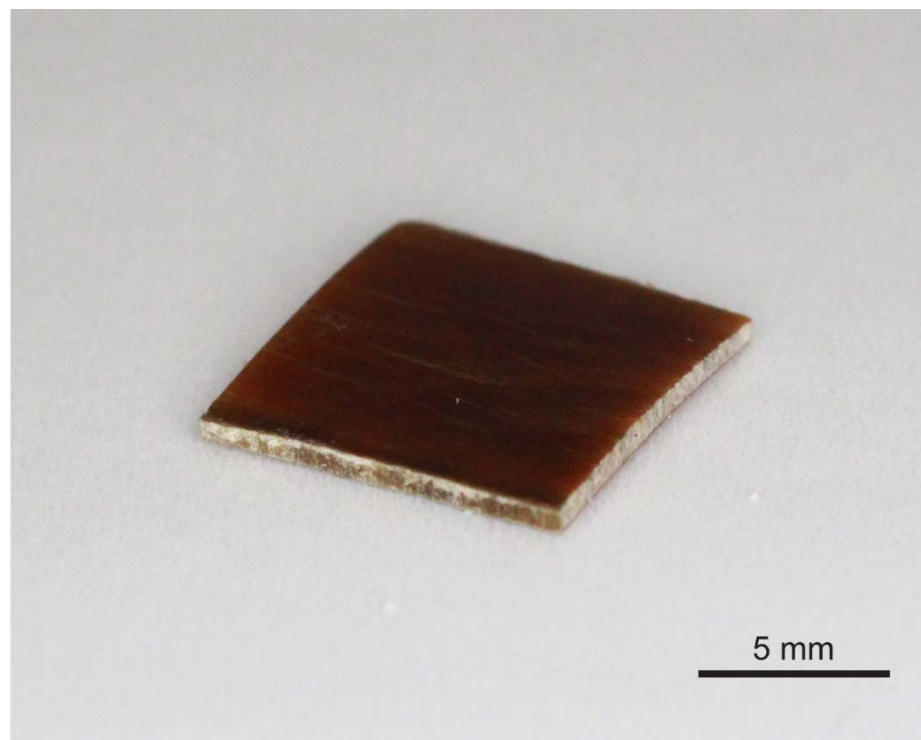


Figure 2.17. Photo of compressed wood template.

The morphological changes induced by mechanical compression were investigated with scanning electron microscopy (SEM) measurements of multiple specimens. Before compressing, microchannels in the wood have proximal cylindrical shape with diameters on average between 10-50 μm (figure 2.18-a, 2.18-b). After compression, most of the previously observed microchannels were squeezed into crack-shaped gaps, and some of the adjacent channels became connected (figure 2.19-a, 2.19-b). Although these open channels were severely deformed after compression, their highly aligned multiscale porous structure remained unchanged (figure 2.20).

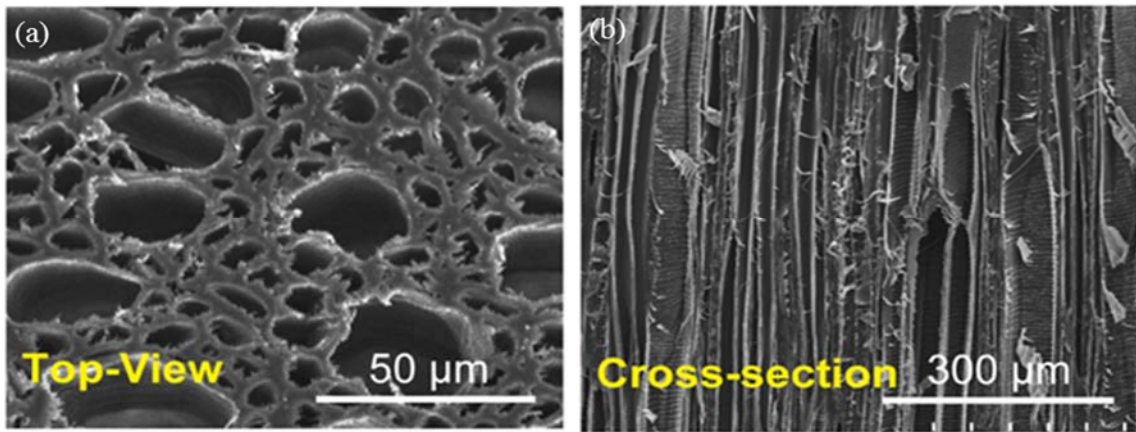


Figure 2.18. (a) Top-view and (b) Cross-sectional SEM image of pristine wood.

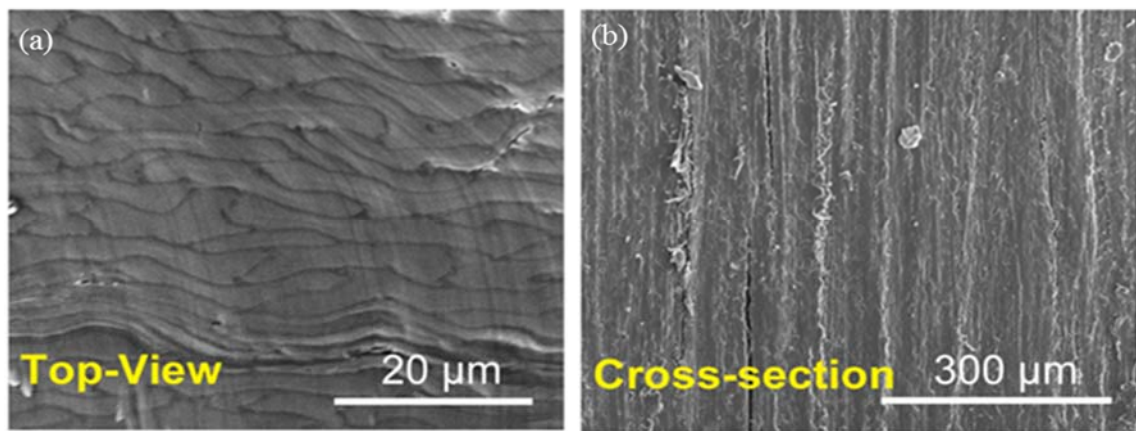


Figure 2.19. (a) Top-view and (b) cross-sectional SEM image of compressed wood.

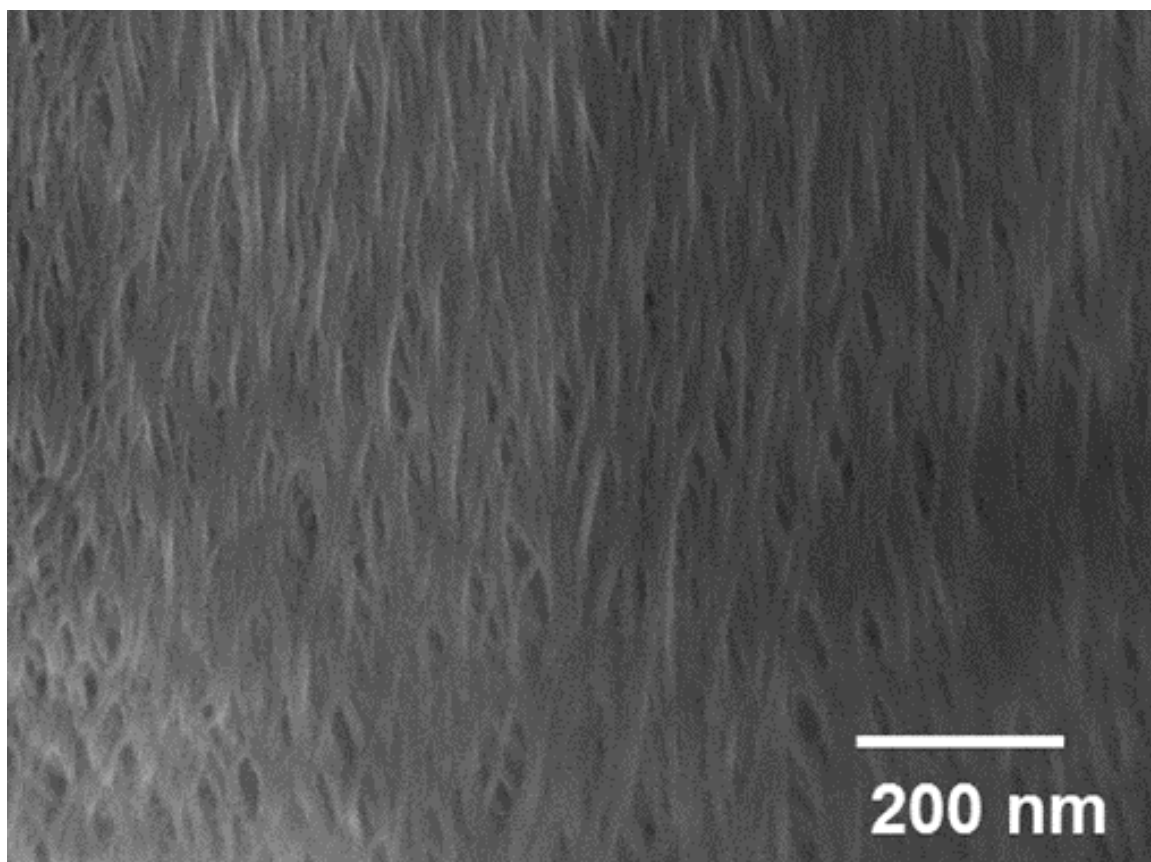


Figure 2.20. SEM image of the aligned nanofiber with a diameter of around 10 nm.

The wood template showed great absorbency when immersed into the precursor solution. For instance, after soaking for 48 hours and drying in vacuum at 70 °C for 4 hours, the mass of the wood template increased 27.8 % from 2.7 mg to 3.45 mg (figure 2.21). The high absorption of precursor solution, pliable nature of the template pores, and scalability of the procedure are indicative of a cost-effective and productive method for fabricating SSEs with aligned mesostructures.

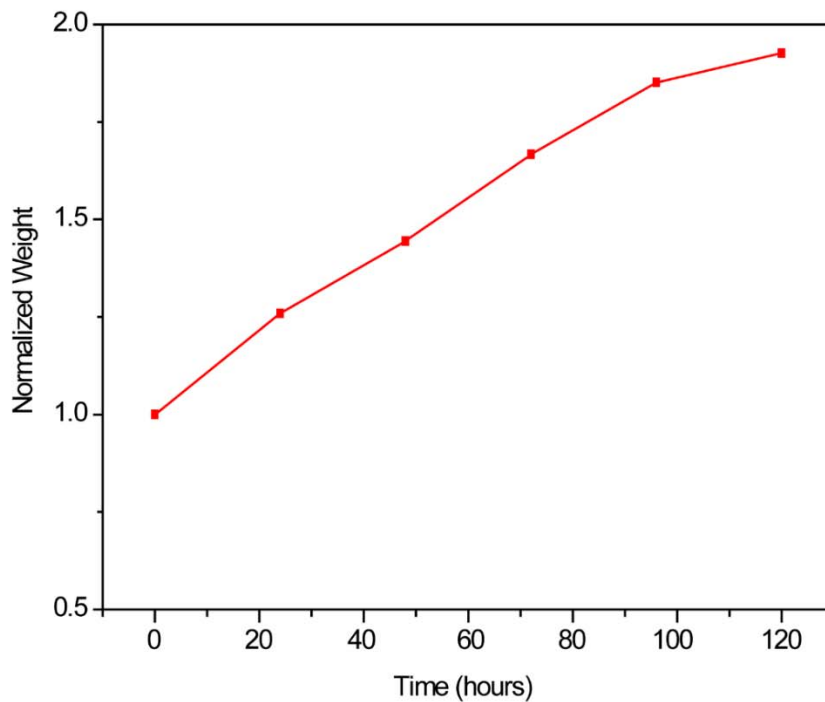


Figure 2.21. Weight change of the wood template during precursor infiltration.

2.2.4. Wood-Templated Sol-Gel Synthesis

The wood with infiltrated garnet precursor was calcined at 800 °C for 4 hours in oxygen to obtain the LLZO membrane (figure 2.22). The wood template with aligned channels has two unique functions. First, the free channels in the wood template provide reservoirs to supply precursor solutions to the template combustion reaction. Second, the aligned nanofibers with a diameter of 2~10 nm in the wood template serve as sacrificial pore formers for additional aligned porosity in the garnet membrane. Morphological changes after calcination were characterized by SEM. The aligned porous structure from the wood template was inherited in the resulting garnet framework at both the microscale (figure 2.23-a) and nanoscale (figure 2.23-b).

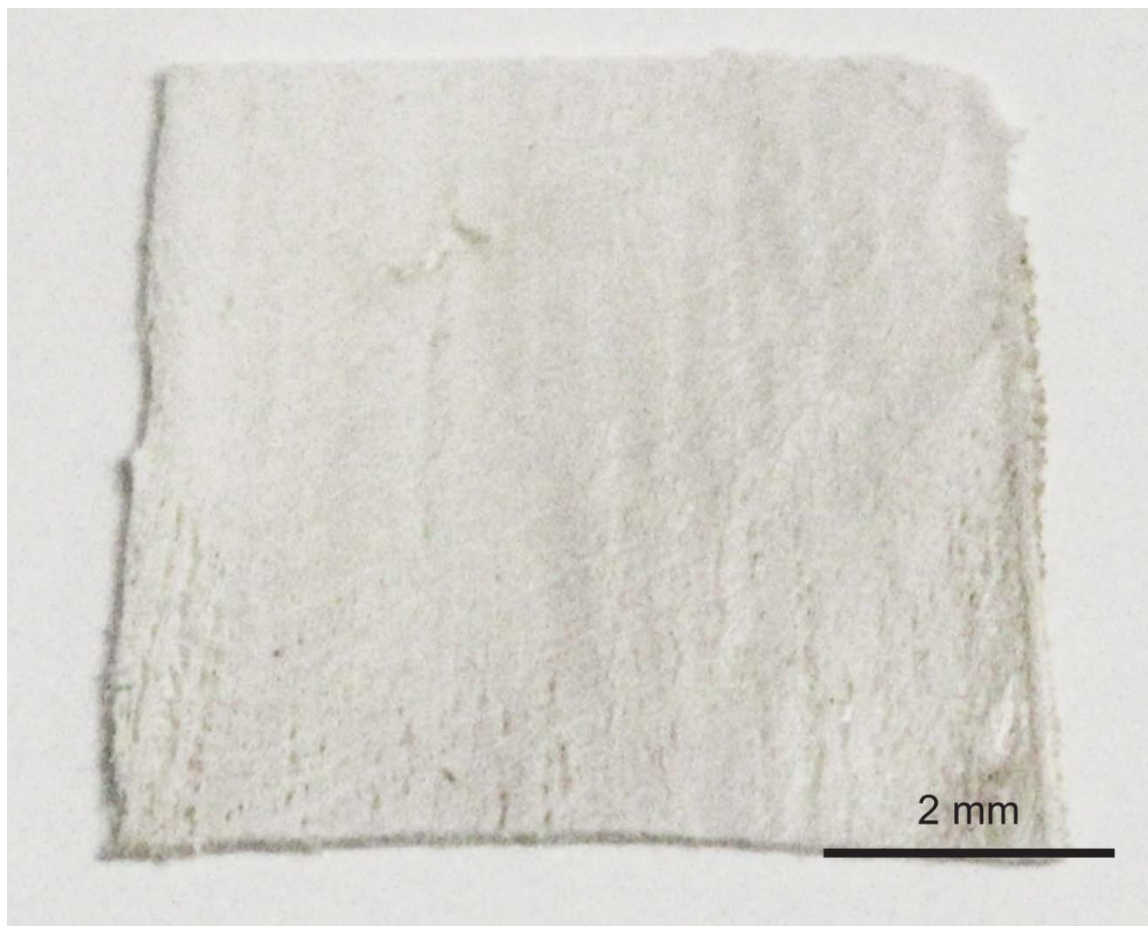


Figure 2.22. Photo of an as sintered aligned mesoporous garnet membrane.

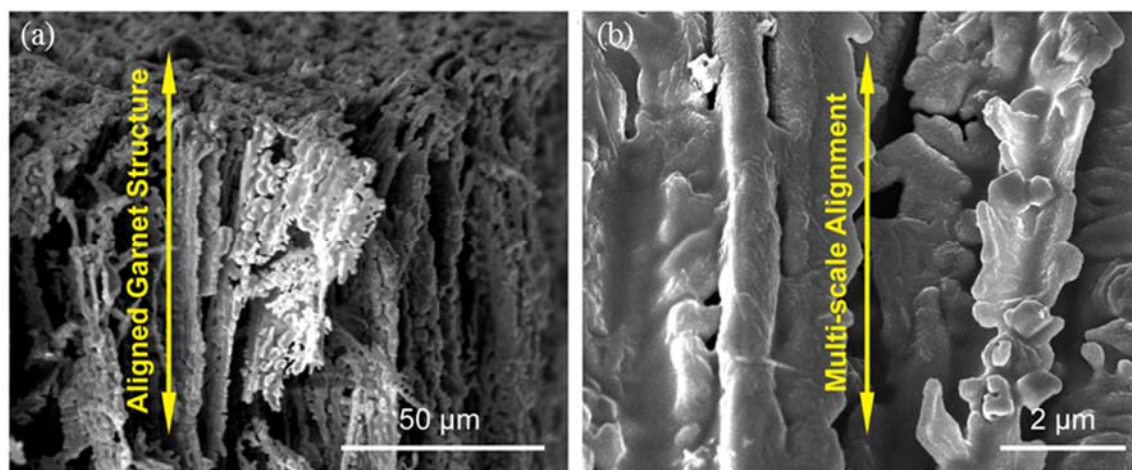


Figure 2.23. Cross-sectional SEM image shows the alignment of channels at both (a) micro-scale and (b) nano-scale.

The well-aligned garnet membrane inherited directly from wood is flexible after infiltration with the PEO based polymer electrolyte. In terms of mechanical properties, we demonstrated the high flexibility of the garnet wood. Figure 2.24 shows the mechanism of the flexibility of garnet wood. Conventional bulk garnet solid-state electrolyte is brittle, which is caused by the unobstructed crack expansion in the highly crystallized structure. The hybrid design of garnet wood consists of polymers and a ceramic network, thereby resulting in a lightweight and flexible composite (Figure 2.25).

X-ray diffraction (XRD) was employed to identify the crystal phase of the garnet membrane. The XRD pattern of the aligned mesoporous garnet synthesized using wood template (figure 2.26) matched well with the cubic-phase garnet $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (JCPDS#80-0457), despite minor peak shifts at higher angles due to aluminum (Al) doping and variations in Li concentration. As a representative structure of fast lithium-ion-conductive garnet, $\text{Li}_5\text{La}_3\text{M}_2\text{O}_5$ ($\text{M} = \text{Nb}, \text{Ta}$) is widely used as a reference to distinguish conductive garnet phases from non-conductive ones.¹¹⁹ The well XRD pattern match of the aligned mesoporous garnet with JCPDS#80-0457 verifies that the wood templated garnet is the conductive cubic phase. The thickness of the garnet-wood structure is mainly determined by the thickness of the wood template. The thin wood templates were prepared by slicing and were further thinned by polishing. The thickness can be reduced to less than 20 μm . Figure 2.27 shows a thin garnet wood sample ($\sim 18 \mu\text{m}$) prepared by slicing and polishing method.

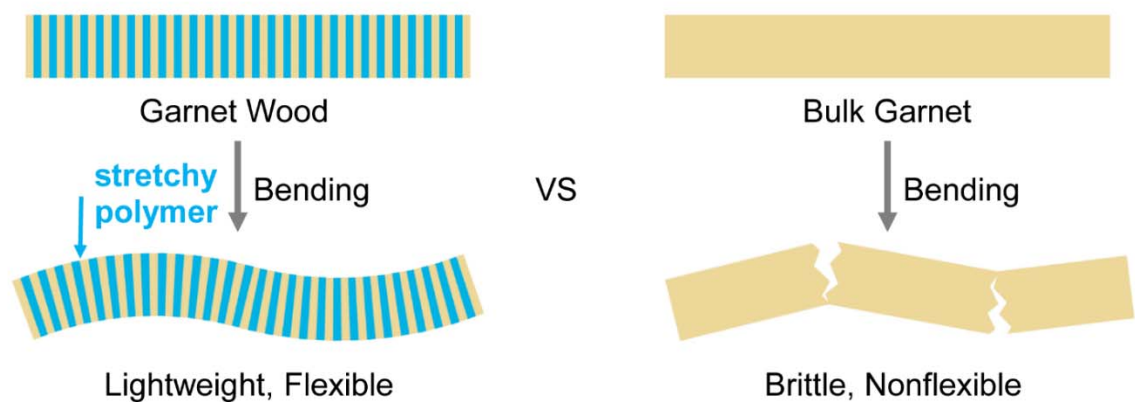


Figure 2.24. Flexibility comparison of garnet-wood to bulk garnet.

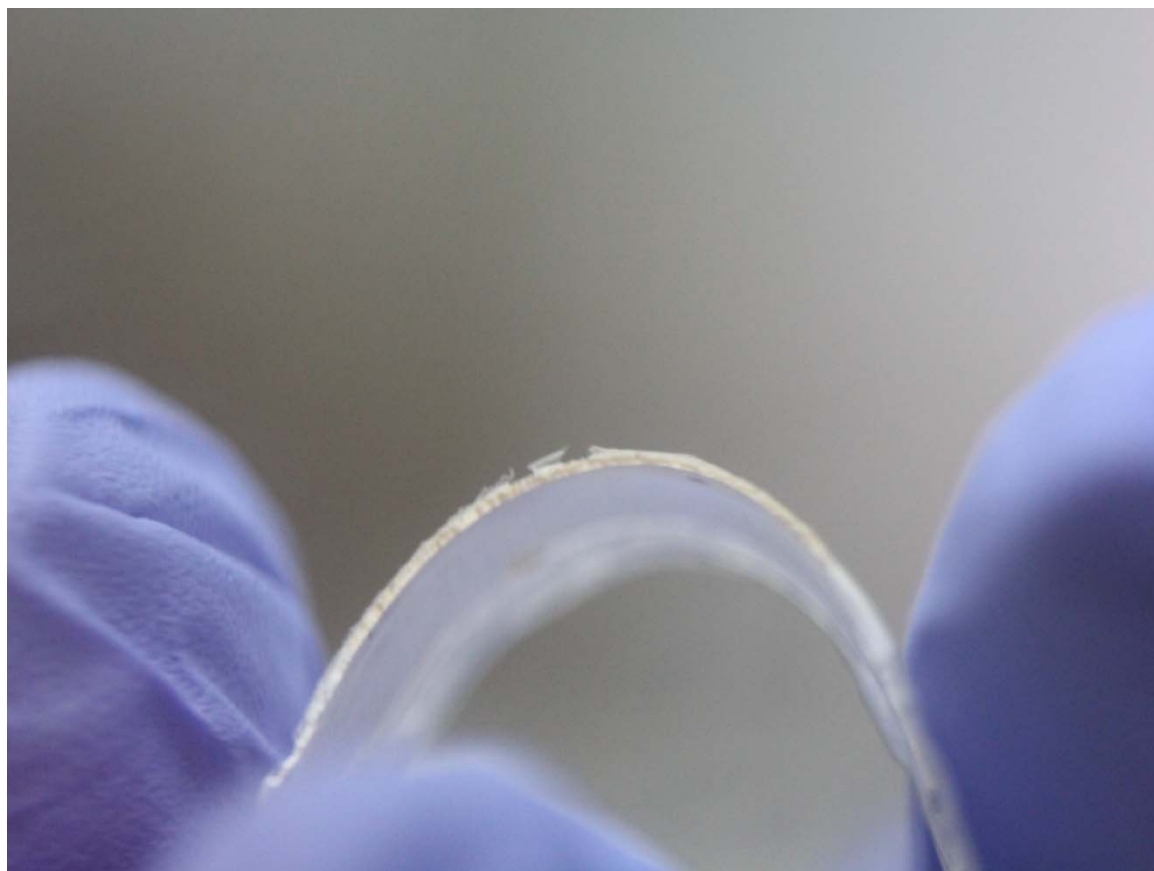


Figure 2.25. Photograph of the flexible garnet-wood consisting of aligned mesoporous garnet and PEO based polymer electrolyte.

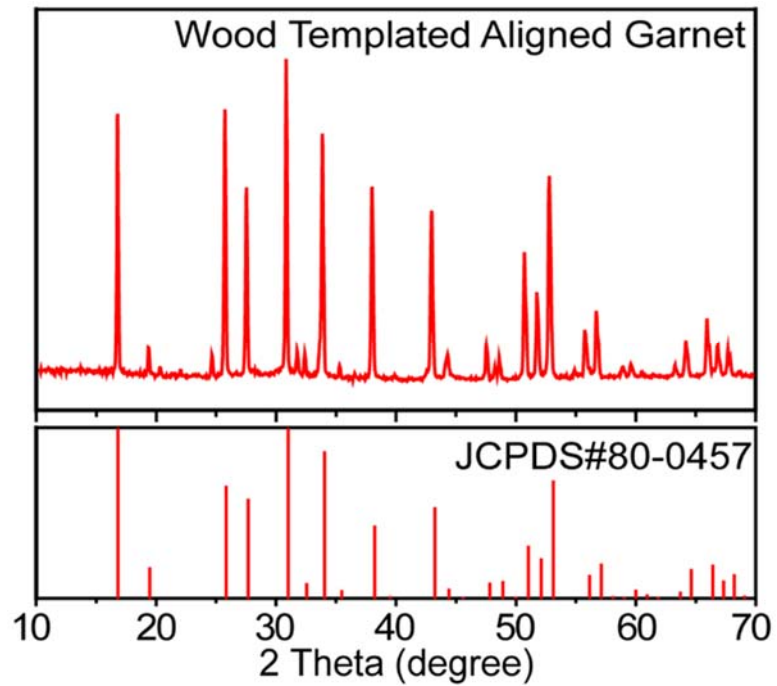


Figure 2.26. XRD pattern of the aligned garnet matches JCPDS#90-0457.

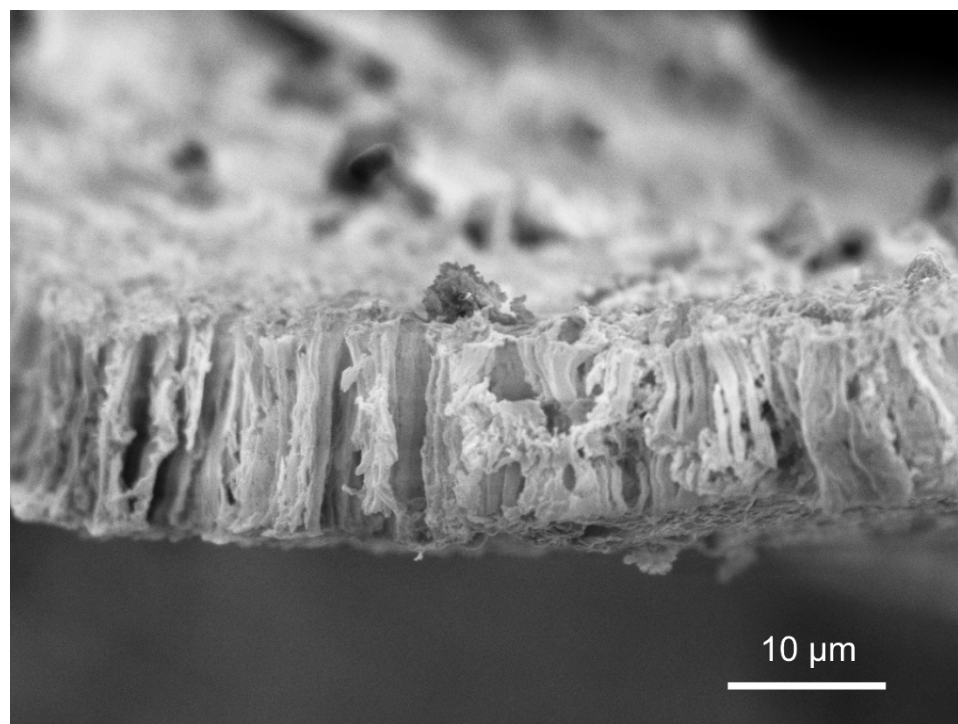


Figure 2.27. Cross-sectional SEM image of the aligned garnet structure with a thickness of 18 μm .

2.2.5. Results and Discussion

High-resolution transmission electron microscopy (HRTEM) of the resulting aligned garnet reveals the clear, well crystallized lattice structure of the garnet (figure 2.28). The miller indices were calculated from the corresponding fast Fourier transform (FFT) pattern (Inset of figure 2.28) and the lattice constant derived from the HRTEM and FFT is 12.982 Å, which agrees with previously reported values.¹²⁰

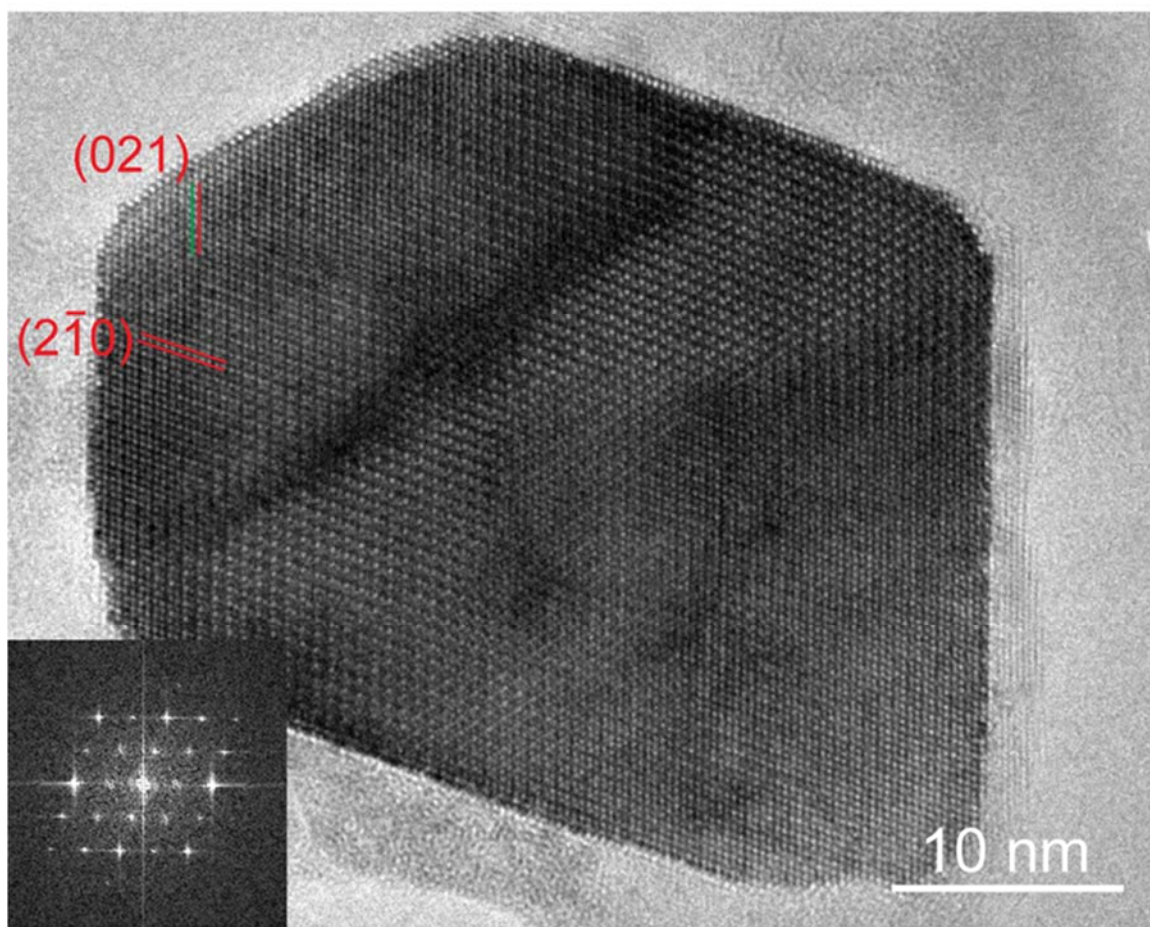


Figure 2.28. HRTEM image of a nanoparticle broken off from the aligned garnet showing the (2̄10) and (021) lattice planes.

Crystal grains with various orientations can be clearly distinguished in the HRTEM image of a larger garnet particle broken off from the structure (figure 2.29). The TEM results indicate that the aligned mesoporous garnet has a highly crystallized, well-connected multicrystalline structure.

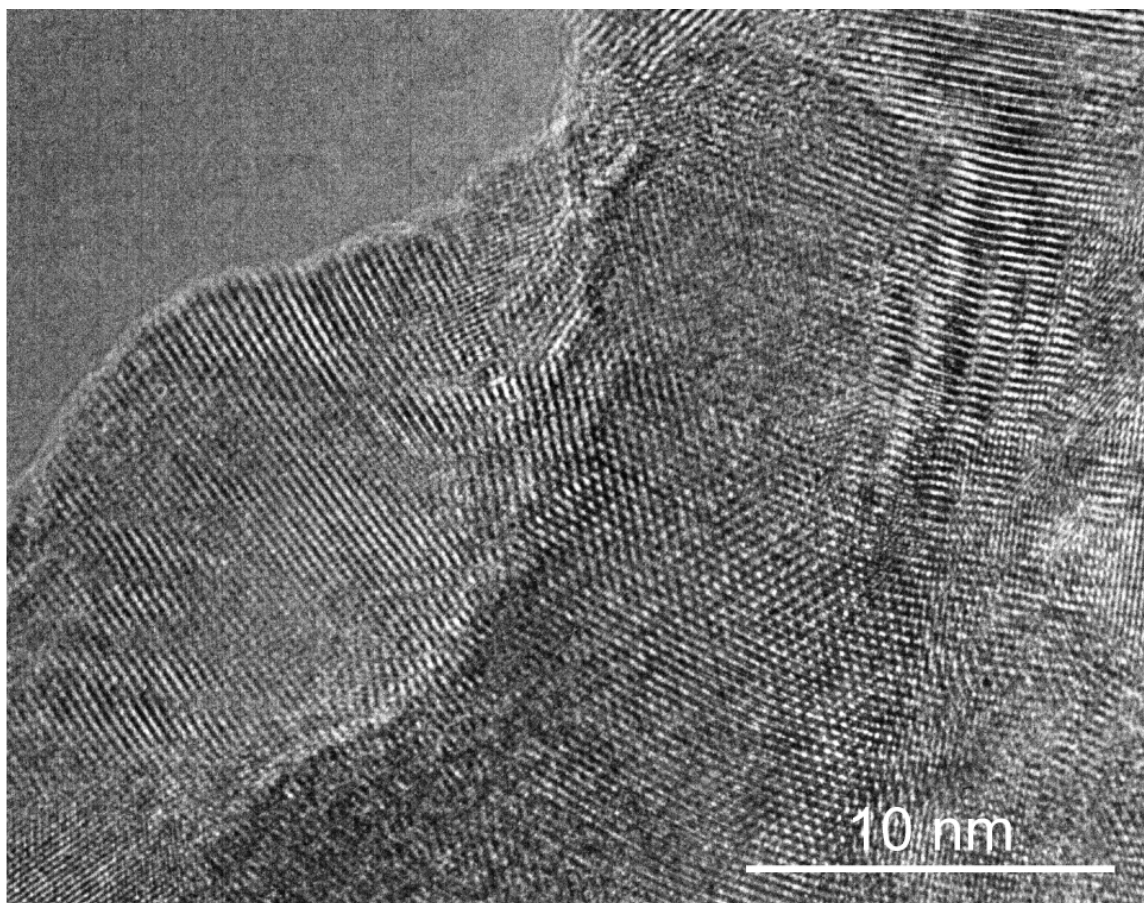


Figure 2.29. TEM image of the edge of a garnet nanoparticle showing a clear multicrystalline structure.

Electron energy loss spectroscopy (EELS) was employed to analyze the composition of the garnet membrane. Figure 2.30 shows the EELS spectrum with the region of interest (ROI) outlined. EELS mapping indicates the relative composition and distribution of oxygen, carbon, and lanthanum. The overlapping region of oxygen k-edge

signal and lanthanum n-edge signal identifies the location of LLZO. Though the carbon k-edge signal is rare throughout the sample, a small overlapping region of oxygen k-edge signal and carbon k-edge signal was identified, which indicates that the Li_2CO_3 impurities caused by calcining in oxygen is minimum.

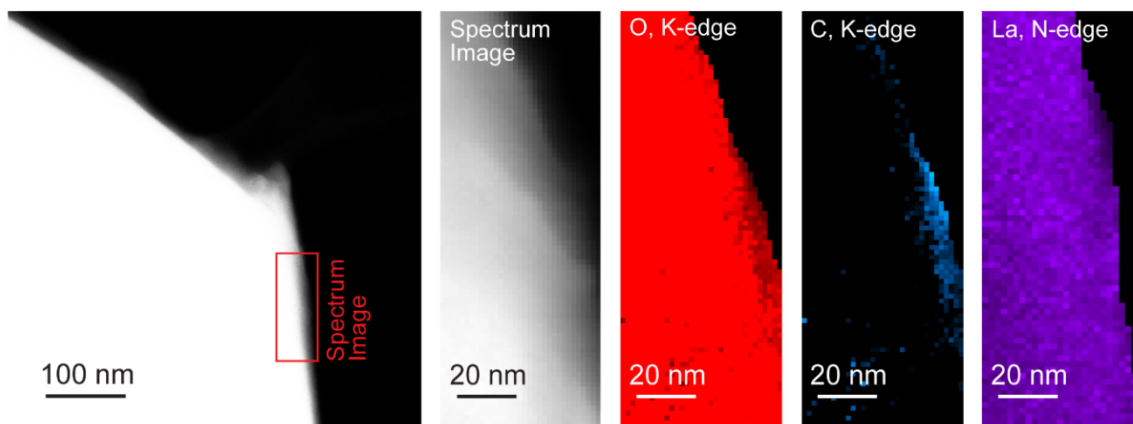


Figure 2.30. EELS spectrum of the garnet surface showing the ROI, spectrum image, and relative composition map of O, C, and La, respectively.

The garnet-wood was fabricated by infiltrating PEO polymer electrolyte into the aligned garnet. Figure 2.31 shows a cross-sectional SEM image of garnet wood with PEO infiltrated. The garnet wood membrane has a thickness of about $30\mu\text{m}$. Figure 2.32 characterizes the polymer infiltration with energy dispersive X-ray spectroscopy (EDX). The evenly distributed carbon signal from the top, down to the aligned garnet channels indicates complete and uniform infiltration of the polymer electrolyte, which is crucial for establishing sufficient Li ion transport pathways. As suggested in the literature, there are three possible Li ion transport pathways.

