

COLD SINTERING OF OXIDE-BASED LLTO AND LLZO SOLID-STATE
ELECTROLYTES AND THEIR INTEGRATION INTO LITHIUM METAL
BATTERIES

by

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B.S., Mechanical Engineering, Yıldız Technical University, 2014

M.S., Mechanical Engineering, Yıldız Technical University, 2018

Submitted to the Institute for Graduate Studies in
Science and Engineering in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Graduate Program in Mechanical Engineering
Boğaziçi University

2025

ACKNOWLEDGEMENTS

The experimental work presented in this thesis was conducted at the laboratories of Boğaziçi University, Penn State University, and the Massachusetts Institute of Technology (MIT). I am deeply grateful to my supervisor, Prof. Nuri Ersoy, and co-supervisor, Dr. Gülin Vardar, for their valuable comments, guidance, and continued support throughout my research. Their insightful feedback and encouragement have been instrumental in shaping the direction and quality of this work. I am especially grateful for their patience and mentorship, which have deeply influenced both my academic and personal development. The trust they placed in me and their constructive criticism helped me overcome the challenges and refine my ideas, making this thesis possible. Their unwavering support has been a source of motivation and inspiration throughout my journey.

It is a pleasure to acknowledge the support of my advisor at Penn State University, Prof. Enrique Gomez, who gave me the opportunity to conduct research at world-class facilities and provided invaluable guidance and unwavering support throughout my visiting period. Our meetings were not only instrumental in shaping the research conducted, but were also filled with insightful and directive discussions that greatly enhanced my understanding of the subject. I would also like to express my gratitude for the financial support provided by the U.S. National Science Foundation under Award Number 2134643. Additionally, this work was supported in part by the U.S. Department of Defense, Army Research Laboratory, and Army Research Office under grant number W911NF-23-2-0229.

I would like to express my sincere gratitude to Dr. Yi-Chen Lan, currently a postdoctoral scholar at Argonne National Laboratory, for her invaluable guidance and support during my research at Penn State University. She patiently taught me how to use a wide range of experimental techniques and equipment, always maintaining a friendly attitude. Dr. Lan was also extremely supportive, always available to answer

my questions and provide guidance whenever I faced challenges. Her outstanding research and advice played a crucial role in the success of my experiments and helped lay the foundation for my work.

I would like to extend my sincere thanks to my advisor at MIT, Prof. Bilge Yildiz, for the invaluable opportunity to carry out research at the Laboratory for Electrochemical Interfaces under her esteemed mentorship. My time at MIT as a visiting Ph.D. student was an intellectually enriching experience that allowed me to engage in cutting-edge research and benefit from a vibrant, interdisciplinary academic environment. Working in such a highly diverse and collaborative environment significantly broadened my scientific perspective and contributed meaningfully to both my personal and professional development. Her guidance and the stimulating research atmosphere at MIT played a key role in shaping the direction and quality of this thesis. I gratefully acknowledge the contributions of Dr. Younggyu Kim and Subhash Chandra for their generous assistance in teaching me the synthesis of LLZO and LLTO solid electrolytes via the solid-state reaction method. Their guidance and hands-on support were instrumental in helping me gain practical experience and confidence in the synthesis process.

I would also like to express my sincere appreciation to my thesis progress committee members, Assoc. Prof. Oktay Demircan and Assist. Prof. Sertan Alkan, for their thoughtful evaluations and valuable insights throughout my research. Their constructive feedback on my progress reports played a vital role in strengthening both the scientific quality and clarity of this thesis. I acknowledge the support provided by the TUBITAK BIDEB 2214-A and 2211-C research programs under Project Codes 1059B142200202 and 1649B032200187, as well as the funding from Boğaziçi University BAP under grant number 19705D. Additionally, I acknowledge the support provided by the Fulbright Ph.D. Dissertation Research Grant.

ABSTRACT

COLD SINTERING OF OXIDE-BASED LLTO AND LLZO SOLID-STATE ELECTROLYTES AND THEIR INTEGRATION INTO LITHIUM METAL BATTERIES

Oxide-based solid electrolytes such as perovskite-type $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) and garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) are promising candidates for next-generation solid-state lithium batteries due to their high ionic conductivities and stability. However, the practical application of these materials is limited by the requirement for high-temperature sintering and challenges in electrode–electrolyte integration. In this thesis, the cold sintering process was investigated as a low-temperature fabrication method for LLTO and LLZO composites; densification was achieved below 150 °C within 30 minutes by using transient solvents and moderate pressure. By optimizing sintering parameters such as solvent type, particle size, and binder-salt content, ionic conductivities greater than $10^{-4} \text{ S cm}^{-1}$ were attained. Co-sintering of LLTO with LiFePO_4 (LFP) and LLZO with LiCoO_2 (LCO) cathodes at approximately 100 °C was successfully demonstrated without any structural or chemical degradation. To prevent instability between LLTO and lithium metal, a PVDF membrane wetted with a small amount of LiPF_6 -based electrolyte was employed, effectively suppressing Ti^{4+} reduction and stabilizing the interfacial resistance. The fabricated Li/PVDF/LLTO/LFP full cells exhibited discharge capacities of 151 mAh g^{-1} and 135 mAh g^{-1} at current rates of 0.1 C and 0.2 C, respectively. Similarly, Li/PPC-LiFSI/LLZO/LCO cells demonstrated discharge capacities of 158 mAh g^{-1} and 141 mAh g^{-1} at 0.1 C and 0.2 C, respectively. Furthermore, the recyclability of LLTO composites through multiple reprocessing cycles was confirmed. Even after ten cycles, LLTO maintained its high crystallinity and phase purity, exhibiting a high ionic conductivity of approximately $\sim 2 \times 10^{-4} \text{ S cm}^{-1}$.

ÖZET

OKSİT ESASLI LLTO VE LLZO KATI HAL ELEKTROLİTLERİNİN SOĞUK SİNTERLENMESİ VE LİTYUM METAL PİLLERE ENTEGRASYONU

Perovskit tipi $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) ve garnet tipi $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) gibi oksit esaslı katı elektrolitler, yüksek iyonik iletkenlikleri ve kararlılıkları sayesinde yeni nesil katı hâl lityum pilleri için umut verici adaylardır. Ancak bu malzemelerin pratik kullanımı, yüksek sıcaklıkta sinterleme gereksinimi ve elektrot-elektrolit entegrasyonundaki zorluklar nedeniyle sınırlanmaktadır. Bu tez kapsamında, LLTO ve LLZO kompozitleri için düşük sıcaklıkta bir üretim yöntemi olarak soğuk sinterleme süreci araştırılmış; geçici çözücüler ve orta seviyede basınç kullanılarak, 150°C 'nin altında ve 30 dakika içinde yoğunlaştırma sağlanmıştır. Sinterleme parametreleri, çözücü türü, partikül boyutu ve bağlayıcı-tuz içeriği optimize edilerek $10^{-4} \text{ S cm}^{-1}$ 'den büyük iyonik iletkenlikler sağlanmıştır. LLTO'nun LiFePO_4 (LFP) ve LLZO'nun LiCoO_2 (LCO) katotlarıyla yaklaşık 100°C 'de birlikte sinterlenmesi, yapısal veya kimyasal bir bozulmaya uğramadan başarıyla gerçekleştirilmiştir. LLTO ile lityum metal arasındaki kararsızlığı önlemek amacıyla, az miktarda LiPF_6 bazlı elektrolitle ıslatılmış bir PVDF membran kullanılmış; böylece Ti^{4+} indirgenmesi etkili bir şekilde bastırılmış ve arayüz direnci kararlı hâle getirilmiştir. Üretilen Li/PVDF/LLTO/LFP tam hücreleri, sırasıyla 0.1 C ve 0.2 C akım hızlarında 151 mAh g^{-1} ve 135 mAh g^{-1} boşalma kapasiteleri sunmuştur. Benzer şekilde, $\text{Li/PPC-LiFSI/LLZO/LCO}$ hücreleri de 0.1 C ve 0.2 C akım hızlarında sırasıyla 158 mAh g^{-1} ve 141 mAh g^{-1} boşalma kapasiteleri sergilemişlerdir. Ayrıca, LLTO kompozitlerinin geri dönüştürülebilirliği de doğrulanmıştır. On döngü sonrasında bile LLTO, yüksek kristal yapısını ve faz saflığını korumuş; $\sim 2 \times 10^{-4} \text{ S cm}^{-1}$ seviyesinde yüksek iyonik iletkenlik sergilemiştir.

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LIST OF SYMBOLS

A	Area
C	Capacitance
d	Spacing Between the Crystal Planes
E	Specific Energy
E_a	Activation Energy
f	Frequency
I	Current
k_B	Boltzmann Constant
L	Inductance
M_w	Molecular Mass
Q	Constant Phase Element
Q_{dis}	Specific Capacity
Q_{th}	Theoretical Capacity
R	Resistance
t	Thickness
T	Temperature
V	Voltage
W	Warburg Impedance
Z	Impedance
λ	Wavelength
ω	Angular frequency
ϕ	Phase Angle
σ	Warburg Coefficient
σ_{ion}	Ionic Conductivity
Θ	Incident Angle

LIST OF ACRONYMS/ABBREVIATIONS

AC	Alternating Current
ACN	Acetonitrile
ALD	Atomic Layer Deposition
A-LLTO	Aluminum Doped LLTO
ASSBs	All-solid-state Batteries
ATR	Attenuated Total Reflection
CCD	Critical Current Density
CE	Coulombic Efficiency
CPE	Constant Phase Element
CSP	Cold Sintering Process
DC	Direct Current
DEC	Diethyl Carbonate
DI	Deionized Water
DMC	Dimethyl Carbonate
DME	Dimethoxyethane
DMF	N, N-dimethylformamide
DMSO	Dimethyl Sulfoxide
EC	Ethylene Carbonate
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ETD	Everhardt-Thornley Detector
FE-SEM	Field Emission Scanning Electron Microscope
FTIR	Fourier-transform Infrared
FWHM	Full Width at Half Maximum
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LAGP	$\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$
LATP	$\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$
LCO	LiCoO_2

LFP	LiFePO_4
LIBs	Lithium-ion Batteries
LiSICON	Li Super Ionic Conductor
LiTFSI	Lithium bis(trifluoromethane sulfonyl)imide
LLTO	Lithium Lanthanum Titanate
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LLZTO	$\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$
LMO	LiMn_2O_4
Ni-Cd	Nickel-Cadmium
NCM	$\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$
NMC	LiNiMnCoO_2
NMC622	$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$
Ni-MH	Nickel-Metal Hydride
NMP	N-methyl-2-pyrrolidone
PEO	Polyethylene Oxide
PET	Polyethylene Terephthalate
PP	Polypropylene
PPC	Polypropylene Carbonate
PVDF	Polyvinylidene Fluoride
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
SEM	Scanning Electron Microscopy
SPEs	Solid Polymer Electrolytes
SSEs	Solid-state Electrolytes
STEM	Scanning Transmission Electron Microscopy
TEGDME	Tetraethylene Glycol Dimethyl Ether
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XANES	X-ray Absorption Near Edge Structure
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

1. INTRODUCTION

Due to the increasing environmental issues arising from fossil fuel resources, such as global warming and air pollution, there is a strong emphasis on transforming the conventional infrastructure of fossil fuel-driven power plants by replacing them entirely or integrating renewable-based energy sources. In addition to power plants, transportation is also one of the leading sources of greenhouse gas pollution. The combustion of gasoline or diesel in vehicles results in substantial emission of carbon dioxide (CO_2) into the atmosphere, underscoring the urgent need to reduce vehicle emissions. In addressing this challenge, a practical approach involves switching from conventional gasoline or diesel vehicles to electric alternatives. This strategic change mitigates the environmental impact and promotes a sustainable transportation paradigm. One of the primary hurdles facing electric vehicles is the design and manufacture of efficient, reliable, durable, and economically viable battery systems. Consequently, the paramount aspiration of the scientific community and industrial enterprises lies in the production of batteries that exhibit high energy density and robustness while simultaneously optimizing cost efficiencies [1].

1.1. Rechargeable Batteries

The swift evolution of technology has led to a diverse spectrum of advanced high-tech devices on the market today. This assortment encompasses an array of versatile innovations, such as smartphones, tablet computers, remotely operated cleaners, drones, and underwater vehicles. One commonality among these technologies is that they are designed with their energy storage systems, enabling them to work without requiring electrical connections. However, electrochemical energy storage systems, or batteries, have not undergone the same rapid rate of change as many other technological innovations. For more than a century, lead-acid batteries remained the primary energy storage technology, with slight notable improvement in energy density, even with significant advancements in their applicability. The widespread use of modern

nickel metal hydride batteries began in the early 1990s and dominated the battery market until the subsequent commercialization of lithium-ion counterparts.

Lithium-ion batteries dominate the portable market in numerous applications due to their high energy density. The evolution of rechargeable batteries can be categorized into three distinct stages: industrial age, portable age, and mobile age, as illustrated in Figure 1.1. The industrial era began with the invention of lead-acid batteries, followed by nickel-zinc and nickel-iron batteries, sealed nickel-cadmium batteries, and nickel-metal hydride batteries. The energy density of the first batteries remained consistently below 50 Wh/kg throughout the industrial age. The second era of battery evolution is known as the portable era, thanks to the invention of the lithium-ion battery, which paved the way to produce modern devices designed for easy mobility and operation by their users. The transition from the industrial to the portable age began with the advent of lithium-ion batteries in the commercial market. Initially, these batteries had an energy density of about 100 Wh/kg. As the first decade of the 21st century approached its end, the energy density of lithium-ion batteries increased substantially, effectively doubling the energy capacity of battery cells. The third distinct period in the development of rechargeable batteries is known as the mobile age, covering the current period in which the energy density of lithium-ion batteries has surpassed the threshold of 250 Wh/kg. This advancement in battery technology has paved the way for the mass production of electric vehicles [2].

In the following subsection, we will present the inherent properties of various rechargeable batteries. This analysis highlights the key advantages that have enabled lithium-ion batteries to surpass earlier secondary battery technologies in multiple applications, from wearable electronics to the automotive industry. The selection of a suitable battery depends on several critical factors, including specific energy, operating voltage, cycle life, susceptibility to memory effects, self-discharge rate, charging efficiency, cost, and recyclability [3].