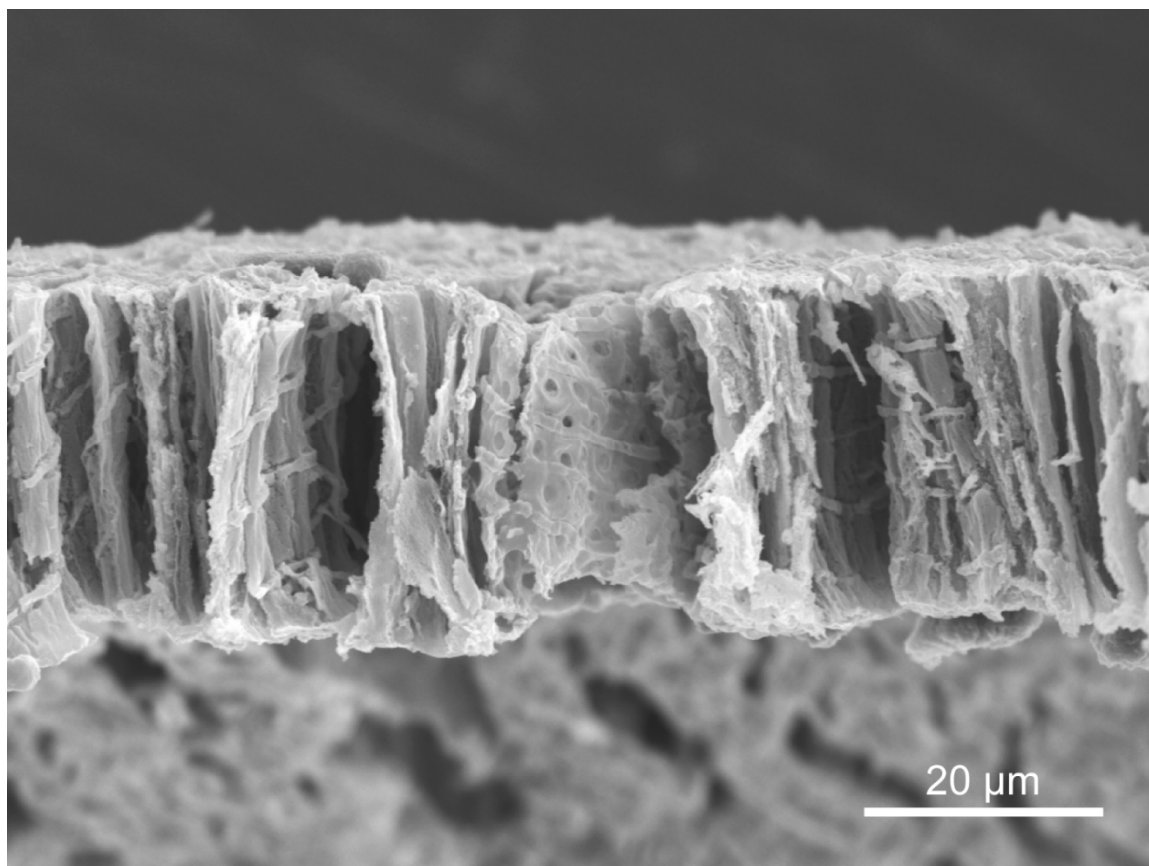


Figure 2.31. Cross-sectional SEM image of garnet-wood with a thickness of $\sim 30 \mu\text{m}$.

The first pathway is the aligned PEO polymer electrolyte, whose bulk ionic conductivity (without fillers) is usually as low as 10^{-7} S/cm at room temperature.¹²¹ The second pathway is the aligned garnet-polymer interface. At the interface, the aligned mesoporous garnet behaves like ceramic fillers that can induce changes to the polymer segmental dynamics, and therefore influences lithium ion transport. Intensive studies on the influence of fillers on the ionic conductivity of polymer electrolyte suggests that ceramic fillers with Lewis acid characteristics can promote the lithium ion transport by anion coupling and providing preferential conductive pathways.^{61,62} The third pathway is transport through the high volume percentage ($\sim 68\%$) aligned garnet nanostructure. Recent studies point out that among three transport pathways in garnet-polymer composite

electrolyte systems, conducting through garnet phase is the most preferred, evidenced by tracking isotope labeled Li ion migration using nuclear magnetic resonance (NMR).¹²² Note that the typical bulk ionic conductivity of dense LLZO achieved in our lab using the same composition is up to 2.2×10^{-4} S/cm at room temperature. However, this bulk ionic conductivity is difficult to achieve in conventional mesoporous structures due to the highly tortuous transport pathways caused by random pores and insufficient solid-solid interfacial contact at the numerous pore gaps.⁴¹ In contrast, the low tortuosity of the aligned mesoporous garnet structure enables unobstructed Li ion transport along the normal direction of the flexible garnet-wood, which effectively promotes ionic conductivity.

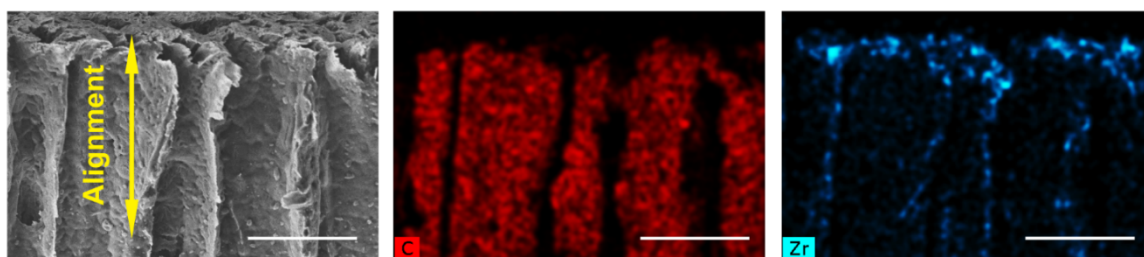


Figure 2.32. SEM and its corresponding EDX images showing the complete, uniform infiltration of polymer electrolyte throughout the aligned garnet. Scale bars, 100 μm .

The ionic conductivity of the garnet-wood was characterized by electrochemical impedance spectroscopy (EIS). A garnet-wood membrane (0.1 cm^2 area, 0.4 μm thick) was assembled into symmetric cells with stainless steel as the blocking electrodes and scanned from 1 MHz to 100 mHz. Figure 2.33 shows the Nyquist plot of the electrolyte membrane tested from room temperature (25 $^{\circ}\text{C}$) up to the melting temperature of PEO (65 $^{\circ}\text{C}$). The experimental ionic conductivity is calculated using the electrolyte membrane thickness and area, and the results are shown in figure 2.34. The garnet-wood membrane achieved an

ionic conductivity of 1.8×10^{-4} S/cm at room temperature. The theoretical ionic conductivity of the composite is the total contribution of each phase weighted by the volume fractions.

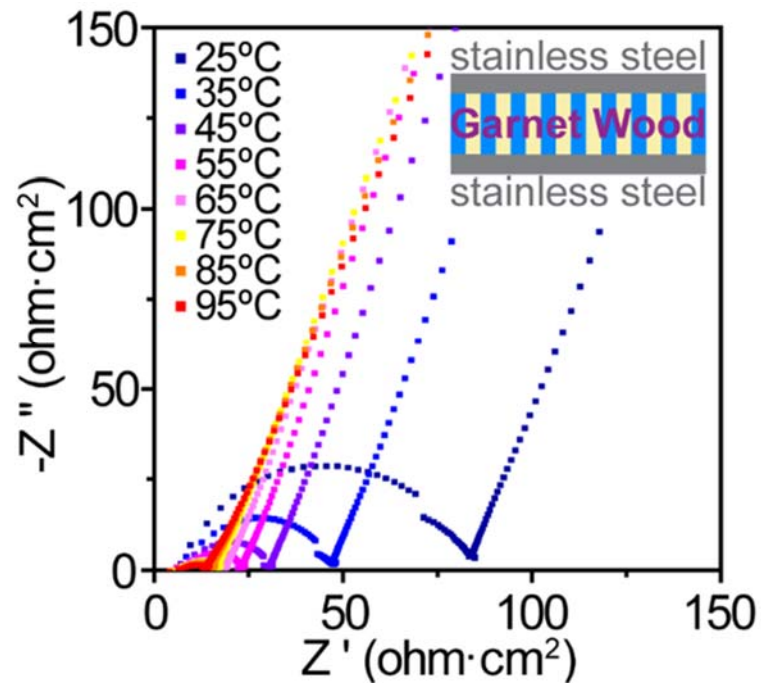


Figure 2.33. Nyquist plot showing the decrease in the impedance of the garnet-wood membrane with increasing temperature, the inset schematic shows the structure of the testing cell.

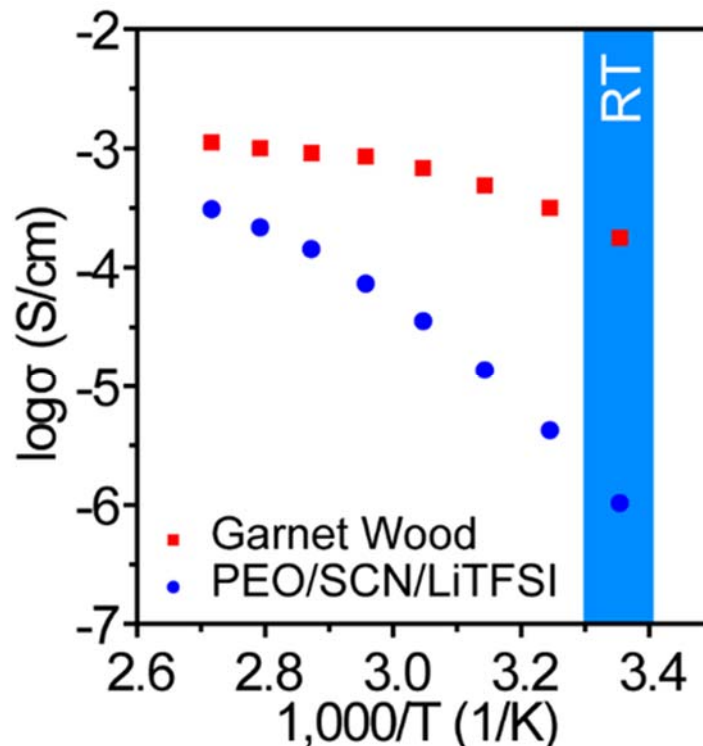


Figure 2.34. Comparison of the ionic conductivity of the garnet-wood and PEO based polymer electrolyte at different temperatures, the blue region indicates measurements performed within the range of room temperature (RT).

The ionic conductivity of the PEO polymer electrolyte without the addition of garnet structure was measured in coin cells at various temperatures. PEO electrolyte contains plasticizer succinonitrile (SCN). The PEO/LiTFSI/SCN polymer electrolyte film was sandwiched by two stainless steel electrodes. A polyethylene (PE) separator ring was placed around the polymer electrolyte film to fix the thickness and avoid shorting at high temperatures. Given the PEO polymer electrolyte conductivity of 1.03×10^{-6} S/cm (figure 2.35 and figure 2.36) and garnet conductivity of 2.2×10^{-4} S/cm, the theoretical conductivity of garnet-wood is 1.5×10^{-4} S/cm at room temperature.¹²³ In this low tortuosity structure with continuous conducting paths in each phase, the theoretical conductivity should hold

unless there is enhanced conductivity at the two-phase interfaces. Therefore, the difference between the theoretical and experimental conductivities should be attributed to an enhanced interface contribution to the total ionic conductivity.

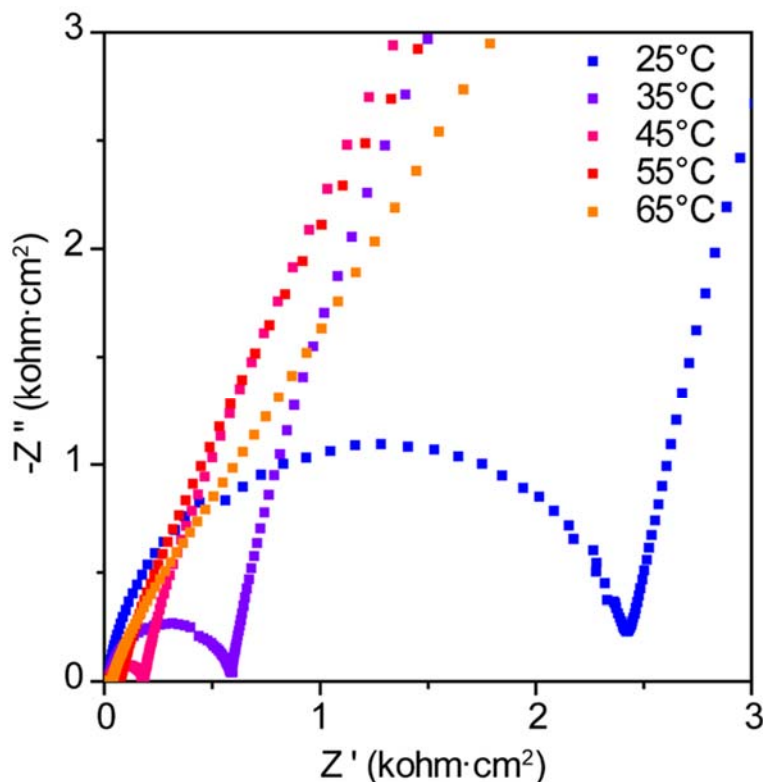


Figure 2.35. Nyquist plot of the PEO/SCN/Li-TFSI electrolyte at different temperatures.

As the operating temperature is increased, the intersection of the semicircle with the real impedance axis decreased, indicating an improved ionic conductivity with elevated temperature. At 95°C, the ionic conductivity increased to 1.1×10^{-3} S/cm, a 6.3 times improvement above the room temperature performance. The temperature dependence of the ionic conductivity for the garnet-wood can be expressed by the Arrhenius equation:

$$\sigma = A \exp\left(-\frac{E_A}{kT}\right) \quad (\text{E 2.4})$$

Where σ is the total ionic conductivity of garnet-wood, A is the pre-exponential factor, T is the absolute temperature, E_A is the activation energy of garnet-wood, and k is the Boltzmann constant.¹²⁴ The calculated activation energy of garnet-wood is 0.38 eV, which can be lowered further by adjusting the proportion of polymer electrolyte. This effect is due to various enhancement effects including the increase in the volume fraction of amorphous conducting phase as well as improvement in the long range polymer chain mobility.⁶²

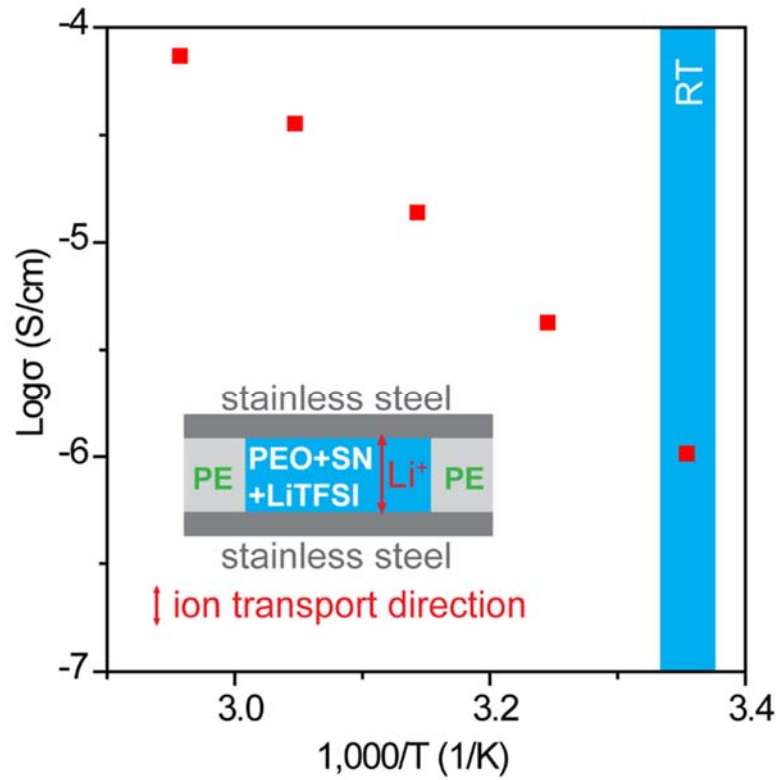


Figure 2.36. Ionic conductivity of the PEO/SCN/Li-TFSI electrolyte at different temperatures. The blue region indicates measurements performed around room temperature (RT). Inset shows the structure of the testing cell.

As a proof-of-concept, a Li metal/garnet-wood/Li metal symmetrical cell was fabricated and a Li stripping/plating test was performed at room temperature. Figure 2.37 shows a characteristic 180 hours of the cycling at a current density of 0.1 mA/cm^2 for 30 min in each direction. The voltage response of the symmetric cell stabled at 50 mV with slight fluctuations. The symmetrical cell cycled well for over 600 hours with small polarization (figure 2.38). The long-term cycling performance indicates that the garnet-wood membrane enhanced with aligned mesoporous garnet can enable fast and stable ion transport. In addition, the polymer electrolyte also largely improves the mechanical flexibility of the aligned garnet, enabling its use in Li metal batteries.

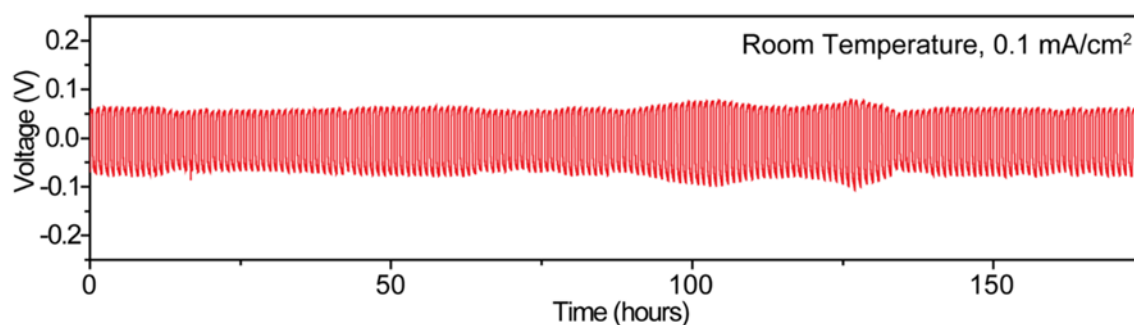


Figure 2.37. Galvanostatic cycling of Li/garnet-wood/Li with a current density of 0.1 mA/cm^2 at room temperature.

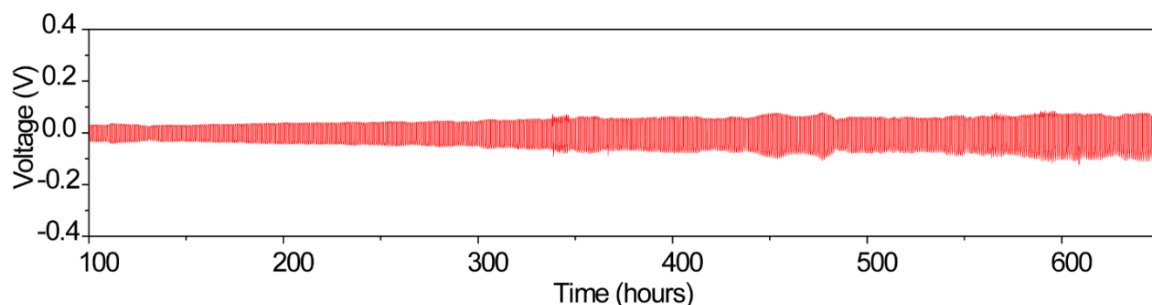


Figure 2.38. Galvanostatic cycling of Li/garnet wood/Li with a current density of 0.1 mA/cm^2 at room temperature for over 600 hours.

2.2.6. Experimental Method

Materials Preparation. The garnet precursor solution was prepared by dissolving stoichiometric LiNO_3 ($\geq 99.0\%$, Aldrich), $\text{La}(\text{NO}_3)_3$ ($\geq 99.9\%$, Aldrich), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\geq 98.0\%$, Aldrich), $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.9%, Aldrich), and acetic acid ($\geq 99.7\%$, Aldrich) in ethanol ($\geq 99.8\%$, Aldrich) at room temperature under magnetic stirring. The total cation concentration of the precursor solution was 2 mol/L. 15% excess lithium nitrate was added to compensate for lithium loss at high calcination temperature.

The wood template was soaked in the above-mentioned solution for 48 h to impregnate the garnet precursors. Excess solution was removed from the wood template and the sample was dried at 70°C for 4h. Subsequent thermal treatment was carried out in oxygen at 800°C for 4 h to burn off the wood template and sinter the dispersed precursors. The sintering process was carefully controlled to retain the microstructure of the wood template. Garnet nanoparticles and nanofibers for TEM studies were obtained by grinding and sonicating the garnet membrane in isopropanol (IPA).

The PEO-based polymer electrolyte was prepared by dissolving PEO ($M_v=600,000$, Aldrich) with bis(trifluoromethane)sulfonimide lithium salt (LiTFSI , $\geq 99.85\%$, Aldrich, $\text{EO}:\text{Li}^+=8:1$) into acetonitrile (ACN, anhydrous, 99.8%, Aldrich) under magnetic stirring in an argon-filled glovebox at room temperature. 15 wt% succinonitrile (SCN, 99%, Aldrich) was added into the solution and the mixture was magnetically stirred until SCN completely dissolved. The drop-cast polymer electrolyte in the aligned mesoporous garnet (garnet-wood) was fully dried in vacuum at room temperature for 1 hour before electrochemical testing.

Materials Characterizations. XRD was performed on a Bruker D8 Advance with Cu K radiation. SEM images and their corresponding EDX images were obtained using a Hitachi SU-70 Field Emission SEM equipped with an energy dispersive x-ray spectrometer. TEM images were obtained using a JEM 2100 Field Emission Gun TEM equipped with an electron energy loss spectrometer for EELS studies. FFT image was computed from the high-resolution TEM image using Gatan Microscopy Suite. The EIS measurement was performed with a Solartron-1260 impedance gain phase analyzer on symmetric cells consisting of the garnet-wood between stainless steel plates as blocking electrodes. The cells were rested in an environmental chamber for 30 minutes at the predetermined temperature before each EIS test to reach thermal equilibrium and then scanned from 1 MHz to 100 mHz to acquire the impedance curves at various temperatures. The Li stripping/plating tests were performed with a BioLogic VMP3 multi-channel potentiostat on symmetric cells consisting of the garnet-wood between Li metal foils as electrodes. The cells were cycled at a current density of 0.1 mA/cm² for 30 minutes in each direction at room temperature in an argon filled glovebox.

2.3. Conclusion

This chapter introduced two structure designs for garnet based solid state electrolytes, and discussed the importance of tortuosity in determining ionic conductivity. In the first work, an ion-conductive 3D interconnected garnet framework was designed and synthesized using electrospun LLZO. A type of SCE consists of the garnet framework and polyethylene oxide (PEO)-based SPE was developed.³⁹ The SCE achieved a high ionic conductivity of 2.5×10^{-4} S/cm at room temperature and exhibited many outstanding

features including good chemical stability against lithium metal, good chemical stability against ambient air and moisture, nonflammability, and good mechanical strength.

In the second work, garnet-wood composite electrolyte with a multiscale aligned mesoporous structure is reported for the first time. The scalable compressed wood template results in the unique low tortuosity and high surface area mesostructure that is critical to the improved electrochemical performance and mechanical stability. Ionically conductive polymer serves as a matrix to reinforce the mechanical strength of the aligned mesoporous garnet membrane and also provide additional ion transport pathways through the amorphous conductive phase and the garnet-polymer interfaces. Benefiting from these structural merits in combination with the intrinsic high ion conductivity and low tortuosity of the aligned mesoporous garnet, the garnet-wood composite electrolyte achieves a high Li ion conductivity of 1.8×10^{-4} S/cm at room temperature and 1.1×10^{-3} S/cm at 95 °C. This is close to the bulk conductivity of garnet itself and moreover exhibits an enhanced contribution from the garnet/polymer interface. The garnet-wood demonstrates great potential as a low-tortuosity structure for highly conductive SSE and it also provides a model study for the design and optimization of solid state SECs.

Chapter 3: Interface Engineering for Solid State Batteries

Solid-state lithium batteries (SSLiBs) are promising solutions to the primary problems encountered in traditional lithium (Li)-ion batteries with liquid electrolytes, such as poor safety, limited voltage, unstable solid-electrolyte interphase (SEI) formation, and poor cycling performance. A key part in the successful development of the SSLiBs is the solid state electrolytes (SSEs). As introduced in previous chapter, the two major challenges facing the SSEs today are (1) maximizing the intrinsic ionic conductivity of the electrolyte and (2) minimizing the interfacial impedance between the electrolytes and electrodes. So far, not much progress has been made in battery development with garnet electrolytes primarily due to the large interface impedance between garnet and electrodes. Quite a few successful approaches have been applied to reduce interfacial impedance between SSEs like garnet and cathodes, including surface coating,¹⁹⁻²² interface softening,^{23,24} and buffer layer, *e.g.* LiNbO_2 ,²⁵ Nb ,²⁶ BaTiO_3 ,¹⁹ and additive in cathode composite, *e.g.* LBO .²⁷

However, the interface between the anode and electrolyte is still rarely studied,²⁸ especially in cells using metallic lithium anodes. Several attempts have been made to understand the cause of the high interfacial resistance between garnet and lithium metal anodes. It has been shown that the poor wettability of lithium metal to the garnet surface is the leading cause of insufficient electrolyte-anode contacts. In addition, Li_2CO_3 naturally formed on the garnet surface is also confirmed to be a contributing factor to the high interfacial resistance. Therefore, improving lithium wetting on garnet and reducing garnet surface impurities are vital issues to address in developing materials and methods for achieving interface with low resistance.

3.1. Negating Interfacial Impedance through Al₂O₃ Coating

3.1.1. Surface Modification with Atomic Layer Deposition

The first successfully demonstrated method is the introduction of an ultrathin Al₂O₃ coating on SSEs through atomic layer deposition (ALD). A thin coating of 5 nm Al₂O₃ lead to a great improvement in the wetting of lithium metal to the SSE and a dramatic decrease in the interfacial resistance. Garnet-structured Li₇La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O₁₂ (LLCZN) was employed as SSE here and was made into thin pellets for the convenience of studies on the interface.

Figure 3.1 illustrates the interface between garnet and Li metal. Without the ALD treatment, the insufficient solid-solid contact between Li metal and garnet leaves numerous voids at the interface, greatly blocking Li⁺ ion transport. With ALD treatment, the ultrathin Al₂O₃ layer greatly improves the wettability of the molten Li metal. As a results, the Li metal can be uniformly coated onto the garnet surface without any interfacial voids. In order to observe how the ALD coating changes the interface contact between garnet and Li metal, a wetting test was conducted by dropping molten Li metal onto polished garnet surface. Figure 3.1 also shows SEM images of two different garnet surface wetting properties with Li. The SEM images clearly demonstrate the enhancement of interfacial contact by applying ALD-Al₂O₃ ultrathin layer on garnet surface. With the presence of ALD coating, Li metal fully contacted with garnet without any voids even at the micron-scale. The spread-out Li on garnet indicates the garnet surface has become lithiophilic that can facilitate better wetting between garnet and Li in molten state.

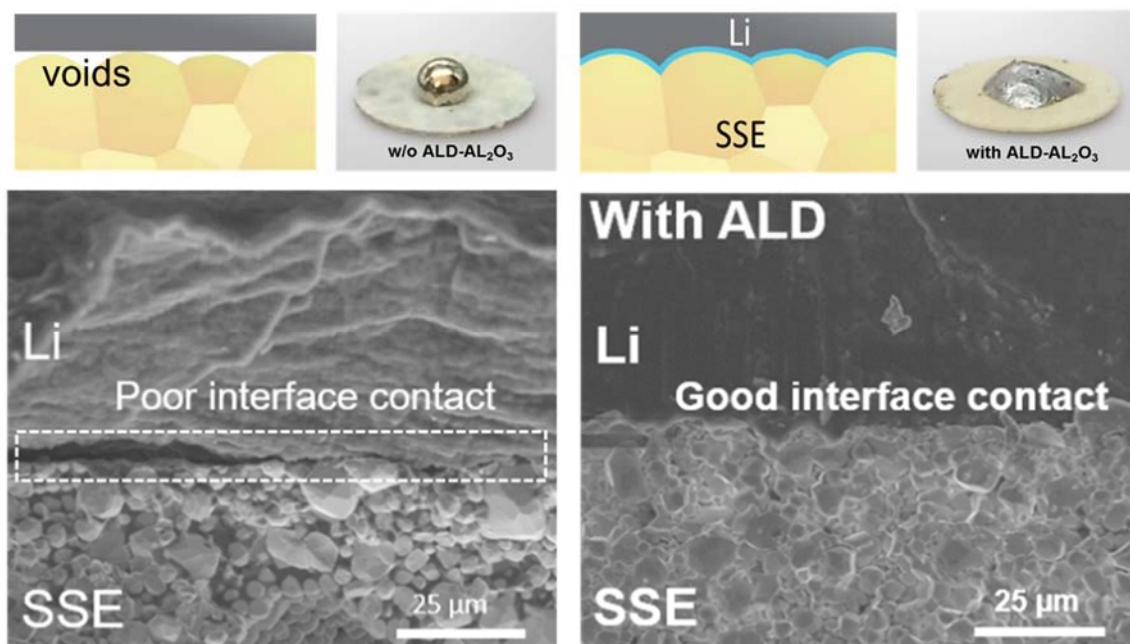


Figure 3.1. Schematic, photo and cross-sectional SEM image comparison of the Li wetting behavior on treated and non-treated garnet.

3.1.2. Electrochemical Analysis on Interfaces

To quantify the effect of ALD on the improvement of garnet/Li interface, symmetric Li/garnet/Li cells were prepared and evaluated by EIS to examine the interfacial resistance. Figure 3.2 shows the EIS curve comparison of the Li/garnet/Li symmetric cell with and without ALD treatment. For both sample, two distinct arcs were identified in the Nyquist plot. The bulk area specific resistances (ASRs), calculated from equivalent circuit fitting, are 26 and 28 $\Omega\cdot\text{cm}^2$ for cells with and without ALD treatment, respectively. The first arc corresponds to the impedance of grain boundary, whose ASRs were found to be 150 $\Omega\cdot\text{cm}^2$ and 4500 $\Omega\cdot\text{cm}^2$ for cells with and without ALD treatment, respectively. The second arc corresponds to the interfacial impedance, whose ASRs can be calculated by subtracting the electrolyte resistance from the total cell resistance, dividing by two (two

garnet/Li metal interfaces in each cell), and then normalizing to the electrode surface area. The calculated interfacial ASR was $16 \Omega \cdot \text{cm}^2$ for the ALD treated sample, which is dramatically lower than that of the sample without ALD treatment ($490 \Omega \cdot \text{cm}^2$). This reduction can be attributed to the conformal contact of Li metal on SSE that increases the effective ionic transfer area. In addition, it is also possible that the Al_2O_3 layer was lithiated by contact with Li metal upon heating, forming a Li-ion conductive layer that can not only effectively transport ions between garnet and Li metal, but also bridge over the impurity and defects on the interfaces, such as Li_2CO_3 patches and surface cracks.

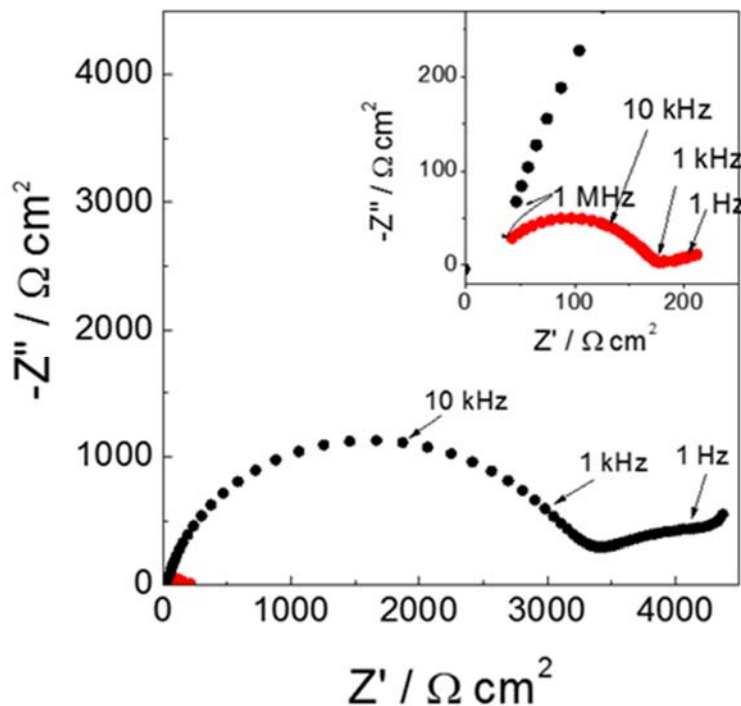


Figure 3.2. EIS of the symmetric Li/ALD garnet/Li: the red curve is the EIS of ALD garnet and black curve is the EIS of bare garnet one.

DC Li plating and stripping experiments were performed to evaluate the interfacial impedance and Li-ion transport capability across the garnet and Li metal interface. Figure 3.3-a compares the direct current (DC) cycling performances for symmetric cells of

Li/bare-garnet/Li and Li/ALD-treated-garnet/Li. For the symmetric cell with ALD treated garnet, it exhibits stable voltage profile with small overpotential. It suggests that the interfacial resistance between garnet and Li metal was effectively reduced with the aid of ALD- Al_2O_3 treatment on garnet solid electrolyte. Inset presents single cycle of the symmetric ALD-treated garnet cell, showing the flat and smooth curve with small overpotential of ~ 15 mV. Figure 3.3-b shows the voltage profile of symmetric cell with bare garnet was unstable with large voltage overpotential, indicating unstable cycling and interfacial impedance, caused by unstable interface of Li/bare garnet. Figure 3.3-c provides a long-term cycling performance of the symmetric ALD-treated garnet cell at the same current density of 0.2 mA/cm^2 . The cell voltage slightly increased from 15 mV and stabilized at 20 mV after 30 hours, implying a little re-arrangement of the interface with a long cycling. Over 130 hours the cell still maintained the stable voltage range around 20 mV. Based on the Ohm's law, the DC cycling has a total resistance of $100 \text{ ohm}\cdot\text{cm}^2$. The obtained interfacial resistance was $5 \text{ ohm}\cdot\text{cm}^2$, calculated by subtracting the overall garnet impedance $\sim 90 \text{ ohm}\cdot\text{cm}^2$ and dividing by two. The $5 \text{ ohm}\cdot\text{cm}^2$ value is consistent with the $1 \text{ ohm}\cdot\text{cm}^2$ interfacial resistance as reported in the main manuscript. It demonstrates that the ALD- Al_2O_3 treatment is effective to alleviate the main challenge of large interfacial impedance for the practical application of garnet electrolyte with Li metal anode.

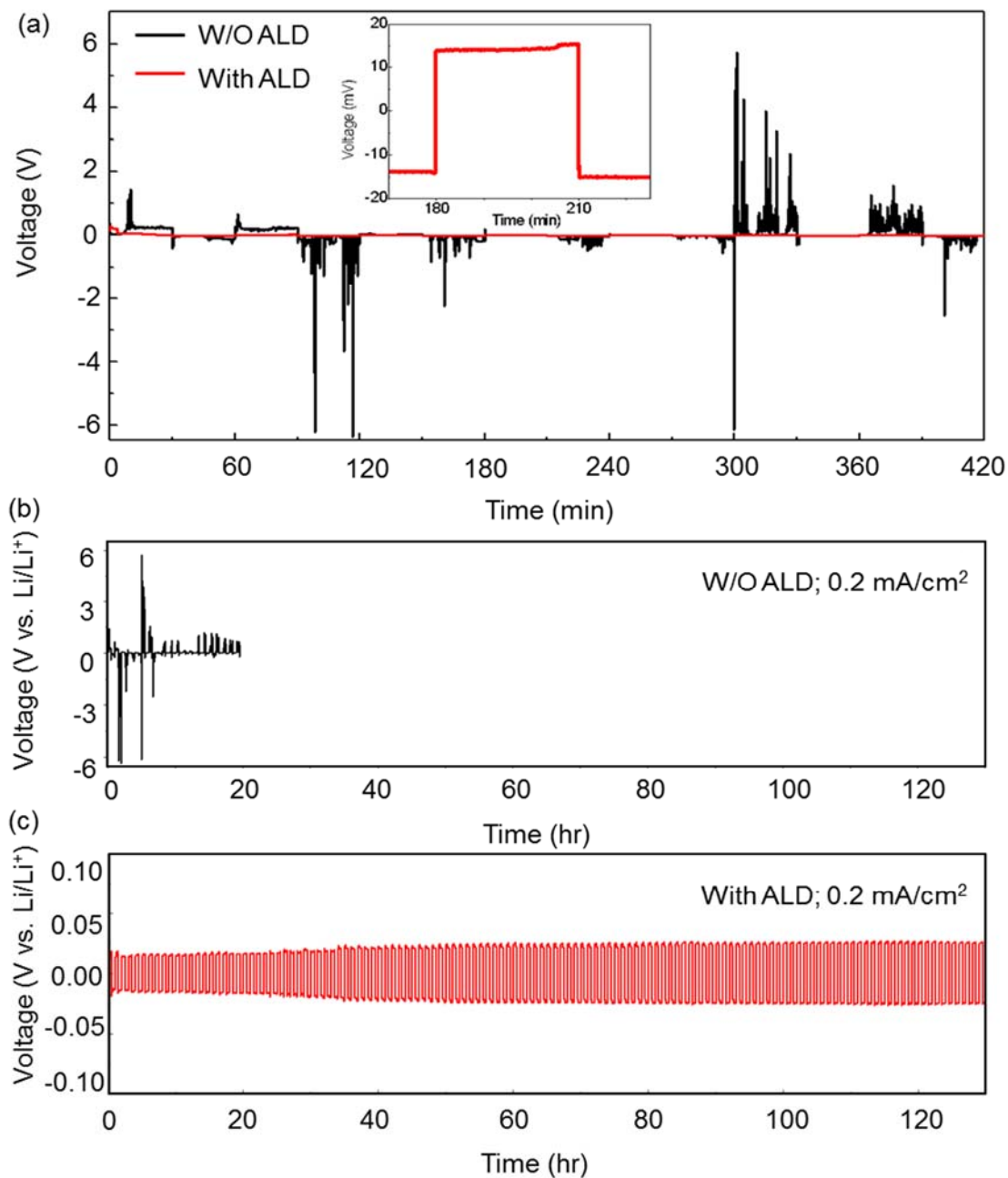


Figure 3.3. (a) Comparison of DC cycling for symmetric cells of Li/bare garnet/Li (black curve) and Li/ALD treated garnet/Li (red curve). The inset is the magnified curve of the ALD treated cell. (b) DC cycling of symmetric cell of Li/bare garnet/Li, showing unstable plating/stripping curve with high overpotential up to 6 V. (c) DC cycling of symmetric cell

of Li/ALD treated garnet/Li, showing stable plating/stripping curve with low overpotential of 20-30 mV.

3.1.3. Interface Imaging and Elemental Analysis

In addition to the electrochemical tests, the Al_2O_3 layer at garnet SSE surface was further investigated by a series of characterizations including transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Focused ion beam (FIB) was used to fabricate TEM samples with exposed Al_2O_3 |garnet interface (figure 3.4).

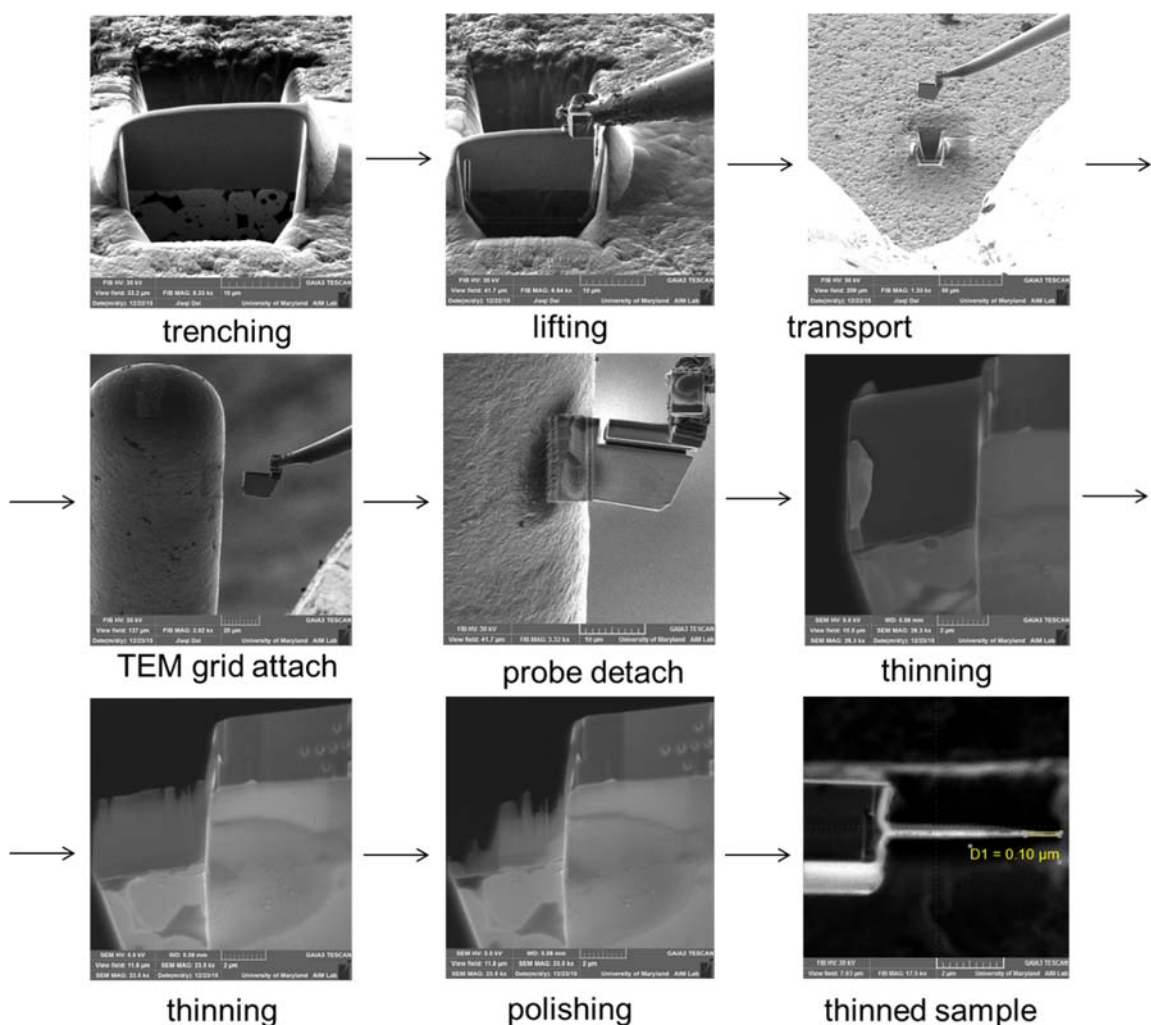


Figure 3.4. TEM sample preparation procedure using FIB.

Figure 3.5-a shows the TEM image and its corresponding EELS elemental mappings for ALD-treated garnet sample prepared by ion milling at low temperature. The cross-section images provide definitive microstructures at the sample's interface. As shown in figure 3.5-c and 3.5-e, the elemental mappings of Al and O are overlapped, especially at the garnet border where uniform Li distribution indicates the garnet location (figure 3.5-d). With further comparison of the relative position of Al, Li, and Ti, (figure 3.5-c, 3.5-d and 3.5-g), Al was found between Ti layer and Li (garnet). These results confirm the existence of Al_2O_3 coating on the garnet surface.

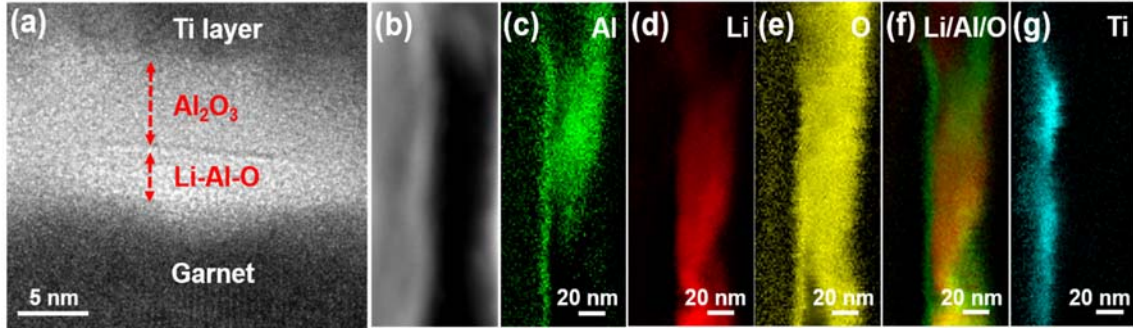


Figure 3.5. (a) Typical TEM image of the Al_2O_3 |garnet interface, (b) the corresponding STEM HAADF image and (c-g) EELS mappings (Al, Li, O, overlapped Al and Li, and Ti, respectively) for the sample Al_2O_3 -treated garnet.

Also, it is worth noticing that between garnet and the ALD- Al_2O_3 coating layer there is a notable interlayer (2~3 nm thick) which is different from the bottom crystallized garnet structure and is obviously separated from the upper ALD coating layer (Figure 3.5a). EELS was performed on different parts of the interlayer. The EELS data suggests the lack of carbon energy loss at ~ 284 eV in the interlayer (Figure 3.6-a), indicating Li_2CO_3 , commonly formed on garnet surface, is excluded from the interlayer. Meanwhile, the energy loss at 58 eV and 76 eV can be assigned to Li K-edge and Al L-edge, respectively

(Figure 3.6-b). Besides element O for charge balance, Li and Al were detected in the interlayer, with Al and O coming from the ALD precursors of trimethyl alumina (TMA) and water.

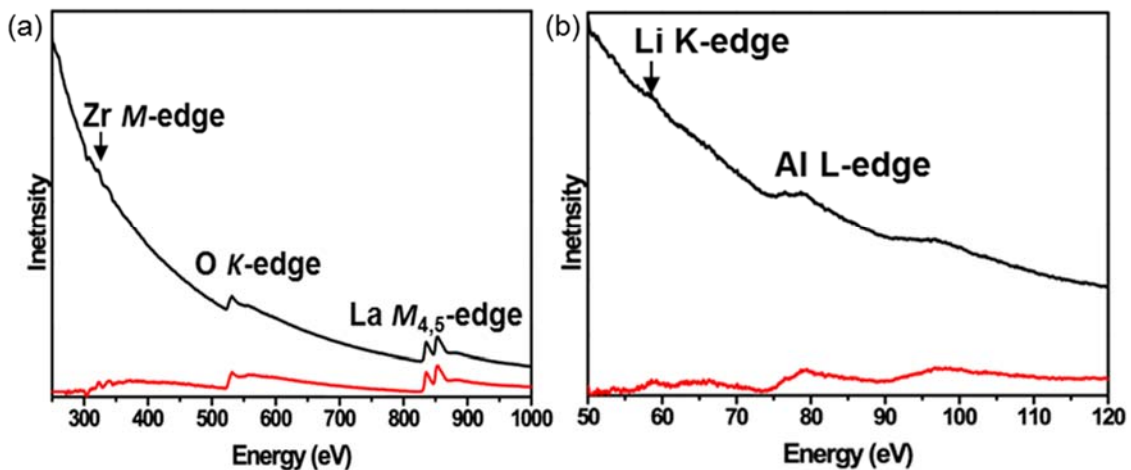


Figure 3.6. (a) EELS with energy 250 – 1000 eV showing peaks of Zr M-edge, O K-edge, and La M_{4,5}-edge; (b) EELS with energy 50 – 120 eV showing peaks of Li K-edge and Al L-edge.

3.1.4. Experimental Method

Materials Preparation. The LLCZN garnet electrolyte was synthesized *via* a sol-gel method. The starting materials were La(NO₃)₃ (99.9%, Alfa Aesar), ZrO(NO₃)₂ (99.9%, Alfa Aesar), LiNO₃ (99%, Alfa Aesar), NbCl₅ (99.99%, Alfa Aesar) and Ca(NO₃)₂ (99.9%, Sigma Aldrich). Stoichiometric amounts of chemicals were dissolved in de-ionized water and 10% excess LiNO₃ was added to compensate for lithium volatilization during high temperature synthesis. Citric acid and ethylene glycol in the mole ratio of 1:1 were consequently added into the solution. The solution was slowly evaporated on hotplate to produce the precursor gel with stirring, which was then heated to 400°C for 10 hours to

burn out the organics. After this, the obtained powder was ball milled and pressed into pellets for calcination at 800°C for 10 hours. And then, the synthesized powders were then uniaxially pressed into pellets, which were sintered at 1050°C for 12 hours in alumina boat covered with the same powder. The atomic layer deposition was performed with Beneq TFS 500 for Al₂O₃ deposition. The Li symmetric cells were assembled by compressing thin lithium foil onto garnet disk upon heating in pure Ar gas at 250°C for 60 min with a pressure of 0.26 psi.

Materials Characterization. Scanning electron microscopy (SEM) was performed with a Hitachi SU-70 analytical scanning electron microscope. Transmission electron microscopy (TEM) was performed on the JEOL 2100f field emission transmission electron microscope equipped with an electron energy loss spectroscopy (EELS) system (TRIDIEM). TEM sample were prepared using a TESCAN GAIA focus ion beam (FIB) system and Fischione 1010 ion milling machine. The electrochemical impedance (EIS) and symmetric cell cycling tests were performed using a BioLogic battery testing system at room temperature via a feedthrough in the glovebox. The cut off voltages were 3.5 V and 5.3 V with a current density of 0.1 C (1C=150 mA/g). The EIS was performed over a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude.

3.2. Critical Factors for the Garnet|Li_{metal} Interfacial Impedance

3.2.1. Diffusivity and Ionic Conductivity

In previous chapters, several ion transport mechanisms in various solid state electrolytes have been introduced. The ion transport properties in the solid state system is a key factor determining electrochemical performances of the battery, including rate

capability, capacity and life-span. In a solid state battery, the mobile species (Li ions for example) need to move from cathode to anode, through the electrolyte and across multiple interfaces. This migration relies on the diffusion of ions through the solid state system. During the migration, the barriers that impede the diffusion of ions are defined as ionic resistivity, and the easiness of ion conduction through the system is defined as ionic conductivity. To investigate the critical factors that influence ionic conductivity at the interface, it is vital to understand the diffusion behavior of the mobile species in the electrolytes.

With an aim of understanding the impedance for LLZO garnet|Li_{metal} interface, especially in the situation where a layer of Al₂O₃ exists, in this section we focus on the diffusion behavior of Li ions in crystalline materials. As introduced in previous chapter, the ion transport mechanism in crystalline materials is ion hopping, which relies on the defects in the crystal. Generally speaking, there are two types of defects that are related to the ion transport: Schottky defects and Frenkel defects. A Schottky defect is a pair of cation vacancy and anion vacancy. Ion transport with assistance of Schottky pairs relies on the migration of vacancies. In other words, ions jump from one equilibrium site to its adjacent vacancy, resulting in the diffusion of vacancies (or ions) through the system. A Frenkel defect is a pair of cation vacancy with a cation interstitial. Frenkel-pair-assisted ion transport relies on the simultaneous movement of a pair of Li ions by pushing a third Li ion from its equilibrium site to an adjacent interstitial site. The continuous movement of ion pairs and the regeneration of interstitials enable the diffusion of vacancies (or interstitials) through the system. In general, the formation energy of a cation vacancy is much higher than that of an interstitial. Especially for Li ions, due to their small ionic

radius, the contribution of Schottky-pair-assisted vacancy diffusion mechanism can be neglected. In other words, the interstitial mechanism is the governing rule for Li ion diffusions in crystalline systems.

The diffusion process can be described using Fick's law:

$$J_i = -D_i \nabla c_i \quad (\text{E 3.1})$$

where J_i is the ionic diffusion flux, D_i is the diffusivity of the ion, and c_i is the concentration of the ion. In solid state systems with dominating interstitial diffusions, the diffusivity of the ion is a dependent of temperature that can be described using Arrhenius relationship:

$$D_i = a_i^2 v^0 \exp\left(-\frac{\Delta G}{k_B T}\right) \quad (\text{E 3.2})$$

where a_i is the jump length, v^0 is the attempt frequency of the order of Debye frequency of the lattice, k_B is Boltzmann constant, T is temperature, and G is the free energy. A pre-exponential factor D_0 and the diffusion activation energy E_A (energy barrier for diffusion) are introduced to simplify the representation of the effect of crystal structure and surrounding potential of the ions. Therefore, the diffusivity can be described as:

$$D_i = D_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (\text{E 3.3})$$

In order to build up the relationship between diffusivity and ionic conductivity, we need to start with relating conductivity with the mobility (u_i) of the charge carriers. Similar to diffusivity that describes the easiness of ions transport through a given media under a concentration gradient, mobility describes the easiness of ion transport under an external electrical field. Considering ion transport under both external electric field and the concentration gradient, the drift velocity of the ions can be expressed as:

$$v_i = -u_i(\nabla\mu_i + z_iF\nabla\varphi), \nabla\varphi = \xi \quad (\text{E } 3.4)$$

where μ_i is the chemical potential, z_i is the valence of ion, F is the Faraday constant, and ξ is electric field. The chemical potential can be calculated as:

$$\nabla\mu_i = \frac{RT}{c_i} \nabla c_i \quad (\text{E } 3.5)$$

where R is the gas constant, and c_i is the concentration of the ion. Therefore, the drift velocity in this case can be written as:

$$v_i = -\frac{u_iRT}{c_i} \left(\nabla c_i + c_i z_i \frac{F\nabla\varphi}{RT} \right) \quad (\text{E } 3.6)$$

Therefore, the ionic flux in this case can be defined as:

$$-j_i = -c_i v_i = u_i RT \left(\nabla c_i + c_i z_i \frac{F\nabla\varphi}{RT} \right) \quad (\text{E } 3.7)$$

From Nernst-Planck Equation we know that the relationship between mobility and diffusivity is:

$$D_i = \frac{u_i RT}{N_A} = u_i k_B T = \frac{v_i}{\xi} k_B T \quad (\text{E } 3.8)$$

Therefore, the current density of the ionic flux can be expressed as:

$$J = q_i j_i = \frac{q_i^2 c_i D_i}{k_B T} \xi \quad (\text{E } 3.9)$$

where q_i is the charge of the carriers. Given that the current density is defined as:

$$J = \sigma \xi \quad (\text{E } 3.10)$$

The relationship between ionic conductivity and diffusivity is then:

$$\sigma = \frac{q_i^2}{k_B T} c_i D_i \quad (\text{E } 3.11)$$

Equation 3.11 relates the ionic conductivity with the diffusivity of the ions in the solid state crystalline electrolytes. This relationship can be used to understand ion transport

behavior at not only the bulk electrolyte, but also the interfaces. Note that in equation E 3.11, all the component are constants except for the diffusivity and concentration of ions, especially at interfaces that are modified by Al_2O_3 coatings as introduced in previous chapter. The ion concentration and diffusivity in the Al_2O_3 layer changes during the lithiation process. In the case of $\text{Li}_{\text{metal}}|\text{Al}_2\text{O}_3|\text{LLZO}$, the interfacial resistance is mainly consisted of the impedance from $\text{Li}_{\text{metal}}|\text{Al}_2\text{O}_3$ interface, $\text{Al}_2\text{O}_3|\text{LLZO}$ interface, and bulk Al_2O_3 . During lithiation, the major resistance change in these three factors takes place in the bulk Al_2O_3 because the ionic conductivity of Al_2O_3 depends on the concentration of charge carriers (Li interstitials or vacant interstitial sites). Therefore, it is vital to study the ion transport in Al_2O_3 during the Lithiation process.

The lithiation of Al_2O_3 is in fact a diffusion process. Note that in Al_2O_3 , the ionic conductivity, self-diffusivity, and diffusion coefficient are all functions of ion concentration, which will greatly complicates the overall relationship if considered all at one time. In order to simplify the calculation and reveal the relationship of ionic conductivity with lithiation parameters qualitatively, it is safe to make following assumptions:

It is assumed that the lithium metal has sufficient supply and the resistance from $\text{Li}_{\text{metal}}|\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3|\text{LLZO}$ interfaces remains constant during lithiation. Therefore the ion concentration distribution in Al_2O_3 can be described with the ion diffusion in a semi-infinite bar with fix concentration on one side. It is also assumed that ion diffusivity and activation energy for diffusion remains independent from ion concentration. In real cases, the ion diffusivity and activation energy is a function of concentration and can be calculated using kinetic Monte Carlo simulations.¹²⁵ Assuming the sample is infinite in the direction

perpendicular to the ion flux to eliminate the sample shape influence (it can be corrected later by considering appropriate edge conditions for different sample shapes). At last, it is assumed that this qualitative relationship is discussed only at low Li ion concentrations, where the insertion of Li interstitial does not lead to phase changes in Al_2O_3 .

Therefore, the diffusivity of Li ion in Al_2O_3 can be written as a function of temperature following an Arrhenius relation described in E 3.2:

$$D_i = \frac{n}{4} a^2 v^0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (\text{E 3.12})$$

where n is the number of adjacent hopping positions, a is the jump length, v^0 is the attempt frequency of the order of Debye frequency of the lattice, and f is a correlation factor that can be neglected. Here n is divided by a factor of 4 because in crystalline Al_2O_3 , Li ions mainly diffuse within the 2-diminsional Li sublattice plain or along the 1-diminsional open channel in Li sublattice. Li ion rarely penetrate through the Al-O lattice layer due to the high energy barrier.

Now consider the diffusion of Li ions through the Al_2O_3 layer with finite thickness. It has been reported that for lithium ions transporting through lithiated Al_2O_3 , there's a maximum amount of Li ions that Al_2O_3 can take to form a stable phase of $\text{Li}_{3.4}\text{Al}_2\text{O}_3$ that has the highest ionic conductivity.¹²⁶ In other words, the concentration of Li ions in Al_2O_3 increases during the lithiation process to a maximum value, which enables the penetration of following Li ions through the fully lithiated Al_2O_3 with minimum impedance. Therefore, the concentration of Li ion during the lithiation process can be described as:

$$c_i = c_0 \operatorname{erf}\left(\frac{z}{2\sqrt{D_i t}}\right), 0 \leq z \leq l \quad (\text{E 3.13})$$

where c_0 is the lithium concentration in lithium metal, erf is the error function, z is the distance from the $\text{Li}_{\text{metal}}|\text{Al}_2\text{O}_3$ interface to the location of interest, l is the Al_2O_3 coating thickness, and t is lithiation time. Combining equation E 3.11, E 3.12, and E3.13 gives:

$$\sigma = a^2 v^0 f \frac{n q_i^2 c_0}{4 k_B T} erf \left[\frac{z a \sqrt{n v^0 f}}{4} \exp \left(\frac{-E_A}{2 k_B T} \right) \sqrt{t} \right] \exp \left(\frac{-E_A}{k_B T} \right) \quad (\text{E 3.14})$$

Note that E 3.14 is based on a series of assumptions and is only used for providing qualitatively prediction of influential factors on ionic conductivity during lithiation. One of The limitations of E 3.14 lies in that it neglects the concentration dependence of ion diffusivity and activation energy. The activation energy has been reported to be a function of x in $\text{Li}_x\text{Al}_2\text{O}_3$ which can be calculated using ab initio molecular dynamics (MD) simulations.¹²⁶ In addition, in real cases the samples are usually cylinders or plates, which adds additional boundary limitations to the diffusion functions. Therefore, equation E 3.14 needs to be corrected by considering concentration dependence of activation energy and diffusivity and shape effects (boundary limitations). The numeric values calculated from E 3.14 in current form may not fully reflect the true values in the real cases.

Despite the limitations of equation E 3.14 in predicting ionic conductivity accurately, it still qualitatively relates the ionic conductivity of the Al_2O_3 coating with lithiation time and temperature. Instead of conducting heavy computational simulations to further develop the model, experimental methods were chosen here to further reveal the relationship of lithiation time and temperature with interfacial ionic conductivity. This qualitative relationship points out that the experiments should focus on discovering the time and temperature dependence of Al_2O_3 coating's ionic conductivity of during lithiation. The experiment results and analysis are discussed in the next section.

3.2.2. Lithiation Time

Electrochemical impedance spectroscopy (EIS) measurement was employed to investigate the interfacial impedance. Figure 3.7 and its inset shows an image of the testing cell structure. The testing cell consists of one dense garnet pellet sandwiched by two lithium metal electrodes. The dense garnet LLZO pellet was coated with Al_2O_3 on both sides using atomic layer deposition (ALD). The surface of lithium metal was polished shiny to remove any possible oxidized layers that may generate additional impedance interface between the lithium electrode and the measuring probe. All the EIS measurements were performed at 30°C in an argon filled glovebox.

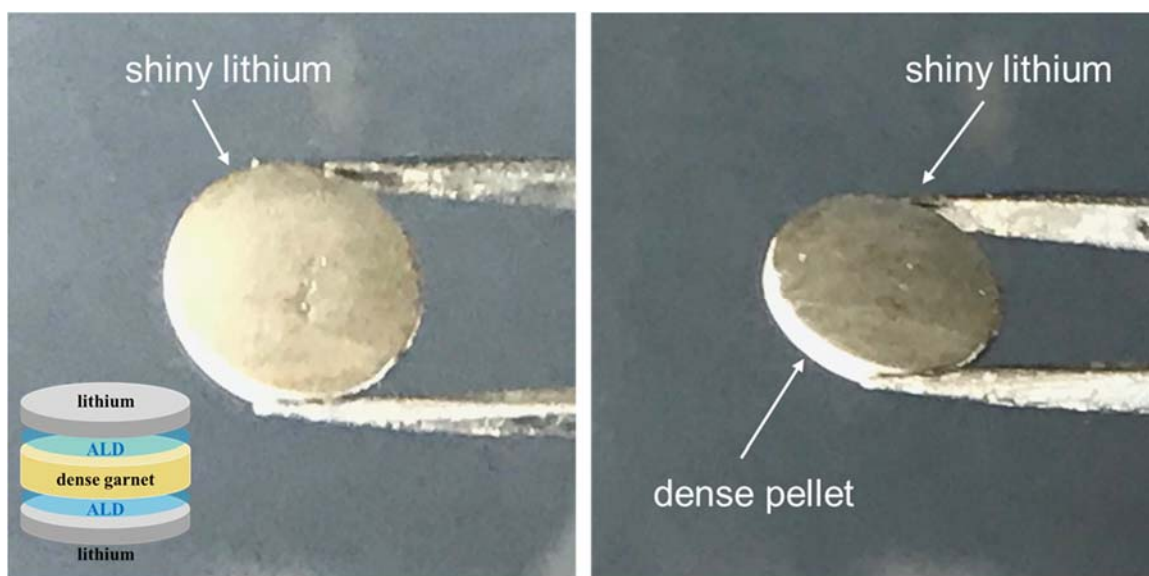


Figure 3.7. Image of a typical testing cell with Al_2O_3 coated dense pellet sandwiched by two lithium metal electrode. Inset shows the structure of the testing cell.

Figure 3.8 shows a typical Nyquist plot of the testing cell using non-blocking lithium metal electrodes. The inset shows the equivalent circuit of the cell. The EIS curve can be fitted with two semi-circles. The first semi-circle corresponds to the bulk impedance of the electrolyte including grain boundary impedances. The second semi-circle

corresponds to the interfacial resistance. Note that the first semi-circle was broken by a sudden drop in the imaginary part of the impedance curve (labeled as ③). This sudden drop is caused by the testing circuit switching from high frequency circuit to low frequency circuit, which is determined by the nature of the testing machine. The switching frequency here is 1MHz.

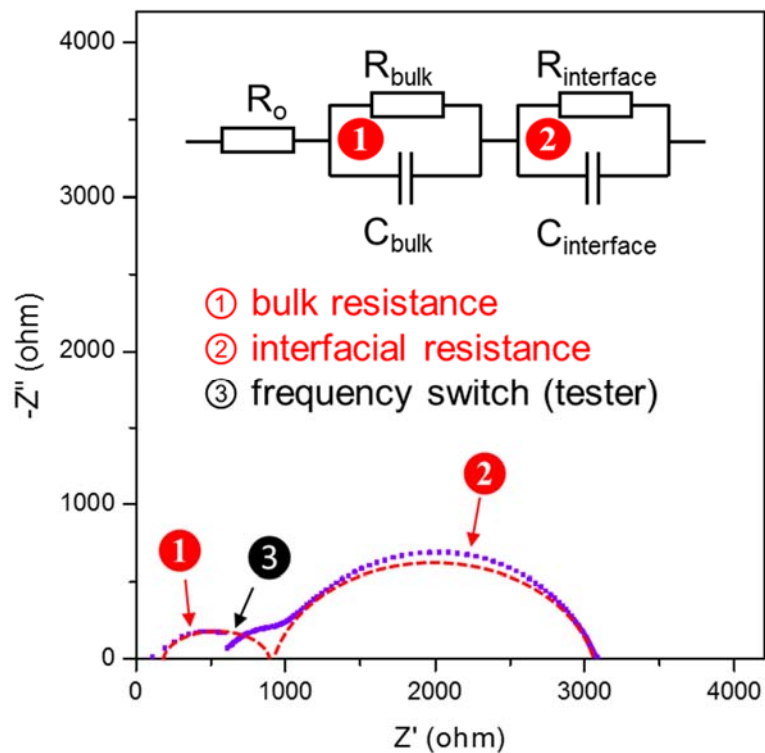


Figure 3.8. Typical EIS curve for testing cells with non-blocking lithium metal electrodes on both sides, the fitted semi-circles, and the corresponding equivalent circuit.

Figure 3.9 compares the EIS curve of testing cells heated with molten lithium for 2-40 minutes at the same temperature. The first semi-circle that corresponds to the bulk resistance remained constant during various heating time, suggesting that the bulk garnet remains stable during the lithiation process. In contrast, the second semi-circle, corresponding to interfacial impedance, decreased with the increasing heating time. The testing cells in this case all had a 3nm Al_2O_3 coating and were heated at 200°C. The

interfacial aerial specific resistance (ASR) can be calculated by deducting the bulk resistance of the garnet pellet from the overall resistance given in EIS results. The minimum interfacial ASR in this case was calculated to be $462.27 \Omega \cdot \text{cm}^2$. Similar trend was observed in testing cells heated at higher temperatures. Figure 3.10 show the EIS curve of another group of testing cells with same Al_2O_3 coating thickness of 3nm but was heated at 250°C . The minimum ASR achieved in this case was calculated to be $33.41 \Omega \cdot \text{cm}^2$.

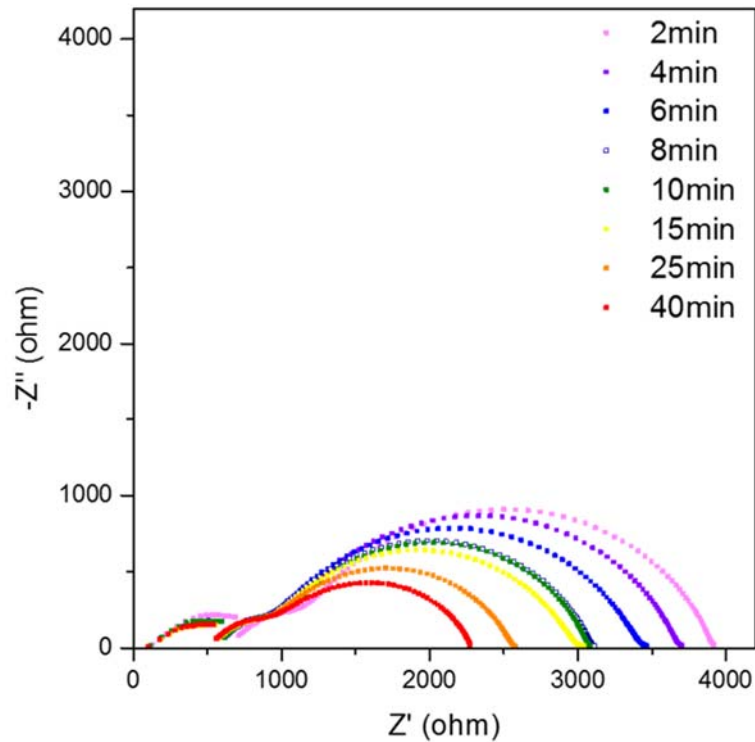


Figure 3.9. Nyquist plot showing the interfacial impedance decreases with the increase of heating time. The testing cells all had a 3nm Al_2O_3 coating and were heated at 200°C .

Therefore, it can be concluded from the results above that the interfacial impedance decreases with the increase of lithiation time. In other words, the ionic conductivity of the Al_2O_3 coating increases along with the heating time. The increase in ionic conductivity is

possibly caused by the increase of charge carrier concentration in the Al_2O_3 coating with longer heating time for lithiation.

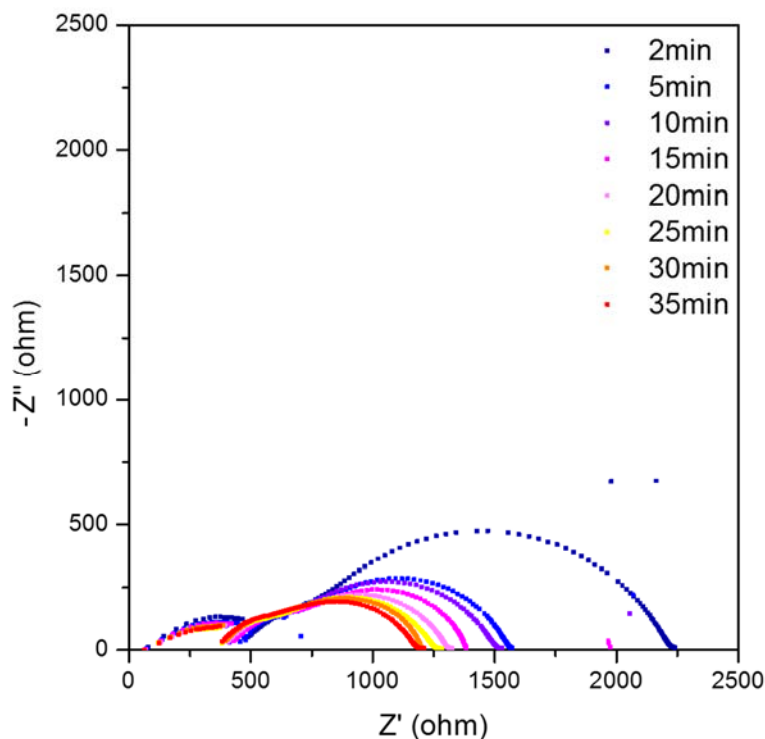


Figure 3.10. Nyquist plot showing the interfacial impedance decreases with the increase of heating time. The testing cells all had a 3nm Al_2O_3 coating and were heated at 250°C.

3.2.3. Lithiation Temperature

As predicted by E 3.14 in the previous section, the lithiation process also depends on the temperature. To investigate the temperature dependence of the ionic conductivity, testing cells with 3 nm Al_2O_3 coating were made and were tested under various temperature for various heating time. Figure 3.11 compares the EIS curve of testing cells heated at 200°C for 2 minutes (melting time of lithium) and 10 minutes. The testing cells were coated with a 3nm Al_2O_3 using ALD. Similar with the EIS results shown in previous section, the

semi-circle for bulk resistance remained constant during lithiation, whereas the semi-circle for interfacial impedance decreased by about 700Ω .

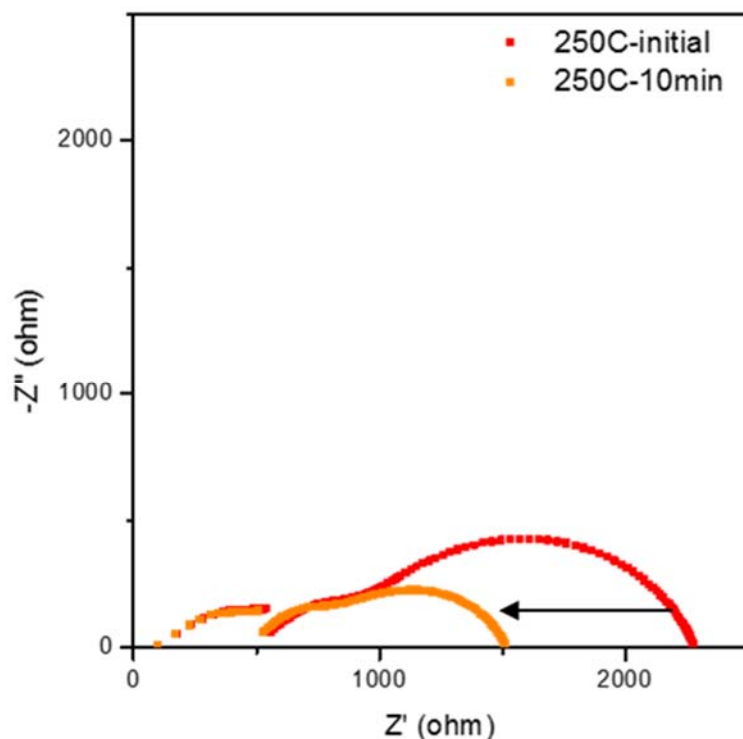


Figure 3.12. Nyquist plot showing the interfacial impedance decrease after being heated at 250°C for 10 minutes.

As comparisons, testing cells with same coating thickness were tested for the same length of lithiation time at higher temperature of 250°C and 300°C . Figure 3.12 shows the testing results from cells heated at 250°C . The interfacial impedance in this case decreased about 800Ω after heating for 10 minutes. However, the interfacial impedance for cells heated at 300°C increased by about 2000Ω after heating for the same amount of time (figure 3.13). Continuing heating leads to further increase of interfacial impedance (figure 3.14).

Combining with the conclusions from previous sections, it can be inferred that the interfacial impedance decreases with time when heating at lower temperature close to 250°C . Long time heating at higher temperature leads to the increase of interfacial

impedance, possibly due to the promoted side reactions and decomposition at higher temperature.

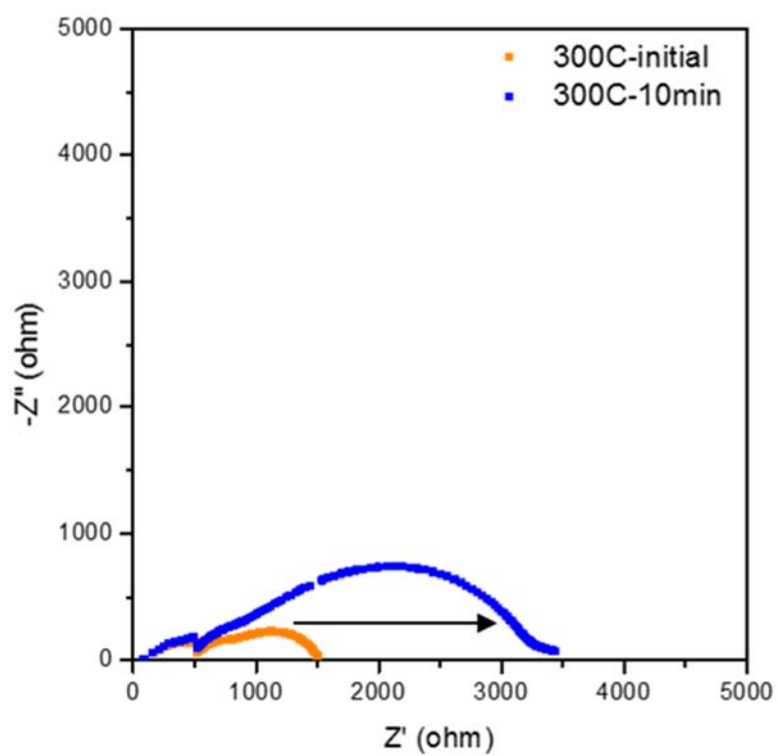


Figure 3.13. Nyquist plot showing the interfacial impedance decrease after being heated at 300°C for 10 minutes.

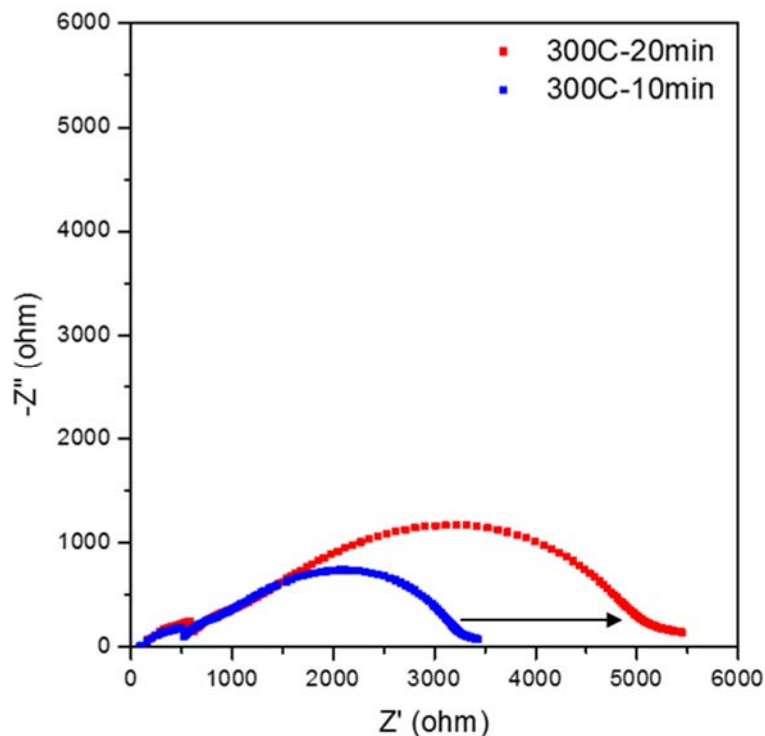


Figure 3.14. Nyquist plot comparison of testing cells after being heated at 300°C for 10 minutes and 20 minutes.

3.2.4. Lithium-Tin Alloy as Anode

In the application of lithium metal on garnet solid state electrolytes, one major component of the interfacial resistance comes from the result of insufficient contact between metallic anode and solid state electrolyte. In other words, the poor wetting of lithium metal on garnet surface often leads to a great interfacial resistance. This poor wetting is fundamentally caused by the large difference in surface energies between garnet and the metallic anode. Therefore the wetting can be improved through two routes. The first route is to introduce an intermediate interface that has better lithium wettability. For example, in previous chapters the wetting between molten lithium and garnet was improved with the assistance of an additional intermedia layer of atomic layer deposited Al_2O_3 . The

second way, however, is to tune the surface energy of the metallic anode itself to match with the garnet surface. The alloying method has been widely reported before to improve the metal-ceramic interfaces. In order to improve the wetting of metallic lithium metal on garnet and to reduce the interfacial impedance, a Li-Sn alloy was developed.

Figure 3.15 shows the wettability of molten Li-Sn alloy with various Sn content on alumina substrates. Though neither pure molten lithium nor pure molten tin wet the surface of alumina, their alloys showed outstanding wetting performance. The wetting performance can be directly evaluated by the wetting angle of the molten metal and the substrate. At a concentration of above 10wt% of Sn, the wetting angle started to decrease with the increasing Sn concentration. At a concentration about 20wt%, the alloy wet the substrate with a contact angle less than 90° . Alloy with 50wt% of Sn sufficiently wet the surface of the substrate with an almost negligible contact angle. In this case, no additional surface treatment (e.g. Al_2O_3 coating) is needed to achieve a sufficient contact between the metallic anode and solid state electrolyte.