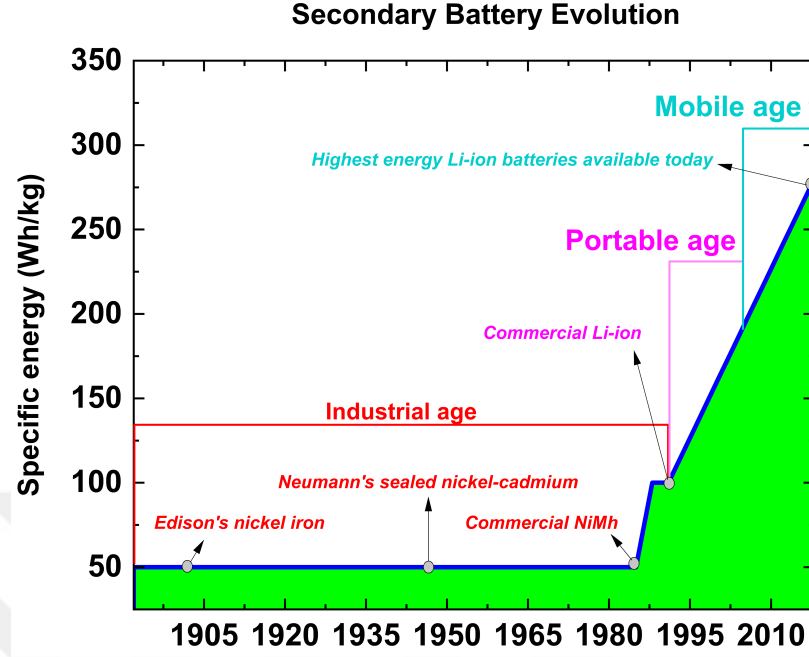


Figure 1.1. The history of the evolution of battery technologies (Plotted according to the information given in [2]).

1.1.1. Rechargeable Batteries Before Lithium-Ion Technology

The lead-acid battery, initially conceptualized by the French physicist Gaston Plante in 1859, is the first commercial secondary battery capable of undergoing numerous recharging cycles [2]. The anode and cathode compartments are made of lead and lead oxide and immersed in a concentrated sulfuric acid solution. Lead-acid battery technology continues to find applications in various fields due to its reasonable price, low self-discharge rate, efficient performance at low temperatures, and high discharge rates [4]. Although possessing merits, lead-acid batteries exhibit inherent limitations such as a limited lifespan (fewer than 500 cycles), elevated toxicity, and slow charging rates. With a gravimetric energy density below 50 Wh/kg, lead-acid battery technology yields a bulky battery pack, significantly restricting its practical use [5].

Developed by the Swedish scientist Waldemar Jungner in 1899, the nickel-cadmium (Ni-Cd) battery features anode and cathode compartments made of Cd and NiO(OH),

respectively. In addition, a liquid electrolyte of KOH alkaline solution is used. Compared with lead-acid batteries, nickel-cadmium batteries show improved ability to withstand extended operational cycles, accompanied by a noticeable increase in gravimetric energy densities. Furthermore, Ni-Cd cells can function efficiently within the temperature range of -20 to 60 °C, exhibiting no discernible loss of efficiency [6]. However, a notable drawback of this particular type of battery cell is its gradual loss of capacity. This decline becomes evident when the battery undergoes recharging after an incomplete discharge cycle, a phenomenon known as the memory effect. Furthermore, cadmium in nickel-cadmium batteries can lead to significant environmental issues. The toxicity of cadmium complicates the disposal of residues from cadmium-based components [6].

Stanford Ovshinsky, a distinguished American scientist, obtained the patent for the nickel-metal hydride (Ni-MH) battery in 1986. The structure of the Ni-MH battery closely resembles that of the Ni-Cd battery, with the distinction that the hydrogen-absorbing alloy replaces the cadmium anode in the Ni-MH battery cell. This modification led to an increase in the gravimetric energy density of 70 Wh/kg and a capacity of 2 to 3 times higher than that of Ni-Cd batteries of equivalent size [7]. In contrast, high self-discharge rates have emerged as a significant challenge in Ni-MH battery technology. The advancement of Li-ion batteries with higher gravimetric energy densities has consequently displaced Ni-MH battery technology from the market [8].

1.1.2. Lithium-Ion Batteries

Lithium-ion technology, introduced to the battery market by Sony Corporation in 1991, currently holds the leading position in battery technology. Lithium-ion batteries offer higher gravimetric and volumetric energy densities than other secondary batteries, making them highly valuable in small- and large-scale applications, introducing a new era of portable electronics [9]. Following the discovery of lithium-ion batteries, conventional secondary batteries experienced a decline in acceptability. The features listed below play a pivotal role in the success of lithium-ion batteries:

- Lithium-ion batteries are noticeably lighter than rechargeable batteries of the same size due to the inherent lightweight nature of lithium [10].
- The gravimetric energy density of lithium-ion batteries exceeds the threshold of 250 Wh/kg, which is significantly higher than that of Ni-MH (~ 100 Wh/kg). In addition, they can store six times as much energy as lead-acid batteries of the same size [11].
- High self-discharge rates are a significant issue in Ni-Cd and Ni-MH batteries; however, the self-discharge rate of lithium-ion batteries is relatively low. Furthermore, Li-ion batteries do not exhibit any memory effect [4].
- In contrast to alternative rechargeable batteries, lithium ion batteries have a longer operating life, sustaining around 2,000 cycles without a noticeable decrease in capacity [12].

Like other battery types, lithium-ion batteries consist of three layers: cathode, electrolyte, and anode, interleaved between current collectors. Figure 1.2 illustrates how a typical lithium-ion battery functions. Lithium exhibits reactivity as a metal when in its pure state; however, it assumes a significantly more stable nature when incorporated into a metal oxide compound. Lithium cations and electrons are formed when external factors, such as electrical current, induce the detachment of lithium atoms from the metal oxide. The key lies in providing two distinct pathways for the movement of lithium cations and electrons, achieved by placing an electrolyte layer between the electrodes. Hence, an optimal electrolyte is characterized by an ionic conductivity that exceeds 10^{-3} S/cm while simultaneously demonstrating negligible electronic conductivity, typically of the order of 10^{-12} S/cm [13]. Thus, lithium cations move through the electrolyte layer, while electrons are compelled through an external circuit, reaching the opposite electrode compartment during the charging process. Upon removal of the power source and connection of the load during discharge, both lithium cations and electrons revert to their initial state by moving in the opposite direction. Reduction (gain of electrons) and oxidation (loss of electrons) reactions occur in the cell's cathode and anode compartments, respectively. These two processes collectively constitute a redox reaction (reduction-oxidation) [2].

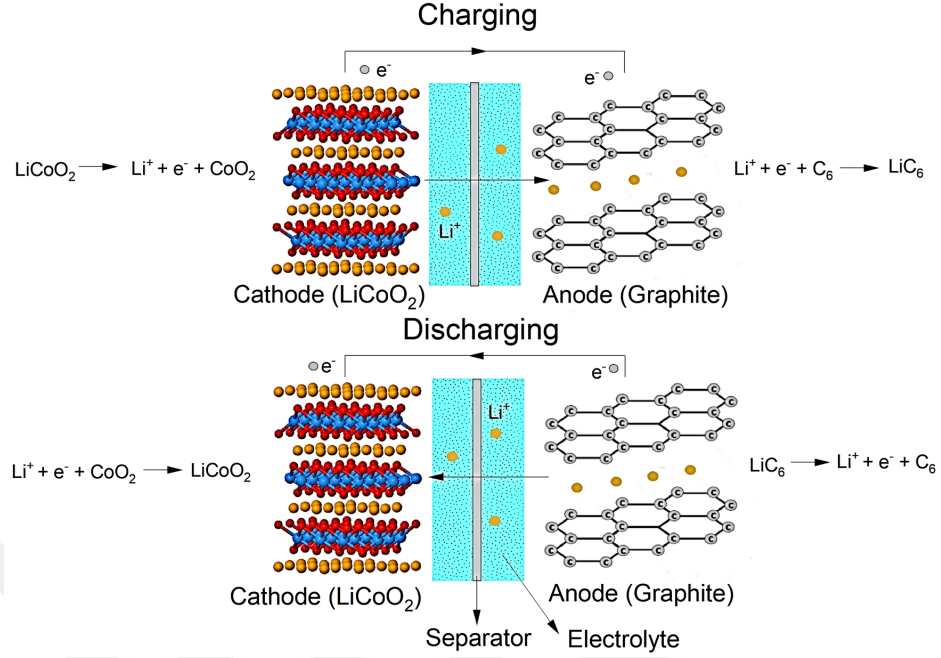


Figure 1.2. The fundamental operating mechanism of a standard lithium-ion battery.

1.2. Solid-State Electrolytes in Lithium-Ion Batteries

The electrolyte within conventional lithium-ion batteries (LIBs) comprises lithium salts dissolved in an organic solvent, forming a critical component that facilitates ion transfer, allowing battery energy storage and release [14]. As LIBs approach the upper limits of the energy density using conventional cathode and anode materials, such as graphite, there is a growing demand for advanced electrode materials to achieve the necessary energy density in next-generation electronic devices [15].

Lithium metal anodes are emerging as a promising solution to meet the high energy requirements of these next-generation devices due to their inherent superior properties, including ultrahigh capacity (3860 mAh g^{-1}) and lowest negative electrochemical potential (-3.040 V versus the standard hydrogen electrode) [16–19]. However, the use of lithium metal as a lithium-ion battery anode raises safety concerns mainly due to the formation of needle-like dendrites between lithium metal and the liquid electrolyte, which result from the uneven dissolution of lithium metal and cause a short

circuit of the battery [20–22]. Furthermore, any chemical or thermal degradation in the separator can trigger uncontrolled reactions at the electrode-electrolyte interface, which can potentially cause excessive heat generation and lead to explosions and fires [23,24]. The flammability of liquid electrolytes has led to significant research in the scientific community on developing all-solid-state batteries (ASSBs) for a wide range of applications [25,26]. ASSBs hold great promise to power next-generation devices, especially electric vehicles, due to their high energy density, reduced risk of fire and explosions, and improved electrochemical and thermal stability [27–29].

Solid-state electrolytes (SSEs) consist of two main types: organic polymer-based electrolytes and inorganic ceramic-based electrolytes [30]. Solid polymer electrolytes (SPEs) exhibit excellent flexibility, ease of fabrication, good electrochemical stability, and interfacial compatibility with existing anode and cathode materials due to their intrinsic material properties. However, the primary obstacle to the practical use of SPEs lies in their limited ionic conductivity, which is lower than $10^{-5} \text{ S cm}^{-1}$ at room temperature [31,32].

Inorganic ceramic-based solid electrolytes can be classified into two main categories: sulfide-based and oxide-based electrolytes. Sulfide solid electrolytes contain sulfur anions and can exist in either a crystalline or glassy structure. The ionic conductivity of glassy sulfide electrolytes varies widely, ranging from 10^{-7} to 10 mS cm^{-1} , with low activation energies between 0.15 and 0.35 eV [33,34]. The most common crystalline sulfide electrolytes are Li-argyrodites and thio-LiSICON (Li Super-Ionic Conductor) materials. Argyrodites ($\text{Li}_6\text{PS}_5\text{X}$, where $\text{X} = \text{Cl, Br, or I}$) show great promise because of their high ionic conductivities exceeding 1 mS cm^{-1} , good interfacial stability, and potential for large-scale manufacturing [35]. Thio-LiSICONs, with the chemical formula $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($\text{M} = \text{Si, Ge, Sn}$), exhibit high ionic conductivities exceeding 10 mS cm^{-1} and a low activation energy range of 0.2 to 0.3 eV [36–38]. The elastic modulus of sulfide-based electrolytes is generally lower than that of oxide-based electrolytes, remaining below 50 GPa. Their lower stiffness and hardness offer both advantages and challenges. For example, these properties facilitate densification

via cold pressing without the need for high temperatures, offering a cost-effective and commercially viable production method. However, increased stiffness is required to inhibit dendritic growth at the lithium metal anode interface during battery operation [39–41]. The main bottleneck of sulfide electrolytes is their instability in air, as exposure to moisture triggers undesired reactions and the production of toxic H_2S gas. Poor air stability requires the handling of sulfide-based electrolytes in dry atmospheres, complicating large-scale production [42–44].

The family of oxide-based electrolytes includes perovskite, garnet, NASICON, and LiSICON, each of which has a unique crystal structure and has its pros and cons. Garnet-type electrolytes exhibit superior ionic conductivity as a result of their cubic crystal structure and demonstrate exceptional chemical and electrochemical stability with lithium metal anodes, making them a promising candidate for solid-state battery applications. NASICON electrolytes, characterized by their three-dimensional structure, exhibit outstanding atmospheric stability and remarkably high ionic conductivity. LiSICON electrolytes are recognized for their strong thermal stability, while perovskite-type electrolytes offer excellent air stability and outstanding bulk ionic conductivity [45].

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is the most widely recognized garnet-type electrolyte, valued for its wide electrochemical stability window, high ionic conductivity reaching 9.28 mS cm^{-1} through doping strategies, exceptional stiffness of 150 GPa, negligible electronic conductivity, and superior thermal stability [46]. LLZO displays both cubic and tetragonal phases. As the sintering temperature increases, the structure undergoes a transition from tetragonal to cubic. The cubic phase, which exhibits ionic conductivity nearly two orders of magnitude higher than that of the tetragonal phase, is therefore preferred for applications that demand superior conductivity [47, 48]. LLZO has a wide electrochemical stability window, typically ranging from 0 to 5 V vs. Li / Li^+ , which makes it suitable for use in high-voltage solid-state batteries. LLZO readily reacts with water and carbon dioxide, resulting in the formation of Li_2CO_3 and LiOH on its surface. The contamination layers impede ionic conductivity at the elec-

trode/LLZO interfaces, complicating its direct handling in air [49]. Inaguma et al. [50] developed the perovskite-type lithium lanthanum titanate (LLTO) with the general formula $\text{Li}_{3x}\text{La}_{(2/3-x)}\text{TiO}_3$. The tetragonal perovskite exhibits a bulk ionic conductivity of 1 mS cm^{-1} , but its total ionic conductivity is approximately two orders of magnitude lower ($2 \times 10^{-2} \text{ mS cm}^{-1}$) due to the high resistance at the grain boundaries. It shows good stability in air and against moisture, high voltage stability, and a high stiffness of 200 GPa, making it an attractive candidate for next-generation batteries. However, Ti^{+4} reduces to Ti^{+3} and even lower oxidation states when in contact with lithium metal, which dramatically increases the electrical conductivity of the solid electrolyte, thus limiting the applicability of LLTO despite its superior properties [51]. Figure 1.3 illustrates the crystal structures of oxide-based electrolytes.

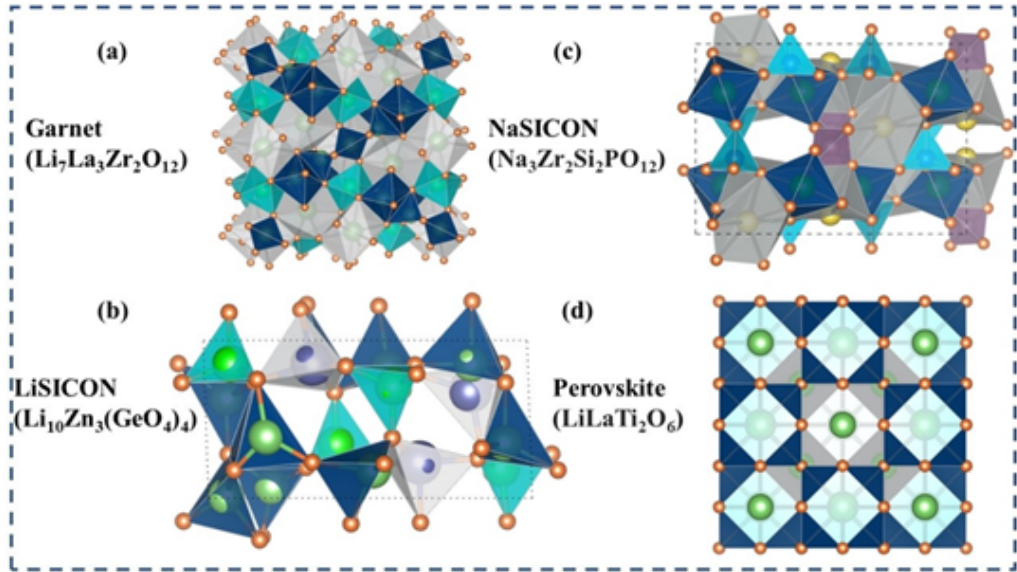


Figure 1.3. Crystal structures of oxide-based electrolytes: (a) Garnet, (b) NaSICON, (c) LiSICON, and (d) Perovskite [45].