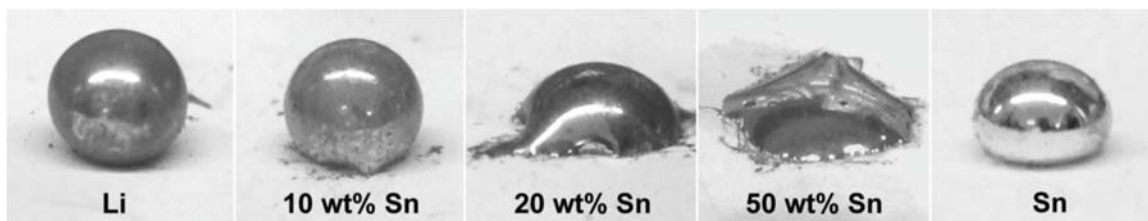


Figure 3.15. Wettability of molten Li-Sn alloys with various Sn content on alumina substrates.

The greatly improved wetting also reduced or even removed the time needed for Al_2O_3 lithiation process. Figure 3.16 shows the effectiveness of Li-Sn alloy on wetting bare garnet surface. The garnet pellet with clean surface can be fully coated with Li-Sn alloy (~20wt% Sn) within 10 s, which is much faster than the Al_2O_3 lithiation process.

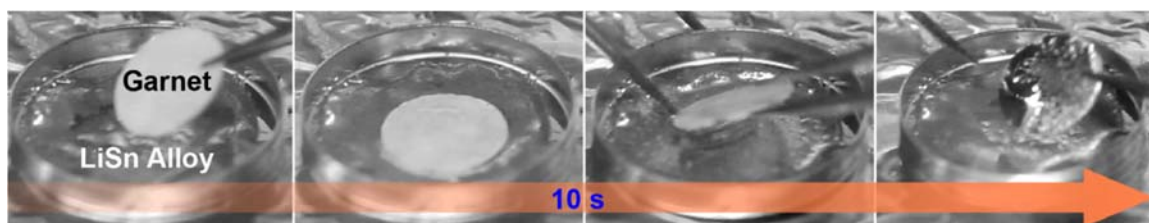


Figure 3.16. Images demonstrating the fast wetting speed of Li-Sn alloy on bare garnet surface.

The morphology of the Li-Sn|garnet interface was characterized with SEM. Figure 3.17 shows a cross-sectional SEM image of the garnet pellet coated with Li-Sn alloy. The SEM image shows that the Li-Sn alloy is closely attached to the surface of the garnet. The interfacial contact is continuous and free of voids. A close-up look at the interface shows that the Li-Sn alloy can cater to the rough surface of the garnet, filling dents and minor cracks (figure 3.18). Therefore a sufficient interface contact can be achieved. In fact, due to the outstanding wettability of Li-Sn alloy on garnet surface, the alloy can even be infiltrated into porous garnet structure while molten. Figure 3.19 shows a piece of porous garnet infiltrated with Li-Sn alloy and a close-up view at the Li-Sn in pores (Figure 3.20). The infiltration into porous structure is extremely hard for pure lithium on garnet with bare surface due to the significant surface energy mismatch. However, it is very easy for Li-Sn alloy to infiltrate the structure. In figure 3.19 the filtration of Li-Sn alloy stopped at the center of the structure due to the blocking of a dense layer in the middle. The Li-Sn alloy enables the application of metallic lithium anode on batteries with more complicated structure designs, especially for the application on solid state electrolyte with complicated porous structure and large specific area.

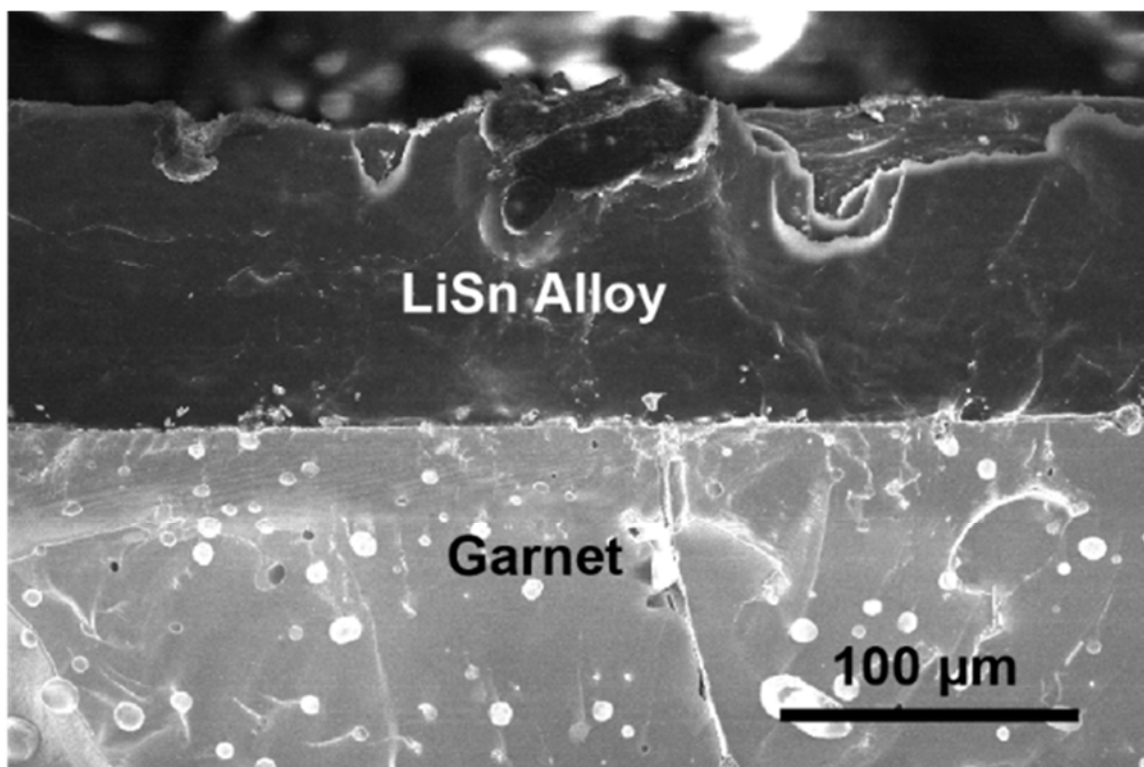


Figure 3.17. Cross-sectional SEM image of a garnet pellet coated with Li-Sn alloy.

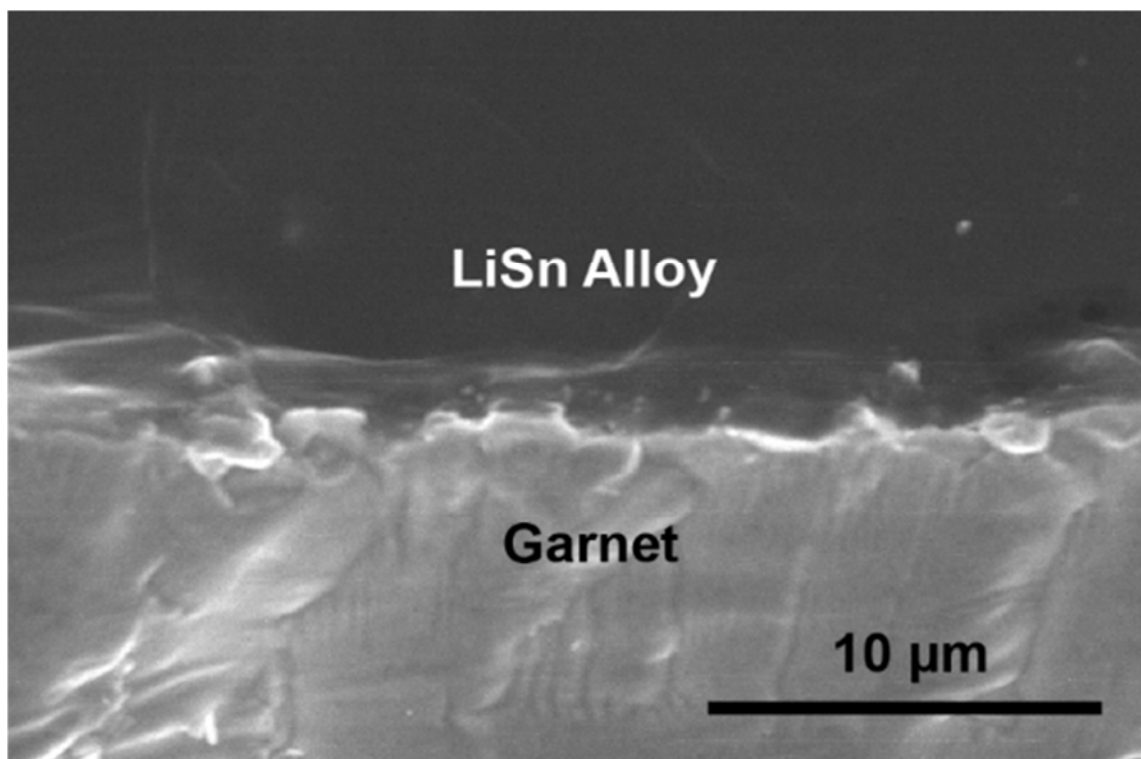


Figure 3.18. SEM image focusing on the Li-Sn|garnet interface.

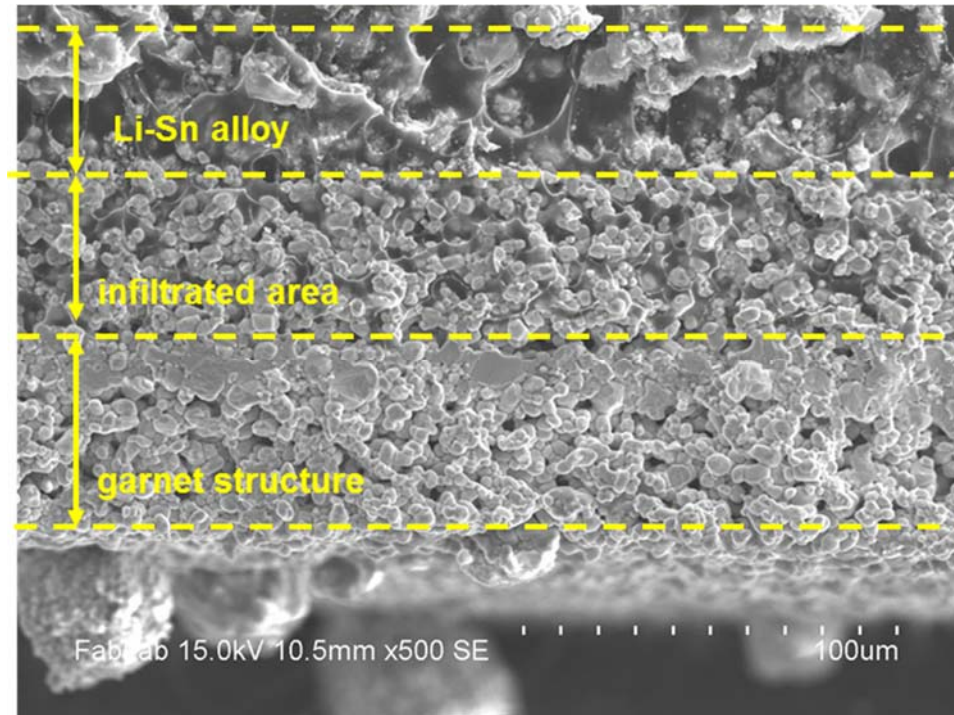


Figure 3.19. Cross-sectional SEM image of Li-Sn alloy infiltrated porous garnet structure.

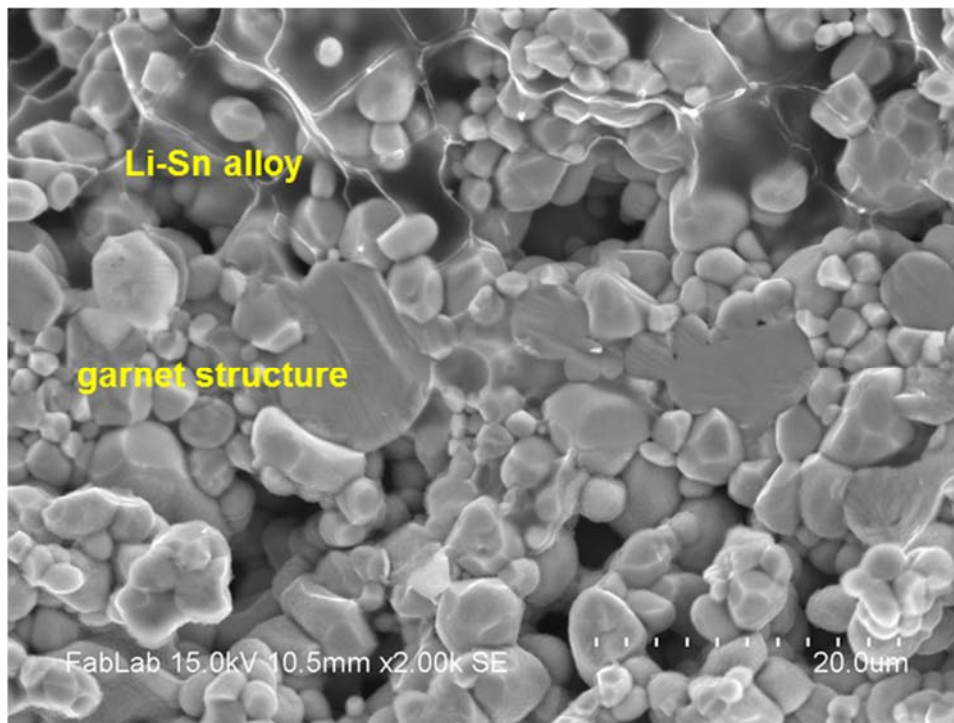


Figure 3.20. A close-up cross-sectional SEM image of a porous garnet structure infiltrated with Li-Sn alloy, focusing on the infiltrated Li-Sn alloy in the pores.

Similar to that in testing cells using pure lithium metal and Al_2O_3 surface coating, the time dependence of interfacial resistance was also observed in testing cells using Li-Sn alloy and bare garnet surface (figure 3.21). Therefore, it can be concluded that the composition of the metallic anode is also an important factor influencing the interfacial resistance. Li-Sn alloy can sufficiently improve the wetting and reduce the resistance of Garnet|Li metal interface.

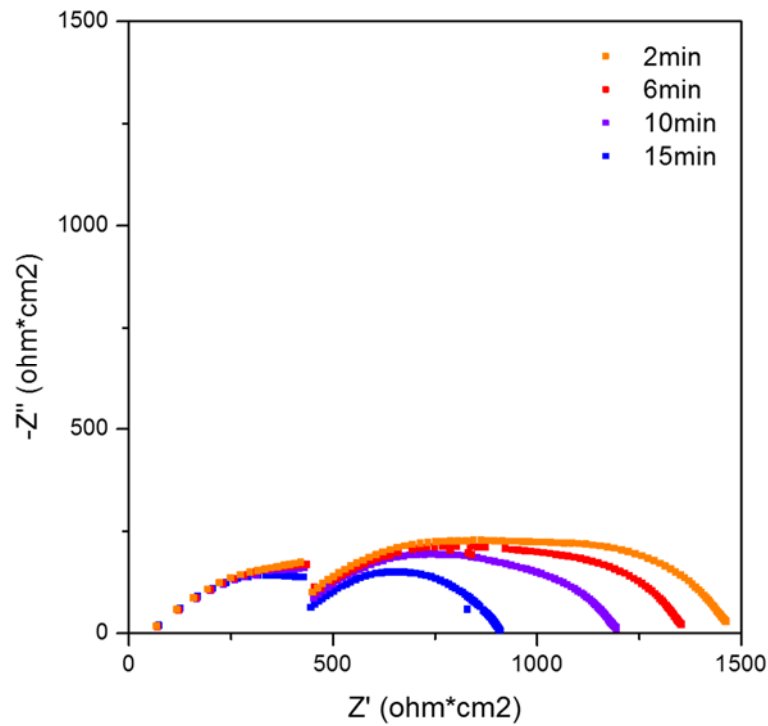


Figure 3.21. Nyquist plot comparison of testing cells after being heated at 250°C from 2 minutes to 15 minutes.

3.2.5. Coating Materials and Configurations

Back to the discussions on reducing interfacial resistance through surface coating, the choice of coating materials also influence the Garnet|Li metal interfacial resistance. In addition to Al_2O_3 , ZnO is also a practical surface coating material that can effectively

improve lithium wetting and reduce interfacial resistance. In order to investigate the effect of ZnO coating on the interface, testing cells with 10nm ZnO coating were fabricated using ALD. The cells were assembled with Li-Sn alloy on both sides as non-blocking electrodes. Similar to that in testing cells using pure lithium metal and Al₂O₃ surface coating, the time dependence of interfacial resistance was also observed in testing cells using Li-Sn alloy and bare garnet surface (Figure 3.22). The testing cells were heated with molten Li-Sn alloy at 220°C. The minimum ASR achieved in this case is about 250.09 $\Omega \cdot \text{cm}^2$, which is higher than that of cells with Al₂O₃ coating under same testing conditions.

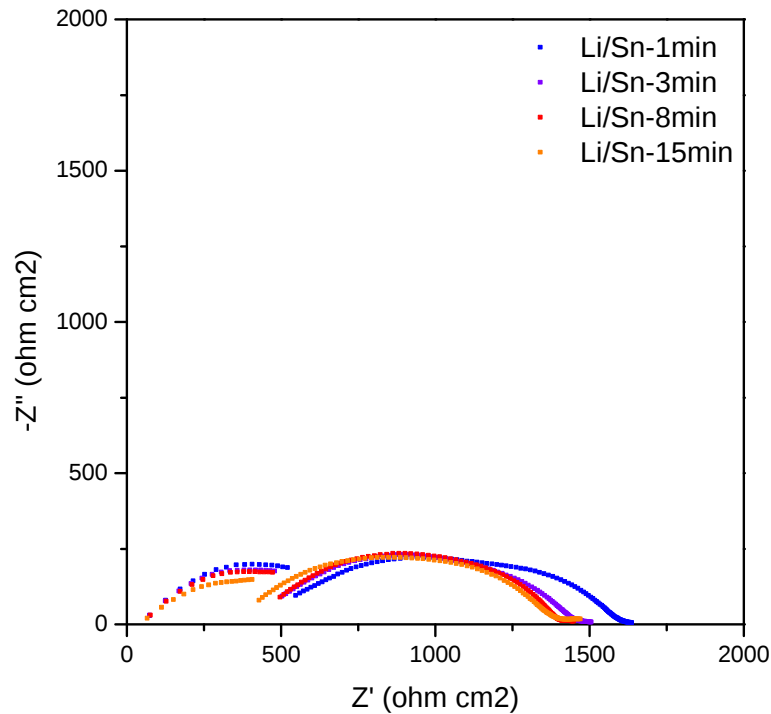


Figure 3.22. Nyquist plot comparison of testing cells after being heated at 220°C from 1 minutes to 15 minutes. The dense garnet in the testing cell is coated with 10nm ZnO.

In addition to different coating materials, the surface coating can chose different coating configurations, too. Figure 3.23 demonstrates a double layer coating configuration where an additional layer of ZnO is coated on top of a piece of Al₂O₃ coated garnet

(ZnO@Al₂O₃@garnet). The purpose of this double layer coating design is to utilize the good wettability of lithium metal on ZnO to build up good contact, then achieve better ionic conduction through the lithiation of Al₂O₃. The ZnO layer here is used as an intermedia to further improve the wetting of molten lithium on Al₂O₃, which can greatly reduce heating time and temperature required by sufficient lithiation.

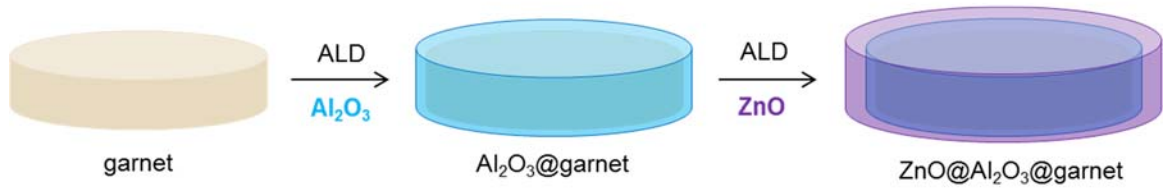


Figure 3.23. Process flow chart of double coating the garnet with Al₂O₃ and ZnO.

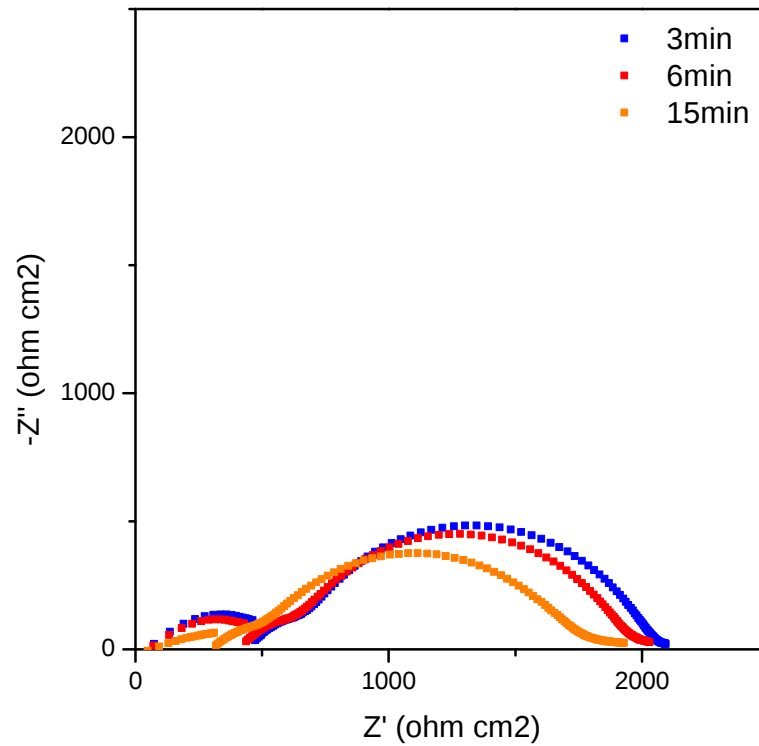


Figure 3.24. Nyquist plot comparison of the testing cells (ZnO@Al₂O₃@garnet) using pure lithium anode after being heated at 220°C from 3 minutes to 15 minutes.

Figure 3.24 and figure 3.25 shows the Nyquist plot of cells with double coating and pure lithium anode and Li-Sn alloy anode, respectively. The dense garnet in the testing cells are all coated with 10nm ZnO on top of a 5nm Al₂O₃ coating. The interfacial resistance in both testing cells decreased with the increasing heating time. With pure lithium anode, the minimum interfacial ASR achieved is 335.79 $\Omega \cdot \text{cm}^2$, whereas in testing cells with Li-Sn alloy anode, the ASR value is 136.81 $\Omega \cdot \text{cm}^2$. The smaller interfacial ASR in testing cells with Li-Sn alloy is possibility caused by the reactions between the coating layer with the alloy under heating. The reactions reduces the total thickness of the intermediate layer consisted of remaining ZnO and lithiated Al₂O₃, resulting in a reduced overall interfacial resistance.

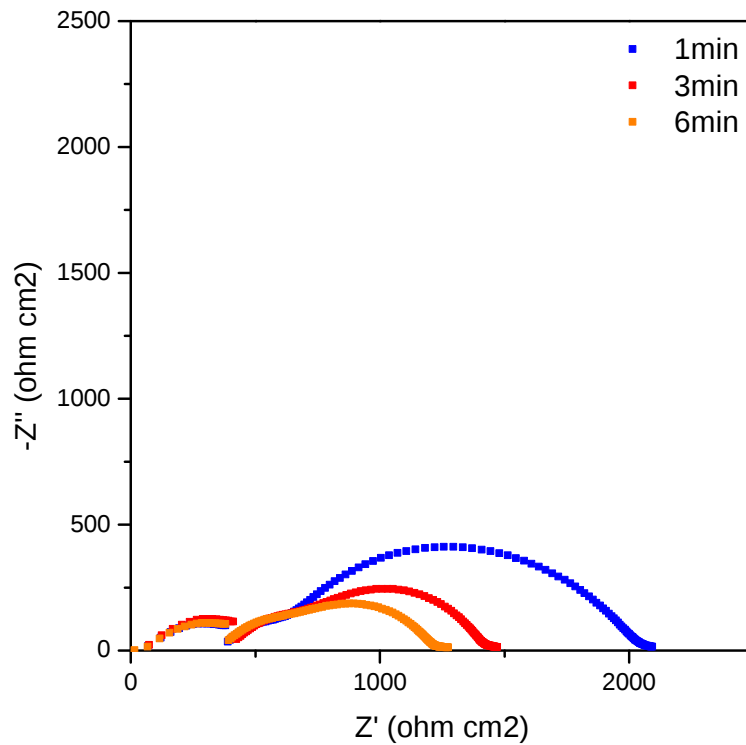


Figure 3.25. Nyquist plot comparison of the testing cells (ZnO@Al₂O₃@garnet) using Li-Sn alloy anode after being heated at 220°C from 1 minute to 6 minutes.

In conclusion, the choice of coating materials and coating configurations are influential factors on interfacial impedance. ZnO can be an alternative surface coating material in substitution of or in addition to Al₂O₃. The application of ZnO layer can be realized in different configurations including single layer coating (ZnO@garnet) and double layer coating (ZnO@Al₂O₃@garnet). The resistance of the Garnet|Li metal interface still has the dependence on heating time and temperature.

3.2.6. Coating Thickness

As introduced in previous sections, the ion conduction through the interface is heavily influenced by the lithiation of the Al₂O₃ layer. Equation E 3.14 suggests that the thickness of the coating (z) is also a key factor that governing the overall ionic conductivity of the lithiated Al₂O₃ layer. The dependence of interfacial resistance on the coating thickness was investigated using EIS tests on identical cells with various coating thicknesses. 4 batches (batch A) of dense garnet pellets were coated with Al₂O₃ with a thickness of 5nm, 10nm, 20nm, and 30nm. This batch of pellets was assembled into testing cells with pure lithium metal using hot press method.

The experimental setup for the hot pressing method is shown in figure 3.26. Lithium metal foil was pressed on to the surface of the dense garnet before heating. Then the Li|garnet|Li cells were sandwiched by two pieces of stainless steel. At last, the whole assembled cell was placed onto a preheated hot plate under a certain pressure. During heating, the lithium metal foil will melt and wet to the Al₂O₃ surface with the help of pressure. This is one of the earliest methods developed for lithium coating. It is easy to operate and convenient to control the temperature and time. However, the biggest drawback of this method is that it takes longer time and thicker Al₂O₃ coating for molten

lithium to sufficiently wet the surface, and the resulting interfacial resistance is usually quite high. The insufficient wetting efficiency of hot press method is caused by the oxidized (or impurity) layer on the surface of molten lithium. This surface layer blocks the fresh lithium from touching the Al_2O_3 layer, resulting in longer lithiation time and higher lithiation temperature. It is very hard to break this surface layer using hot press method. Therefore the resulting interfacial resistance and the coating thickness is usually less satisfying.

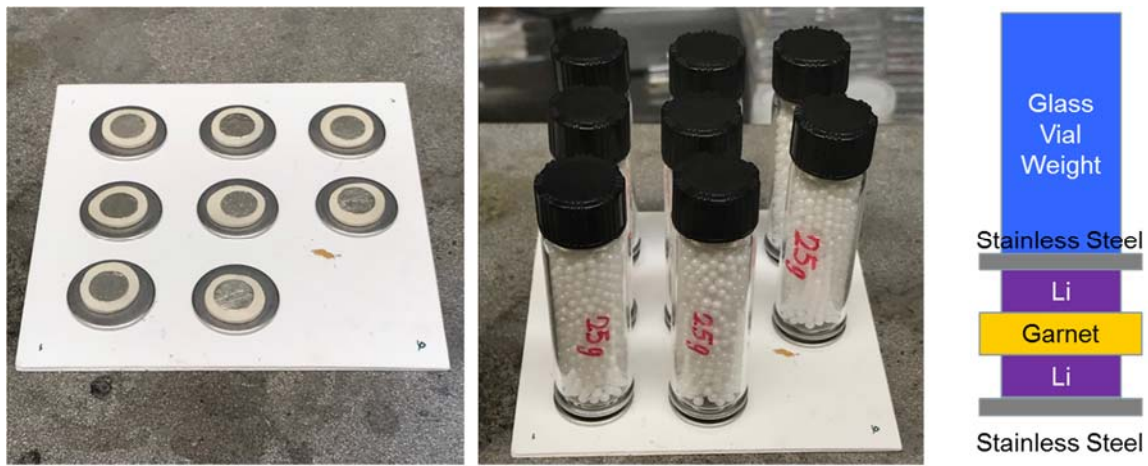


Figure 3.26. The experimental setup for lithium coating using hot pressing method.

Figure 3.27 and figure 3.28 show the EIS curve comparison of testing cells from batch A. All the testing cells were heated together using hot press method at 300°C for 1 hour. The pressure was 6.125 kPa on each cell and the mass of lithium metal was 4.5mg/electrode. Two semicircles can be identified from each EIS curve. Despite the huge interfacial resistance value, a clear trend can be resolved from the EIS results. The interfacial impedance decreased with the increasing coating thickness from 5nm to 20nm, and a minimum value was achieved at 20nm. Further increasing the coating thickness from 20nm to 30nm results in an increase in interfacial resistance again. In order to validate the

trend and eliminate the influence of huge interfacial resistance, another batch (batch B) of testing cells were made using a newly developed dip-coating method.

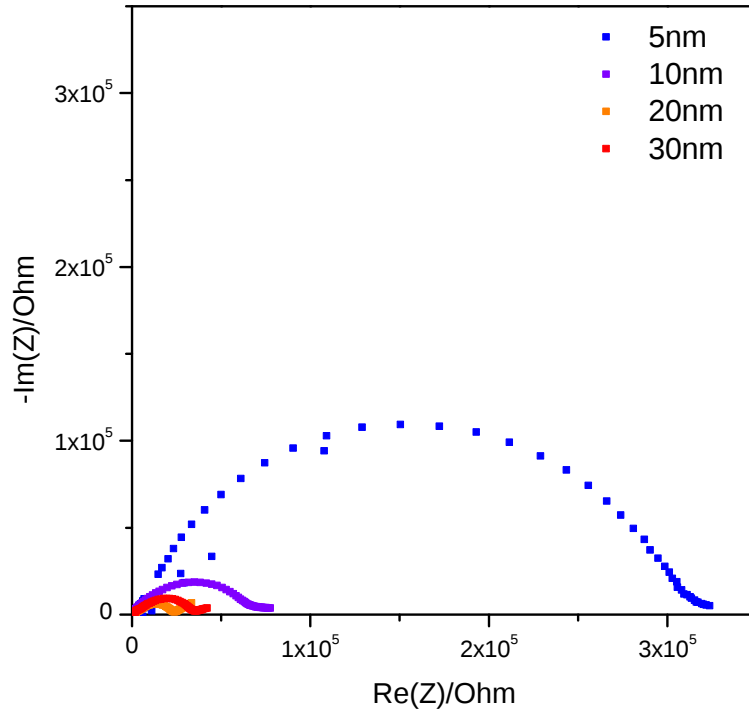


Figure 3.27. Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses.

Figure 3.29 shows the experimental set up of the dip-coating method. During dip-coating, lithium metal was first melted in a stainless steel crucible. Then the garnet pellet was dipped into the molten lithium metal and gently rubbed against the molten lithium until lithium fully wet the surface. The gentle rubbing helps to break the continuous surface layer on top of the molten lithium that blocks the direct contact of molten lithium with the surface coating layer. It was observed from the experiments that though the initial attachment of lithium onto the garnet was hard, once the surface layer broke, the molten lithium could instantly wet several points on the pellet surface and then expand to wetting the whole surface.

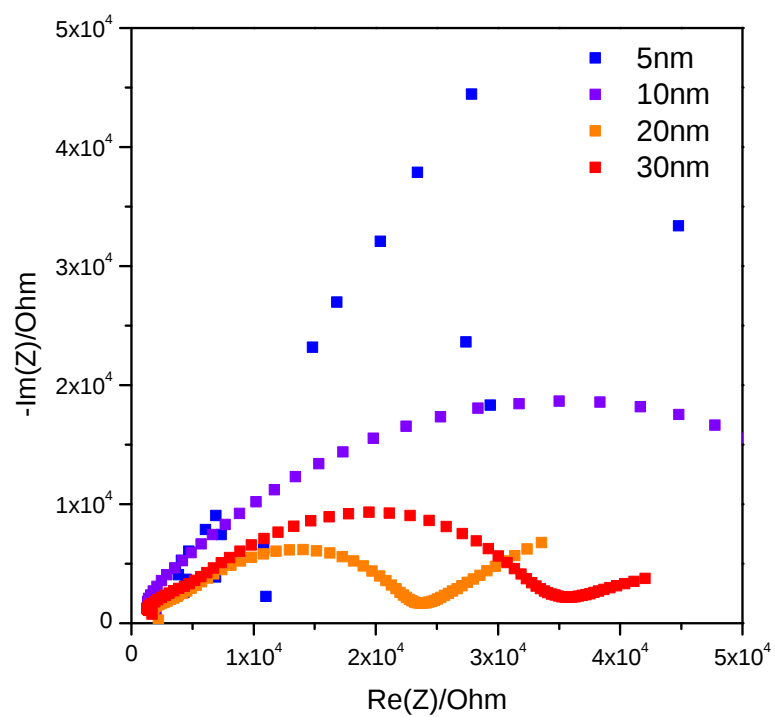


Figure 3.28. A zoom-in at high frequency of the Nyquist plot comparison of testing cells with various Al₂O₃ coating thicknesses.

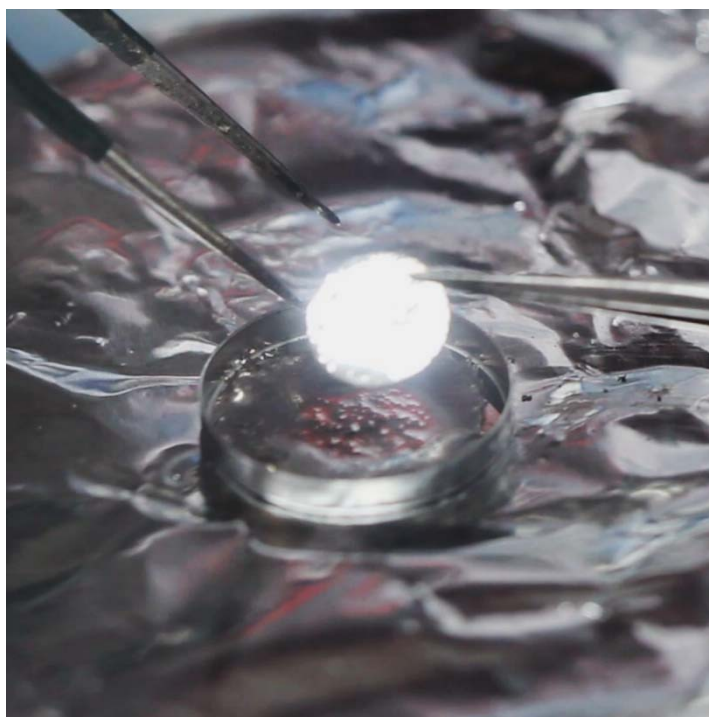


Figure 3.29. The experimental setup for lithium coating using dip-coating method.

Figure 3.30 shows the EIS curve comparison of testing cells from batch B. The interfacial impedance decreases then increase with the increasing coating thickness. This trend matches with the previous trend observed in batch A cells. Note in this test, the garnet pellets were very thin. Therefore the semi-circle for their bulk resistance can hardly be resolved from the EIS curves. In order to reveal both semi-circles, the same test was performed again on a new batch of garnet pellets (batch C) with Al_2O_3 coating of various thicknesses. Batch C pellets has thicker thickness, smoother surface, and better conductivity. It can be told from the EIS curves that even though the 3 cells has similar overall resistance, the size of the second semi-circle (corresponding to interfacial resistance) varies significantly. Batch C cells reveal the same trend, where the interfacial impedance decreases then increase with the increasing coating thickness (figure 3.31).

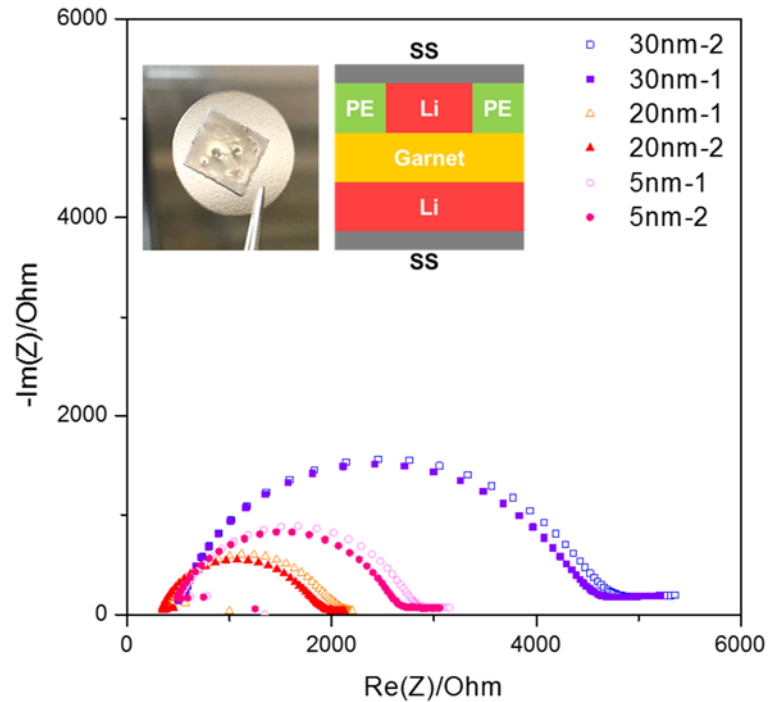


Figure 3.30. Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses. Inset shows an image and a structure schematic of the testing cell.

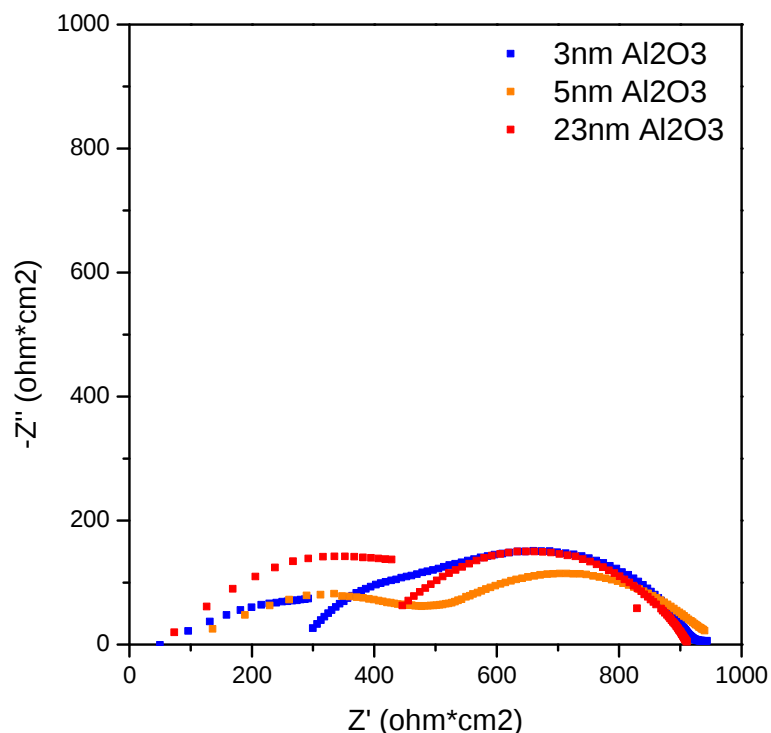


Figure 3.31. Nyquist plot comparison of testing cells with various Al_2O_3 coating thicknesses.

3.2.7. Experimental Method

Materials Preparation. The LLCZN garnet electrolyte was synthesized *via* a sol-gel method. The starting materials were $\text{La}(\text{NO}_3)_3$ (99.9%, Alfa Aesar), $\text{ZrO}(\text{NO}_3)_2$ (99.9%, Alfa Aesar), LiNO_3 (99%, Alfa Aesar), NbCl_5 (99.99%, Alfa Aesar) and $\text{Ca}(\text{NO}_3)_2$ (99.9%, Sigma Aldrich). Stoichiometric amounts of chemicals were dissolved in de-ionized water and 10% excess LiNO_3 was added to compensate for lithium volatilization during high temperature synthesis. Citric acid and ethylene glycol in the mole ratio of 1:1 were consequently added into the solution. The solution was slowly evaporated on hotplate to produce the precursor gel with stirring, which was then heated to 400°C for 10 hours to burn out the organics. After this, the obtained powder was ball milled and pressed into

pellets for calcination at 800°C for 10 hours. And then, the synthesized powders were then uniaxially pressed into pellets, which were sintered at 1050°C for 12 hours in alumina boat covered with the same powder. The atomic layer deposition was performed with Beneq TFS 500 for Al₂O₃ deposition. Li-Sn alloy was made by direct mixing of Sn powder with molten Li in glovebox on a hotplate at about 250 °C.

Materials Characterization. Scanning electron microscopy (SEM) was performed with a Hitachi SU-70 analytical scanning electron microscope. The electrochemical impedance (EIS) and symmetric cell cycling tests were performed using a BioLogic battery testing system at room temperature in the glovebox. The EIS was performed over a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude.

3.3. Conclusion

This chapter introduced techniques to negate the interfacial resistance between garnet and metallic anode through surface modification and anode alloying. A thin layer of atomic layer deposited Al₂O₃ on garnet surface was found to be efficient in improving the wetting of molten lithium, which led to much lower interfacial resistance. The surface coating method provides a promising solution to lithium wetting issues through tuning the surface energy of garnet substrate.

The ion transport mechanism in Al₂O₃ was also investigated. The second half of this chapter focused on discovering critical factors influencing the garnet|Li_{metal} interfacial impedance. Based on the relationship of ion diffusivity and ionic conductivity, a qualitative function was proposed to indicate possible influencing factors including lithiation time, lithiation temperature, and surface coating thickness. In addition, factors like alloying effects, coating materials, and coating configurations were also studied through systematic

experimental analysis. Table 3.1 concludes several representative interfacial ASR for various coating materials, configurations, and anode compositions.

Table 3.1. Interfacial ASR summary for various coating materials, configurations, and anode compositions.

Materials	Thickness	Pellet Size		Pellet Resistance	Total Resistance	ASR
	nm	cm ²	cm	Ω	Ω	Ωcm ²
Al ₂ O ₃	3	0.78	0.092	1123.32	1184	23.66
Al ₂ O ₃	5	0.82	0.103	1055.24	1141.5	35.49
Al ₂ O ₃	23.52	0.78	0.083	1013.43	1206	75.10
Li-Sn	10wt%Sn	0.78	0.074	903.54	943	15.39
Li-Sn	13.6wt%Sn	0.78	0.099	1208.79	1290	31.67
ZnO-Li	10	0.78	0.095	1159.95	1255	37.07
ZnO-Alloy	10wt%, 10	0.78	0.094	1147.74	1789	250.09
Al ₂ O ₃ @ZnO@Li	Al:5; Zn:10	0.78	0.119	1452.99	2314	335.79
Al ₂ O ₃ @ZnO@Li-Sn	Al:5; Zn:10	0.78	0.101	1233.21	1584	136.81

Chapter 4: High Voltage Cathode for Solid State Batteries

The development of electric vehicles (EVs) and hybrid electric vehicles (HEVs) has become increasingly attractive as an effective solution to the growing need for an already limited supply of fossil fuels. Recent advances in vehicle technologies, for example light-weight materials and high-efficient engines, have made EVs more competitive and reliable. Increasing the energy density of lithium-ion batteries (LIBs) is a key solution to improve the driving ranges of EVs, and has always been an alluring target for research in LIB. General approaches include reducing current collector weight¹²⁷⁻¹²⁹, raising electrode capacity¹³⁰⁻¹³⁴, and increasing the working voltage of the cathode. The application of high voltage cathodes was limited by the low decomposition voltage of traditional liquid electrolytes⁸⁹⁻⁹¹. With the emergence of solid state electrolytes⁴² and advances in high voltage electrolytes⁹³⁻⁹⁵, improving energy density by increasing cell voltage has become possible.

4.1. High Voltage Cathode $\text{Li}_2\text{FeMn}_3\text{O}_8$

Many spinel structured oxides have been reported as high voltage cathodes for LIBs, for example, $\text{Li}_2\text{NiMn}_3\text{O}_8$ (4.7 V)^{97,98}, $\text{Li}_2\text{CrMn}_3\text{O}_8$ (4.8V)⁹⁹, $\text{Li}_{2.02}\text{Cu}_{0.64}\text{Mn}_{3.34}\text{O}_8$ (4.9V)¹⁰⁰, $\text{Li}_2\text{FeMn}_3\text{O}_8$ (4.8V)^{101,102}, and LiCoMnO_4 (5.1V)⁸⁸. Compared with cathodes containing nickel, chromium, and cobalt, $\text{Li}_2\text{FeMn}_3\text{O}_8$ (LFMO) is more attractive due to its low cost, abundance, and non-toxicity. As in figure 4.1-a, typically LFMO has a spinel structure which provides a stable framework and 3D pathways for Li diffusion. However, in real situations, LFMO usually has abundant oxygen vacancies, as shown in figure 4.1-b. LFMO has two reversible plateaus at ~4.1V and ~4.9V vs. Li/Li^+ , caused by the valence

change of Mn^{3+} to Mn^{4+} and Fe^{3+} to Fe^{4+} respectively¹⁰¹. The theoretical capacity of LFMO is around 148 mAh/g.¹⁰² Moreover, LFMO delivers a working potential of 4.8 V^{101,102} and it would be highly beneficial for practical applications if the working voltage could be further increased. General methods of improving cathode electrochemical performances including doping^{135,136}, nanostructure constructions^{137,138}, and surface modifications^{139,140}.

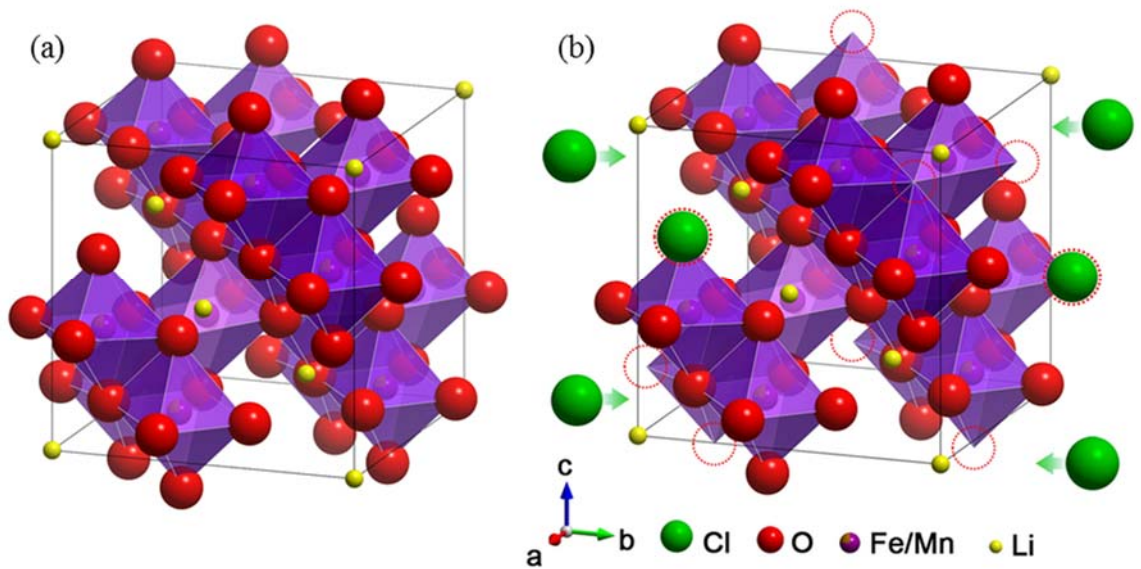


Figure 4.1. Crystal structure comparison of LFMO in (a) ideal and (b) real situation. The abundant oxygen vacancies in LFMO crystal provide sites for chlorine to occupy.

In terms of stabilizing cycling performance and improving capacity, various kinds of spinel coated layered Li-rich cathodes have been reported by many pioneering works¹⁴¹⁻¹⁴⁷. As to increasing the working potential, elemental doping is very effective. For example, chromium (Cr)^{148,149}, boron (B)¹⁵⁰, fluorine (F)¹⁵¹, and chlorine (Cl) doping have been reported as effective dopants to improve the electrochemical performances of various electrode materials for LIBs¹⁵²⁻¹⁵⁵ including LiMnPO_4 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and LiFePO_4 . However, its effect on increasing cathode voltage is rarely reported. Cl ions are easier to lose electrons than oxygen (O) ions, Cl insertion into oxide cathodes will, therefore,

influence the distribution of electrons between various ions and oxidation state of transition metals, which would facilitate more efficient Li^+ ions insertion and extraction¹⁵⁶.

4.2. Halogen Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$

4.2.1. Synthesis of Chlorine Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$

$\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ is used here to denote Cl doped LFMO (LFMO-Cl), where value x represents the nominal atomic ratio of Cl added in the synthesis, and varies from 0 to 1.5 for the different sample groups. $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ nano-powder was prepared by a combustion method using glycine and nitrate as combustion agents¹⁵⁷⁻¹⁵⁹. Lithium nitrate, cobalt nitrate, iron nitrate, lithium chloride, and manganese nitrate were mixed according to stoichiometric molar ratios and dissolved in de-ionized (DI) water. Glycine was then dissolved in DI water and added into the nitrate solution under stirring. The molar ratio¹⁰² of glycine to nitrate was 1:2. The mixture solution was heated to 300 °C and a sudden ignition occurred after the complete evaporation of water, leaving black powders. The final product was obtained by calcining these black powders at 700 °C for 2 hours in air.

4.2.2. Synthesis of Fluorine Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$

$\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{F}_x$ is used here to denote F doped LFMO (LFMO-F), where value x represents the nominal atomic ratio of F added in the synthesis, and varies from 0 to 1.5 for the different sample groups. The synthesis of LFMO-F is exactly the same with the synthesis of Cl doped LFMO except for the use of doping agent. $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{F}_x$ nano-powder was prepared by a combustion method using glycine and nitrate as combustion agents¹⁵⁷⁻¹⁵⁹. Lithium nitrate, cobalt nitrate, iron nitrate, lithium fluoride, and manganese nitrate were mixed according to stoichiometric molar ratios and dissolved in de-ionized

(DI) water. Glycine was then dissolved in DI water and added into the nitrate solution under stirring. The molar ratio¹⁰² of glycine to nitrate was 1:2. The mixture solution was heated to 300 °C and a sudden ignition occurred after the complete evaporation of water, leaving black powders. The final product was obtained by calcining these black powders at 700 °C for 2 hours in air.

4.2.3. Results and Discussion

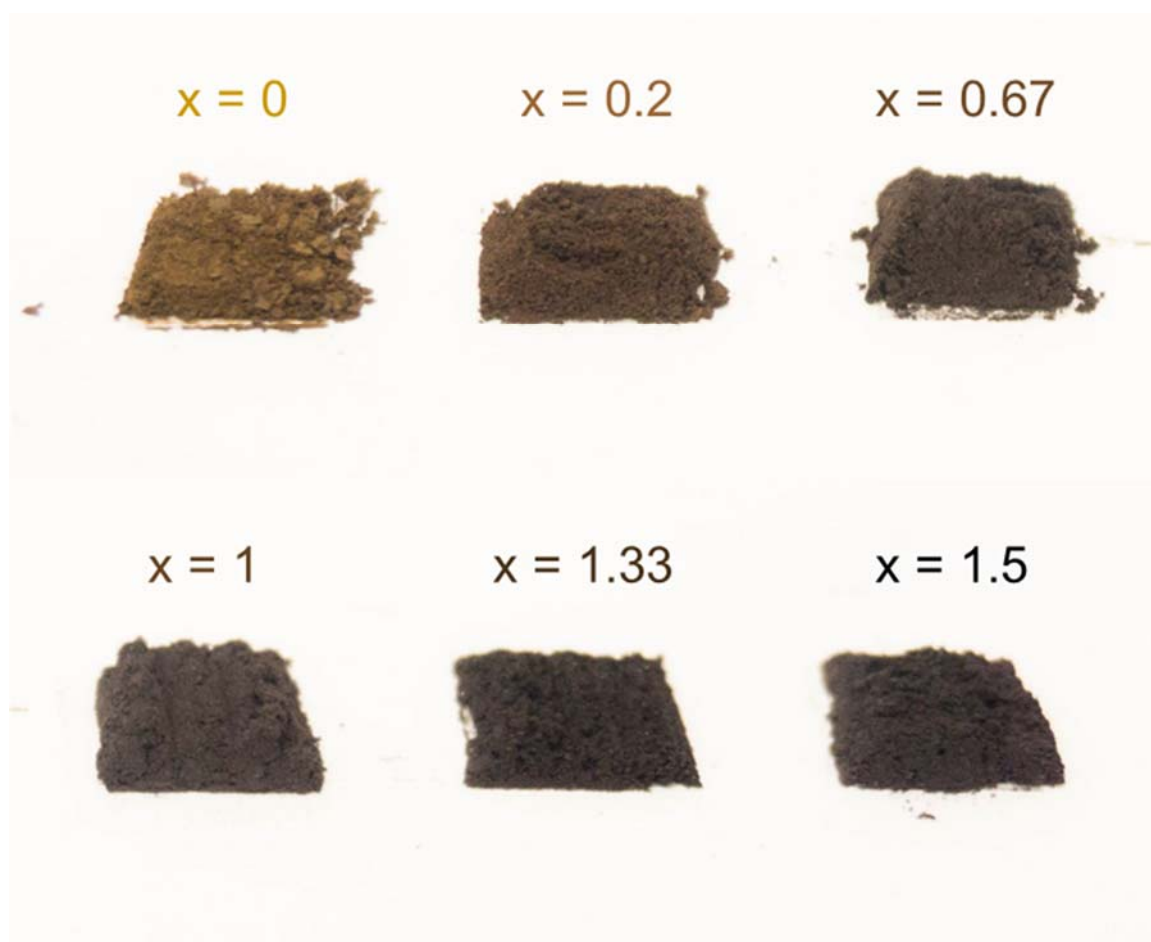


Figure 4.2. Photo of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ powder shows that the cathode color gets darker as the x increases from 0 to 1.5.

Figure 4.2 shows the appearance of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ powder with x ranging from 0 to 1.5. The color of the LFMO-Cl powder gets darker with the increase of the

chlorine concentration. The color change indicates that the increase in chlorine concentration introduces changes in the crystal structure (lattice parameter). With higher dopant content, the concentration of intrinsic oxygen vacancies will decrease. Therefore the lattice parameter will change as well. In order to quantitatively investigate the influence of Cl concentration on lattice parameter, it is very important to first to quantify the ratio of each element in the LFMO-Cl. Here, the x value in $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ is defined as the “nominal concentration” for the clarity of illustration.

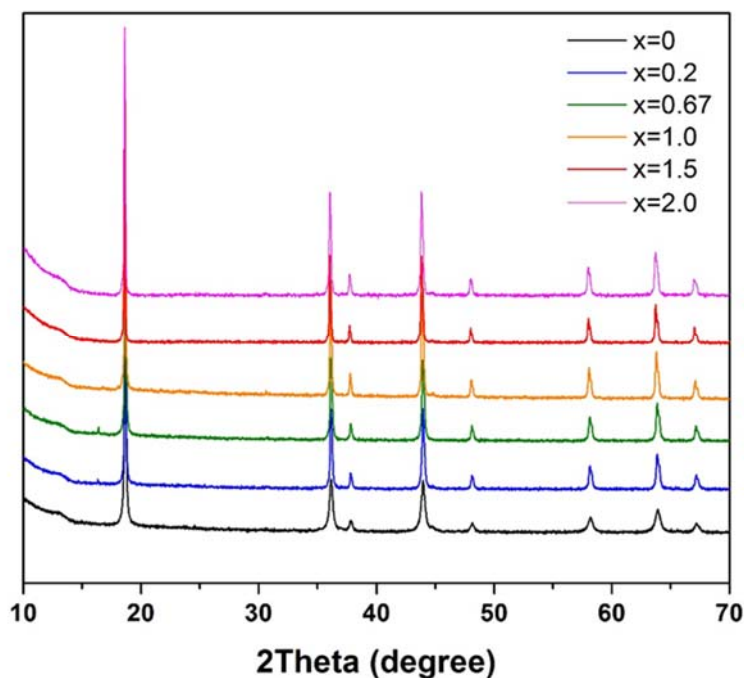


Figure 4.3. XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various chlorine concentrations.

The synthesis of LFMO-Cl requires calcining and annealing in high temperature. High-temperature treatment can possibly change element ratio by causing losses of cations (decomposition), deficiency of oxygen, and losses of chlorine (decomposition or escape as gas). Given the calcining temperature around 700°C, lost cations usually form oxides, which can be detected as impurity phases by XRD. Previous XRD result shows that all the

synthesized $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ powder was free of impurities when x was below 2 (figure 4.3). These XRD results indicate no loss of Fe and Mn in synthesizing, thus the Fe: Mn ratio should be their stoichiometric ratio 1: 3. Fe and Mn can be used as a reference in determining the elemental ratio of the compound.

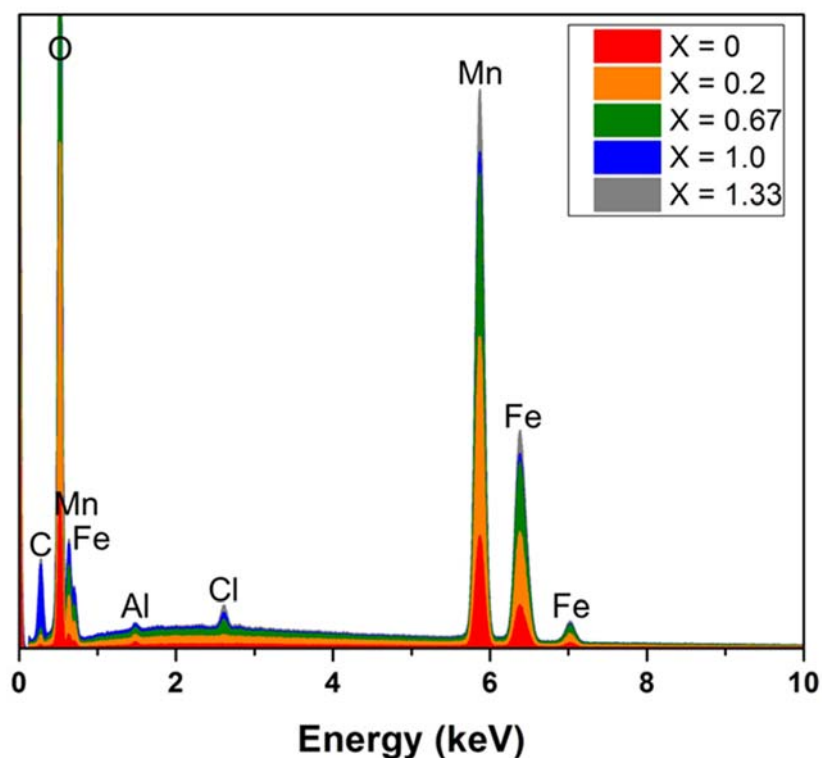


Figure 4.4. EDX spectrum of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various chlorine concentrations.

Oxygen concentration is hard to be measured accurately because of the surface oxygen adsorption and intrinsic oxygen deficiency. However, the elemental ratio of oxygen can be calculated from the chlorine concentration based on the charge neutrality of the compound. Chlorine can escape the compound by forming chlorides or chlorine gas. The Cl concentration can be quantified using X-ray Photoelectron Spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDX), or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). EDX is used here to quantify the chlorine content in

the final compound. EDX is less accurate but it can give quick estimation of the elemental ratio. Figure 4.4 shows the EDX spectra of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations.

Note that due to the overlap of Mn $K\beta$ peak around 6.49 keV with Fe $K\alpha$ peak at 6.40 keV, their intensity ratio of Fe and Mn peak is not 1: 3 as indicated by $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$. In order to use Fe and Mn as a reference, their concentration should be considered as a whole so that we can eliminate the influence of peak overlap. The elemental ratio of chlorine (x) can be calculated by

$$x = \frac{(1 + 3) \times \text{Mole Fraction of Cl}}{\text{Mole Fraction of (Fe + Mn)}} = 4 \times \frac{\frac{\text{Cl wt\%}}{M[\text{Cl}]}}{\frac{\text{Fe wt\%} + \text{Mn wt\%}}{\frac{3}{4}M[\text{Mn}] + \frac{1}{4}M[\text{Fe}]}} \quad (\text{E 4.1})$$

Table T 4.1 summarizes the concentration of each elements detected and the calculated chlorine content (x) in $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$. Despite the inaccuracy of EDX, the experimental chlorine concentration is lower than the nominal concentration. However, this mismatch of nominal and real concentration does not affect the trend and performance, therefore nominal concentration of chlorine is used for the clarity of illustration.

Table 4.1. Quantified content of each element and normalized chlorine concentration (x) of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ obtained from EDX.

Sample	Elements (wt%)						Mole Fraction of Cl %	Mole Fraction of (Fe+Mn) %	x
	C	O	Al	Cl	Mn	Fe			
0	0.54	29.14	0.73	0.09	46.66	22.84	0.003	1.260	0.008
0.2	0.57	32.78	0.10	0.19	45.56	20.80	0.005	1.203	0.018
0.67	0.47	30.86	0.16	0.90	42.92	24.69	0.025	1.226	0.083
1	16.83	28.57	0.26	1.78	35.69	16.87	0.050	0.953	0.211
1.3	1.99	29.32	0.18	2.46	40.80	25.25	0.069	1.197	0.232

Figure 4.5 shows the XRD patterns of Cl doped LFMO with various dopant concentrations (a-e). The diffraction peaks matched the cubic phase $\text{Li}_2\text{FeMn}_3\text{O}_8$ (JCPDS#48-0258), which was in agreement with Hiroo Kawai's results⁸⁸. Compared with the un-doped LFMO ($x=0$), samples with various Cl content showed no differences in XRD patterns (b-e). This result indicates that Cl was doped into the lattice site instead of forming impurities, or the impurities formed were too little to be detected. Figure 4.5-inset also shows the shift of peak locations. As the Cl content increases, all the peaks especially those at higher angles shift towards lower angles. The shifting of the peaks indicates changes in the lattice constant. A shrinking two theta value is a result of growing d-spacing, which also reflects an expanding inter-lattice distance, according to Bragg's Law¹⁶⁰.

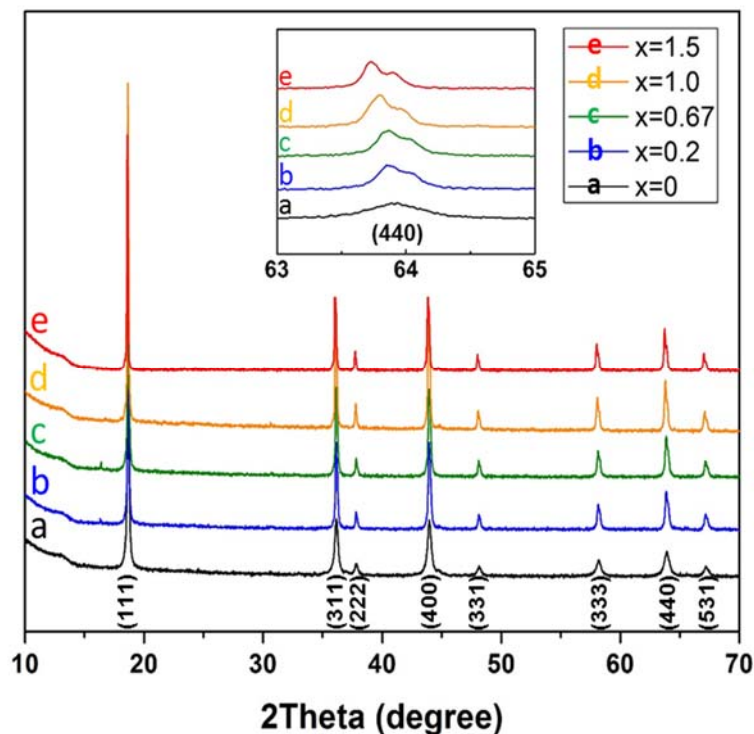


Figure 4.5. XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations: (a) $x=0$; (b) $x=0.67$; (c) $x=1.0$; (d) $x=1.5$, inset figure shows the comparison of (440) peak location.

To confirm the changes in the lattice constant, a Rietveld refinement was performed on all samples. Figure 4.6 shows the lattice constant of cubic $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various Cl content (x value). The lattice constant of standard $\text{Li}_2\text{FeMn}_3\text{O}_8$ is plotted as a single round dot in the figure for comparison. Both the standard LFMO (JCPDS #48-0258) and the un-doped samples ($x=0$) used in this study was synthesized in same conditions. However the standard LFMO was annealed in oxygen for 2 days after the synthesis, which ensured that almost all the possible vacancies were fully occupied. The dramatic difference between the un-doped samples and the standard LFMO was a result of oxygen deficiency, which was also strong evidence proving the existence of abundant oxygen vacancies in the

undoped LFMO. As Cl enters the lattice, these oxygen vacancies will be gradually filled up. Cl ions have larger size than oxygen ions. Therefore, the occupation of Cl on oxygen sites expands the lattice with an increasing concentration of Cl until, finally, the lattice constant exceeds that of a perfect LFMO crystal. These results not only prove that Cl was doped into a host site, but also reveal that the host site was the intrinsic oxygen vacancy.

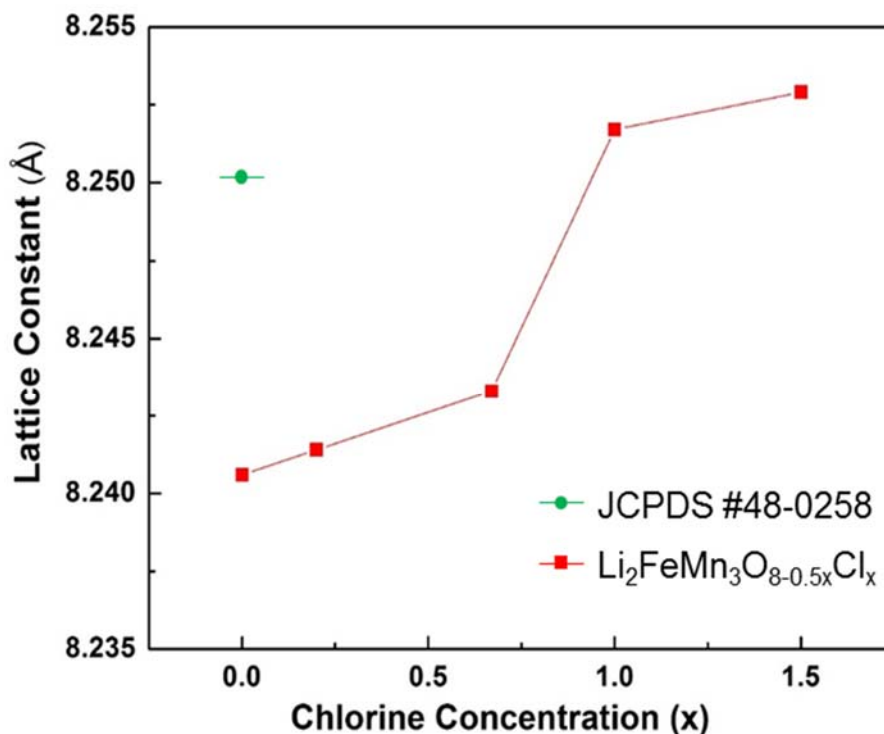


Figure 4.6. Lattice constant comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations: $x=0\sim1.5$.

The dopant concentration has a saturation value. Figure 4.7 compares the XRD pattern of LFMO-Cl with different chlorine concentration. As chlorine concentration increases, the LFMO-Cl remains pure phase then shows impurities when chlorine concentration passes a critical value. XRD result reveals that the impurity phases are mainly consisted of Li_2MnO_3 and Fe_2O_3 , which are the products of LFMO decomposition.

Excessive amount of chlorine generates dramatic lattice distortion, which leads to the breakdown of the crystal structure in the end. Note that the concentration denoted in the figure is nominal value, and the real chlorine concentration is usually smaller than the nominal value.

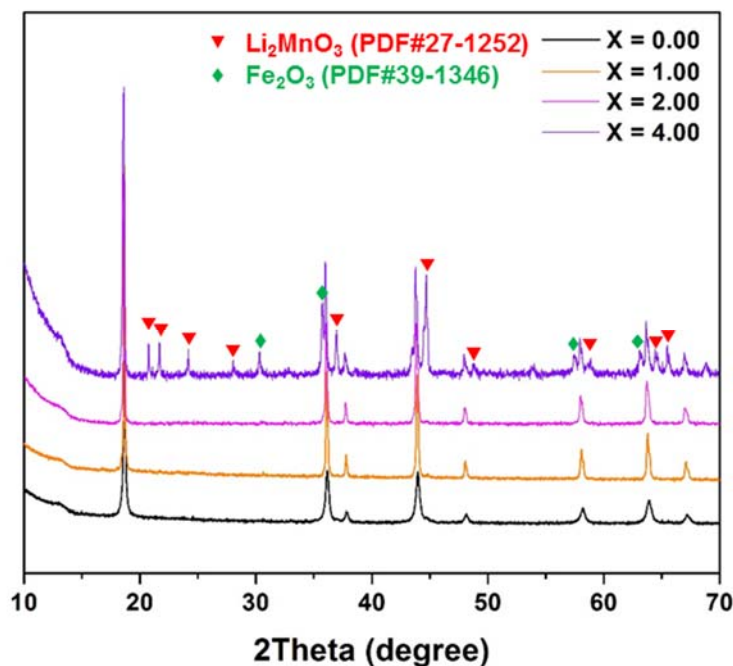


Figure 4.7. XRD pattern of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations showing a saturation dopant concentration.

The morphology of the LFMO-Cl is studied using SEM. According to A Pimpinelli's book *Physics of Crystal Growth*, the equilibrium shape of the crystal is mainly dominated by its surface free energies. Difference in surface energy of different crystal faces causes a mismatch in their growth rates, thus the equilibrium shape of crystal varies. Xu et al reported the shape evolution of cubic crystal from cubic to octahedral form using cuprous (Cu_2O) as an example (figure 4.8).¹⁶¹ Crystal faces with higher surface energy tend to grow faster towards its normal direction. For cubic crystal, when the growth rate ratio

of $\langle 100 \rangle$ direction over $\langle 111 \rangle$ direction is above a critical value (1.73 for cuprous), the crystal will grow into octahedral form. The emergence of clear facets and edges in chlorine doped LFMO samples matches the shape prediction of cubic crystal. Well-defined octahedron shape indicates strong direction preferences of the growth.

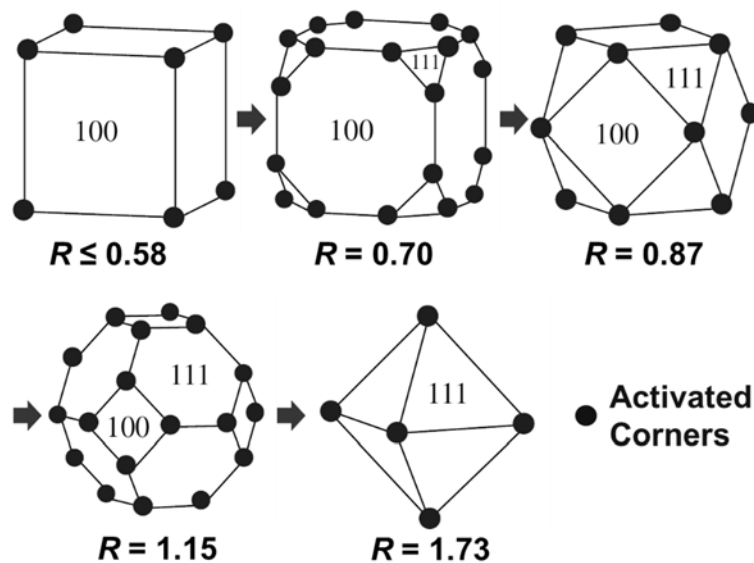


Figure 4.8. Shape evolution of cuprous (Cu_2O) from cubic to octahedron reported by Xu J et al. Blue dots represent activated corners. R is defined as the growth rate ratio along the $\langle 100 \rangle$ direction over the $\langle 111 \rangle$ direction.

Figure 4.9 to figure 4.12 shows the SEM images of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with x equal to 0, 0.67, 1, and 1.5, respectively. The un-doped LFMO particles did not show any specific shapes. The particle size was about 200nm; however, most of the small particles grew on each other, forming secondary particles which were larger than 10 μm (figure 4.9). With an increase in the chlorine content, small crystal seeds started to grow and develop into individual large crystal particles with an octahedron shape (figure 4.10). Particles with higher chlorine content (figure 4.11 and figure 4.12) showed clear facets and edges resulting from a typical cubic crystal growth with strong direction preferences.¹⁶¹ The well-

defined octahedron shape indicates that the crystals were well developed.¹⁶² In addition, an increasing chlorine content was correlated with increasing particle size. For example, the particle size of $\text{Li}_2\text{FeMn}_3\text{O}_{7.5}\text{Cl}$ ranged from 500 nm to 1 μm , but for $\text{Li}_2\text{FeMn}_3\text{O}_{7.25}\text{Cl}_{1.5}$, it was about 2 μm . The change in morphology and particle size was a direct result of chlorine doping. Oxygen, manganese, and iron ions build up the framework of LFMO. The lower occupancy on the oxygen sites generally obstructs the crystal growth. Upon doping, chlorine ions get into oxygen sites (vacancies), which provides more “building blocks” to construct the crystal framework. Therefore the particles grow larger and octahedron shape become more apparent when the chlorine content in $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ increases.

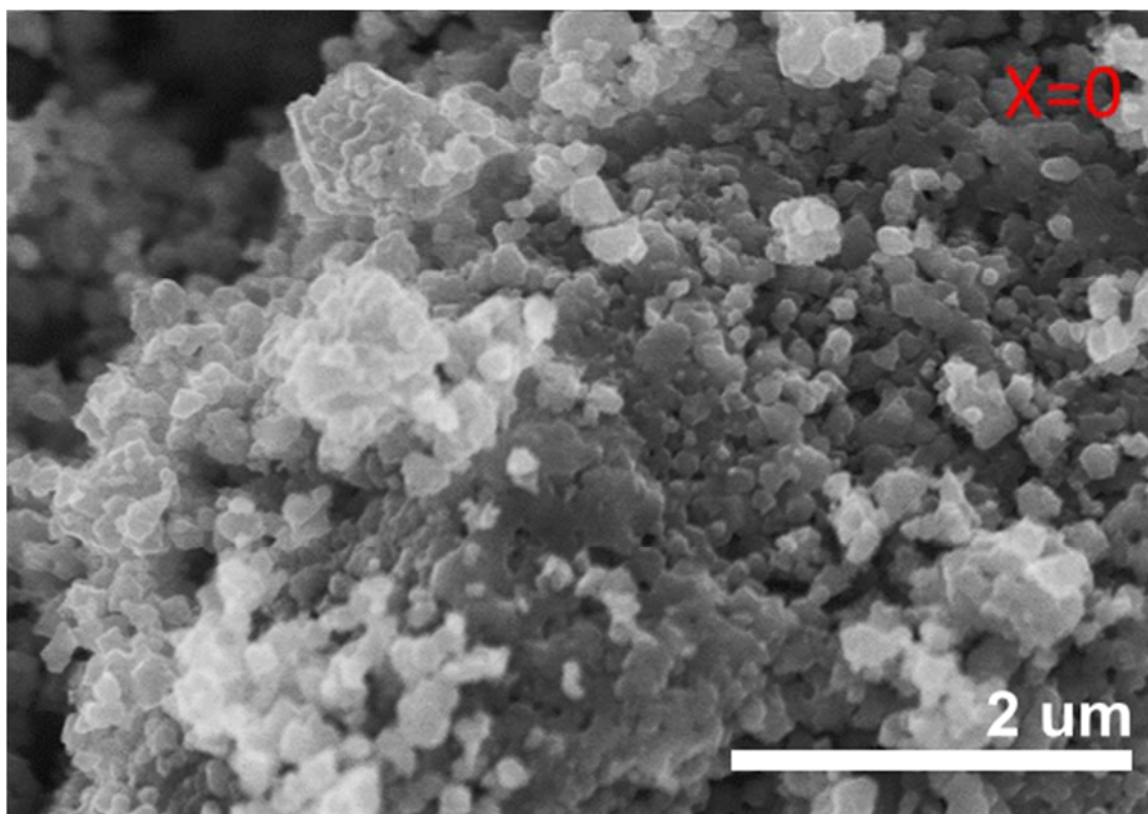


Figure 4.9. SEM image of undoped pristine $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ (x=0).

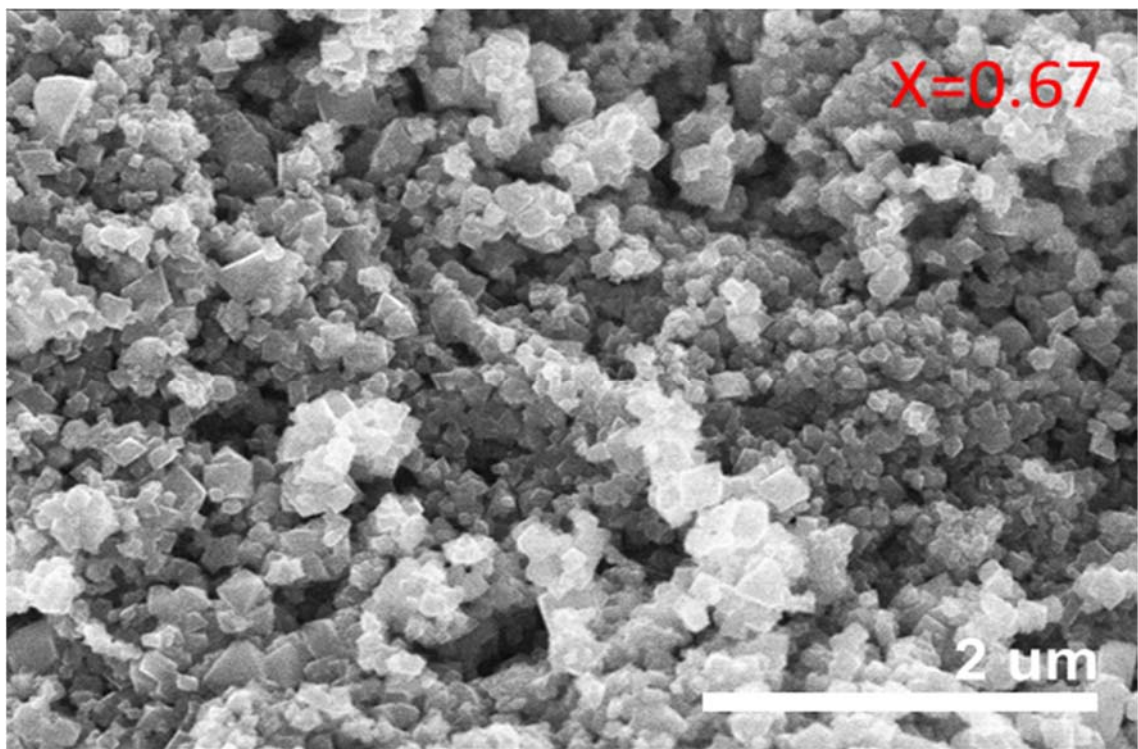


Figure 4.10. SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=0.67$).