1.3. Cathode Materials in Lithium-Ion Batteries

A cathode is the electrode in a battery where reduction occurs during charging and oxidation occurs during discharging, allowing lithium ions to move between

electrodes through the electrolyte, which is a key component in determining battery cell performance. The main commercial cathode materials have three different crystal structures: layered oxides, spinels, and olivines, as shown in Figure 1.4. Layered structures are known for their high capacity, making them attractive for various applications. However, they are prone to thermal instability and voltage degradation, which can significantly affect their performance. At elevated temperatures, these materials can undergo structural changes, leading to a loss in capacity and overall efficiency. Furthermore, the electrochemical processes occurring within the structure can induce crystal rearrangements, further exacerbating the decline in voltage and stability over time. These factors highlight the need for careful consideration of the thermal and electrochemical behavior of layered materials in practical applications [52].

Spinel materials are recognized for their stability but tend to fall short in capacity. Olivines are particularly notable for their excellent safety profile, attributed to the robust P–O bonds that effectively prevent thermal runaway, a critical feature in improving the reliability of energy storage systems. Moreover, olivine-based compounds are renowned for their outstanding cycle life, with some variants capable of enduring thousands of charge-discharge cycles, making them ideal for long-term use. Olivines are also environmentally friendly, consisting of abundant and nontoxic elements, which contribute to their sustainability. However, despite their many advantages, the energy density of olivine materials tends to be lower than that of certain layered materials, which poses a limitation for applications where high energy density and extended range are paramount. This trade-off between safety, cycle life, and energy density must be carefully evaluated in the context of specific application requirements [53, 54].

LiCoO_2 (LCO) is a well-known cathode material, with a theoretical capacity of 274 mAh g^{-1} [55]. LCO has a layered crystal structure in which one cobalt atom is surrounded by six oxygen atoms arranged in octahedral sites, with alternating layers of cobalt oxide and lithium. The oxidation state of Co alternates between $3+$ and $4+$ during the charging and discharging processes, facilitating reversible redox reactions in the electrochemical system. Despite its high energy density, LCO suffers from poor

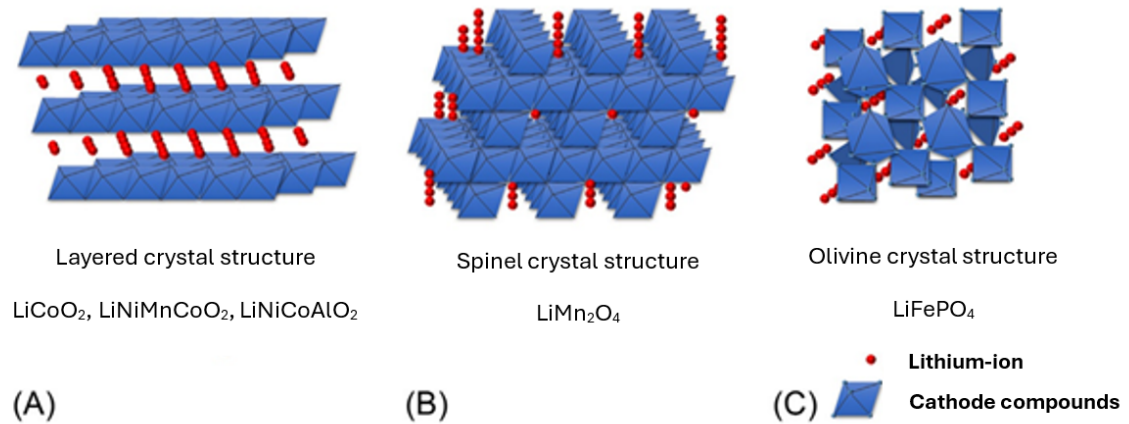


Figure 1.4. Illustration of three different cathode crystal structures commonly used in commercial batteries: (a) layered oxides, (b) spinels, and (c) olivines [2].

cyclic stability due to structural instabilities [56]. Lithium nickel manganese cobalt oxide, commonly known as LiNiMnCoO₂ (NMC), is a relatively new layered oxide material that has garnered significant interest in lithium-ion battery applications due to its high energy density, low cost, and high voltage capabilities. Using a combination of different transition metals in NMC provides distinct performance advantages compared to any single metal used alone. For example, nickel-rich NMC formulations are known for their high discharge capacity, making them ideal for applications that require substantial energy output. Manganese-rich variants enhance cycle life and thermal stability, making them more durable and suitable for long-term, high-performance use. Cobalt-rich combinations, on the other hand, are favored for their excellent rate capacity, which allows for quick charging and discharging [57].

Lithium iron phosphate, LiFePO₄ (LFP), is a three-dimensional olivine-type cathode material. Iron (Fe²⁺) forms octahedral coordination with six oxygen atoms, while phosphorus is arranged in tetrahedral coordination with four oxygen atoms. Lithium ions exist in distorted octahedral sites within the PO₄ framework. Strong covalent P-O bonds result in a more stable and safer structure than other lithium-ion chemistries [58]. The LFP cathode exhibits excellent thermal stability and remains chemically stable

without reacting with electrolytes at temperatures below 350 °C. Additionally, the use of iron as a key component makes the cathode inherently non-toxic and environmentally friendly, offering a safer and more sustainable alternative to other lithium-ion cathodes. However, its nominal voltage is relatively low, approximately 3.3 volts, resulting in a lower energy density than other lithium-ion chemistries. However, their superior safety, longer cycle life, and thermal stability often outweigh this drawback in many practical applications [2]. Table 1.1 provides a comparative analysis of the cathode materials.

Table 1.1. Comparison of cathode materials (Data from [2]).

	LFP	LCO	NMC
Specific energy (Wh/kg)	90–120	150–200	150–280
Energy density (Wh/L)	190–300	400–600	325
Specific power (W/kg)	4000	1000	1000–4000
Power density (W/L)	10,000	2000	2000–10,000
Volts (per cell)	3.3 V	3.6 V	3.7 V
Cycle life	5000–6000	500–1000	3000–4000

Note: All values are based on cells using a graphite anode. Cycle life values are based on tests conducted at 100% depth of discharge, 1 C rate, and 23 °C.

1.4. Challenges Arising at the Cathode-Oxide Electrolyte Interface in All-Solid-State Lithium-Ion Batteries

Despite their advantages, the main challenge of oxide-based electrolytes is their densification, which requires a conventional high-temperature sintering process that exceeds 900 °C [34, 48, 59]. High-temperature processing leads to several drawbacks, such as the formation of impurity phases, lithium loss, and high processing costs [60]. Furthermore, the co-sintering process involving oxide-based electrolytes and readily accessible cathodes is performed at elevated temperatures to ensure intimate physical contact between the layers. However, interfacial sintering above 500 °C leads to the

formation of secondary lithium-ion blocking phases and structural changes at the solid electrolyte/cathode interface induced by elemental diffusion. Park et al. [61] studied the chemical stability and electrochemical performance of the buried LCO/LLZO interface. High-density LLZO pellets were fabricated using a high-temperature sintering process at 1150 °C. The X-ray diffraction (XRD) pattern of the fabricated pellets matched that of $\text{Li}_{6.06}\text{Al}_{0.20}\text{La}_3\text{Zr}_2\text{O}_{12}$, with Al contamination resulting from the alumina crucible. The lithium-ion conductivity of the pellets was measured to be $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. To form a cathode interface, LCO powder was placed on the LLZO surface and annealed at 700 °C for 1 hour.

XRD results showed that the tetragonal phase of LLZO formed at the interface after the annealing process. The results of transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) revealed significant Al cross-diffusion across the cathode layer. The deficiency of Al destabilized the cubic phase, leading to a transformation of the cubic to tetragonal phase. This transformation increased the interfacial impedance, as the tetragonal LLZO has an ionic conductivity two orders of magnitude lower than the cubic phase. The electrochemical performance of Li/LLZO/LCO battery cells was tested, and the initial discharge capacity was only 35 mAh g^{-1} with a Coulombic efficiency of 54.7%.

Vardar et al. [62] studied the effect of interface sintering temperature on the charge transfer kinetics of the LLZO|LiCoO₂ (LCO) interface. LCO cathode material was coated on LLZO pellets as thin films using the radio frequency sputtering technique and then annealed at different temperatures to determine the onset temperature of structural and chemical degradations at the interface. They utilized TEM to analyze the interface morphology and X-ray photoelectron spectroscopy (XPS) to obtain the compositional profiles across the interface. TEM images show that there is a smooth and distinct interface between the LCO and LLZO layers for the as-deposited sample; however, after annealing at 500 °C, the interface deviates from its continuous and uniform structure, resulting in a reduction in the interlayer contact area. The depth profiles obtained by XPS demonstrate the diffusion of Co into the solid electrolyte layer

by the increase of the annealing temperature, proving the elemental mixing between the layers. They fabricated Au|LCO|LLZO|LCO|Au symmetric cells to determine interfacial impedance using electrochemical impedance spectroscopy (EIS). The results show that the interfacial impedance of the as-deposited sample is almost eight times lower than that of the annealed pellets at 500 °C. The high interfacial resistance exhibited after annealing at 500 °C is attributed to the formation of poor Li-ion conductor secondary phases and elemental mixing.

Kim et al. [63] studied the onset temperature of the interfacial reactions between $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC622) and LLZO, as many inorganic solid electrolytes and oxide cathodes are susceptible to forming secondary phases at elevated temperatures. NMC622 cathode material was deposited on LLZO pellets as thin films using the radio frequency sputtering technique and then annealed at 300 °C, 500 °C, and 700 °C for 4 h. Interfacial sintering was performed in air to reveal the possible contribution of CO_2 to the formation of secondary phases. The results show that the intermixing and oxidation of the cations begin at 300 °C, and the effect becomes more severe as the temperature increases in the air. Furthermore, the formation of Li_2CO_3 was detected at the interface at 500 °C, while after exposure to 700 °C, $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}(\text{Ni}, \text{Co})\text{O}_3$ phases also came into existence. They fabricated Au|NMC622|LLZO|NMC622|Au symmetric cells to determine the interfacial impedance using electrochemical impedance spectroscopy. The interfacial resistance of the samples treated with as-deposited and 500 °C was determined to be $1.4 \text{ k}\Omega \text{ cm}^2$ and $2.1 \text{ k}\Omega \text{ cm}^2$, respectively, while it increased significantly to $102 \text{ k}\Omega \text{ cm}^2$ for samples treated with 700 °C. $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{La}(\text{Ni}, \text{Co})\text{O}_3$ are the main contributors to increased interfacial resistance.

Kim et al. [64] investigated the effect of the sintering temperature and the furnace atmosphere on the formation of secondary phases at the interface of NMC622|LLZO. In the first stage, NMC622 cathode material was deposited on LLZO pellets as thin films using the radio frequency sputtering technique. The solid electrolyte and cathode layers were subjected to an interfacial sintering process for 4 h at different temperatures in environments of pure oxygen (O_2), pure nitrogen (N_2), humidified oxygen (2 wt.% H_2O

in O_2), and pure carbon dioxide (CO_2). As a result of the sintering process carried out in a pure oxygen environment and at 300 °C, the findings show that secondary phases do not form between the solid electrolyte and the cathode, so sintering in a pure oxygen environment is ideal to reduce interfacial resistance.

Ren et al. [65] studied the high-temperature chemical compatibility between the garnet-like solid-state electrolyte $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO) and four main lithium battery cathode materials: LCO, $LiMn_2O_4$ (LMO), $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM), and LFP. XRD, Raman spectroscopy and X-ray photoelectron spectroscopy were used to analyze the phase stability of these blends after heat treatment between 400 °C and 900 °C. The results showed that LMO and LFP reacted with LLZTO at around 500 °C, while LCO and NCM exhibited chemical reactions at approximately 700 °C, forming secondary phases $LaCoO_3$ and $LaCo_{1-x}Mn_xO_3LaNiO_3$, respectively. In the case of LFP, its reaction with LLZTO led to the formation of Li_3PO_4 and Fe-containing phases. Furthermore, $La_2Zr_2O_7$ was detected, suggesting the decomposition of LLZTO. These findings indicate that high-temperature processing leads to undesired reactions between the cathodes and the garnet electrolyte, forming secondary phases that may negatively impact battery performance.

The perovskite LLTO ceramic solid electrolyte is a promising candidate for ASSBs because of its superionic lithium ion conductivity. To advance the understanding of thermally induced chemical and electrochemical reactions at the LCO|LLTO interface, 100 nm thick LCO cathode material was deposited on top of the LLTO solid electrolyte [66]. Chandra et al. [66] fabricated Au|LCO|LLTO|LCO|Au symmetric cells and annealed them in air at 300 °C, 500 °C and 700 °C for 4 hours. Atomic percentages of gold, cobalt, titanium, and oxygen were determined using XPS over a depth range ranging from the gold surface of the fabricated cell to the interior of the bulk LLTO layer. XPS analysis reveals that the thermal energy at 300 °C is sufficient to initiate the diffusion of Co into the bulk LLTO layer. Increasing the annealing temperature intensifies the migration of Co atoms to the solid electrolyte layer, which eventually leads to the complete disappearance of the LCO layer at 700 °C. Even if

secondary phase formation was not detected at the LCO|LLTO interface at a temperature as high as 700 °C, high-temperature co-sintering resulted in the complete loss of the cathode layer.

Ichihara et al. [67] sintered the composites made from the high-capacity cathode material LCO and the oxide-based solid electrolyte $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) at different temperatures, and the resulting products were analyzed using XRD and X-ray absorption near edge structure (XANES). At a temperature of 300 °C, a reaction between LCO and LATP leads to the formation of Co_3O_4 , amorphous TiO_2 , and Li_3PO_4 . When the sintering temperature is increased to 500 °C, the crystalline structure of LCO breaks down completely. This allows LATP to react with the remaining low-crystalline or amorphous forms of LCO, as well as with Co_3O_4 , generating LiCoPO_4 and TiO_2 . As the temperature reaches 700 °C, Co_3O_4 and TiO_2 continue to react, producing CoTiO_3 . At the highest sintering temperature of 900 °C, the final reaction products include LiCoPO_4 , CoTiO_3 , TiO_2 , and Li_3PO_4 . The findings indicate that LATP and LCO are chemically unstable above 300 °C and their chemical reactivity increases with increasing sintering temperature. Thermally driven structural and chemical degradations at the solid electrolyte-cathode interfaces are summarized in Figure 1.5.