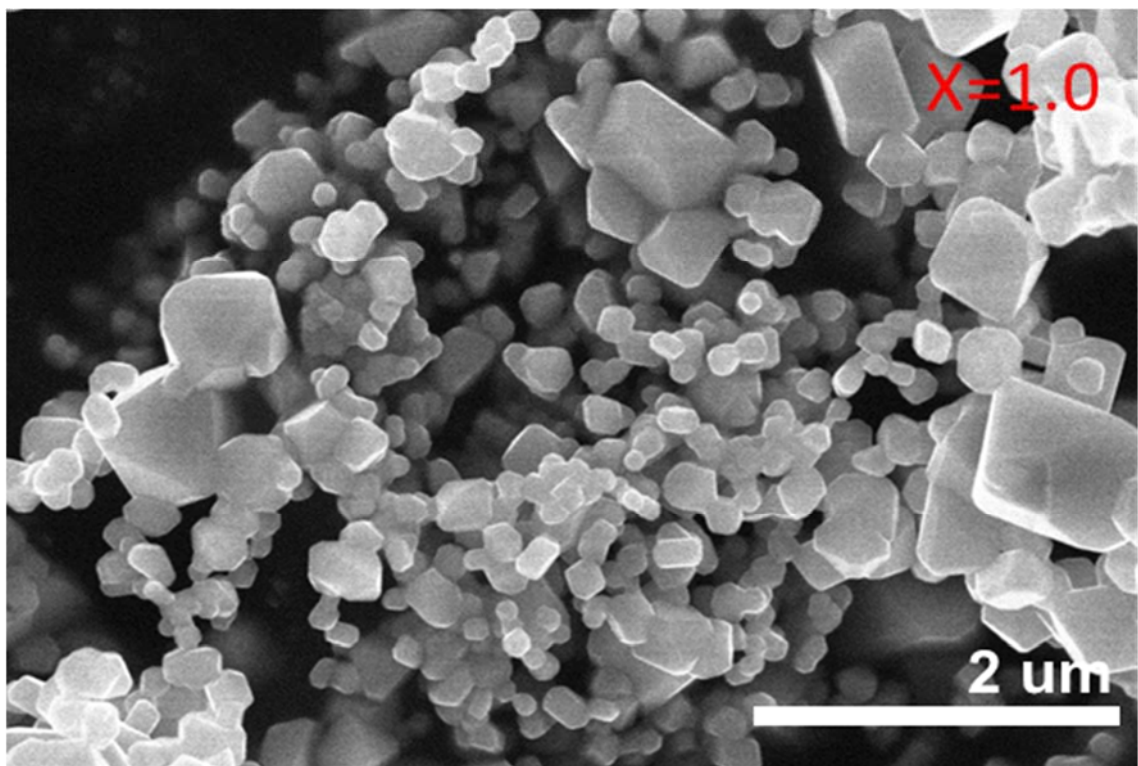


Figure 4.11. SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=1$).

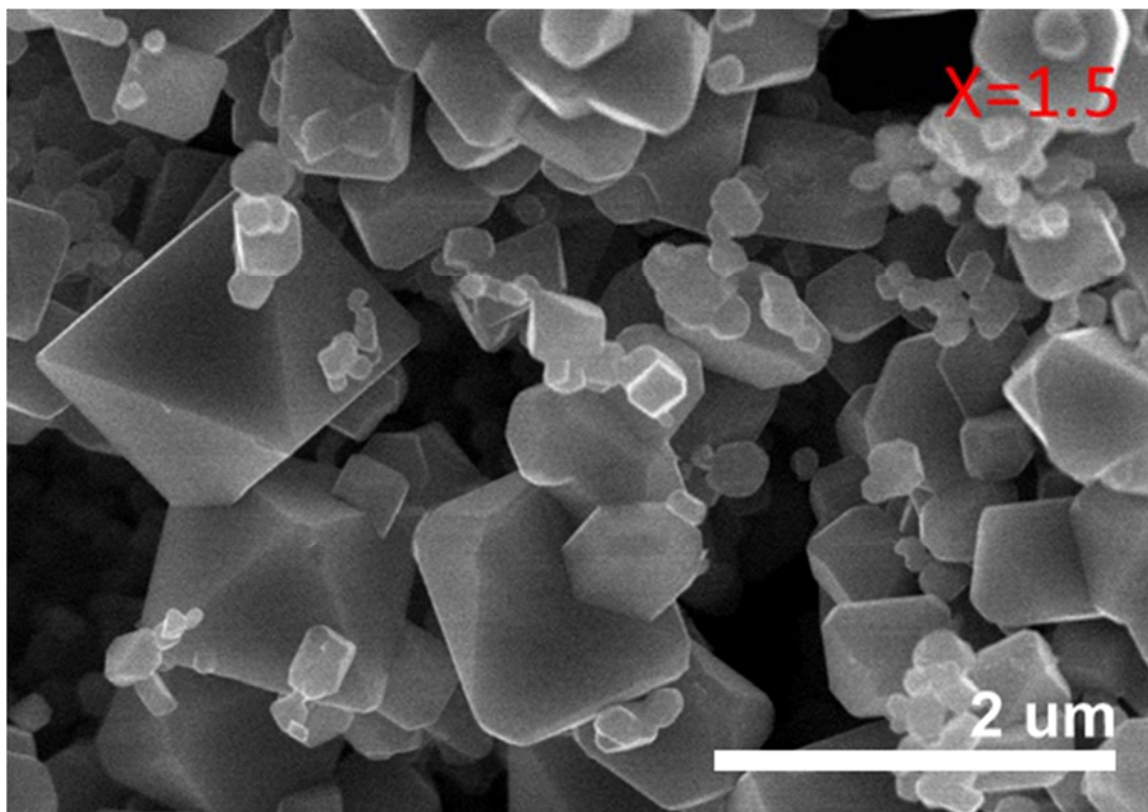


Figure 4.12. SEM image of Cl doped $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=1.5$).

XPS analysis was performed on $\text{Li}_2\text{FeMn}_3\text{O}_{7.25}\text{Cl}_{1.5}$ to investigate how chlorine doping influences ions adjacent to oxygen vacancies. Figure 4.13 shows the total XPS survey spectrum, the spectra of Cl 2p electrons, Mn 3s electrons and Mn 2p electrons of the specimen. XPS survey spectrum indicates that the sample surface consisted of C, O, Fe, Mn, and Cl. The presence and atomic percentage of Li is unable to be confirmed or calculated from the survey spectrum due to the overlap of the Li 1s with the Fe 3p signal. Disregarding the lack of Li information, the relative atomic percentage of the rest elements was confirmed and calculated. As direct evidence of chlorine doping, Cl 2p signal can be found in the survey spectrum, and the atomic percentage is 0.5% (figure 4.14). Figure 4.15 shows the separation in the multiplet spin states of the Mn 3s, which indicates that the majority of the Mn is in the 4+ state in the specimen. However, a shoulder found on the

low binding energy side of the Mn 2p indicates that there exists a small amount of Mn in a lower oxidation state (figure 4.16). Given the fact that the distinct shakeup satellite for Mn^{2+} at 647eV cannot be found, the lower oxidation state Mn is most likely to be Mn^{3+} . The valence state drop of Mn compensates for the valence state difference between oxygen and chlorine. Similar effects are also found on Fe, which can be identified by the distinct shakeup satellite about 8eV above its main peak. This evidence suggests that the chlorine ions reduced the valence state of the adjacent ions, which increases the energy barrier of the redox reactions. In addition, the binding energy of Mn 2p electrons in the studied specimen is larger than the previously reported un-doped LFMO.¹⁶³ In conclusion, the doping of chlorine ions increase the energy barrier for the redox reactions by reducing valence state and increasing electron binding energy of cations, which leads to a higher working voltage of the electrodes.

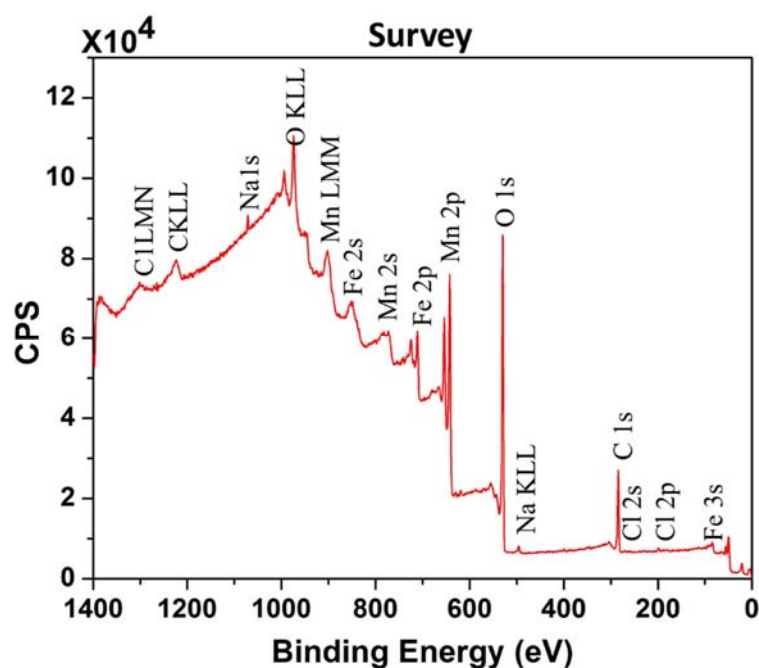


Figure 4.13. XPS Survey spectrum of $\text{Li}_2\text{FeMn}_3\text{O}_{7.25}\text{Cl}_{1.5}$.

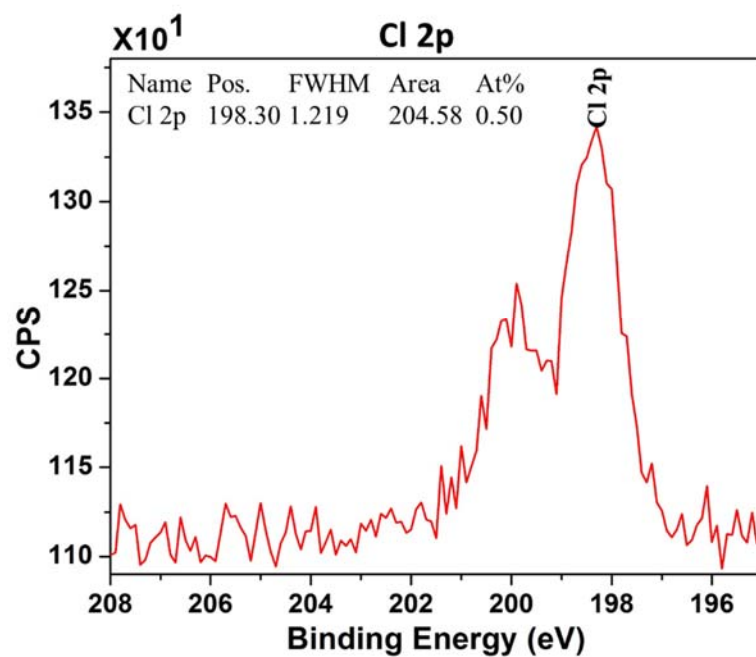


Figure 4.14. Detailed XPS spectrum plot showing Cl 2p.

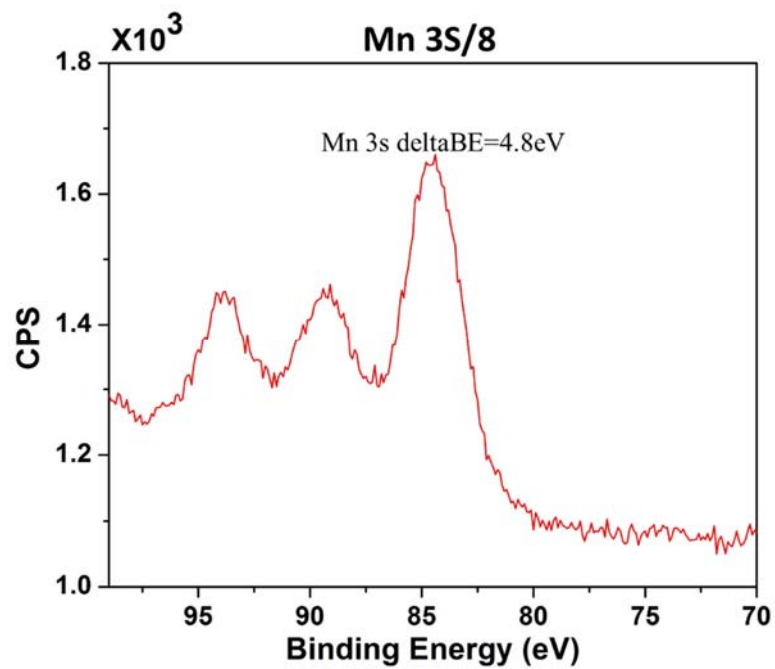


Figure 4.15. Detailed XPS spectrum plot Mn 3s.

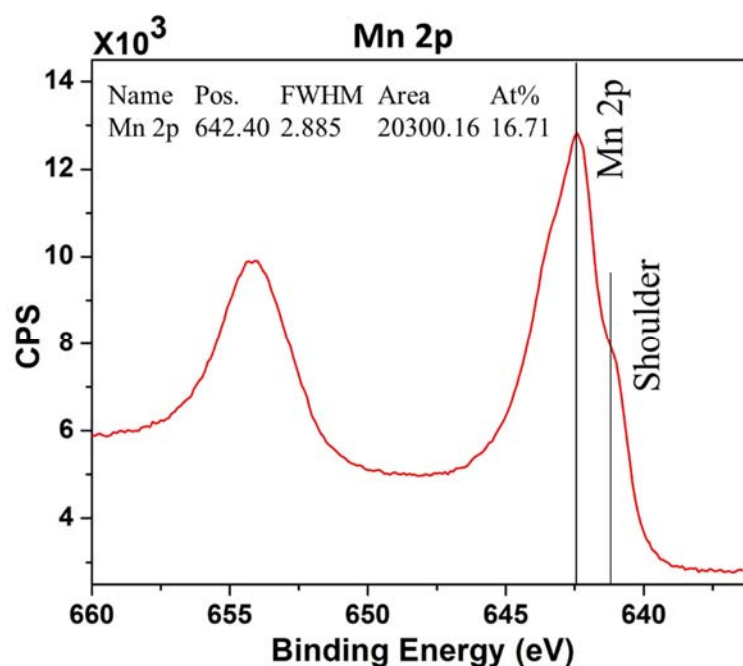


Figure 4.16. Detailed plot showing Mn 2p XPS spectrum, where the shoulder is marked with a short black line.

Figure 4.17 shows the Cyclic Voltammetry (CV) curve comparisons of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ cathode with various Cl content. The test cell consisted of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ cathode slurry-coated on aluminum foil, high-voltage LiPF_6/FEC electrolyte, and lithium metal as counter electrode. The scanning range was 3V to 5.3V with a rate of 0.1mV/s. All the samples showed signature peaks around 4.3V and 4.9V which resulted from the valence change of Mn^{3+} to Mn^{4+} and Fe^{3+} to Fe^{4+} respectively. The sample with the higher chlorine concentration shows smaller polarity, which indicates better reversibility. Figure 4.18 compares the rate performances of the $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ cathode with various Cl content. Despite the difference in specific capacity, cathodes with different chlorine concentration behave similarly in the rate performance. After cycling at high rate (5C), cathode capacity recovers 87.5%, 87.0%, and 79.4% of its initial capacity

respectively. Concluding from the results, chlorine doping has little help on the rate performance improvement.

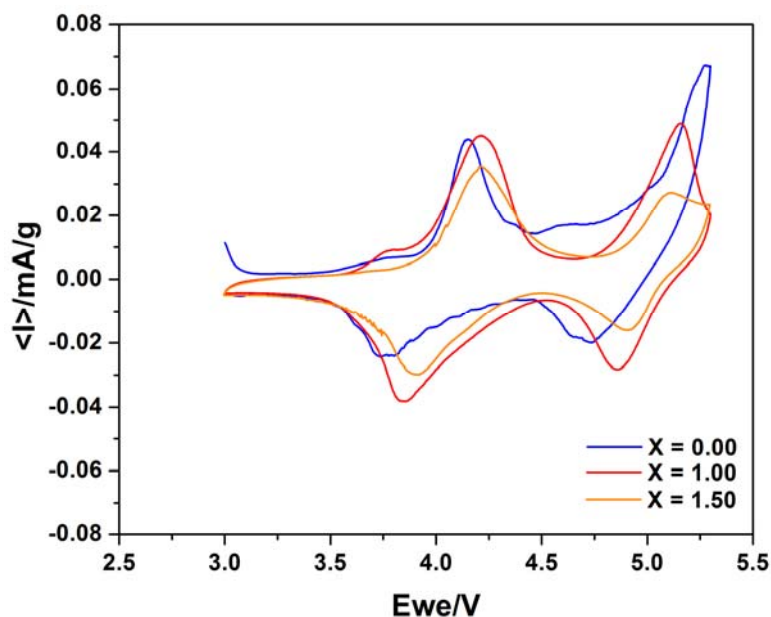


Figure 4.17. Cyclic voltammetry comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations ($0 \leq x \leq 1.5$).

Figure 4.19 shows the cycling performances of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various chlorine concentrations. The cells were cycled between 3.5V and 5.3V, which exceeded the stability window of the electrolyte⁸⁷. Therefore, the capacity gradually faded during charging/discharging as a result of the slow decomposition of both the electrolyte and electrode. With the increase of chlorine concentration, the capacity increases then drops. $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ ($x=1.5$) achieved the best performance among all the tested compositions. This trend can be explained by the increased crystal structure instability due to the over-distorted lattice generated by the excessive amount of chlorine.

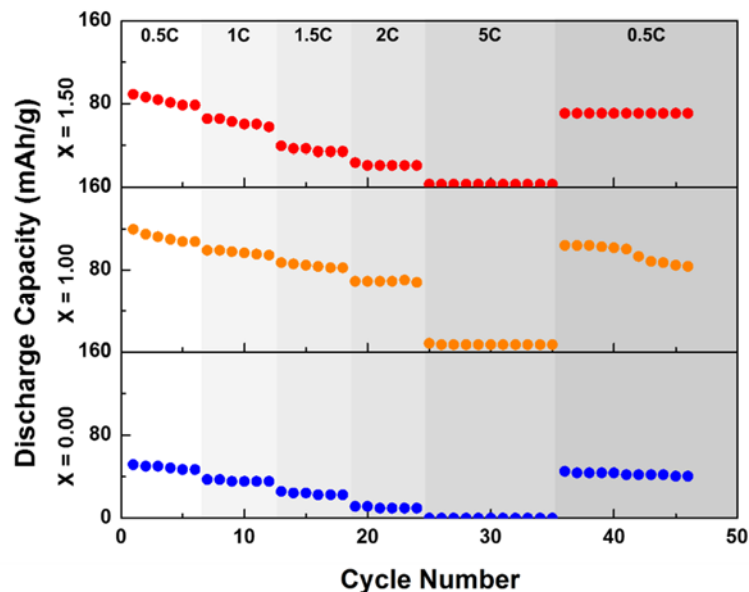


Figure 4.18. Rate performance comparison (from 0.5C to 5C) of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations.

With low chlorine content, the distortion caused by intrinsic oxygen vacancies is neutralized by dopant insertion, thus stabilizes the crystal structure. However, when chlorine content exceeds a critical value, the excessive dopants will over-distort the lattice, which leads to the structural breakdown. Figure 4.20 shows the voltage profile of $\text{Li}_2\text{FeMn}_3\text{O}_{7.5}\text{Cl}$ and $\text{Li}_2\text{FeMn}_3\text{O}_8$. Both samples show two reversible plateaus for $\text{Mn}^{3+}/\text{Mn}^{4+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couple respectively; however, the charging/discharging voltage of the chlorine doped LFMO is higher. The specific capacity of LFMO was about 130 mAh/g, which was 2.6 times the capacity of the undoped LFMO capacity and approached 90% of theoretical capacity. The electrochemical performance suggests that chlorine doping can effectively increase the specific capacity and working voltage of the LFMO cathode.

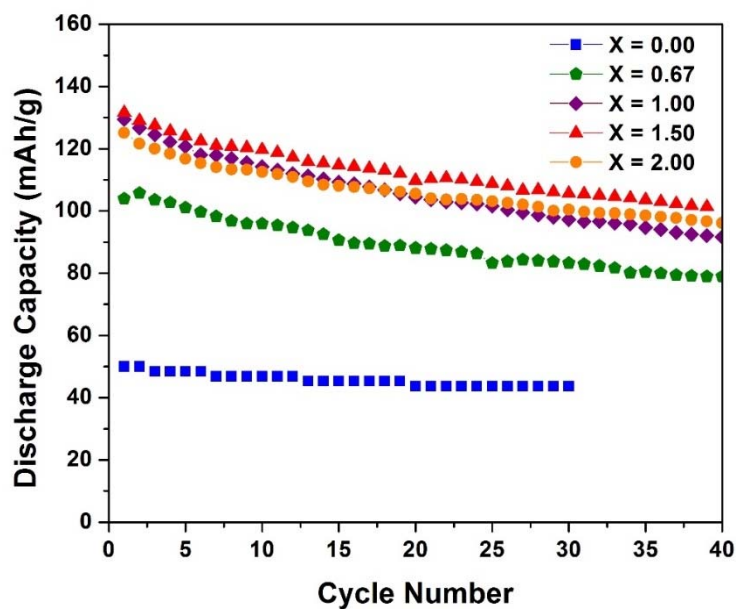


Figure 4.19. Cycling performance comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with different chlorine concentrations ($0 \leq x \leq 2$).

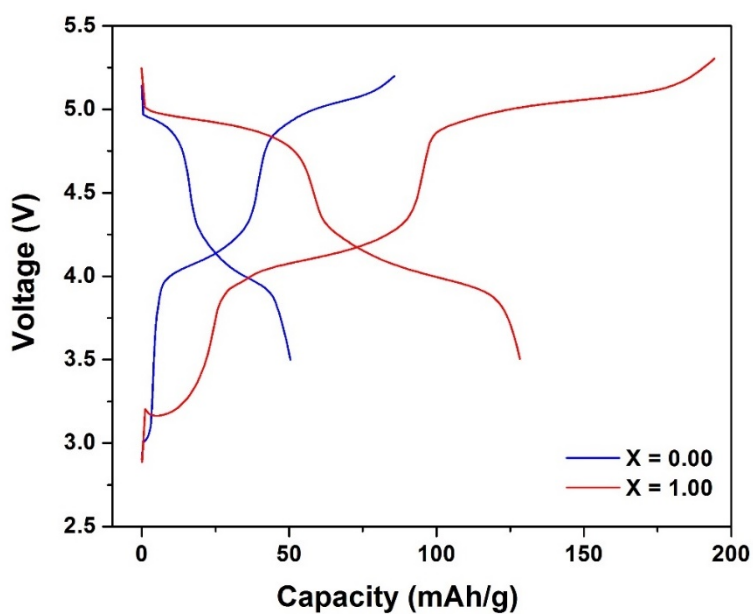


Figure 4.20. Voltage profile comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with $x=1$ and $x=0$.

Figure 4.21 shows the comparison of theoretical capacity and experimental capacity of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various Cl content. The experimental capacity for each Cl content is the max capacity obtained from multiple tests. The experimental results show that Cl doping will not only increase working voltage, but also improve capacity performance. It is true that due to the large atomic number of Cl, the theoretical capacity of the $\text{Li}_2\text{FeMn}_3\text{O}_8$ cathode decreases as Cl content increases. However, the experimental capacity increases then decreases with the increasing Cl content. The critical Cl content that balances the advantage and disadvantage should minimize the difference between theoretical and experimental capacity.

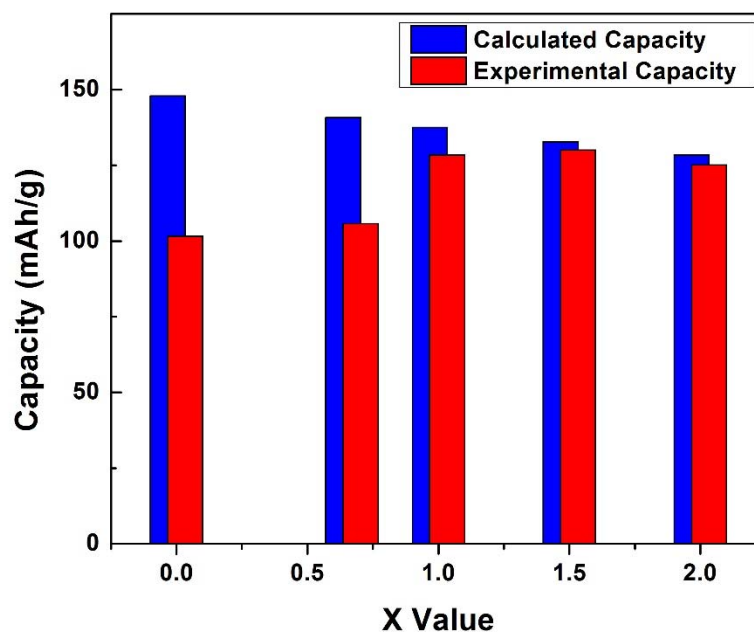


Figure 4.21. Theoretical and experimental capacity comparison of $\text{Li}_2\text{FeMn}_3\text{O}_{8-0.5x}\text{Cl}_x$ with various Cl content.

4.2.4. Experimental Method

Materials Preparation. To prepare the electrodes for battery testing, the cathode powder was mixed with carbon black using hand grinding. Then a 2 wt% solution of polyvinylidene fluoride (PVDF) in n-methyl-2-pyrrolidone (NMP) was added into the powder mixture. The proportion of carbon black and PVDF was both 10 wt%. The mixture was hand-grinded for an hour to obtain a homogenous slurry. Then the slurry was coated onto aluminum foil using a doctor blade (the as-coated thickness was 30 μm). The resulting electrode sheet was then dried in a vacuum oven at 90 $^{\circ}\text{C}$ for 12 hours and then punched into round disks for battery assembly. The electrode was assembled into coin cells with lithium metal as the counter electrodes and high-voltage-stable electrolyte containing fluoroethylene carbonate (FEC) and lithium hexafluorophosphate (LiPF_6) salt⁷.

Materials Characterization. Transmission electron microscopy (TEM) was performed on the JEOL 2100f field emission transmission electron microscope equipped with an energy dispersive x-ray spectrometer (EDX). TEM sample were prepared by sonicating powder followed by drop-casting on lacey TEM grid. X-ray Diffraction (XRD) was performed on a Bruker D8 Advance with Cu K radiation. The electrochemical impedance (EIS) and symmetric cell cycling tests were performed using a BioLogic battery testing system at room temperature in ambient air. The EIS was performed over a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude. The cells were cycled at 0.5 C rate in a potential range of 3.5 - 5.3 V vs. Li/Li^+ using a Bio-Logic SAS Battery Testers (SP-150 & VMP3).

4.3. Aluminum Doped $\text{Li}_2\text{FeMn}_3\text{O}_8$

High-capacity and high voltage cathode materials are crucial for high energy density batteries, which are highly demanded by emerging electrical vehicles. With the application of novel electrolytes with high decomposition voltages, high voltage cathode materials can now fully display their capability in increasing battery energy density. However, the massive application of high voltage cathodes is severely limited because most of these cathodes suffer from three major interfacial issues: interface reaction with electrolyte, poor interface contact, and dissolution of the material.

Ultrathin oxide coatings can dramatically refine the surface properties of Li-ion battery anodes and cathodes. Especially in solid state batteries, lithiated alumina coating over the cathode particles was found to be effective in preventing cathode-electrolyte interface reactions, enhancing solid-solid interface contacts and suppressing cathode dissolution. However, currently the alumina thin coatings can only be achieved by conformal atomic layer deposition (ALD) process, which is way too expensive to be applied in industrialized fabrications.

High voltage cathode materials with self-formed alumina coatings are the best candidate to not only solve the aforementioned issues, but also greatly reduce the fabrication cost. Self-formed alumina coating is therefore a forward-looking solution to the interfacial issues in batteries. Surface aggregation induced by aluminum diffusion usually happens in ceramic sintering, however, its application on the self-formation of alumina coatings in batteries has never been reported before, and the mechanism remains to be explored. Hence, it is of great value to construct cathode particles with self-formed alumina coatings,

and to investigate fundamental mechanism of formation and electrochemical properties including mixed electronic and ionic conductivity.

4.3.1. Diffusion-Induced Self-Formation of Core-Shell Structure

Figure 4.22 explains the formation mechanism of the Al_2O_3 shell and the lithiation process. During annealing, Al ions diffuse to the surface of the cathode where they are oxidized to form a layer of Al_2O_3 . Upon contacting with garnet under heating, Al_2O_3 layer is lithiated with Li ions from the garnet, forming a soft, ionic conductive shell. Figure 4.23 illustrates the synthesis process of Al-doped LFMO (LFMO-Al). Upon annealing, Al ions in the cathodes migrate to the surface, where they are oxidized into alumina and form uniform coatings as a result. The alumina coating formed at this stage can effectively separate the cathode and the solid electrolyte, thus preventing potential interfacial reactions. When the cathode is mixed with solid state electrolytes, lithium ions diffuse from the electrolyte to alumina coating during co-heating, which lithiated the alumina coating as a result. The lithiated alumina coating is a good solid state lithium conductor which connects the cathode and electrolyte like a “glue”. Thus refines the solid-solid interfacial contact between electrolytes and cathodes. Besides, the uniform alumina coating over the cathode particle can block manganese ions from diffusion, which effectively suppress the dissolution of cathode and extends the battery life.

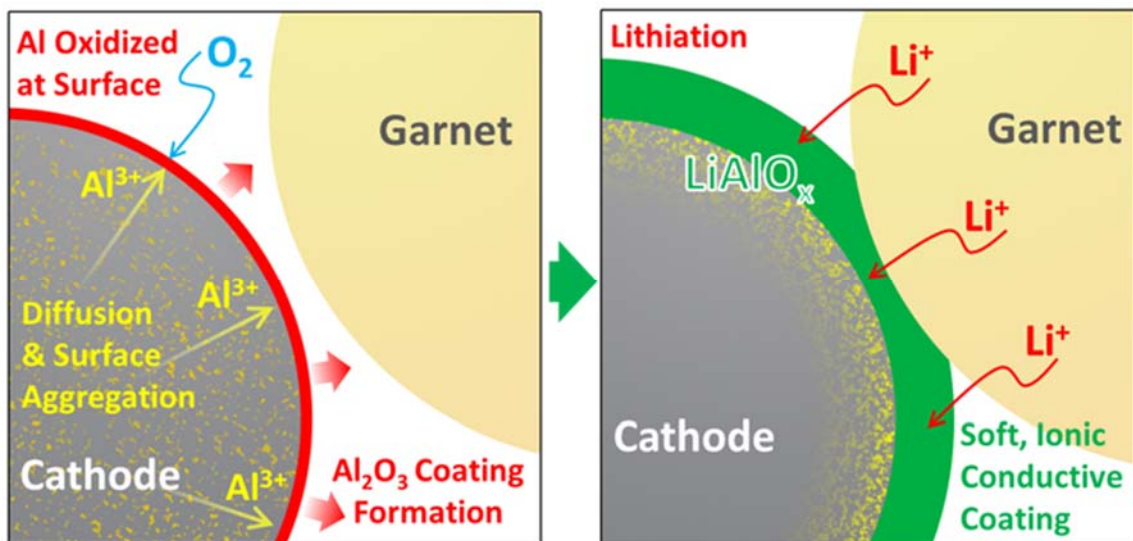


Figure 4.22. Mechanism of the Al_2O_3 coating self-formation, and the lithiation process of the Al_2O_3 coating.

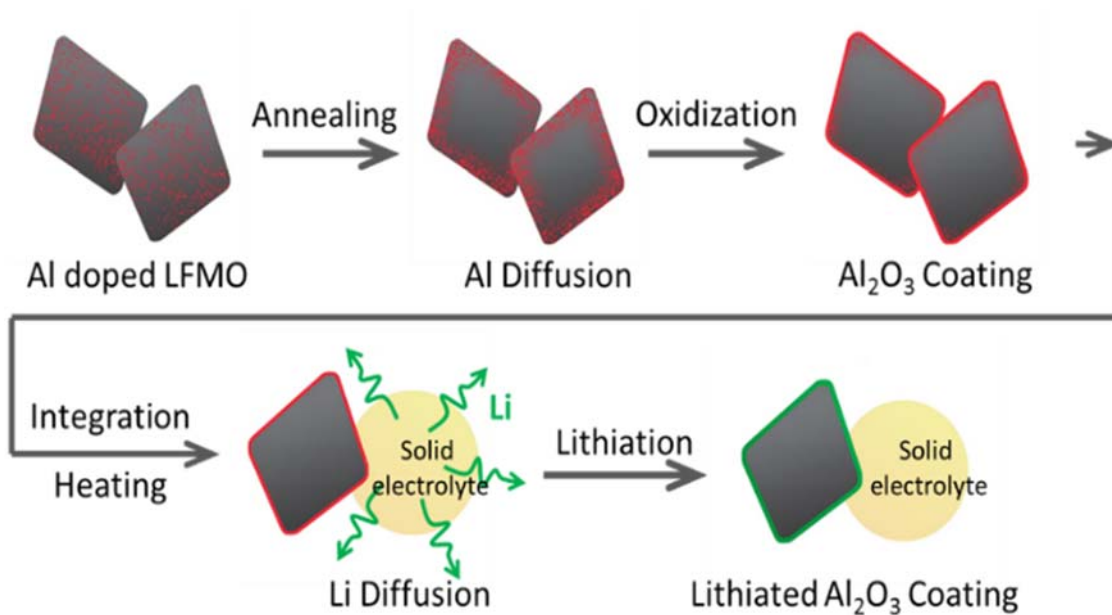


Figure 4.23. A process flow chart for synthesizing cathode particles coated with self-formed alumina layer, and their lithiation when integrated with solid state electrolytes.

4.3.2. Results and Discussion

The morphology of the LFMO-Al is characterized by TEM to confirm the existence of Al_2O_3 shell. Figure 4.24 shows the SEM image of a pristine LFMO particle without Al doping annealed at 500°C for 1 hour. The particle has a clean surface and sharp edges. In comparison, figure 4.25 shows the TEM image of a LFOM-Al particle annealed at the same temperature for the same length of time. For Al doped samples, the particle surface is covered with a thin layer of shell structure. The shell is evenly coated on most of the particles with small thickness variations.

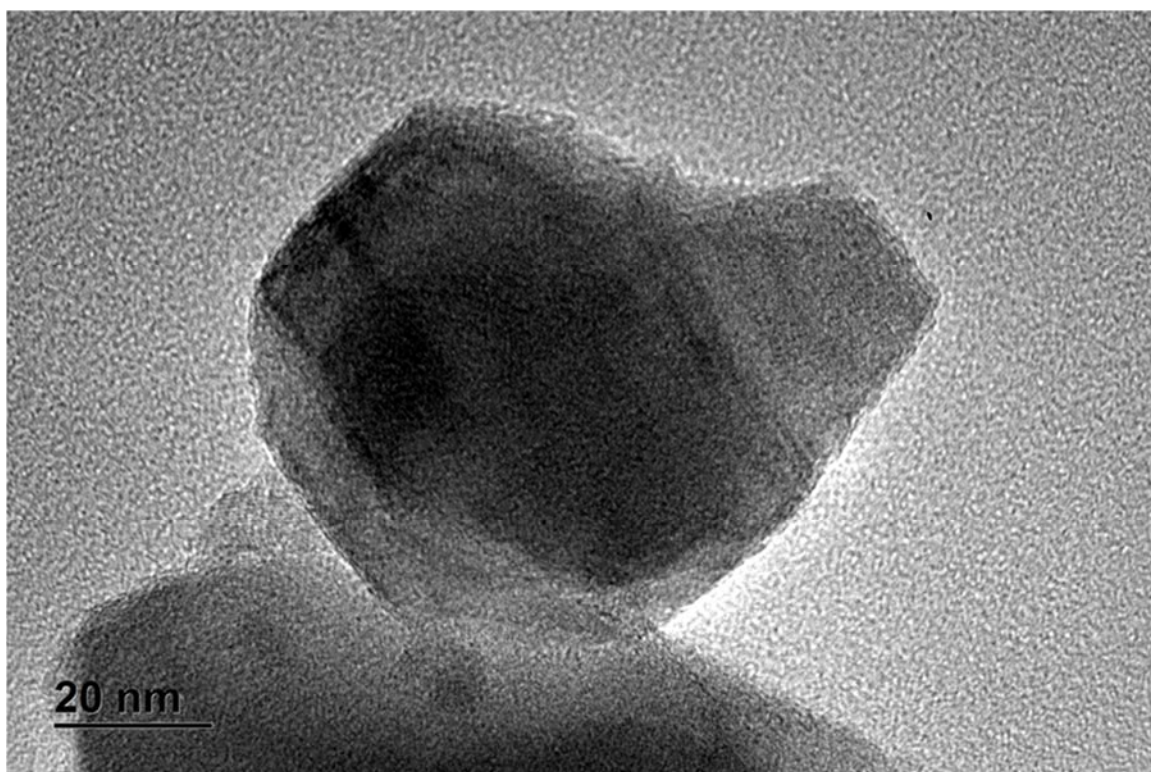


Figure 4.24. TEM image of pristine LFMO particles annealed at 500°C for 1 hour.

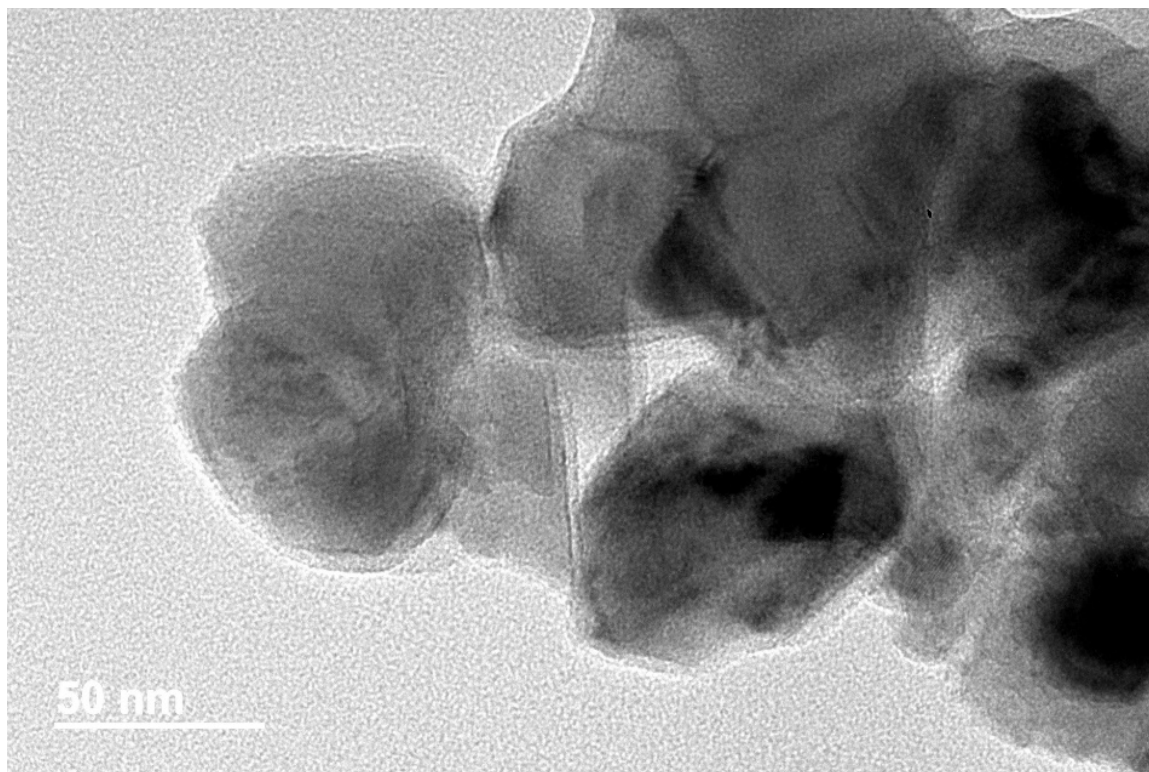


Figure 4.25. SEM image of Al doped LFMO particles annealed at 500°C for 1 hour showing a uniform coating on the particles.

A close-up TEM image shows that the thickness of the coating is about 3 nm (figure 4.26). EDX spectrum shows a clear, strong Al peak, which confirms the existence of Aluminum in the sample. XPS was employed to investigate the chemical environment of the Al. XPS results shown in figure 4.27 shows a clear Al-O bonding signal, indicating the existence of Al-O bonding on the surface. The binding energy of Al 2p is very close to that in Al_2O_3 . Therefore it can be inferred that the shell on LFMO-Al particles is Al_2O_3 .

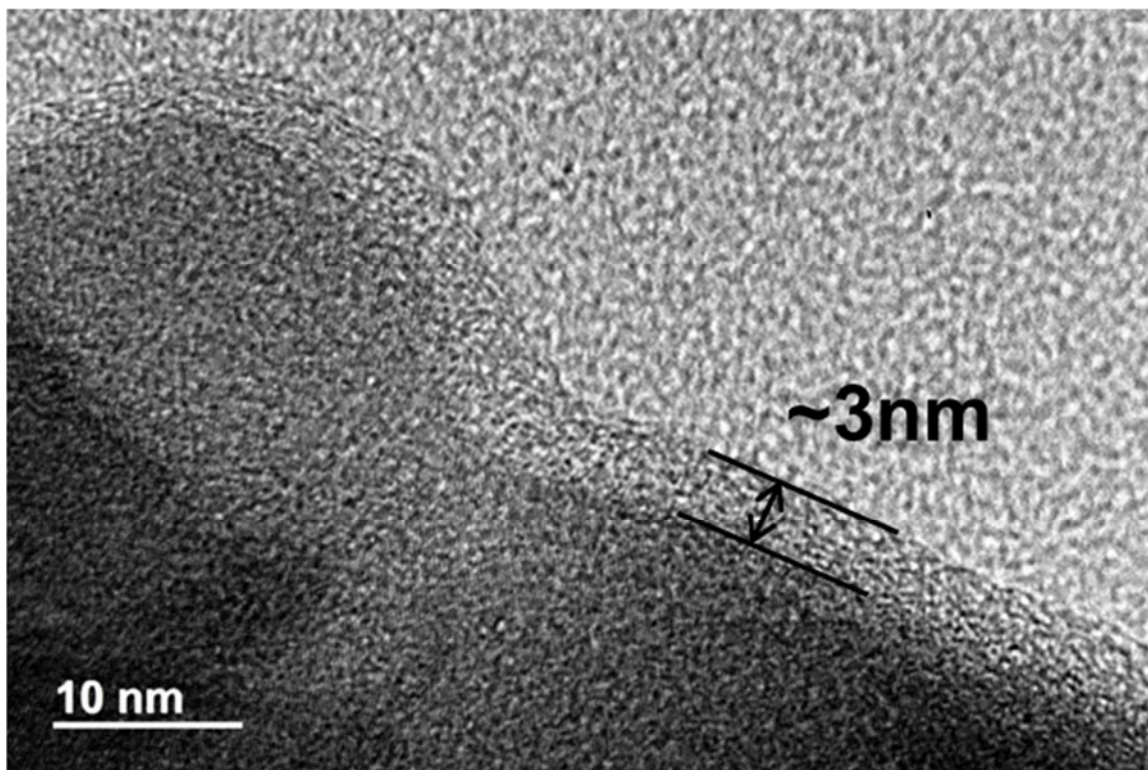


Figure 4.26. Close up SEM image of Al doped LFMO annealed at 500°C for 1 hour showing that the coating thickness is about 3 nm.

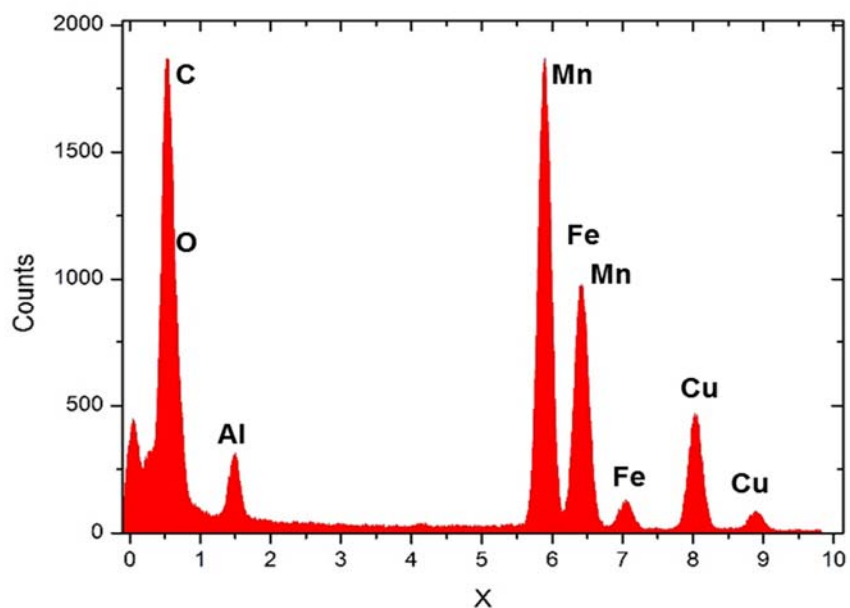


Figure 4.27. EDX spectrum of Al doped LFMO annealed at 500°C for 1 hour shows strong Al signal.

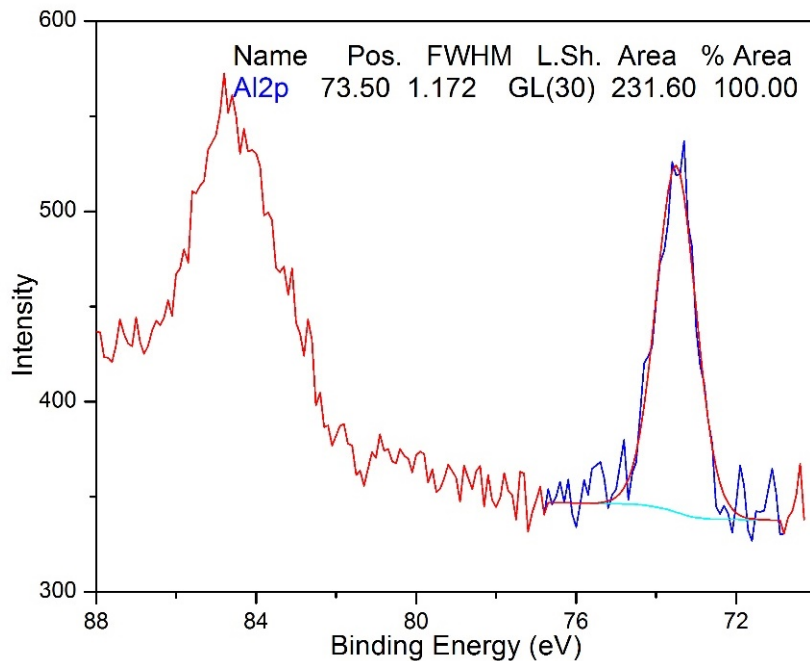


Figure 4.28. XPS results focused on Al 2p signal of Al doped LFMO annealed at 500°C for 1 hour. The binding energy for Al 2p indicates that the Al is in the form of Al_2O_3 on the surface of the LFMO particles.

A great advantage of the Al_2O_3 shell is that it separates the cathode from direct contacting the electrolytes, which prevents side reactions that happen at the electrolyte-electrode interfaces. Figure 4.29-a shows the XRD pattern comparison of the 500°C annealed garnet LLZO mixture with pristine LFMO, and LFMO-Al, respectively. The LFMO/LLZO mixture broke down to multiple oxides after annealing, indicating chemical reactions between the two components. The LFMO-Al/LLZO mixture remains the same pattern before and after annealing, indicating the absence of chemical reactions. Figure 4.29-b shows the XRD pattern of LFMO-Al annealed together with garnet LLZO at 700°C with addition of LiOH. The XRD pattern of the mixture after annealing is an integral of both components. Therefore, no side reactions occurred during the annealing. These results

suggest that the addition of LiOH can further improve the stability of cathode and electrolyte interface, in addition to the protection from Al_2O_3 shell.

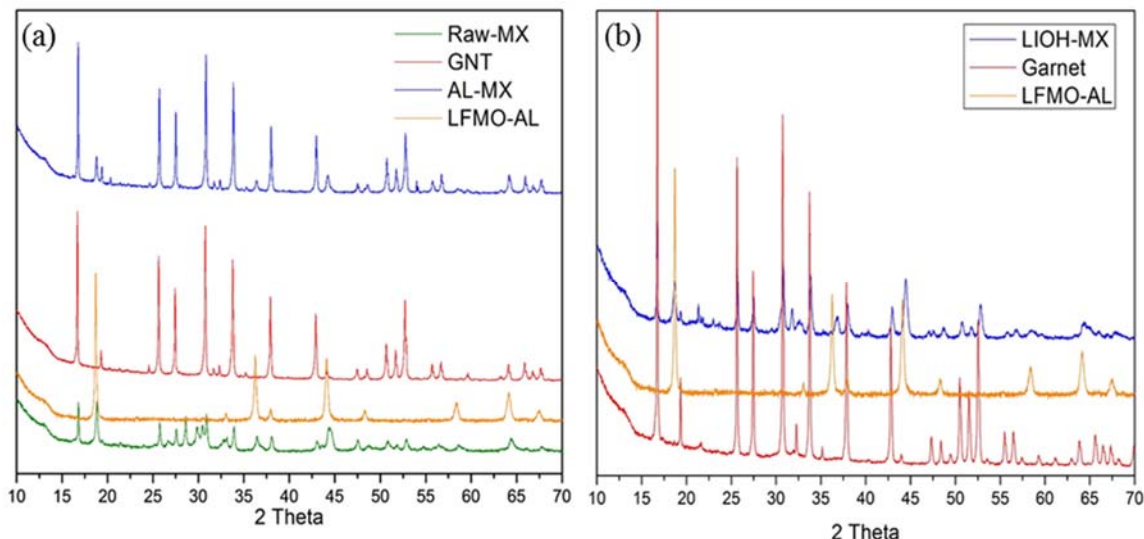


Figure 4.29. (a) XRD pattern comparison of garnet LLZO, pristine LFMO and garnet LLZO mixture, Al-doped LFMO and garnet LLZO mixture, and Al-doped LFMO. All the samples were annealed at 500°C for 1 hour. (b) XRD pattern comparison of pristine garnet LLZO, Al-doped LFMO, and a mixture of Al-doped LFMO, garnet LLZO, and LiOH. All the samples were annealed at 700°C for 1 hour.

In addition to the improvement on chemical stability, the Al_2O_3 coating also improves the ionic conductivity of the LFMO-Al cathode. Figure 4.30-a shows the EIS curve of pristine LFMO, 500°C annealed LFMO-Al, and 900°C annealed LFMO-Al. The EIS tests were performed on cold pressed cathode pellets with gold electrodes on both sides. The bulk conductivity of LFMO-Al is about 7 times higher than that of the pristine LFMO. A zoom-in plot at higher frequencies shows better the ionic conductivity of 900°C annealed LFMO-Al (figure 4.30-b). It can be concluded from the EIS results that the Al_2O_3

shell can improve the ionic conductivity of the LFMO cathode. Higher annealing temperature of LFMO-Al can lead to higher ionic conductivity.

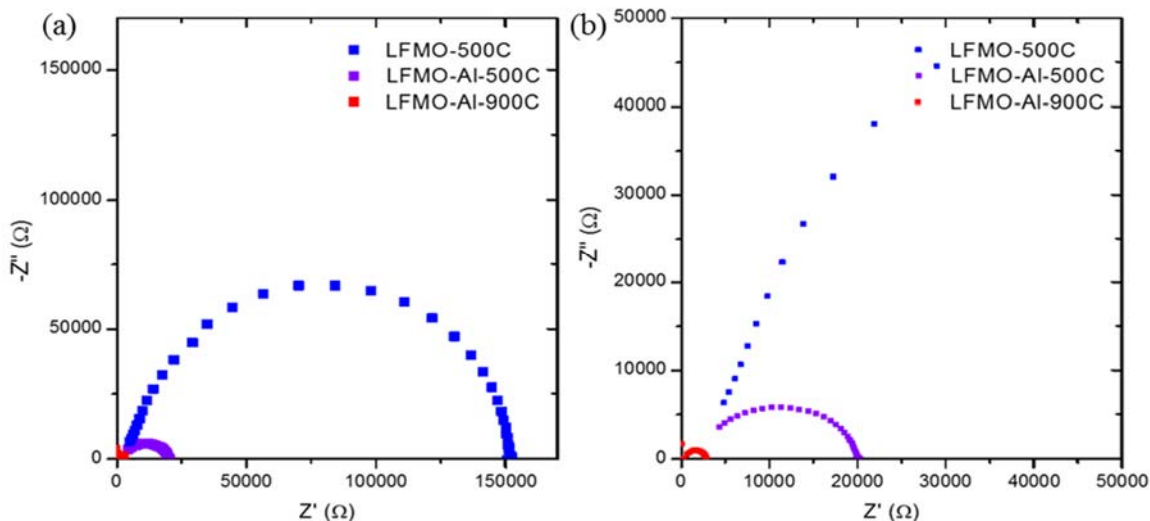


Figure 4.30. (a) Nyquist plot comparison of 500°C annealed LFMO, 500°C annealed Al doped LFMO, and 900°C annealed Al doped LFMO. (b) A zoom-in of EIS curve at higher frequencies.

4.3.3. Experimental Method

Materials Characterization. Transmission electron microscopy (TEM) was performed on the JEOL 2100f field emission transmission electron microscope equipped with an energy dispersive x-ray spectrometer (EDX). TEM sample were prepared by sonicating powder followed by drop-casting on lacey TEM grid. X-ray Diffraction (XRD) was performed on a Bruker D8 Advance with Cu K radiation. The electrochemical impedance (EIS) and symmetric cell cycling tests were performed using a BioLogic battery testing system at room temperature in ambient air. Samples for EIS tests were fabricated by pressing cathode powder into disks. The cathode disks were then coated on both sides

with gold electrode then annealed at high temperature. The EIS was performed over a frequency range of 1 MHz to 100 mHz with a 50 mV perturbation amplitude.

4.4. Conclusion

This chapter introduced several attempts to improve the voltage, capacity, and electrochemical stability of the high voltage cathode material $\text{Li}_2\text{FeMn}_3\text{O}_8$. Chlorine doped and fluorine doped $\text{Li}_2\text{FeMn}_3\text{O}_8$ high-voltage cathodes with various dopant concentrations were successfully synthesized using a simple combustion method. The influence of chlorine doping on the performance of the LFMO cathodes was investigated with X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and battery cycling tests. The performance enhancement was studied using X-ray photoelectron spectroscopy (XPS). Our results show that chlorine ions filled up intrinsic oxygen vacancies in LFMO crystals upon doping, which led to the lattice expansion, valence state reduction, and electron binding energy increase of cations adjacent to the vacancies. Thus, the energy barrier for the redox reactions of the cathode was increased. Accordingly, the electrochemical performance was effectively improved by chlorine doping. The $\text{Li}_2\text{FeMn}_3\text{O}_{7.5}\text{Cl}$ cathode showed superior performance over the undoped LFMO with a specific discharge capacity of 130 mAh/g at 0.5C and a working voltage of 5V. The specific capacity was 2.6 times of the undoped LFMO capacity and approached 90% of the theoretical capacity. These results reveal the electrochemical improvement in the LFMO to be due to chlorine doping. This simple, low-cost fabrication method can also be applied on other spinel cathodes, following a similar mechanism.

In addition, a core-shell structure self-formation mechanism was raised up for the aluminum doped LFMO. The Al was found to migrate towards the surface of the high

voltage cathode upon heating. At the surface, the Al will be oxidized to form Al_2O_3 shells. The shell uniformly coats the whole LFMO-Al particle with a thickness of about 3nm. The Al_2O_3 shell can also be lithiated through co-heating with Li rich electrolytes. After lithiation, the shell delivers good ionic conductivity and outstanding protection to the LFMO particles at high temperature up to 900°C.

Chapter 5: A Solid State Energy Storage Device with a Hybrid Design

5.1. Battery-Supercapacitor Hybrid Devices

High power and high energy density are attractive attributes in energy storage devices for applications such as mobile electronic devices, electric vehicles, and high-rate energy storages for militaries.^{66,164} However, in conventional energy storage devices, like supercapacitors and batteries, improved power density often results in a tradeoff with lower energy density. The inevitable dichotomy between energy density and power density is caused by the reliance of most devices on a single ion storage mechanism. Supercapacitors utilize the electric double layer mechanism to store ions, which enables fast charge carrier kinetics but offers limited capacity.¹⁶⁵⁻¹⁶⁷ Batteries employ electrochemical reactions to store ions in bulk electrode materials, which can provide large capacity, but suffer from comparatively slow ion transport.^{2,168,169} The key to overcoming the energy-power conflict lies in the design of a hybrid device that utilizes the advantages of both supercapacitors and batteries storage mechanisms.

Past studies have focused on achieving ion storage hybridization through the design of novel electrode materials.¹⁷⁰⁻¹⁷² For example, a nanocomposite anode containing capacitive carbon materials and intercalative oxides was reported with improved energy density and high stability as a hybrid supercapacitor.¹⁷³ In addition, hybrid devices using asymmetric electrodes (e.g. capacitive cathode paired with intercalative anode) were reported with stable high power, high energy performance.^{174,175} The successful design of a hybrid device relies on the proper selection of the electrodes that can merge

supercapacitor and battery chemistries.¹⁷⁶ In other words, the device should be able to adopt both the electric double layer and ion intercalation storage mechanisms.

5.2. Hybrid Design of Solid State Energy Storage Device

In this work, I designed a hybrid energy storage device that performs as both a double-layer supercapacitor and intercalative lithium-ion battery with high power and energy density. The device possesses outstanding features including 1) an asymmetric cell configuration consisting of an intercalative cathode and capacitive anode; 2) ultrathin, lightweight Al leaf current collectors; 3) a free-standing carbon anode that also works as its own current collector; and 4) a quasi-solid-state gel polymer electrolyte that diminishes liquid electrolyte leakage risks.

As a proof-of-concept, LiFePO_4 (LFP) was selected as the cathode for hybrid cells due to its good cycling stability and high rate performance among various cathode materials.^{3,177,178} With structural modifications, such as nanocrystallization,¹⁷⁹ conductive coatings,¹⁸⁰ and nano-compositing,⁶⁵ LFP can deliver over 110 mAh/g at 10 C.¹⁸¹ The ultrathin Al leaf with 1 μm thickness was used in our device as current collectors for the cathode to reduce the volume and mass of inactive material. For the anode, the main challenge lies in their limited capacity, which is determined by the specific active surface area.¹⁸²⁻¹⁸⁴ One effective way to improve the anode capacity is to use nanomaterials with high surface areas, such as carbon nanotubes (CNTs) and graphene.¹⁸⁵⁻¹⁸⁷ A freestanding reduced graphene oxide (RGO)/CNT membrane was selected in our device to serve as a current-collector-free anode. A poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) membrane was employed as the gel polymer electrolyte to minimize potential electrolyte leakage.¹⁸⁸ Compared with conventional liquid electrolyte, gel polymer

electrolytes have the advantages of comparable ionic conductivity at ambient temperatures, good mechanical strength, stable electrochemical performances, and no liquid electrolyte leakage risks.¹⁸⁹

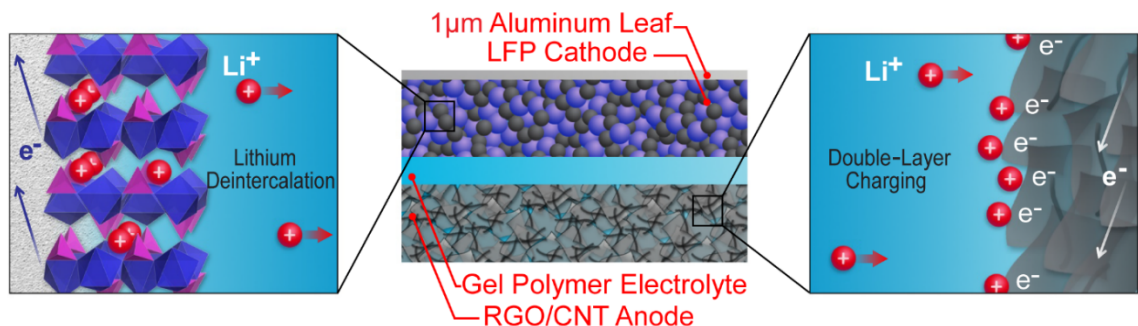


Figure 5.1. Schematic of the hybrid device consisting of LFP cathode, gel polymer electrolyte, and RGO/CNT composite anode. Zoom-in schematic shows the working mechanism of the hybrid device.

Figure 5.1 shows a structural schematic of the hybrid device. During charging, lithium ion deintercalate from the cathode, diffuse through gel polymer electrolyte, and form an electric double layer on the anode. Note that the RGO/CNT film is used as both an electrode material and a lightweight current collector for the anode. A thin Al leaf (only 1 μm thick) is the current collector for the cathode to save weight. Gel polymer is used as the quasi-solid-state electrolyte. In other words, during charging, the lithium ions deintercalate from the LFP cathode, migrate through gel polymer electrolyte, and form an electric double layer on the surface of the RGO/CNT anode. The application of the ultrathin Al leaf current collector and current collector free anode greatly reduces the weight of inactive materials, which improves the energy and power density. The hybrid device delivered simultaneously an energy density of 180 Wh/kg and a power density of 218 W/kg at the materials level based on the total weight of the cell except for packaging. In addition,

during the cycling tests, the hybrid device retained over 97% of its initial capacity after 100 cycles with high coulombic efficiencies.

5.3. Developing Solid State Gel Electrolyte

Gel polymer electrolyte consisting of lithium salt and bonding solvent inside a porous PVdF-HFP membrane was used in the hybrid cell. PVdF-HFP was chosen as the polymer electrolyte due to its outstanding ionic conductivity and electrolyte absorbency enabled by its amorphous structure.^{36,190} It can be easily made into membranes with high porosity, which is highly beneficial to achieve fast lithium ion transport.

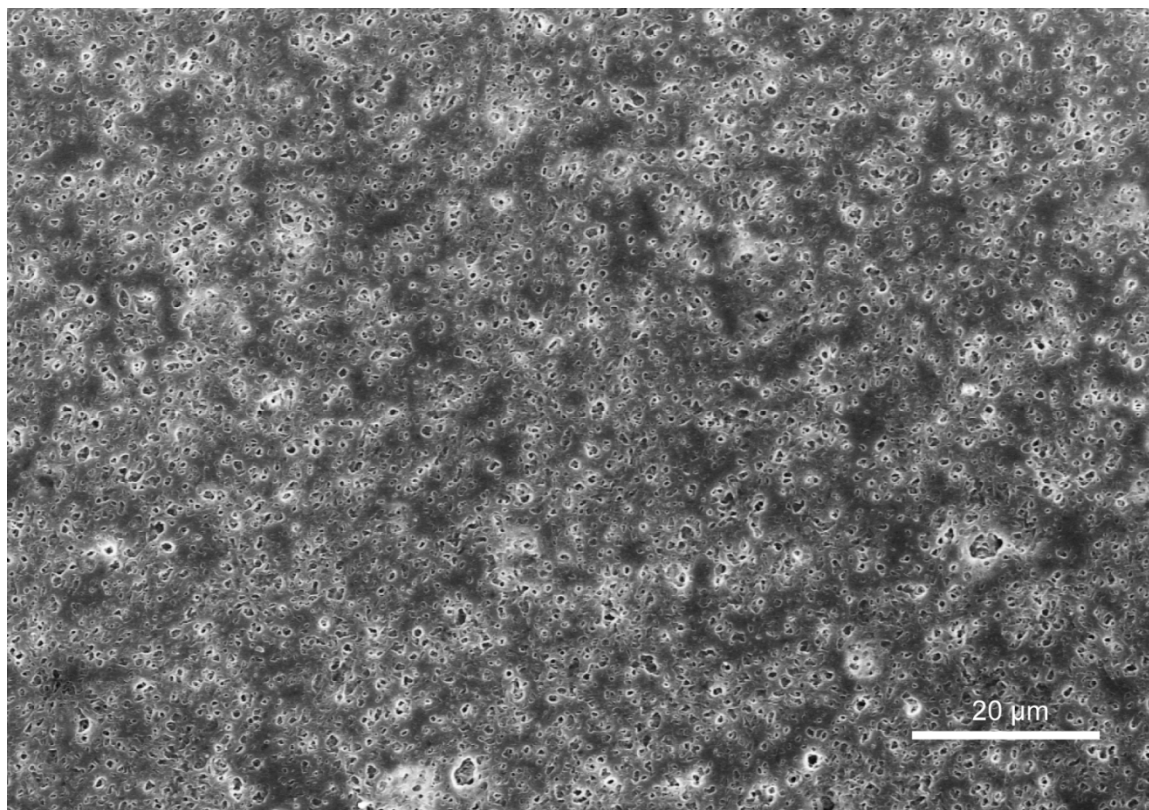


Figure 5.2. SEM image of a piece of dry PVdF-HFP co-polymer top surface.

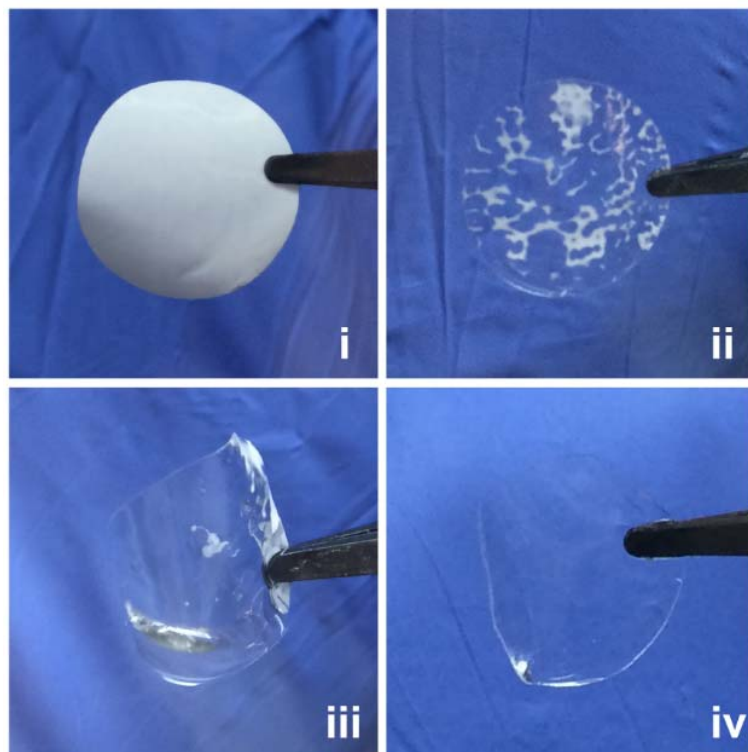


Figure 5.3. Photo image of a piece of PVdF-HFP membrane absorbing liquid electrolyte during gelation.

The morphology of the polymer membrane and the electrochemical performance of the gel polymer electrolyte were studied to understand its structure, electrochemical stability, and ionic conductivity. Figure 5.2 shows the scanning electron microscopy (SEM) image of the pristine PVdF-HFP membrane. The membrane was prepared by dissolving PVdF-HFP in acetone and drying in vacuum to obtain the hierarchically porous structure. Pores were uniformly distributed with pore sizes ranging from 0.5 μm to 2 μm . These pores allow lithium salt and solvent to penetrate into the porous polymer membrane and increase their affinity in the polymer molecular structure. The preparation of gel polymer electrolyte is shown in Figure 5.3. Firstly, 1M lithium hexafluorophosphate (LiPF_6) dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) solvent mixture was dropped onto the

PVdF-HFP membrane (figure 5.3-I). Then the membrane was left in the glovebox at room temperature for 1 minute to ensure complete gelation (figure 5.3-II). Then the remaining liquid electrolyte on the gel membrane surface was wiped off to form the quasi-solid-state gel electrolyte (figure 5.3-III). After gelation, the membrane had a solvent uptake of approximately 120 wt% (figure 5.3-IV).

To investigate the electrochemical stability window of the gel electrolyte, cyclic voltammetry (CV) was performed on a symmetric cell in which the gel electrolyte membrane was sandwiched between two stainless steel blocking electrodes (figure 5.4). The CV was scanned from 0 to 5 V with a scan rate of 1 mV/s. The CV profile shows one significant oxidation peak at 4.3V with a reaction current up to 55 μA , which is associated with electrolyte decomposition. The CV profile below 3.8 V remains stable.

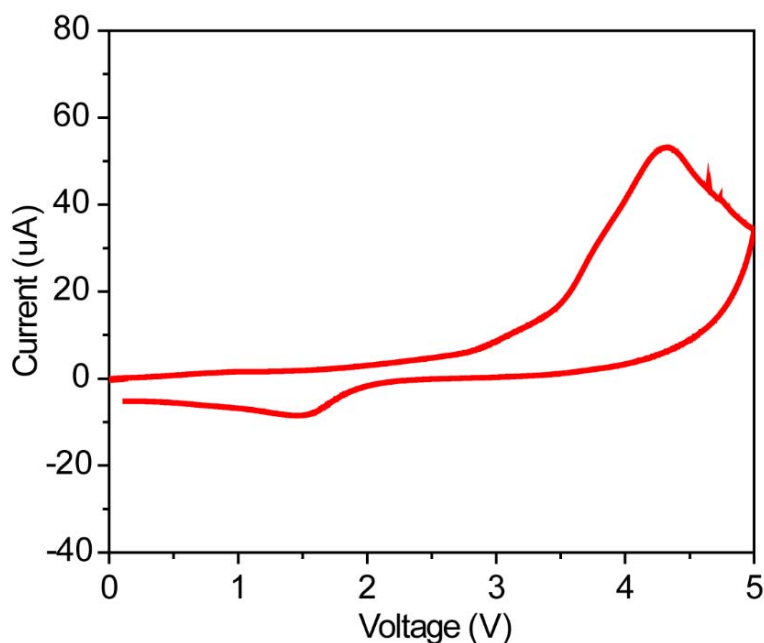


Figure 5.4. CV profile of the gel electrolyte membrane composed of PVdF-HFP and organic electrolyte at the scanning rate of 1 mV/s within a potential window of 0-5 V.

Figure 5.5 shows the Nyquist plots of the gel electrolyte membrane compared to a commercial polyethylene (PE) separator with the same amount of electrolyte. Both the gel electrolyte (thickness 56 μm) and separator (thickness 24 μm) were assembled into symmetric cells using stainless steel as electrodes, and were tested for electrochemical impedance spectroscopy (EIS) at a scan rate from 1 MHz to 100 mHz with a perturbation amplitude of 50 mV.

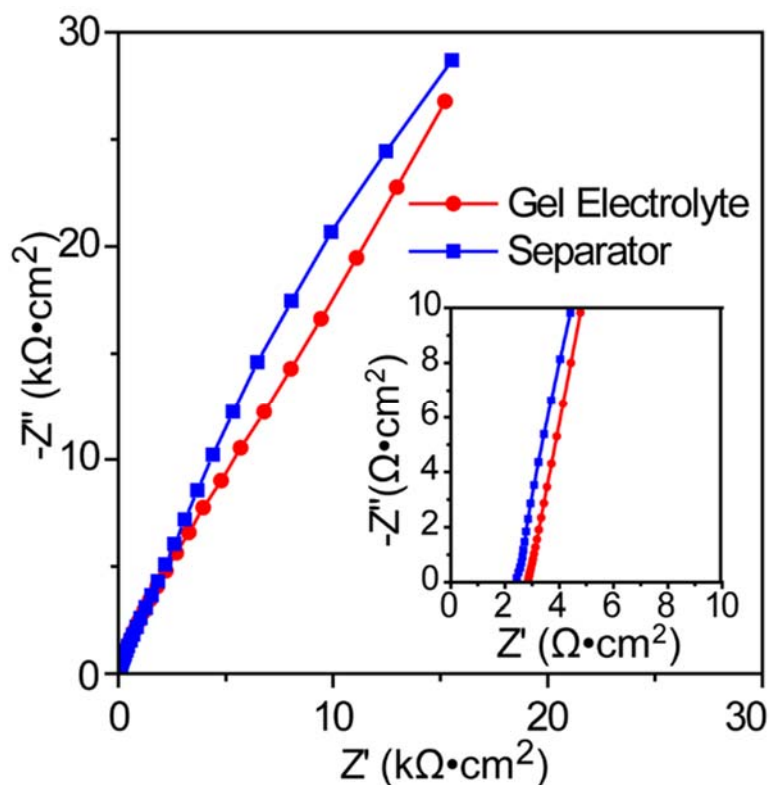


Figure 5.5. Impedance comparison of the gel and liquid electrolyte shows the similar ionic conductivity of gel electrolyte with organic liquid electrolyte. (Inset plot shows their intersections with the Z' axis).

The total impedance of the symmetric cell includes the bulk resistance of the gel electrolyte and charge transfer resistance from two electrolyte-electrode interfaces. The inset graph shows the magnified region of the Nyquist plots at high frequency. The

intersection of the semicircle on the x-axis for the PE separator and gel polymer electrolyte are 2.2 ohm•cm² and 2.7 ohm•cm², respectively, indicating the bulk resistance of the electrolyte-filled membrane. The ionic conductivity of the electrolyte can be calculated by

$$\frac{1}{\sigma} = R \frac{S}{l} \quad (\text{E } 5.1)$$

where σ is the conductivity of the electrolyte, R is the resistance, S is the area, and l is the thickness. Therefore, the calculated ionic conductivity was 1.08 mS/cm for PE separator, and 2.07 mS/cm for gel electrolyte, suggesting that the gel polymer electrolyte has a comparable ionic conductivity with the traditional liquid electrolyte-filled separator.¹⁹¹

5.4. Results and Discussion

To evaluate the electrochemical performance of RGO/CNT as an anode material for hybrid devices, a testing electrode was prepared by filtering and drying RGO/CNT ink. A SEM image of the hybrid anode composite shows that the RGO flakes were wrapped by CNTs (figure 5.6-a). The CNTs can link large pieces of RGO flakes together so as to enhance the anode structure stability. In addition, the interconnected structure builds a porous network with a high specific surface area, which is favorable for ion adsorption. The mass loading of the anode was 0.42 mg/cm² (figure 5.6-b). Galvanostatic measurements were carried out at elevated current densities of 0.1 A/g, 0.5 A/g and 1 A/g. Figure 5.6-c shows the voltage profile of the RGO/CNT half-cell. The initial coulombic efficiency was about 50% due to the irreversible capacity of the high surface area of the carbon electrode, which quickly increased to 92.7% in the second cycle. In the following cycles, the coulombic efficiency fluctuated around 94%. The anode electrode delivered a capacity of 570 mAh/g and remained stable in the following cycles. Figure 5.6-d shows the

relation between current density and the corresponding capacity. Note that the RGO/CNT anode can deliver a high capacity of 230 mAh/g at a high current density (1 A/g), which is important for achieving both high energy density and high power density in our hybrid device. The outstanding electrochemical performance of the RGO/CNT anode can be attributed to the greatly expanded surface area imparted by the 3-dimensional nanocarbon networks. In addition, the high porous structure constructed by the linked CNT and RGO also provided sufficient transport pathways for lithium ions.^{192,193}

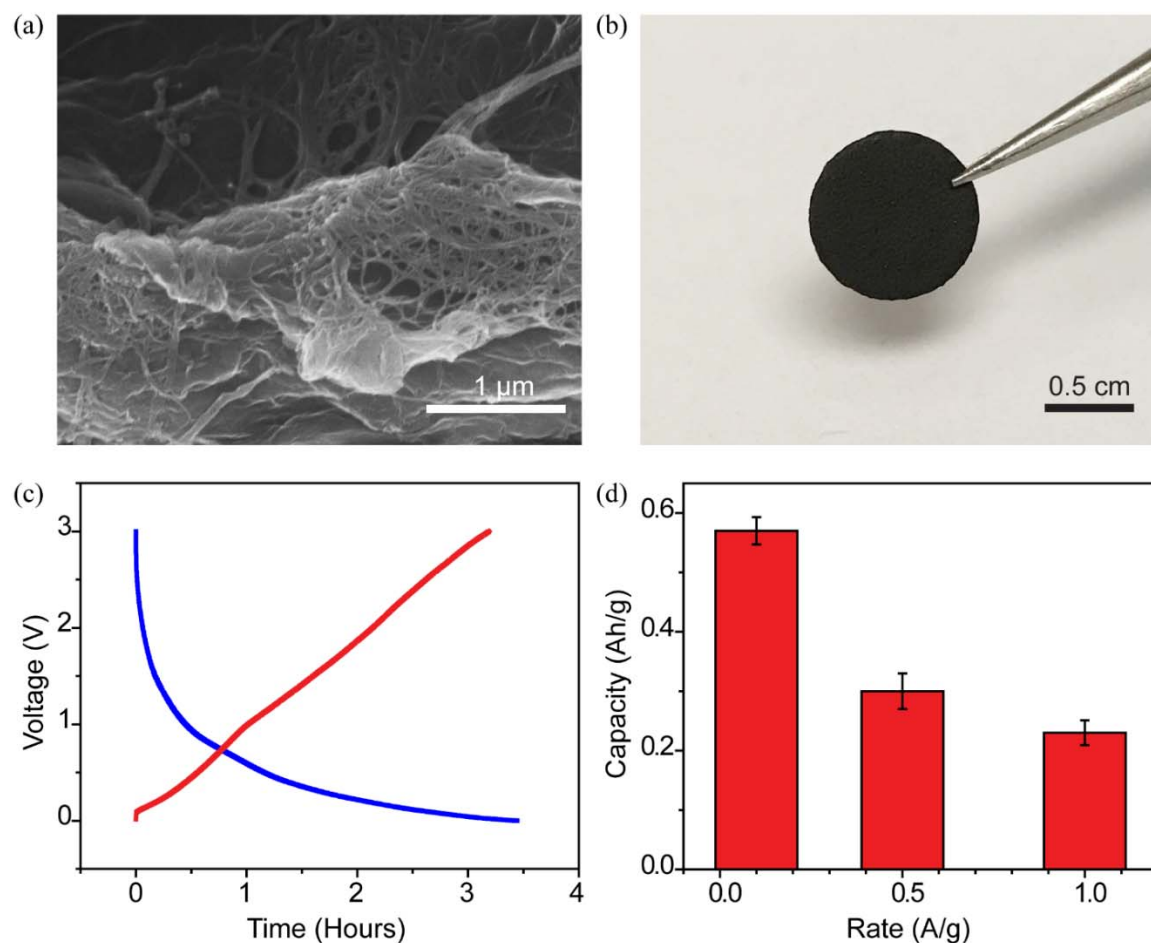


Figure 5.6. (a) SEM image of the anode material shows the interconnected porous network of CNT and RGO. (b) Photograph of a piece of the RGO/CNT anode. (c) Voltage profile of the RGO/CNT material in a half cell configuration against a Li metal reference electrode

shows a high columbic efficiency from the second cycle. (d) Capacity comparison of the RGO/CNT material at different currents densities shows the superior capacity of the anode at high rates.