Given the above studies, it is evident that ceramic solid electrolytes coupled with oxide cathodes are prone to structural and chemical degradation on high-temperature annealing. A critical bottleneck for developing high-capacity all-solid-state batteries is fabricating the battery cell without secondary phase formation and elemental mixing at the solid electrolyte-cathode interface to achieve desired charge transfer properties. The above findings suggest that low-temperature ($T_{\text{sintering}} < 300$ °C) bonding can play a crucial role in eliminating secondary phase formation and intermixing at the ceramic solid electrolyte-cathode interfaces.

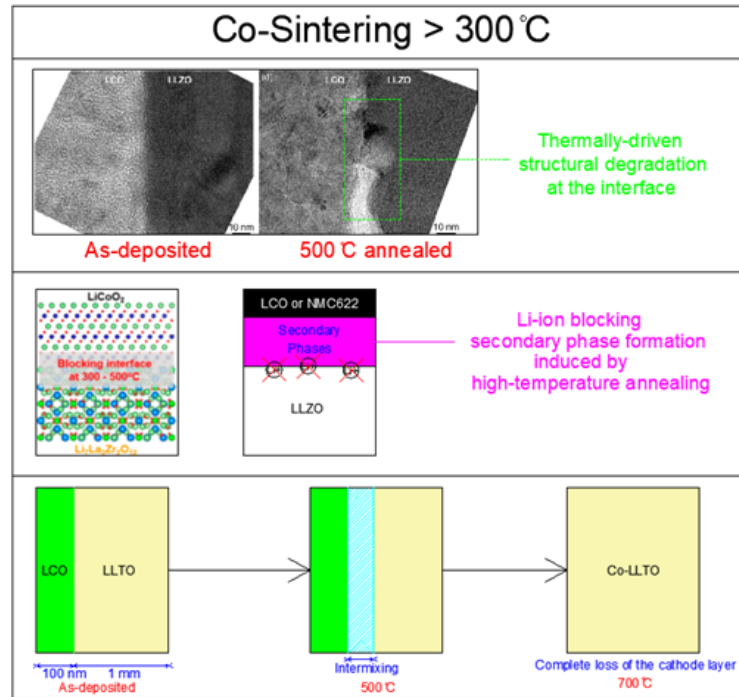


Figure 1.5. The structural and chemical degradations at the solid electrolyte-cathode interfaces induced by high-temperature annealing (Data from [62, 63, 66]).

1.5. Cold Sintering Process

The sintering process dates back to ancient times and is commonly used to densify powders of materials in the form of metals, ceramics, and polymers. The application of heat and pressure binds the granular material, giving the material a compact and strong final solid form. There are several types of sintering techniques in which the compaction and firing processes can be applied sequentially or simultaneously. Researchers have extensively researched the fundamental physical processes that govern sintering to optimize the sintering parameters. The conventional sintering process comprises two distinct stages: pressing and sintering. In the pressing stage, a press and a die compact the powder, causing the particles to move against each other and fill the voids. As the sintering phase begins, the applied thermal energy triggers atomic diffusion and forms interparticle necks. The driving force for densification is the change in surface free energy, and the necking formation between particles consumes surface

free energy, reducing the total surface area of the particles. As the sintering process advances, the pores between adjacent particles gradually shrink, adopting a smaller spherical morphology. Conventional ceramic sintering usually occurs at temperatures exceeding 1000 °C and requires extended holding times ranging from 12 to 36 hours [68].

In 2016, Prof. Clive Randall from Penn State University proposed a new sintering technique called 'Cold Sintering'. Unlike conventional sintering, the cold sintering process (CSP) uses an aqueous solution as a transient solvent to promote densification through a dissolution-precipitation process, reducing the sintering temperature to below 300 °C. The cold sintering process includes the stages of particle rearrangement, dissolution-precipitation, evaporation of the liquid solvent, and grain growth [69]. At the beginning of the first stage, the powder is uniformly wetted with an aqueous solution, the intentionally introduced liquid phase facilitates the movement of the particles, and the liquid-assisted particle rearrangement occurs under the applied external pressure. The sharp edges of the particles dissolve in the solution and the dissolved species diffuse in the direction of decreasing chemical potential, the transferred species aggregate in a low-stressed site, filling the pores between the particles. The evaporation of the liquid solvent follows this stage.

In the final phase of the cold sintering process, the diffusion of atomic species continues, leading to an increase in grain size and removal of porosity [69]. The sintering mechanism requires mass transfer between particles to consolidate the particulate matter. The conventional sintering process occurs at relatively high temperatures because mass transfer occurs at the solid-solid interface. In solids, the crystal lattice imposes significant barriers to the transport of atomic species; however, the introduction of a liquid phase can facilitate the mobility of particles, thus lowering the energy required for their movement [69]. Figure 1.6 illustrates the stages of the cold sintering process from a microstructural evolution point of view.

Researchers have successfully applied the cold sintering process to oxide-based electrolyte materials. Berbano et al. [70] densified $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) solid

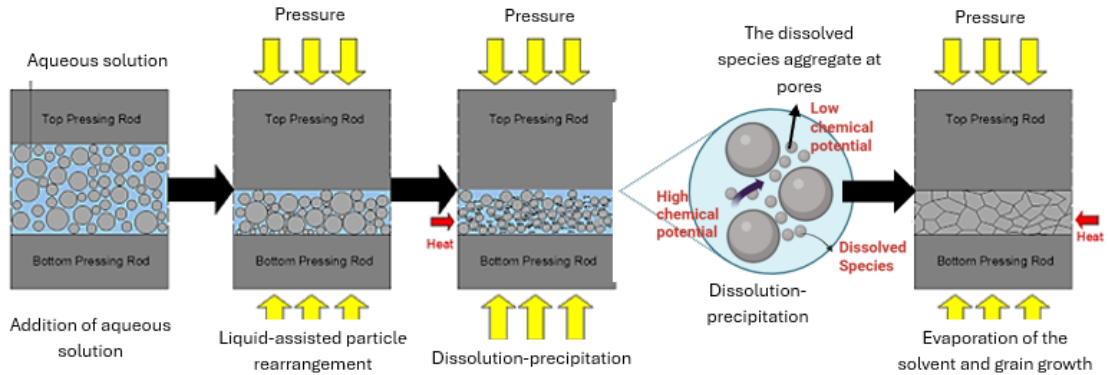


Figure 1.6. The stages of the cold sintering process.

electrolytes by the cold sintering process in the temperature range from 40 °C to 160 °C. Deionized water (30-39 vol.%) or ethanol (50-56 vol.%) is poured into the synthesized powder to promote densification. Low-temperature treatment (<200 °C) and rapid solvent evaporation lead to amorphous grain boundaries in solid electrolytes, which is not conducive to high total ionic conductivity. Heat treatment at 650 °C for 5 min transformed the grain boundaries of cold sintered samples from an amorphous to a partially crystalline structure, increasing the ionic conductivity by approximately an order of magnitude from $3.6 \times 10^{-6} \text{ S cm}^{-1}$ to $5.4 \times 10^{-5} \text{ S cm}^{-1}$.

In cold-sintered ceramic-polymer composites, increasing ionic conductivity by heat treatment at 650 °C is not applicable, considering the thermally driven structural and chemical degradation in polymers, which occurs at temperatures much lower than the applied heat treatment temperature. Therefore, an alternative solution approach rather than a high-temperature post-treatment should be considered to reduce the detrimental effects of the amorphous grain boundaries formed due to the low-temperature sintering process. In this regard, after the cold sintering process (100-x) LAGP – x (PVDF-HFP) (for x= 5, 10, 20, 30, 40), ceramic-polymer composite electrolytes were soaked with a liquid electrolyte (1 M LiPF₆ solution in ethylene carbonate and dimethyl carbonate (50:50 vol.%)). Soaking LAGP- (PVDF-HFP) in a liquid electrolyte causes the noncrystalline regions of PVDF-HFP to expand, and the polymer that absorbs the liquid electrolyte can create a connection across resistant grain

boundaries. The ionic conductivity of the cold-sintered ceramic–polymer composite electrolytes soaked in 5 wt.% liquid electrolytes reached $1.0 \times 10^{-4} \text{ S cm}^{-1}$, which is three orders of magnitude higher than those of the counterparts without liquid electrolyte. Figure 1.7 provides an overview of the processing conditions, the resulting conductivities at 298 K, and the proposed lithium-ion conduction mechanism.

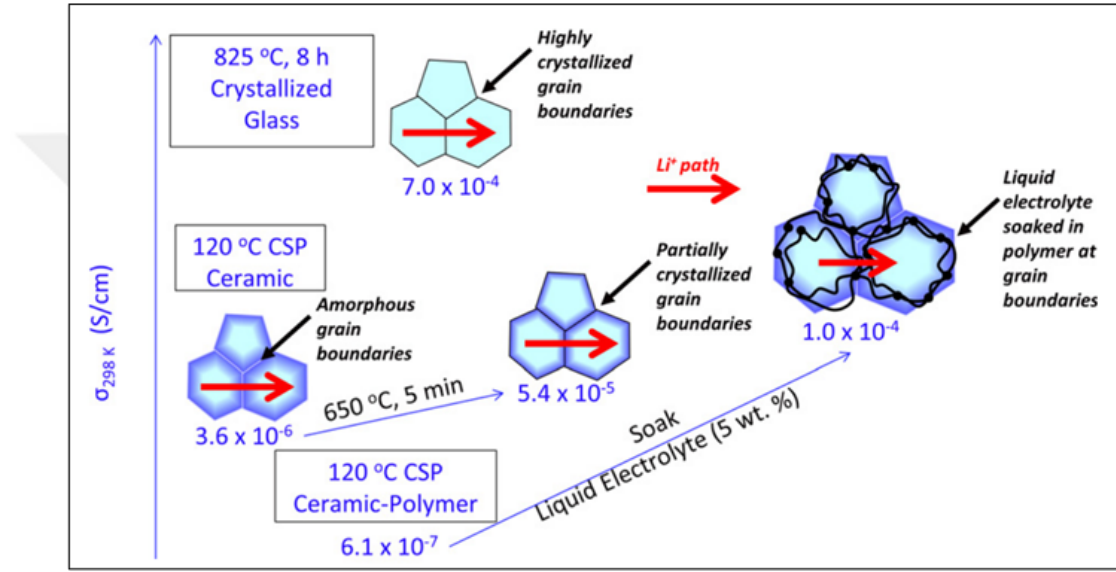


Figure 1.7. The effect of processing techniques on the total ionic conductivities [70].

Takashima et al. [71] conducted a comparative study for the densification of LAGP solid electrolytes using different solvents or processing routes to reveal the effect of LiNO_3 - LiOH as a transient solvent in the cold sintering process. Using LiNO_3 - LiOH mixtures with varying ratios as solvent, the LAGP particles were exposed to a temperature of 220 °C and a uniaxial pressure of 400 MPa for 5 h. While the transient solvent was deionized water, the LAGP particles were exposed to a temperature of 130 °C and a uniaxial pressure of 400 MPa for 2 h. A LAGP pellet sample was sintered above 800 °C following a conventional sintering procedure for comparison. Although the specific secondary phases varied, XRD and SEM analysis confirmed the presence of impurity phases in all samples after the cold sintering process.

In cold-sintered samples using the LiNO_3 – LiOH mixture, there is direct contact between the LAGP grains due to the absence of impurity phases at the grain-to-grain interfaces, although impurity phases were found segregated within the grains. However, due to incongruent dissolution, a thick layer of AlPO_4 was detected at the grain boundaries of the cold-sintered samples with water. The atomic Li, Ge, and Al species were dissolved in the LiNO_3 - LiOH mixture, while water preferentially dissolved Li and Ge from the surface of the LAGP grains, leaving Al behind. The undissolved aluminum subsequently formed the impurity phase AlPO_4 , which can hinder lithium-ion migration at the grain boundaries.

Electrochemical impedance spectroscopy measurements are consistent with the elemental composition data obtained across grain boundaries. The selection of LiNO_3 – LiOH as transient solvent instead of water increased the ionic conductivity of the cold sintered samples by approximately one order of magnitude from $1.9 \times 10^{-6} \text{ S cm}^{-1}$ to $1.8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. However, it remained lower than the samples manufactured by a conventional high-temperature sintering technique ($4.4 \times 10^{-4} \text{ S cm}^{-1}$). Figure 1.8 shows the scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) images of the cold-sintered samples using LiNO_3 – LiOH or water.

Liu et al. [72] investigated the grain boundary structure of a NASICON-type $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) fabricated by CSP and annealed at 650°C . The effects of the selected solvent, applied pressure, and sintering conditions on the relative density and ionic conductivity of the fabricated LATP pellets were explored. LATP solid electrolytes were sintered by different sintering routes: conventional at high temperature, dry press, and cold sintering (using two primary solvents, water and acetic acid). The relative density of the solid electrolyte sintered by the dry-press sintering technique was determined to be relatively low. However, during the cold sintering process in which water was used as the solvent, the relative density of LATP increased from 74% to 79% compared to the dry-press sintering method.

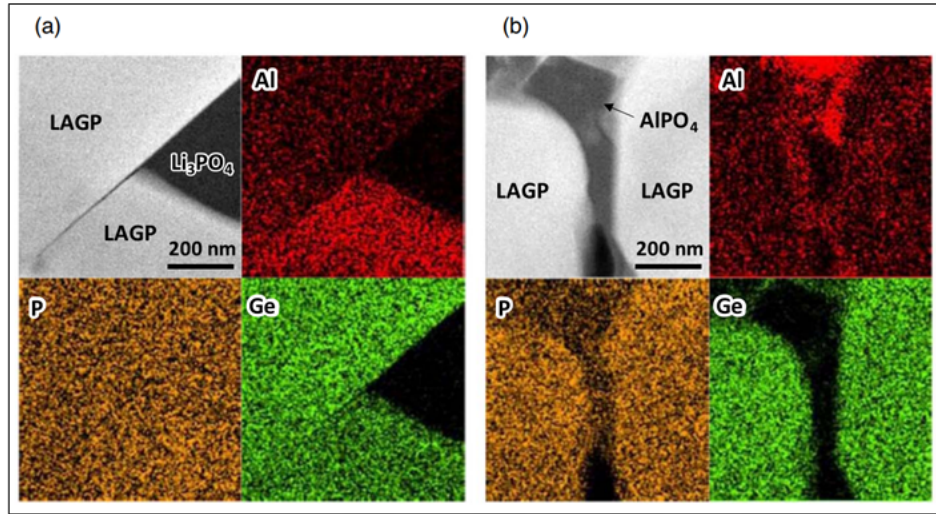


Figure 1.8. STEM images and elemental mapping at LAGP grain boundaries for (a) LiNO₃-LiOH, (b) Water [71].