For the cathode design, decreasing the weight of inactive materials (current collectors for example) in the battery is a practical and straightforward way to increase the energy density of the cells.^{129,194,195} Here, we use an Al leaf with a thickness of 1 μm as the current collector. Figure 5.7 is the SEM image of the LFP cathode. The LFP slurry was coated onto the Al leaf to obtain an ultrathin, flexible electrode. Figure 5.8 shows that a piece of the Al leaf can easily stand on a flower stamen, demonstrating the ultra-lightweight feature of the Al leaf.

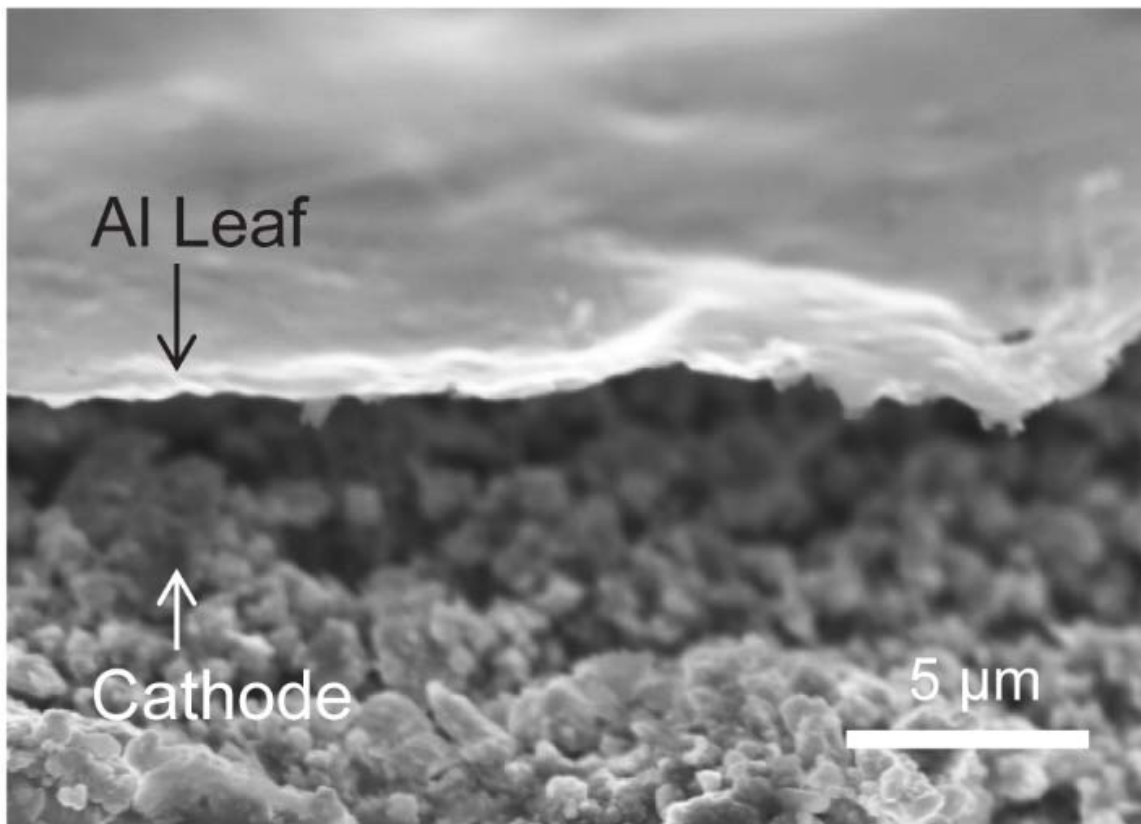


Figure 5.7. SEM image of the cathode shows the 1 μm thickness of Al leaf on top of the LFP-CB-PVdF cathode.



Figure 5.8. Photograph of a piece of Al leaf supported by the stamen of a flower showing the ultra-lightweight feature of the Al leaf as a current collector.

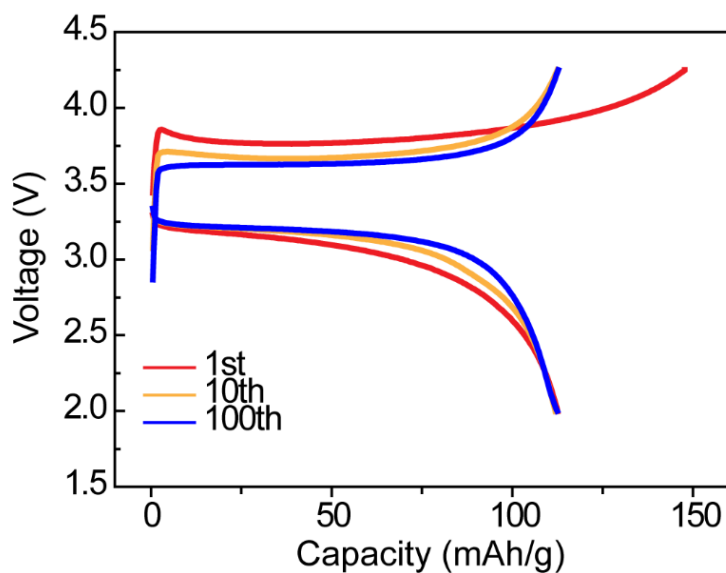


Figure 5.9. The comparison of the charge and discharge capacities of the integrated LFP cathode at the 1st cycle, 10th cycle, and 100th cycle under a current density of 10 C shows the superior capacity and high coulombic efficiency.

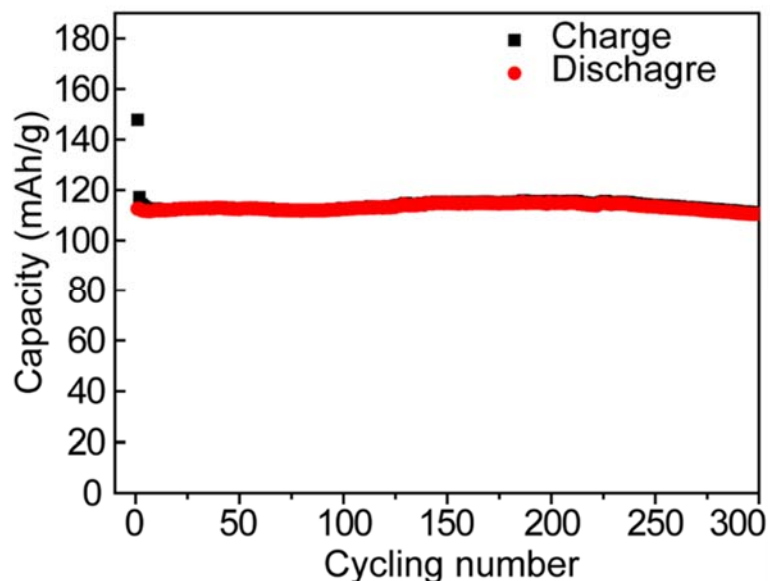


Figure 5.10. Cycling performance of the integrated Al leaf/ LFP cathode at a current density of 10 C for 300 cycles without obvious capacity decay shows the outstanding stability of the integrated cathode.

To enhance the mechanical properties of the LFP cathode, we designed a cathode by laminating an Al leaf and LFP cathode directly onto the dry PVdF-HFP membrane. The integrated cathode was dried in a vacuum oven at 50 °C for 10 hours to remove the solvent. Then it was assembled into a coin cell with lithium metal as a counter electrode. The half-cell was cycled between 2.0 and 4.2 V with a current density of 10 C (1 C = 170 mA/g). Figure 5.9 shows the voltage profile of several characteristic cycles. In the first cycle, the charge specific capacity was 150 mAh/g, and discharge specific capacity was 110 mAh/g, with an initial coulombic efficiency of 73%. The charging and discharging plateaus were at 3.7 V and 3.1 V, respectively, exhibiting a voltage difference of 0.6 V. In the following cycles, this voltage difference gradually decreased to less than 0.4 V, indicating the improved kinetics of the cathode during long-term cycling. From the 10th to the 100th cycle, the charge and discharge capacities remained stable around 110 mAh/g. In addition

to the superior capacity and high coulombic efficiency, the battery also exhibited a stable cycling performance over 300 cycles without obvious capacity decay (figure 5.10).

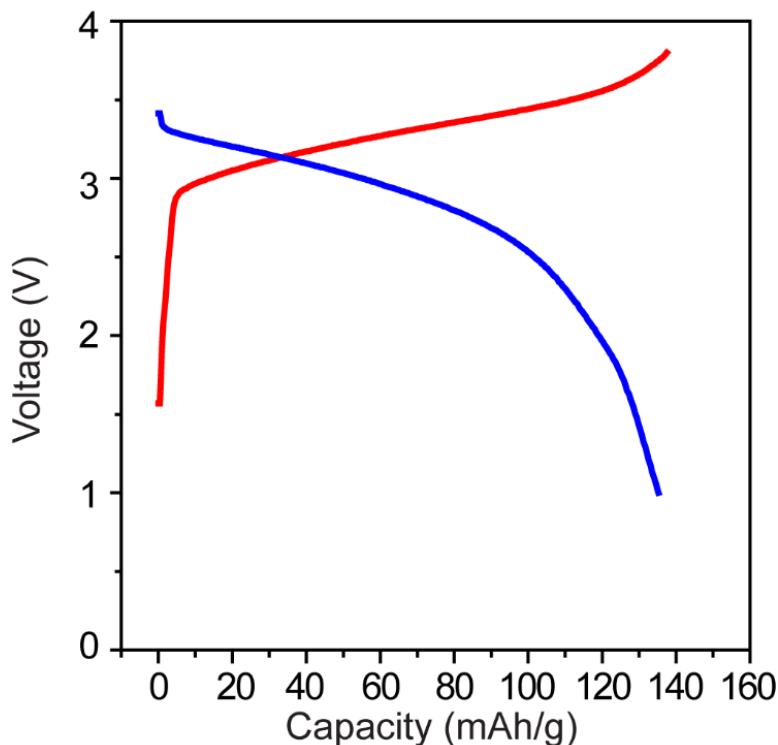


Figure 5.11. Voltage profile of the hybrid cell using gel electrolyte.

The RGO/CNT anode and integrated cathode (Al leaf and LFP cathode laminated on gel polymer electrolyte) were then assembled into a hybrid cell. The electrochemical performance of the hybrid cell is shown in figure 5.11 with the charge and discharge curves at 1 C. In the 1st cycle, the hybrid cell shows a charge capacity of 136 mAh/g and a discharge capacity of 135 mAh/g, with an initial coulombic efficiency over 99%. The anode was pre-lithiated before assembled into the hybrid cell to eliminate capacity loss due to solid electrolyte interface (SEI) formation. Figure 5b shows the EIS curve of the hybrid cell scanned from 1 MHz to 100 mHz with a perturbation amplitude of 50 mV. The

intersection of the impedance semi-circle was at $170.9 \text{ ohm}\cdot\text{cm}^2$, which is the charge transfer resistance.

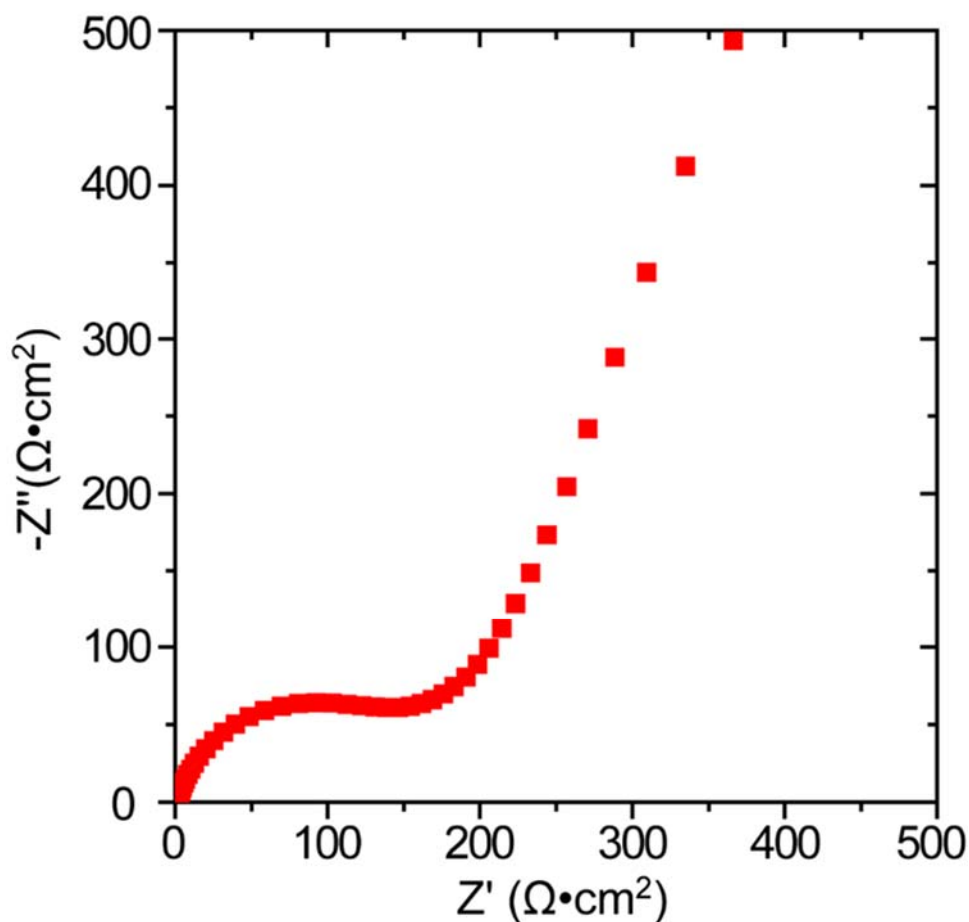


Figure 5.12. EIS curve of the hybrid cell using gel electrolyte.

In the following cycles, the capacity gradually increased and then stabilized at 140 mAh/g (figure 5.13). The hybrid cell exhibited an outstanding cycling performance over 100 cycles with over 97% capacity retention. The calculated energy density was about 180 Wh/kg, and the power density was about 218 W/kg, normalized to the total weight of electrodes and current collectors. Figure 5.14 gives a Ragone plot to compare different types of energy storage devices.¹⁹⁶ For conventional batteries, for example, state-of-the-art Li-ion batteries today have an energy density up to 240-260 Wh/kg and a power density of

about 150W/kg,¹⁹⁷ and commercial capacitors usually have a high power density of over 10 kW/kg but an energy density lower than 100Wh/kg.^{198,199} Our hybrid cell can simultaneously deliver an energy density of 180 Wh/kg with a high power density of 218 W/kg, which indicates that the hybrid design has a promising future for developing high power and energy density devices.

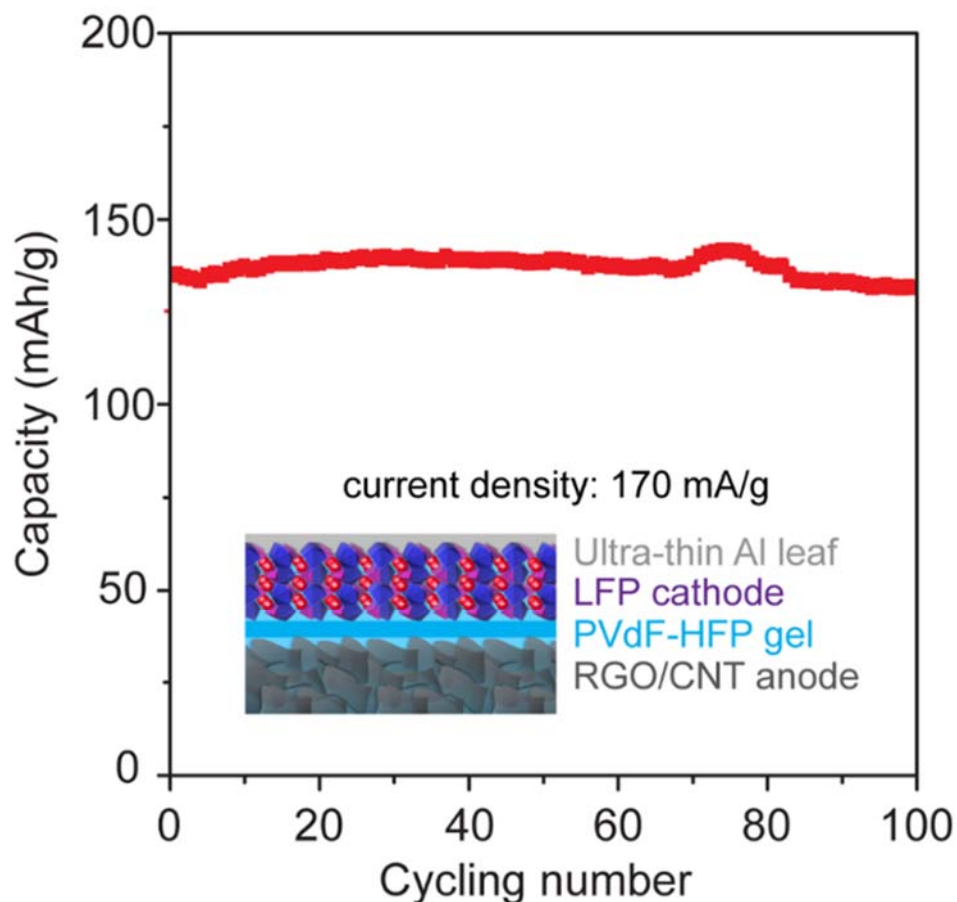


Figure 5.13. Cycling performance of the hybrid cell under a current density of 170 mA/g shows the great stability and high capacity of the hybrid device.

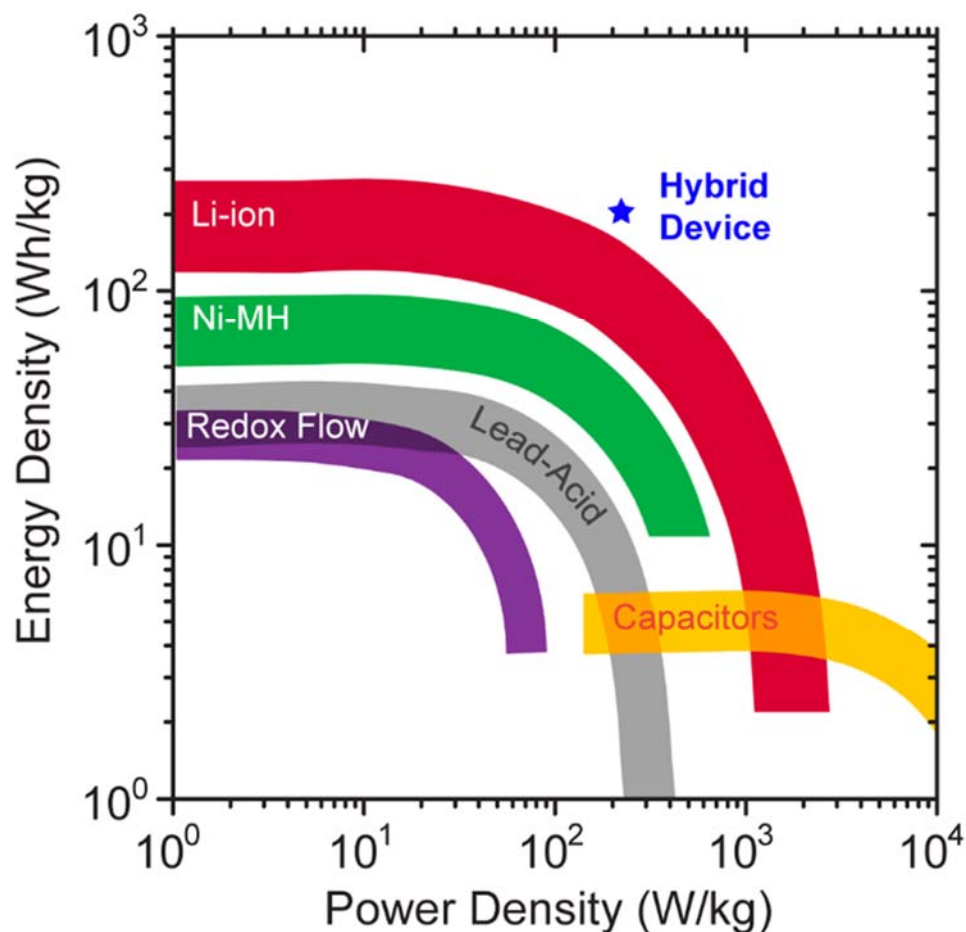


Figure 5.14. The Ragone chart shows energy density versus power density for various energy storage devices. Our hybrid devices exhibit both high energy density and power density of 180 Wh/kg and 218 W/kg, respectively.

5.5. Experimental Method

Materials Preparation. The gel electrolyte membrane was prepared by dissolving PVdF-HFP (Aldrich) powder into acetone ($\geq 99.9\%$, Aldrich) at room temperature under magnetic stirring. The solution was then dried on a petri-dish in an environmental chamber at room temperature with 50% humidity to remove acetone. Then the membrane was dried in vacuum at 60 °C to fully remove water. At last, several drops of 1M LiPF₆ ($\geq 99.99\%$,

Aldrich) dissolved in a mixed solvent of EC/DEC (EC, 99%, Aldrich; DEC, $\geq 99\%$, Aldrich) was dropped onto the dry gel electrolyte membrane and rested for 1 minute at room temperature in an argon filled glovebox. The remaining solvent on the gel membrane surface was wiped off to form the quasi-solid-state gel polymer electrolyte. The anode was prepared by filtering and drying RGO/CNT ink at 80 °C in vacuum. The ink was prepared by mixing RGO and CNT composite in distilled water with a weight ratio of 3:1, followed by multiple times of washing in sodium hydroxide (NaOH, $\geq 98.5\%$, Aldrich) solution to remove carboxylated carbon fragments.²⁰⁰ The RGO was prepared by dispersing graphene oxide (GO, prepared using a modified Hummer's method²⁰¹) in water, followed by a reduction reaction using urea ($\geq 98\%$, Aldrich), with a weight ratio of GO: urea=1: 12, at 95 °C for 30 hours to obtain high quality RGO flakes.^{187,202} The cathode was prepared by slurry coating LFP/PVdF/carbon black (weight ratio 8:1:1) directly onto the PE separator (in the half cell preparation), or the dry PVdF-HFP polymer membrane (in the hybrid cell preparation), followed by laminating a layer of ultra-thin Al leaf on top. The prepared cathode was dried in a vacuum oven at 50 °C for 10 hours to remove the remaining solvent in cathode slurry.

Materials Characterization. The SEM images of the electrolyte and electrodes were obtained using a Hitachi SU-70 Field Emission SEM. The EIS measurement was performed with a Biologic VMP3 Potentiostat equipped with impedance measuring modules. The EIS measurement for the electrolyte was performed on symmetric cells consisting of the gel electrolyte film (or PE separator in the reference group) between stainless steel plates as blocking electrodes. The EIS measurement for the hybrid cell was performed directly on a hybrid cell consisting of the integrated Al leaf/ LFP cathode, gel

electrolyte, and current-collector-free RGO/CNT anode. The cells were scanned from 1 MHz to 100 mHz with a perturbation amplitude of 50 mV. The cycling test was performed on a Biologic VMP₃ Potentiostat at room temperature in air.

5.6. Conclusion

In conclusion, we designed a high power, high energy density hybrid energy storage device by integrating a lightweight intercalative battery cathode, a capacitive carbon anode, and a quasi-solid-state gel polymer electrolyte to combine the merits of batteries and supercapacitors. Ultrathin Al leaf (1 μm) current collector for cathode and free of current collector for anode were designed to enhance the energy and power density of the hybrid device by reducing the inactive materials. Compared with conventional supercapacitors and lithium-ion batteries, our hybrid device exhibits great performance with both high energy density (180 Wh/kg) and high power density (218 W/kg), and enhanced safety imparted by the quasi-solid-state gel electrolyte, representing one new direction for developing next-generation energy storage devices with high energy density, high power density and high safety.

Chapter 6: Conclusions and Outlook

6.1. Thesis Summary

In this work we focused on developing nanomaterials and corresponding processing techniques to improve the comprehensive performance of solid state batteries from the perspectives of electrolyte design, cathode improvement, metallic anode modification, and full cell construction. Chapter 2 and Chapter 3 mainly focuses on the electrolyte design in terms of structure engineering, interface engineering, and ion transport mechanism. The metallic anode modification was briefly explored in the second half of Chapter 3. The cathode improvement was discussed in Chapter 4 with a focus on voltage elevation and core-shell structure construction. The full cell design was included in Chapter 5.

Chapter 2 explored approaches of improving the ionic conductivity through nanostructure designing. The first design introduced an ion-conductive 3D interconnected garnet framework synthesized using electrospun LLZO. A type of SCE was developed by infiltrating PEO-based SPEs into the garnet structure. The SCE achieved a high ionic conductivity of 2.5×10^{-4} S/cm at room temperature and exhibited many outstanding features including good chemical stability against lithium metal, good chemical stability against ambient air and moisture, nonflammability, and good mechanical strength. The second design is a nature-inspired garnet-wood composite electrolyte with a multiscale aligned mesoporous structure. The garnet-wood exhibits outstanding ionic conductivity of 1.8×10^{-4} S/cm at room temperature and 1.1×10^{-3} S/cm at 95 °C and great flexibility, benefiting from the aligned, low tortuosity structure.

Chapter 3 introduced techniques to negate the interfacial resistance between garnet and metallic anode through surface modification and anode alloying. A novel technique of

Al_2O_3 coating on garnet via ALD was developed. This method is widely applicable to many different surfaces with a vast selection of coating materials. The surface coating method provides a promising solution to lithium wetting issues through tuning the surface energy of garnet substrate. Chapter 3 also provided a systematical understanding about influential factors for the interfacial impedance in solid state energy storage devices using metallic anodes. A qualitative function was derived from the diffusivity-conductivity relation to indicate possible influencing factors including lithiation time, lithiation temperature, and surface coating thickness. In addition, factors like alloying effects, coating materials, and coating configurations were also studied through systematic experimental analysis.

Chapter 4 introduced how doping techniques could be employed to improve the voltage, capacity, and electrochemical stability of the high voltage cathode material $\text{Li}_2\text{FeMn}_3\text{O}_8$. The first technique utilizes halogen elements to dope LFMO. The resulting doped cathode exhibits better electrochemical stability and higher working voltage. The $\text{Li}_2\text{FeMn}_3\text{O}_{7.5}\text{Cl}$ cathode showed superior performance over the undoped LFMO with a specific discharge capacity of 130 mAh/g at 0.5C and a working voltage of 5V. The specific capacity was 2.6 times of the undoped LFMO capacity and approached 90% of the theoretical capacity. The second technique utilize aluminum to dope LFMO. The resulting doped cathode possesses a self-formed core-shell structure where the cathode is protected by a layer of ionically conductive lithiated Al_2O_3 . The doping successfully improved the stability of the LFMO cathode and also promoted its ionic conductivity.

Chapter 5 presented a high power, high energy density hybrid energy storage device consisted of a lightweight intercalative battery cathode, a capacitive carbon anode, and a quasi-solid-state gel polymer electrolyte. The supercapacitor-battery hybrid design

combines the merits of both system. In other words, the hybrid device was designed to achieve higher power density than batteries, and higher energy density than supercapacitors. Compared with conventional supercapacitors and lithium-ion batteries, the hybrid device exhibits great performance with both high energy density (180 Wh/kg) and high power density (218 W/kg), and enhanced safety imparted by the quasi-solid-state gel electrolyte.

6.2. Future Work

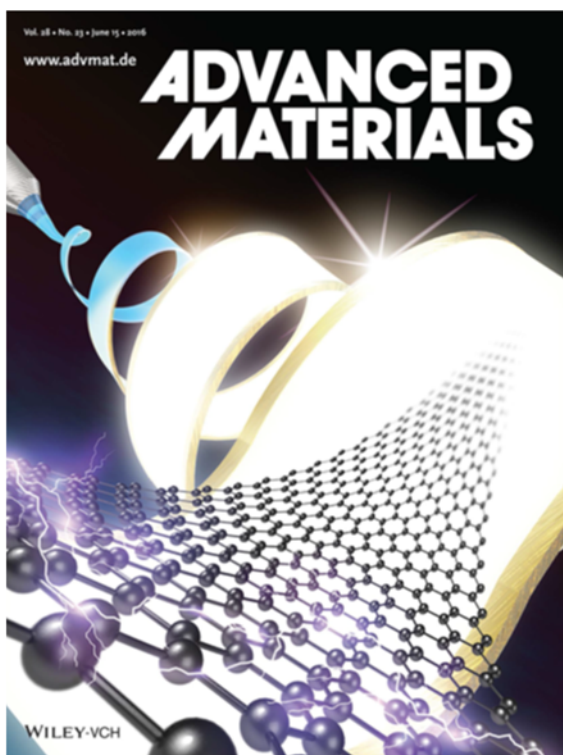
The research detailed in this thesis work has been published in several scientific journals and has the potential to impact the future development of garnet-based solid state energy storage technologies, especially the ones using metallic anodes. The techniques, materials, and mechanisms discussed in this thesis also have the potential to be further developed, improved, and further detailed, respectively. Following is a list of potential future work of the research.

- **Full cell fabrication using garnet-wood.** The garnet wood has been reported to exhibit outstanding ionic conductivity, great flexibility, and satisfying electrochemical stability. However, the application of garnet-wood in full cell has never been demonstrated. Therefore, it will be interesting to design and fabricate a flexible solid state battery using garnet-wood and lithium metal electrode.
- **Quantitative study and computational modeling of interfacial impedance's dependence on various factors.** Chapter 3 explored several key factors influencing the interfacial impedance. The equations derived are based on various assumptions that greatly simplified the question. Though the equation can be used to qualitatively study the critical factors influencing the interfacial impedance, a quantitative analysis or even computational

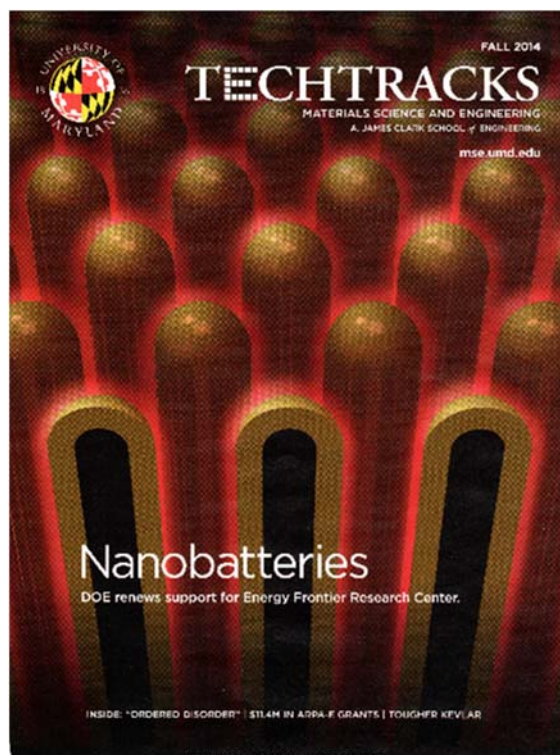
modeling will be of great help to further understand the ion transport behaviors through the interfaces and within the coating layer. It will also be of great help to determining processing parameters for industrialized mass production of the solid state batteries using garnet based SSEs and lithium metal anodes.

Appendices I. Scientific Visualizations

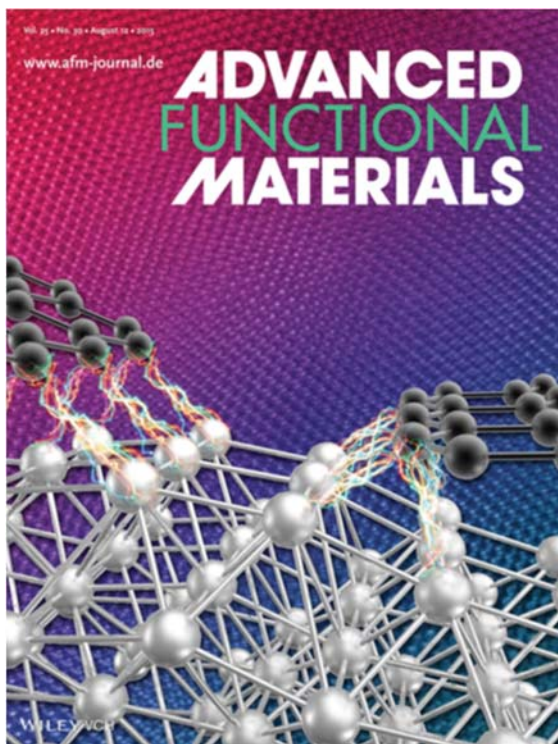
Scientific visualization is an interdisciplinary branch of science. Nowadays, it has become an important tool for scientific researches in all fields. With the help of scientific visualization, devices, structures, and even abstract scientific theories can now be conveyed, presented, and understood vividly through visual effects. Along with my PhD studies, I developed my skill in scientific visualizations, including 3D modeling, schematic illustration, data visualization, and cover art designing. Following is a selected list of published cover arts during my PhD studies.



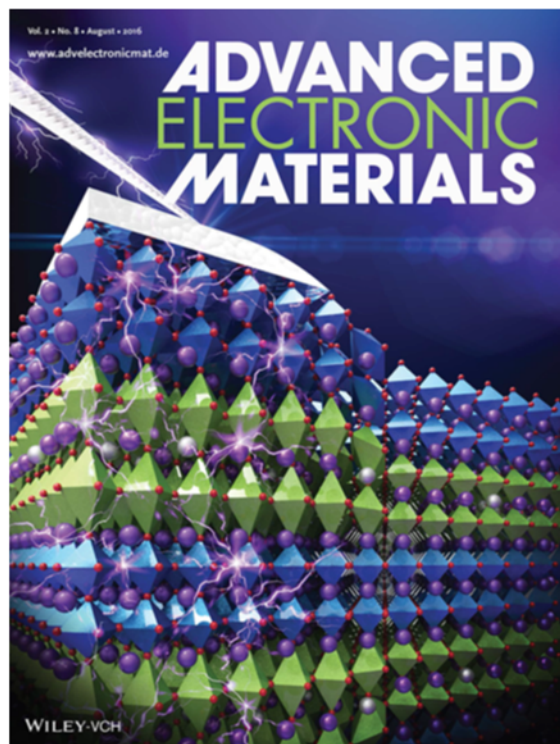
Advanced Materials. 28.23 (2016)



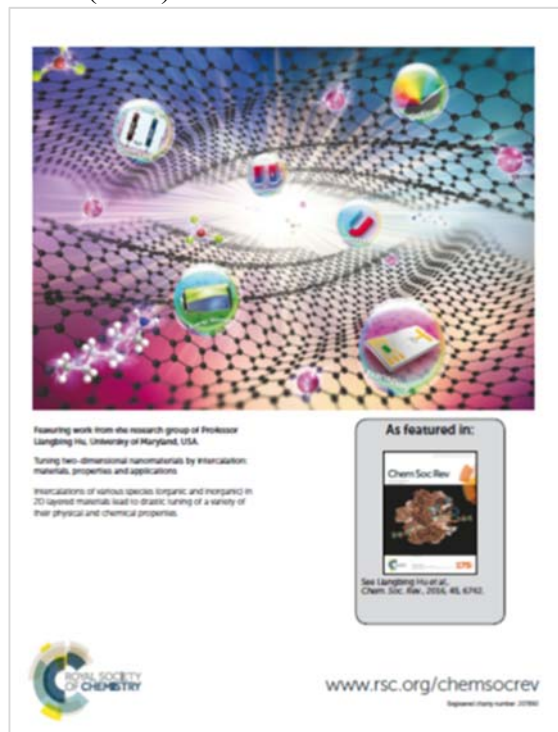
TechTracks. Fall (2014)



Advanced Functional Materials.
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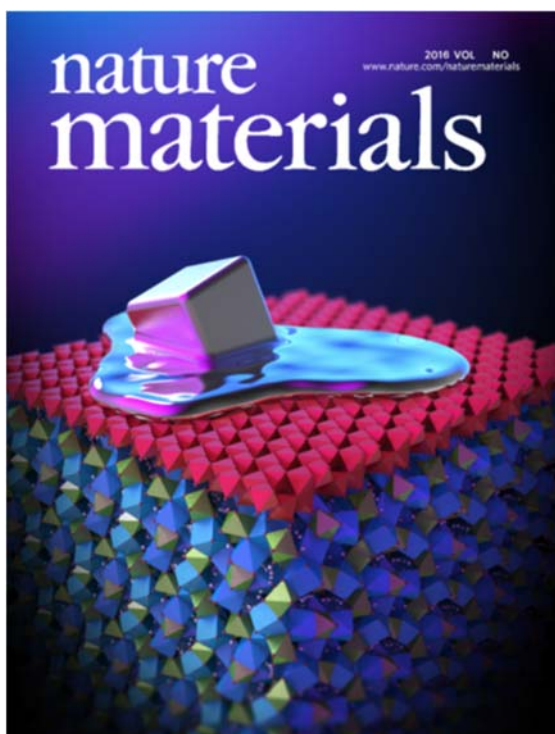
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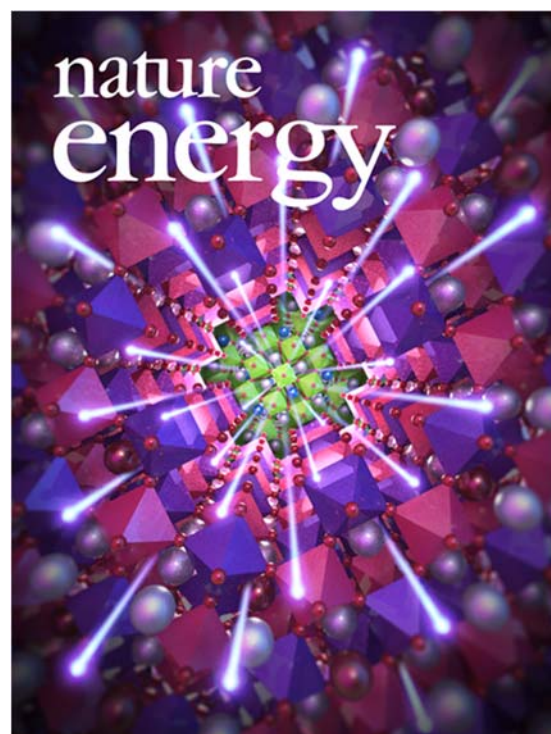
Chem. Soc. Rev. 45 (2016)



Chemistry of Materials. 28.11 (2016)



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Nature Energy. Submitted



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