Furthermore, the use of acetic acid instead of water further increased the relative density of the fabricated pellet to 93%, which is slightly lower than that of high-temperature sintering by a margin of 3%. The ionic conductivity of LATP pellets manufactured by CSP using water and acetic acid is $2.79 \times 10^{-5} \text{ S cm}^{-1}$ and $8.04 \times 10^{-5} \text{ S cm}^{-1}$, respectively, which is about one order of magnitude less than that of conventionally sintered pellets. The reason for the relatively high ionic conductivity of conventionally sintered pellets is the resulting average grain size and smooth grain boundaries. High-temperature sintering accelerates diffusion kinetics, eventually leading to more prominent grains and reduced porosity. Different solvent combinations were investigated to elucidate the influence of the liquid phase on ion dissolution during the CSP process. The mechanical strength of the LATP pellets manufactured by the CSP using water is insufficient. The pellets tend to crack due to rapid evaporation of water at 120 °C, leading to an incomplete dissolution-precipitation process, negatively affecting the cold sintering performance. The high boiling point N-Methyl-2-pyrrolidone (NMP) solvent was mixed with water to inhibit the rapid evaporation of water from the mold, resulting in improved mechanical properties.

Lee et al. [60] proposed the incorporation of bis(trifluoromethanesulfonyl)imide (LiTFSI) salts into the LATP solid electrolyte to resolve the issue of high resistance at amorphous grain boundaries resulting from the extremely low processing temperature applied in cold sintering. First, LiTFSI was dissolved in deionized water (DI). Subsequently, the prepared salt solution was mixed with LATP powder, and the resulting mixture was subjected to a uniaxial pressure of 620 MPa at 130 °C for 2 hours. Highly dense microstructures are obtained for solid composite electrolytes with relative densities between 85% and 90%, depending on the amount of LiTFSI salt added. In addition, the LiTFSI salt at the grain-to-grain interfaces in LATP facilitates ion transport, effectively bridging the gap at the grain boundaries and resulting in a high ionic conductivity of 10^{-4} S cm $^{-1}$.

Seo et al. [73] revealed the importance of the addition of dimethylformamide (DMF) in the cold sintering process of Mg- and Sr-doped LLZO solid electrolytes. The cold sintering temperature, pressure, and holding time for $\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$ solid electrolyte were selected as 100 ~ 150 °C, 400 MPa, and 1.5 ~ 3 h, respectively. A polymer-salt solution was prepared by stirring polypropylene carbonate (PPC) and lithium perchlorate (LiClO_4) in acetonitrile for several hours. The binder solution was mixed with the synthesized solid electrolyte powder and a small amount of DMF was added as a plasticizer. Impedance measurements have demonstrated that the presence of DMF in the as-prepared solution is critical to achieving desirable ionic conductivity in the composite LLZO solid electrolyte fabricated by the cold sintering process. Without DMF, the ionic conductivity was extremely poor (10^{-9} S cm $^{-1}$). However, the addition of a small amount of DMF (~ 3 wt.%) led to a dramatic increase in the ionic conductivity of the cold-sintered pellets, reaching 10^{-4} S cm $^{-1}$. The drastic change in the ionic conductivity was attributed to the decrease in polymeric grain boundary resistance, as the addition of DMF decreased the viscosity of the binding polymer, thereby facilitating the movement of ions at the grain boundaries.

He et al. [74] introduced polyethylene oxide (PEO)- LiTFSI mixtures into Ta-doped LLZO ($\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$) solid electrolytes to investigate how varying con-

centrations of polymer-lithium salt mixtures influence the ionic conduction mechanism in solid composite electrolytes. Solid electrolytes designated as LLZTO-PEO_x-LiTFSI (where $x = 1, 1.5, 2, 5, \text{ and } 8$) were fabricated through the cold sintering process, incorporating varying ratios of EO to Li. The sintering process was carried out at temperatures ranging from 120 °C to 270 °C, with deionized water as a transient solvent.

LLZTO-PEO₂-LiTFSI exhibited the highest ionic conductivity of $2.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature among the cold-sintered pellets. Achieving a densely packed microstructure is essential to enable the formation of additional lithium-ion transport pathways by incorporating polymer-lithium salt mixtures into the interstitial spaces between grains. Significant voids between the grains may hinder the adequate bonding of bulk ceramic particles with polymeric binders. The findings suggest that, as a result of the increase in polymer content, excessive polymer reduces the density of the composite electrolytes, resulting in larger pores between the particles. Therefore, when the molar ratio of EO: Li increases from 2 to 8, the ionic conductivity of the composite solid electrolytes decreases by about an order of magnitude.

In summary, the cold sintering performance of LLZO, LAGP, and LATP solid electrolytes has been investigated under a range of processing conditions, incorporating various additives and solvents. These studies highlight how changes in the sintering temperature, pressure, duration, solvent selection, and binder-salt additives influence the densification and ionic conductivity of solid electrolytes. A comprehensive summary of these parameters and the corresponding electrochemical performance is presented in Table 1.2. The ionic conductivity of solid electrolytes exceeded $10^{-4} \text{ S cm}^{-1}$ only when polymer-lithium salt additives were incorporated, which likely facilitated the formation of additional lithium-ion transport channels along the grain boundaries [60,73,74]. To the best of our knowledge, no studies have yet reported on the cold sintering performance of perovskite LLTO solid electrolytes, highlighting a gap in current understanding and presenting an opportunity for further investigation.

Table 1.2. Cold sintering parameters and resulting performance metrics of LAGP, LLZO, and LATP solid electrolytes.

	LAGP [60]	LAGP [70]	LAGP [71]	LLZO [73]
Additives	LiTFSI	–	–	PPC-LiClO ₄
Solvent	DI Water	DI Water	LiNO ₃ -LiOH	ACN-DMF
Pressure (MPa)	380	400	400	400
Temperature (°C)	130	120	220	120
Duration (h)	2	0.5	5	1
Relative Density (%)	87	79	88	85
Conductivity (S cm ⁻¹)	2.3×10^{-4}	7.9×10^{-6}	1.9×10^{-5}	4.0×10^{-4}
	LLZO [74]	LLZO [75]	LATP [72]	LATP [76]
Additives	PEO-LiTFSI	–	–	–
Solvent	DI Water	LiCl	Acetic Acid	DI Water
Pressure (MPa)	300	500	420	600
Temperature (°C)	150	150	120	200
Duration (h)	1	0.5	1	1
Relative Density (%)	83	80	93	94
Conductivity (S cm ⁻¹)	2.4×10^{-4}	3.0×10^{-5}	8.0×10^{-5}	1.3×10^{-5}

1.6. Summary, Problem Statement and Objectives

Oxide-based solid-state electrolytes have been widely studied for their high chemical stability and ionic conductivity, making them promising candidates for next-generation solid-state batteries. However, their fabrication typically requires high temperature sintering, often exceeding 1000 °C, to achieve sufficient densification and intergranular connectivity. The high-temperature processing presents several critical challenges. One major issue is the formation of unwanted secondary phases, which can significantly degrade the electrolyte’s ionic conductivity and overall electrochemical performance. In addition, when oxide-based electrolytes are co-sintered with cathode materials, elemental interdiffusion and phase decomposition can occur, leading to

structural changes that negatively impact electrochemical characteristics. This incompatibility makes it difficult to directly co-sinter oxide electrolytes with cathodes, forcing researchers to rely on alternative approaches such as interfacial buffer layers. In addition, prolonged sintering durations and extreme temperatures result in high energy consumption, increased production costs, and environmental concerns.

Cold sintering is an emerging low-temperature processing technique that offers a promising alternative for the fabrication of oxide-based composite electrolytes. Unlike conventional high-temperature sintering, cold sintering operates below 200 °C, providing several advantages. One key benefit is its ability to integrate ceramics with polymers without degrading the polymer phase, enabling the design of composite electrolytes that combine the benefits of both materials. Despite advances in the cold sintering of LLZO, LATP, and LAGP solid electrolytes, the cold sintering of perovskite LLTO remains underexplored.

Cold sintering performance is influenced by various parameters, including sintering temperature, pressure, duration, particle size, solvent selection, the weight percentage of binder-salt additives, and their molar ratios. Therefore, the cold-sintering parameters and performance of the LLTO solid electrolyte should be systematically studied. In addition, the mechanical properties of solid electrolytes are crucial in determining battery performance and degradation mechanisms. However, no studies have been conducted to evaluate the mechanical properties of cold-sintered ceramic-polymer composite electrolytes.

The low processing temperature of cold sintering minimizes elemental diffusion and secondary phase formation, making it feasible to co-sinter oxide-based electrolytes with commercial cathode materials while preserving their electrochemical integrity. Thus far, co-sintering of solid electrolytes and cathodes via cold sintering has only been applied to LLZO/LFP interfaces. Investigating its applicability to other oxide electrolyte-cathode interface combinations is necessary. Furthermore, with a significantly reduced processing time—approximately one hour—cold sintering drastically

lowers energy consumption, making it an environmentally friendly approach that reduces both production costs and carbon emissions. Recent studies have demonstrated that cold sintering enables the reprocessing of LLZO solid electrolytes up to five times while retaining their superior pristine properties, enhancing its potential as an environmentally benign and effective recycling technique for solid-state electrolytes. However, reprocessing performance via cold sintering is dependent on several parameters, such as the crystal structure and the solubility of the constituent elements in the process solvents. Therefore, the recyclability of each solid electrolyte should be studied separately. So far, no research has been conducted on the reprocessing performance of LLTO solid electrolytes, and a thorough investigation is needed to assess and compare its performance with other oxide-based electrolytes.

Despite LLTO's high bulk ionic conductivity and chemical compatibility with cathode materials, successful operation of battery cells at room temperature using LLTO as a solid electrolyte with a Li metal anode remains rare. This limitation arises because LLTO is not stable with Li metal, necessitating interlayer designs to mitigate interfacial reactivity. Based on the challenges outlined above, the main objectives of this thesis are as follows:

- To explore the cold-sintering parameters and performance of LLTO composite solid electrolytes.
- To analyze the mechanical properties of LLTO-based composites.
- To co-sinter the LLTO/LFP and LLZO/LCO interfaces via cold sintering while preventing elemental mixing and secondary phase formation.
- To mitigate the chemical reactivity between LLTO and the Li metal anode by introducing a small amount of liquid electrolyte-soaked PVDF membrane at the interface.
- To fabricate Li/LLTO/LFP and Li/LLZO/LCO battery cells and achieve high discharge capacities.
- To investigate the reprocessing performance of LLTO composite solid electrolytes via cold sintering.

1.7. Organization of the Thesis

Chapter 2 presents an overview of the characterization techniques used throughout this thesis. The chapter begins with an introduction to electrochemical impedance spectroscopy (EIS) and battery performance evaluation, outlining their fundamental principles and key concepts. Following this, the chapter briefly describes the operating principles and procedures of various materials characterization methods used in this thesis. These include techniques for probing the structural, morphological, thermal, mechanical, and chemical properties of the processed materials. The specific role of each method is discussed in the context of how it contributes to the comprehensive analysis and interpretation of the material systems explored in this thesis.

Chapter 3 investigates the optimization of cold sintering parameters for LLZO- and LLTO-based solid electrolytes. The study begins with the cold sintering of LLZO using deionized water as the transient solvent, during which key processing parameters—temperature, pressure, sintering duration, and particle size distribution—are systematically varied. Both fine and coarse LLZO powders are examined to assess the influence of initial particle size on densification and ionic conductivity. However, the results reveal that water-based cold sintering leads to incongruent dissolution and the formation of secondary phases, which significantly limit the ionic conductivity of the resulting pellets across all processing conditions. In response to these limitations, the next part presents the modification of the solvent system to a binary mixture of acetonitrile and dimethylformamide (DMF). A binder-salt solution is prepared by dissolving PPC-LiClO₄ in acetonitrile, which is then added to the ceramic powder along with DMF. This formulation promotes densification and enhances lithium-ion transport through the formation of additional conductive pathways along amorphous grain boundaries. Given the flammability of the organic solvents, all cold sintering procedures in this stage are conducted inside an argon-filled glovebox to ensure operational safety. This improved binder-assisted cold sintering strategy enables the successful fabrication of LLZO and LLTO composite electrolytes with ionic conductivities exceeding 10^{-4} S cm⁻¹, marking a significant performance improvement over the initial

water-based approach and demonstrating the effectiveness of the solvent and additive modification.

Chapter 4 begins by addressing the integration of cold-sintered LLTO composite electrolytes into lithium metal battery architectures. The key challenge in this process is the formation of a steadily growing interphase layer at the direct contact between lithium metal and LLTO, which leads to a substantial increase in interfacial resistance over time. To suppress this chemical reactivity, a PVDF membrane soaked in 1 M LiPF_6 dissolved in a 1:1 volumetric mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) is introduced as an interlayer at the Li/LLTO interface. This interfacial strategy stabilizes the growth of the interphase between the lithium metal and the solid electrolyte. Next, symmetric Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li cells are fabricated and evaluated for their critical current density and long-term cycling stability. Full-cell Li/PVDF/LLTO-PS (13 vol%)/LFP configurations are then assembled to assess rate capability and extended cycling performance. Although the full cells initially exhibit stable operation, a sharp capacity fade is observed at 0.1 C after approximately 30 cycles. Finally, to determine the root cause of this degradation, a comprehensive post-mortem analysis is conducted. XPS and FTIR results reveal significant degradation of the PVDF membrane and carbonate-based electrolyte solvents, leading to increased interfacial resistance at the anode side. Importantly, XRD and XPS analyses confirm the structural and chemical stability of the LLTO solid electrolyte, indicating that the failure mechanism originates from interfacial degradation rather than intrinsic electrolyte instability.

Chapter 5 presents the integration of cold-sintered LLZO composites into lithium metal batteries. The first part demonstrates the fabrication of a PPC-LiFSI interlayer and its effectiveness in reducing the interfacial resistance at the Li/LLZO interface. Next, Li/i/LLZO/i/Li (i: PPC-LiFSI interlayer) symmetric cells are constructed for critical current density and long-term cyclic stability evaluation. Subsequently, Li/i/LLZO/LCO battery cells are fabricated to test battery performance at different C-rates. SEM (EDS) images are provided to show that cold sintering is an effective

method for co-sintering the LLZO/LCO interface without structural changes or elemental mixing at 100 °C for 30 minutes.

Chapter 6 presents the exploration of the reprocessing performance of LLTO composites via cold sintering. The chapter begins with the tracking of ionic conductivity and relative density across multiple reprocessing cycles, demonstrating that LLTO perovskites retain excellent phase stability and nearly pristine ionic conductivity even after ten reprocessing cycles. Next, a detailed comparison between pristine and reprocessed ($\times 10$) electrolytes is conducted using XRD, SEM, FTIR, Raman spectroscopy, and particle size analysis to evaluate their structural and chemical properties. To further investigate the origin of LLTO's exceptional stability in cold sintering solvents, inductively coupled plasma atomic emission spectroscopy (ICP-AES) is employed to quantify the dissolution concentrations of constituent elements in LLTO and LLZO electrolytes. The chapter then proceeds with mechanical characterization of the cold-sintered LLTO composites, comparing their elastic modulus, hardness, and fracture toughness to those of conventionally sintered LLTO. Finally, the reprocessed ($\times 10$) LLTO composites are integrated into both half-cell and full-cell configurations to evaluate their electrochemical performance.

Finally, Chapter 7 presents a comprehensive summary of the main findings of this thesis, followed by a critical evaluation of the results obtained throughout the study. The chapter begins by revisiting the core objectives and research questions, emphasizing the systematic development of LLZO- and LLTO-based composite solid electrolytes using the cold sintering process. The transition from the initial water-based sintering approach, which was limited by poor phase stability and low ionic conductivity, to the development of an improved binder-assisted strategy using organic solvents, significantly improved the electrochemical performance. The chapter critically examines the challenges encountered, particularly interfacial degradation in full-cell configurations, and evaluates the effectiveness of the proposed interfacial architectures. The results also discuss the success of the cold sintering process in co-sintering LLTO and LLZO solid electrolytes with common cathode materials such as LFP and LCO, demonstrat-

ing its compatibility with practical battery interfaces. A comparative analysis of LLTO and LLZO electrolytes is provided, outlining their respective advantages and limitations in terms of processability, conductivity, and interfacial stability. Furthermore, the reprocessing performance of LLTO composites is summarized, with a focus on the experimental findings that explain the exceptional structural and electrochemical stability of LLTO in multiple reprocessing cycles. This final chapter consolidates key contributions from the thesis and provides insight into the future potential of cold sintering in solid-state battery applications.



2. CHARACTERIZATION TECHNIQUES

This chapter provides an overview of the characterization techniques employed in this thesis. First, the electrochemical impedance spectroscopy technique and battery characteristics will be introduced, along with their fundamental principles and key concepts. This section aims to equip the reader with the necessary knowledge to understand the underlying mechanisms governing these techniques and to effectively interpret the electrochemical performance of the solid electrolytes and battery cells examined in this work. Next, the operating parameters and procedures of various material characterization techniques used in this study will be briefly discussed. The role of each method in the analysis of the structural, morphological, thermal, mechanical, and chemical properties of the materials investigated in this thesis will be highlighted.

2.1. Electrochemical Impedance Spectroscopy

In a standard EIS measurement, a potentiostat or galvanostat is used to apply a small alternating current (AC) or voltage signal to the electrochemical cell across a broad frequency range, typically from millihertz to megahertz. Under direct current (DC) conditions, the relationship among resistance (R), voltage (V), and current (I) follows Ohm's law, expressed as $R = \frac{V}{I}$. However, when an AC voltage is applied, the impedance of the system $Z(\omega)$ adheres to the AC form of Ohm's law, $Z(\omega) = \frac{V(\omega)}{I(\omega)}$. The applied and measured voltage and current are in the sinusoidal form as:

$$V = V_m \sin(\omega t) \quad (2.1)$$

$$I = I_m \sin(\omega t - \phi) \quad (2.2)$$

$$\omega = 2\pi f. \quad (2.3)$$

The complex impedance $Z(\omega)$ can be written as:

$$Z(\omega) = \frac{V_m}{I_m} \cos(\phi) + \frac{V_m}{I_m} \sin(\phi)j \quad (2.4)$$

$$\phi(\omega) = \tan^{-1} \left(\frac{\text{Re}(Z(\omega))}{\text{Im}(Z(\omega))} \right). \quad (2.5)$$

In this context, V_m and I_m represent the peak voltage and current values, respectively, while ω denotes the angular frequency of the applied AC signal. This frequency-dependent impedance provides critical insight into the electrochemical processes that occur within the system, including the charge-transfer resistance, diffusion characteristics, and interfacial properties [77]. The real part of $Z(\omega)$ denotes the resistance, while the imaginary part represents the contributions of capacitance and inductance. A Nyquist plot in battery impedance measurements displays the real and imaginary components of impedance over a range of frequencies, helping to analyze charge transfer resistance, solid electrolyte interphase (SEI) behavior, and ion transport properties [78]. Impedance arises from the combined effects of resistors, inductors, and capacitors, each contributing uniquely to the circuit's overall response to electrical signals. Therefore, equivalent circuit models are used to fit the actual data and accurately represent the electrochemical behavior of the system. The commonly used equivalent circuit elements and their formula are presented in Table 2.1.

The constant phase element (CPE) models non-ideal capacitive behavior, commonly observed at electrode-electrolyte interfaces due to the formation of an electrical double layer. Meanwhile, the Warburg impedance (W) represents the semi-infinite diffusion of lithium ions within the bulk phase, constrained by the planar electrode surface [77]. When a circuit includes a resistance R_1 in parallel with a double-layer capacitance C_1 , represented as (R_1C_1) , its Nyquist plot exhibits a semicircular shape. The real component of the impedance corresponds to the resistance R_1 . The capacitance C_1 can be determined from the peak of the semicircle in the Nyquist plot, where $\omega = \frac{1}{R_1C_1}$. If a resistor R_0 is connected in series with the circuit (R_1C_1) , denoted as $R_0(R_1C_1)$, the semicircle shifts along the real axis to a value equal to the ohmic resis-

tance of R_0 . When a second parallel (R_2C_2) circuit is connected to $R_0(R_1C_1)$, forming the $R_0(R_1C_1)(R_2C_2)$ circuit, the Nyquist plot shows two semicircles [79].

Table 2.1. The commonly used equivalent circuit elements [77].

Equivalent Circuit Element	Formula
Resistance (R)	R
Capacitance (C)	$\frac{1}{\omega C j}$
Inductance (L)	$\omega L j$
Warburg Impedance (W)	$\sigma \omega^{-1/2}(1 - j)$, σ : Warburg coefficient
Constant Phase Element (CPE, Q)	$\frac{1}{Q(\omega j)^\alpha}$, $\alpha = 1$ for ideal capacitor

In a Nyquist plot, impedance data are plotted with the real part (Z') on the x-axis and the imaginary part (Z'') on the y-axis, as a function of decreasing frequency from left to right. As the frequency is swept from high to low, different electrochemical processes are activated, allowing the separation of bulk, grain boundary, and interfacial contributions in the impedance spectrum. A typical Nyquist plot for a ceramic solid-state electrolyte is shown in Figure 2.1. The plot exhibits two distinct features, each corresponding to a different ionic transport process within the material. The first feature, located in the high-frequency region, is attributed to the bulk resistance, which reflects the intrinsic ionic conductivity of the well-ordered crystalline grains. The second feature, observed at lower frequencies, corresponds to the grain boundary resistance, which arises from ionic transport across grain interfaces. This resistance originates from factors such as grain orientation mismatch and poor crystallinity at the grain boundaries, which impede ion movement [78].

In this study, the impedance spectra of the samples were acquired with a 10 mV AC amplitude within the frequency range of 1-10⁶ Hz (Modulab XM, Solartron Analytical). ZView software was used by Scribner Associates (USA) to perform EIS data fitting through equivalent circuit modeling. The ionic conductivity (σ_{ion}) of the

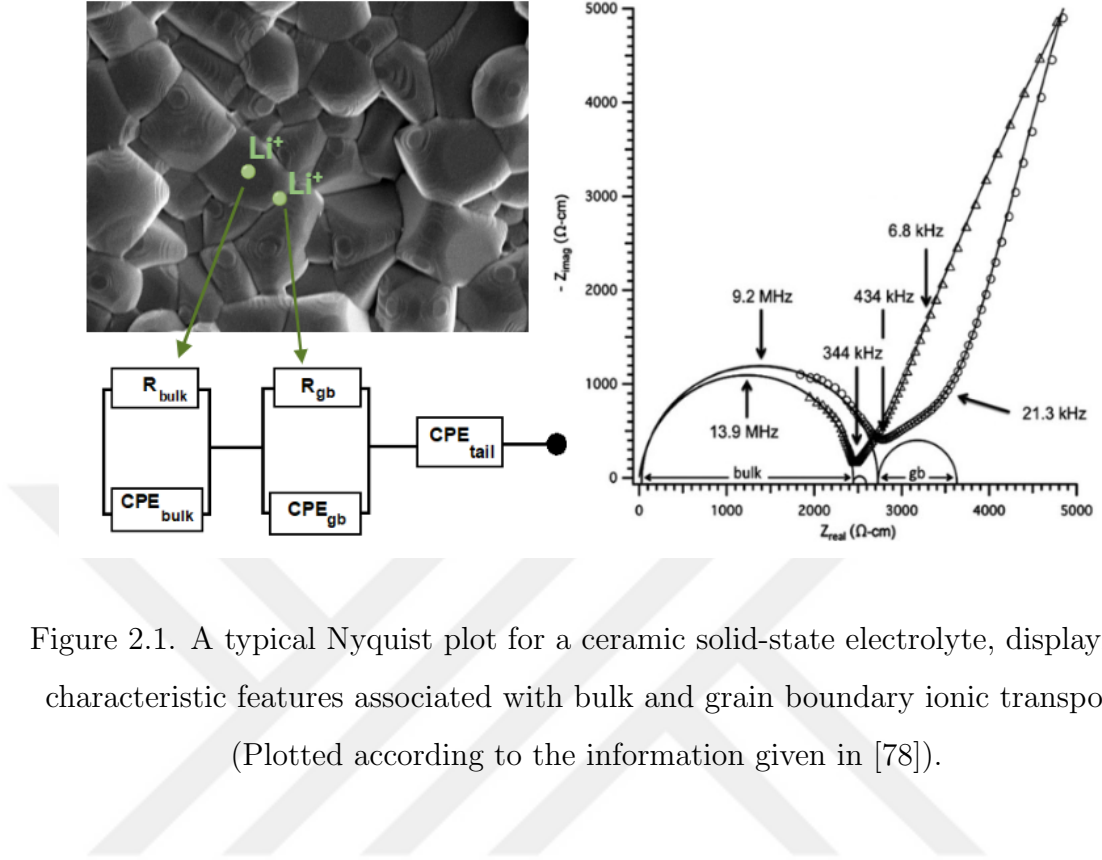


Figure 2.1. A typical Nyquist plot for a ceramic solid-state electrolyte, displaying characteristic features associated with bulk and grain boundary ionic transport (Plotted according to the information given in [78]).

solid electrolytes is calculated using the following equation [78]:

$$\sigma_{\text{ion}} = \frac{t}{R_{\text{total}}A}, \quad (2.6)$$

where R_{total} and t represent the total resistance and thickness of the solid electrolyte, respectively, while A represents the area of ion-blocking electrodes. The overall resistance (R_{total}) consists of multiple contributing factors, including resistance from the bulk phase of grains, grain and phase boundaries, and impedances arising from physical or chemical changes at the electrode interfaces. The ionic conductivity of the samples was measured from 0 to 100 °C in 20 °C intervals to elucidate the temperature dependence of the ionic conductivity of the samples. At each measurement point, the temperature stabilized for 10 minutes. The activation energies of the sintered solid electrolytes were calculated from the slope of the Arrhenius plot using the following equation [80]:

$$\sigma_{\text{ion}} = \exp\left(-\frac{E_a}{k_B T}\right), \quad (2.7)$$

where A is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature.

2.2. Relative Density Calculations

The density of each composite solid electrolyte was calculated by measuring the mass and thickness of the pellet and determining the mass-to-volume ratio. The relative density of the composite solid electrolytes was calculated as the ratio of the measured density to the theoretical density of the composite, which consists of the ceramic LLTO phase ($\rho_{\text{LLTO}} = 5.09 \text{ g/cm}^3$), PPC ($\rho_{\text{PPC}} = 1.26 \text{ g/cm}^3$), and LiClO_4 ($\rho_{\text{LiClO}_4} = 2.42 \text{ g/cm}^3$). The theoretical density of the composite solid electrolytes was calculated using the following equation [68]:

$$\rho_{\text{composite}} = \rho_{\text{LLTO}} f_{\text{LLTO}} + \rho_{\text{PPC}} f_{\text{PPC}} + \rho_{\text{LiClO}_4} f_{\text{LiClO}_4}, \quad (2.8)$$

where ρ_{LLTO} , ρ_{PPC} , and ρ_{LiClO_4} denote the densities of LLTO, PPC, and LiClO_4 , respectively, and f_{LLTO} , f_{PPC} , and f_{LiClO_4} represent their corresponding volume fractions.

2.3. Battery Characteristics

Several key parameters are used to evaluate battery performance, including critical current density, energy density, C-rate, cycle life, and coulombic efficiency. This section provides a brief introduction to each of these parameters.

2.3.1. Critical Current Density

In all-solid-state batteries that utilize lithium metal anodes, the main factor that causes short circuits is the penetration of lithium dendrites. To better understand the interfacial chemistry of lithium, most studies assessing anodic behavior in solid-state batteries rely on symmetric cell configurations. This method enables researchers to isolate and analyze the interactions at the interface between the lithium electrode and the solid electrolyte, offering critical insights into the underlying mechanisms that influence battery performance, stability, and long-term reliability [81].

The critical current density (CCD) is the maximum current density that a solid-state battery can sustain without undergoing short circuiting due to the formation of lithium dendrites or other failure mechanisms. This parameter serves as a crucial indicator of the battery's ability to operate safely under high current conditions. A higher CCD suggests improved interfacial stability between the lithium anode and the solid electrolyte, reducing the likelihood of dendrite penetration and ensuring reliable long-term performance. Understanding and optimizing CCD is essential for the development of high-power, durable solid-state battery technologies [82].

As solid-state battery research progresses, several measurement protocols have been developed to assess CCD effectively. Unlike EIS, which employs an AC signal, CCD evaluation involves applying DC to the electrochemical system while monitoring the resulting voltage response. This approach provides valuable insight into the battery's ability to withstand high current loads without short circuiting. Figure 2.2 presents schematic representations of microstructural changes within cells under different CCD measurement protocols, along with their respective charge and discharge profiles. These protocols can be broadly classified into four distinct approaches, each designed to provide a comprehensive understanding of CCD and its impact on battery performance. The following sections will detail these approaches and their significance in solid-state battery research [82].

–(I) Time control

The time-controlled test method evaluates the CCD by gradually increasing the applied current density in each cycle while maintaining a fixed time duration, typically set to 10 minutes, 30 minutes, 1 hour, or longer. This approach allows researchers to systematically assess the battery response to increasing current loads over controlled time intervals. The time-voltage profiles obtained from this method (Figure 2.2c) reveal a continuous increase in polarization until a sudden voltage drop occurs, signaling the onset of a short circuit due to the penetration of lithium dendrites or other failure mechanisms. By simultaneously increasing both current density and capacity, this

(a) Time Control

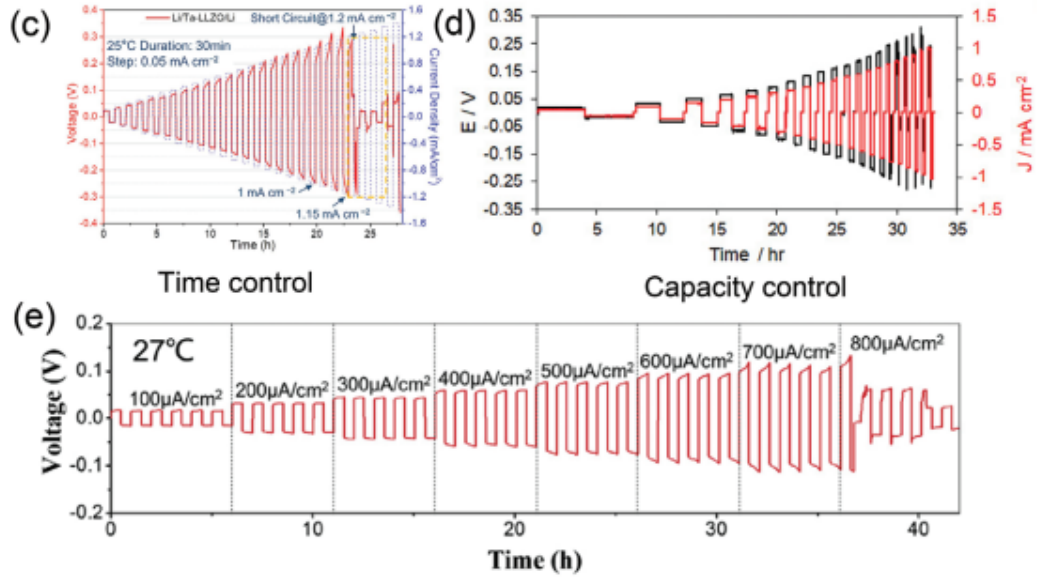
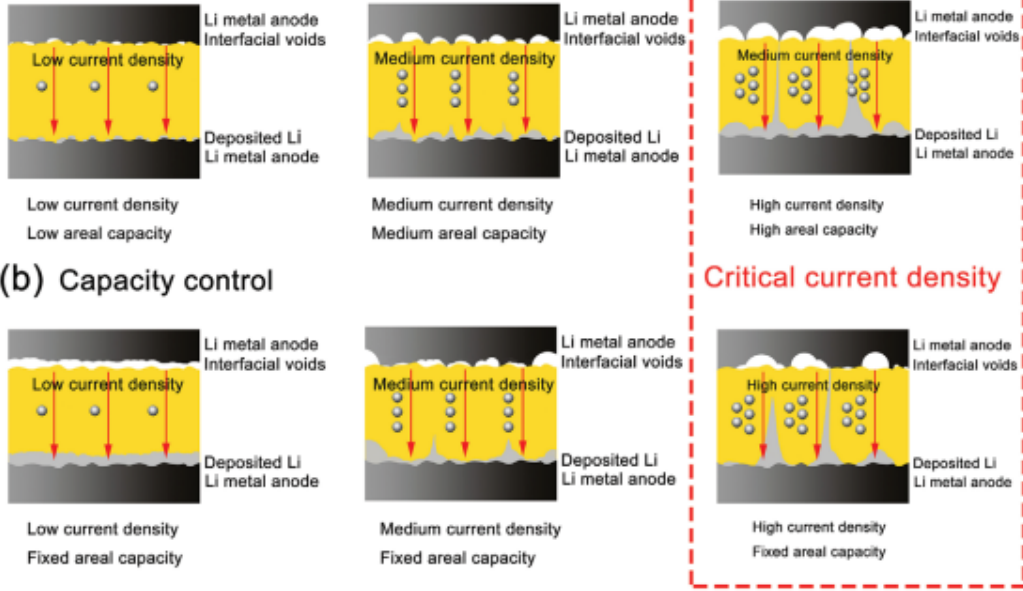


Figure 2.2. Schematic representation of the microstructural evolution in cells under different measurement protocols, along with their corresponding charge and discharge profiles: (a) and (c) time-controlled method, (b) and (d) capacity-controlled method, and (e) endurable time-controlled method [82].

technique provides valuable insights into the endurance of the cell under progressively harsher operating conditions, helping to determine its reliability and stability over time.

– (II) Capacity control

The capacity-controlled method evaluates the CCD by applying progressively increasing current densities while keeping the areal capacity constant at predefined values, such as 0.2, 0.5, or 1 mAh cm⁻² per cycle. To maintain a fixed capacity, the duration of the cycle is adjusted accordingly, decreasing as the current density increases (Figure 2.2d). This measurement protocol is particularly useful for investigating the influence of capacity on battery performance during cycling, providing insight into how different charge storage conditions affect the stability and endurance of a solid-state battery.

– (III) Endurable time control

This technique involves applying a fixed current density for a set duration and repeating the procedure for multiple cycles at each current level (Figure 2.2e). By subjecting the cell to repeated cycling at a given current density before increasing it, this method provides a more comprehensive assessment of battery performance. This method simultaneously accounts for the effects of both the current density and the number of cycles, providing valuable insights into the long-term stability and endurance of the solid-state electrolyte under continuous operation. This approach helps to determine how prolonged exposure to specific current conditions influences the onset of short-circuiting and overall battery reliability.

– (IV) Long-term cycling

This method is widely used to assess the stability of the lithium-metal/solid electrolyte interface in symmetric cells subjected to repeated cycling at a constant current density. By maintaining a fixed current for an extended period, researchers

can monitor any changes or degradation occurring at the interface between the lithium-metal anode and the solid electrolyte.

The CCD is identified at the point of anodic failure, with unique voltage profiles providing insight into different lithium dendrite growth mechanisms. In solid-state lithium metal batteries, four primary failure mechanisms have been recognized. Sudden death occurs when thick lithium dendrites rapidly form and bridge the anode and cathode, resulting in an irreversible short circuit. This failure is prevalent in inorganic solid electrolytes, where weak grain boundaries and structural defects promote dendrite propagation [83, 84]. Partial short circuits represent an early stage failure in which lithium filaments penetrate the interfacial regions of the solid electrolyte without fully reaching the opposite electrode. This leads to a minor drop in polarization voltage, indicating a partial reduction in bulk impedance, but the battery remains operational [85, 86].

Soft short circuits are common in polymer-based or hybrid electrolytes, where small, temporary dendrites form and dissolve, causing voltage fluctuations. Although these dendrites can fuse back, allowing battery recovery, they contribute to overcharging and energy inefficiency [87]. Contact loss results from the accumulation of vacancies and volume changes during lithium stripping, leading to interfacial pore formation and a decrease in the effective electrode-electrolyte contact. This, in turn, increases polarization and interfacial resistance [88]. A comprehensive understanding of these failure mechanisms is essential to improve the stability and lifespan of solid-state batteries [82].

Various types of LLZO-based symmetric lithium metal cells were fabricated to determine the CCD and evaluate both the lithium dendrite suppression capability of the solid electrolytes and the stability of the lithium–solid electrolyte interface (Table 2.2). The reported CCD values for LLZO-based symmetric lithium metal cells generally lie between 0.75 and 1.28 mA cm⁻², with most measurements centered around 1 mA cm⁻².

Table 2.2. Reported CCD values for various symmetric Li cells.

Reference	Symmetric Li Cell	CCD (mA cm^{-2})
[89]	Li 0.15LiBr-LLZO Li	1.00
[90]	Li 5 wt.% Li_3BO_3 -LLZO Li	0.05
[91]	Li/LLZO/Li	0.95
[92]	Li/ $\text{Li}_{6.85}\text{La}_{2.95}\text{Yb}_{0.05}\text{Zr}_{1.85}\text{Ta}_{0.15}\text{O}_{12}$ /Li*	1.10
[93]	Li/ $\text{Li}_7\text{La}_{2.75}\text{Ca}_{0.25}\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ /Li, LiAlO_2 coated	0.75
[94]	Li-Al/LLZO/Li-Al	0.90
[95]	Li/ $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ /Li	1.28
[96]	Li/PP/ $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ + 1 wt.% Bi_2O_3 /PP/Li	0.70

* Based on the capacity control method. The others are based on the time control method.

Because of the chemical instability of LLTO solid electrolytes in contact with lithium metal, reports on LLTO-based symmetric lithium metal cells are relatively scarce. Wu et al. [96] reported a CCD value of 0.70 mA cm^{-2} for an LLTO-based symmetric lithium cell incorporating polypropylene (PP) interlayers, which mitigate chemical reactivity at the Li/LLTO interface. The reported CCD values for LLZO- and LLTO-based symmetric lithium metal cells are summarized in Table 2.2.

2.3.2. Energy Density

The performance of batteries in various applications is primarily determined by specific energy, specific power, and energy density. Specific energy (Wh kg^{-1}), which represents the energy stored per unit mass, is crucial for large-scale applications such as public transportation systems, including electric buses. In contrast, energy density (Wh L^{-1}), which measures energy storage per unit volume, is more critical for compact devices such as smartphones and laptops. The specific energy is calculated by discharging a battery at a given current using the formula [97]:

$$E = V_{\text{oc}} \times Q_{\text{dis}}, \quad (2.9)$$

where V_{OC} is the operating potential (V) and Q_{dis} is the specific capacity (Ah kg^{-1}). The theoretical capacity can be determined as follows [2]:

$$Q_{th} = \frac{26.8 \times n}{M_w}, \quad (2.10)$$

where M_w is the molecular mass of the limiting electrode material and n denotes the number of electrons transferred.

2.3.3. C-rate

The C-rate is a standardized measure that indicates how quickly a battery is charged or discharged relative to its total capacity. It helps compare the performance of different batteries regardless of their size. A C-rate of nC means that the battery will be fully charged or discharged in $1/n$ hour. For example, if a 10 Ah battery operates at a rate of $C/5$ (2 A), it will take 5 hours to completely discharge. Similarly, at a $2C$ rate (20 A), the same battery would be discharged in 0.5 hours (30 minutes). C-rate is a key factor in battery design and selection, affecting efficiency, lifespan, and heat generation. Higher C-rates allow for faster charging and discharging but can cause greater heat buildup and capacity loss over time. Conversely, lower C-rates result in slower charging/discharging but help preserve capacity and extend battery life. Optimizing the C-rate is essential for applications ranging from portable electronics to electric vehicles and energy storage systems.

2.3.4. Cycle Life

With the growing use of rechargeable batteries in consumer electronics, their cycle life has become an essential measure of longevity. It indicates how many full charge and discharge cycles a battery can complete before its capacity drops to a level that is no longer adequate for its intended function. Generally, this limit is reached when the battery retains only 70-80% of its initial capacity [2].

2.3.5. Coulombic Efficiency

Coulombic efficiency (CE) quantifies the efficiency with which a battery can store and retrieve electrical charge during each charge-discharge cycle. It is determined by the ratio of the discharge capacity (Q_{DCH}) to the charge capacity (Q_{CH}). Mathematically, it is expressed as [97]:

$$CE (\%) = \frac{Q_{DCH}}{Q_{CH}} \times 100\%. \quad (2.11)$$

Discharge capacity (Q_{DCH}) is a measure of the total amount of electric charge a battery can deliver during a full discharge cycle. To determine the discharge capacity in mAh/g, the total charge delivered during the discharge process is divided by the mass of the active material in the electrode. A Coulombic efficiency of 100% means complete charge retention, where all the energy stored during charging is fully recoverable during discharge. However, in practical applications, CE is usually lower due to losses caused by self-discharge, unwanted side reactions, and gradual decline in capacity.

2.4. Materials Characterization Techniques

This section presents the operating parameters and procedures of the various material characterization techniques employed to analyze the structural, thermal, morphological, chemical, and mechanical properties of the materials. These details outline the specific conditions and methodologies followed during the experimental analyses.

2.4.1. X-ray Diffraction (XRD)

XRD is a widely used and non-destructive technique for analyzing the crystal structure of materials in the crystalline phase. Because most solid materials exhibit crystallinity, X-ray diffraction (XRD) is an essential tool in materials science for structural characterization. In crystalline solids, atoms are arranged in a repeating lattice

structure, allowing them to diffract incident X-rays in a well-defined manner. When an X-ray beam strikes these atomic planes, the scattered waves interfere constructively or destructively, producing a unique diffraction pattern. This phenomenon, known as X-ray diffraction, occurs only when the conditions defined by Bragg's law are satisfied. Bragg's law defines the fundamental relationship between the wavelength of incident X-rays, the spacing between atomic planes, and the diffraction angle at which constructive interference occurs, expressed as [98]:

$$n\lambda = 2d \sin \theta. \quad (2.12)$$

In this equation, n is a positive integer, λ denotes the wavelength of the incoming wave, d is the spacing between the crystal planes, and θ is the angle between the incident X-ray beam and the crystal plane. In this thesis, phase identification and crystal structure determination were performed using an Empyrean X-ray diffractometer (Malvern Panalytical). XRD patterns were obtained with Cu-K α radiation generated at 45 kV and 40 mA in the 2θ range of 10° to 70° , using a step size of 0.013° . The collected XRD patterns were analyzed using MDI Jade software.

2.4.2. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS)

SEM is used to observe the surface morphology and microstructure of the samples. High-resolution images are captured using a Field Emission Scanning Electron Microscope (FE-SEM), providing detailed insights into the particle size, shape, and distribution. To further analyze the elemental composition, the SEM is equipped with EDS, which enables elemental mapping of the images. This allows for a comprehensive examination of the spatial distribution of elements within the samples, as well as the identification of potential compositional heterogeneity, defects, and grain boundaries.

The microstructural analysis of the specimens was performed on fractured surfaces using a Thermo Fisher Scientific Verios scanning electron microscope equipped with an EDS detector. Before SEM analysis, a thin iridium layer (~ 5 nm) was sputtered on the fractured surfaces to prevent charging [98]. In this thesis, the SEM was

operated in field-free mode with an Everhardt-Thornley detector (ETD) for secondary electron collection. This mode allows for the collection of secondary electrons emitted from the sample's surface when bombarded with the electron beam. The accelerating voltage was set to 5 kV, providing optimal imaging conditions for high-resolution surface morphology analysis. The combination of these settings enabled for detailed imaging of the surface features, allowing for the observation of fine textures and grain boundaries. An accelerating voltage of 20 kV was used for EDS mapping to achieve optimal interaction between the electron beam and the sample. This higher voltage enhances the generation of X-rays from deeper regions of the sample, improving the depth of analysis, and ensuring more accurate elemental characterization.

2.4.3. X-ray Photoelectron Spectroscopy (XPS)

XPS was employed to examine the surface composition and chemical states of the samples. The method uses an X-ray source to irradiate the sample, which leads to the ejection of core electrons from surface atoms. The kinetic energy of the emitted photoelectrons is measured, and the binding energy is calculated by subtracting the kinetic energy from the energy of the incident X-rays. In this thesis, XPS measurements were carried out on a VersaProbe III system (Physical Electronics), which utilizes a monochromated Al K α radiation source and a concentric hemispherical analyzer. To counteract surface charging, a dual beam charge neutralization method was applied employing low-energy electrons (under 5 eV) and Ar⁺ ions. Measurements were performed at a 45° take-off angle relative to the sample surface plane, resulting in a typical sampling depth of 3–6 nm, with 95% of the signal originating from this depth or shallower. XPS data analysis was performed using CasaXPS software.

2.4.4. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was employed in attenuated total reflection (ATR) mode to analyze the vibrational modes and chemical bonding characteristics of the samples. In this configuration, an infrared beam is directed

onto a crystal with a high refractive index, where it undergoes total internal reflection and generates an evanescent wave that penetrates a few micrometers into the sample. This evanescent wave is absorbed at characteristic frequencies corresponding to specific molecular vibrations, providing a fingerprint of the sample's chemical structure [99]. Measurements were carried out using a Bruker Vertex 70 spectrometer equipped with a diamond crystal ATR accessory. Spectra were recorded in the range of 500–4000 cm^{-1} with a resolution of 6 cm^{-1} . The ATR configuration allows for the direct analysis of solid samples without the need for pellet pressing or other complex preparation techniques.

2.4.5. Raman Spectroscopy

Raman spectroscopy was employed to investigate the vibrational modes and structural characteristics of the cold-sintered composites. In Raman spectroscopy, monochromatic laser light is scattered by molecular vibrations, leading to energy shifts that provide information about the chemical bonds and symmetry of the material. Unlike infrared spectroscopy, which measures dipole moment changes, Raman spectroscopy detects changes in the polarizability of molecules. As a non-destructive technique, Raman spectroscopy is particularly useful for characterizing structural features, phase composition, and crystallinity [100]. The Raman spectra of the cold-sintered composites were recorded using a LabRAM HR Evolution spectrometer (HORIBA Scientific) equipped with a 532 nm excitation laser and a 1800 g/mm grating.

2.4.6. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), is a quantitative elemental analysis technique widely used to detect trace metal concentrations in complex matrices. In this method, samples are nebulized and introduced into a high-temperature argon plasma, which is typically operating at approximately 8000 K. The thermal energy of the plasma excites the atoms and ions of the elements present

in the sample. As these excited species return to lower energy states, they emit light at characteristic wavelengths specific to each element. The emitted light is separated by a spectrometer and detected, allowing simultaneous multi-element analysis with high sensitivity and precision [101].

To evaluate the dissolution behavior of elements in LLTO or LLZO powders, 1.00 g of the pristine powder was immersed in an acetonitrile/dimethylformamide (ACN/DMF) solution and heated at 125 °C for 5 and 30 hours. After thermal treatment, the suspensions were extracted using a syringe and passed through a 0.22 µm PTFE syringe filter to remove any undissolved solids. The filtrates were collected and adjusted to a final volume of 5000 µL. Subsequently, these filtered solutions were dried at 120 °C to remove organic solvents and then redissolved in 2% (v/v) trace metal grade HNO₃ to ensure compatibility with ICP-AES analysis. Elemental analysis was carried out using a Thermo iCAP 7400 Duo ICP-AES instrument. Calibration standards were prepared using certified single-element solutions purchased from High Purity Standards (North Charleston, SC), ensuring accurate quantification of dissolved metal species.

2.4.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was employed to investigate the thermal stability and residual solvent content of the cold-sintered composite solid electrolytes. In TGA, the mass of a sample is continuously measured as it is heated under a controlled atmosphere, allowing detection of decomposition, desorption, or other mass-change events. This technique is particularly useful for identifying the presence of residual solvents or other volatile species [102]. Thermal analysis was performed using a Q600 SDT thermogravimetric analyzer (TA Instruments). Samples were first equilibrated at 50 °C for 10 minutes to remove moisture, and then heated from room temperature to 400 °C at a rate of 10 °C/min under a nitrogen atmosphere to quantify the amount of dimethylformamide (DMF) residue.

2.4.8. Hardness, Fracture Toughness and Elastic Modulus Measurements

Before mechanical characterization, conventionally sintered and cold-sintered pellets were embedded in resin. Their surfaces were polished with 600, 800, 1200, and 2400 grit grinding paper to achieve the desired surface flatness, without using any solvent. For microindentation and nanoindentation measurements, parallel surfaces are required to minimize measurement errors. Microindentation measurements were performed using a Vickers indenter on the HV-1 and HV-10 scales to determine the hardness and fracture toughness of the samples. In this method, a diamond-shaped indenter is pressed into the polished surface under a controlled load, and the diagonals of the resulting indentation are measured optically. The hardness is calculated based on the applied load and the size of the indentation, providing information on the resistance of the material to localized plastic deformation [103]. Fracture toughness was estimated using the following analytical equation:

$$K_{IC} = 0.16 \times H \times d^2 \times C^{-1.5}, \quad (2.13)$$

where H is the Vickers hardness, d is half the diagonal of the Vickers indent, and C is the radius of the critical crack [104]. The elastic modulus of the pellets was evaluated by nanoindentation testing. Measurements were performed using a Hysitron TI-900 TriboIndenter equipped with a Berkovich diamond tip, applying a maximum load of 10 mN. The modulus was extracted from the unloading segment of the load-displacement curves using the Oliver-Pharr method, which allows the determination of elastic properties by analyzing contact stiffness during indentation [105]. This technique provides a reliable means to assess local mechanical properties at the sub-micrometer scale.

2.4.9. Particle Size Analysis

Particle size analysis of both the pristine ceramic powders and the crushed composite powders obtained from sintered pellets was performed using a laser diffraction particle size analyzer (Mastersizer 3000+, Malvern Panalytical). Isopropyl alcohol was used as the dispersing medium to minimize agglomeration and ensure stable suspension of the particles during the measurement. The laser diffraction method determines the

particle size distribution based on the angle and intensity of light scattered by particles suspended in a liquid medium. Larger particles scatter light at smaller angles, while smaller particles scatter at wider angles. This technique provides reliable information on the size distribution of powders [106].



3. COLD SINTERING PROCESS OF OXIDE-BASED SOLID ELECTROLYTES

The remainder of this thesis presents the performed experimental studies, focusing on the fabrication, characterization, and optimization of solid electrolytes for solid-state batteries and their integration with cathode materials. This chapter explores the cold sintering conditions of LLZO- and LLTO-based composite electrolytes that were systematically investigated to enhance ionic conductivity through an innovative, cost-effective, and energy-efficient approach. Before co-sintering these composite electrolytes with cathode layers, identifying the optimal cold sintering parameters for solid electrolytes is crucial to achieve high ionic conductivities exceeding $10^{-4} \text{ S cm}^{-1}$. Through systematic optimization of processing conditions, this thesis aims to establish a fundamental understanding of cold sintering for the development of next-generation solid-state battery electrolytes.

3.1. Cold Sintering Process of LLZO Composite Solid Electrolytes

3.1.1. Introduction

LLZO is a promising solid electrolyte for all-solid-state lithium batteries as a result of its high ionic conductivity and excellent chemical stability against the lithium metal. Its cubic phase, which is stabilized through doping, enables fast lithium-ion transport while maintaining good mechanical properties. The densification of oxide-based electrolytes requires high sintering temperatures ($T_{\text{sintering}} > 900 \text{ }^{\circ}\text{C}$) to achieve ionic conductivities greater than $10^{-4} \text{ S cm}^{-1}$. Conventionally sintered Al-doped LLZO solid electrolytes achieve ionic conductivities between $2.11 \times 10^{-4} \text{ S cm}^{-1}$ and $4.48 \times 10^{-4} \text{ S cm}^{-1}$, depending on sintering conditions and processing methods [107–109]. The reported sintering temperatures range from 900 to 1230 $^{\circ}\text{C}$, with durations varying between 6 and 36 hours, an energy intensive process used to achieve dense samples. This prolonged high-temperature treatment is essential for obtaining large grains and

ensuring intimate contact between them, helping to reduce grain boundary resistance and enhance lithium-ion transport [108].

This section examines the cold sintering performance of LLZO solid electrolytes as a potential alternative to conventional sintering techniques. Cold sintering aims to significantly reduce the required sintering temperature by an order of magnitude, allowing densification at much lower temperatures while maintaining or even improving the ionic conductivity of the material. This approach not only minimizes energy consumption but also mitigates issues such as lithium loss and unwanted phase formation, which are common in high-temperature sintering processes. The cold sintering performance is influenced by factors such as the chemistry and composition of the solvent, the amount of electrolyte additives, applied pressure, temperature, sintering duration, and the solubility of the sintered particles in the solvent. Therefore, the primary motivation of this section is to identify the optimal cold sintering parameters for $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, to achieve high ionic conductivity ($\sim 10^{-4} \text{ S cm}^{-1}$).

3.1.2. Experimental Methods

$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ powders were purchased from MSE Supplies. In the first stage, the ceramic powder is mixed with deionized water (30 wt.% of the ceramic powder), milled using an agate mortar and pestle for 5 minutes, and then placed into a cold sintering die with an inner diameter of 10 mm. The die was then surrounded by a bracelet connected to a heating element, equipped with a thermocouple, and placed on a uniaxial compression machine to apply pressure and heat simultaneously (Figure 3.1). To evaluate the impact of temperature, pressure and sintering duration on the cold sintering performance of the pellets, the cold sintering process was carried out within a controlled pressure range of 300 to 600 MPa and a temperature range of 100 °C to 160 °C, with a rate of increase of 10 °C per minute. The sintering duration varied between 1 and 4 hours. The cubic LLZO exhibits a relatively high bulk ionic conductivity ($> 5 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature). However, the main challenge in the cold sintering process is achieving high ionic conductivity between grain boundaries

due to the formation of amorphous grain boundaries and porosity at the grain-to-grain interface caused by low-temperature processing [110].

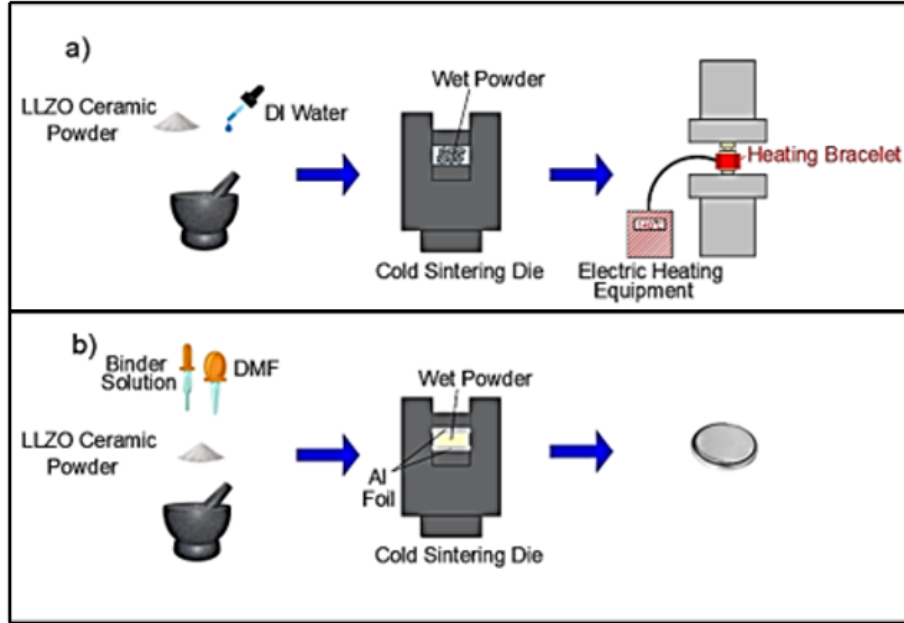


Figure 3.1. Cold sintering process of LLZO using (a) Deionized water, (b) Binder-salt solution, and DMF.

To establish conductive pathways across grain boundaries, a binder-salt solution was prepared using polypropylene carbonate (PPC) and lithium perchlorate (LiClO_4) with weight ratios of PPC to LiClO_4 of 1, 2, 4, and 8. PPC (average $M_n \approx 50,000$ Da) and LiClO_4 were purchased from Sigma-Aldrich. In the preparation of the binder-salt solution, the binder and lithium salt were dissolved in acetonitrile (ACN), where acetonitrile constitutes 80% of the total mass of the PPC- LiClO_4 -ACN mixture. The resulting mixture was stirred overnight using a magnetic stirrer at 25 °C. Afterward, the Al-doped LLZO powder was mixed with the binder-salt solution and DMF, milled using an agate mortar and pestle for 5 minutes, and then placed between aluminum foil disks in a cold sintering die with a 13 mm inner diameter. The LLZO powder was incorporated with a weight percentage of 95% and the weight ratio of PPC to LiClO_4 was studied for values of 1, 2, 4, and 8, designated LLZO-PS1, LLZO-PS2,

LLZO-PS4 and LLZO-PS8, where PS stands for polymer-salt. The weight percentages of the constituents in the LLZO composites are shown in Table 3.1. The amount of DMF added is 9 wt.% of the LLZO-PPC-LiClO₄ composites. The composite powder was subjected to uniaxial pressure of 300 MPa at 120 °C for 1 h with a ramp-up rate of 10 °C/minute. The composite pellet was then assembled within a 2032-coin cell to perform EIS measurements. Both the preparation of the binder-salt solution and the cold sintering process of the composite powder were performed in an Ar-filled glovebox (Figure 3.1b).

Table 3.1. The weight percentages of the constituents in the LLZO composites.

Composite	LLZO (wt.%)	PPC (wt.%)	LiClO ₄ (wt.%)
LLZO-PS1	95	2.50	2.50
LLZO-PS2	95	3.33	1.66
LLZO-PS4	95	4.00	1.00
LLZO-PS8	95	4.44	0.55

3.1.3. Results and Discussion

The cold sintering process employs a transient solvent to facilitate densification through a dissolution-precipitation mechanism, effectively lowering the sintering temperature below 300 °C. CSP is governed by several key parameters, such as the type and quantity of solution introduced, the applied pressure, the sintering temperature, the duration, and the size of the powder particles. Consequently, the effects of initial particle size, temperature, pressure, sintering duration, and additive incorporation on the performance of cold sintering for Al-doped LLZO solid electrolytes were investigated.

The density of the cold-sintered pellets fabricated by adding deionized water as a transient solvent was measured. This measurement used Archimedes' principle and involved a precision balance (Precisa XB 220A) and a dedicated density determination kit. Initially, the dry weight of the pellet was measured, followed by suspension in water

to determine its soaked weight. The device recorded the density of water as $1.00069 \text{ g cm}^{-3}$. It automatically calculated the density of the pellets based on their dry and wet weights. The relative density of the pellets was determined in comparison to the theoretical density of LLZO, which is 5.093 g cm^{-3} . The cold sintering conditions and the relative density of the pellets are summarized in Table 3.2.

The observed trends reveal a notable correlation between the sintering temperature and the relative density of the samples. Specifically, as the sintering temperature increases from $100 \text{ }^{\circ}\text{C}$ to $160 \text{ }^{\circ}\text{C}$, a discernible reduction in relative density becomes evident, decreasing from 84.39% to 75.06%. This finding underscores the critical role of sintering temperature in densification, paving the way for a comprehensive understanding of cold sintering dynamics. The liquid added in the cold sintering process significantly alters the mechanism, distinguishing it from conventional sintering techniques.

During cold sintering, liquid-assisted mass transfer occurs. In the absence of this liquid phase, atomic species diffuse only at the solid-solid interface. In other words, the introduction of the liquid phase facilitates the movement of the particles, reducing energy requirements. The difference in governing mechanisms explains why powder densification can occur at much lower temperatures through cold sintering than conventional sintering techniques. It is reasonable to assert that one of the limiting factors for the cold sintering process is the boiling temperature of the added liquid phase. The cold sintering temperature must be determined based on the boiling temperature of the liquid phase. If the sintering temperature exceeds this boiling point, the evaporation rate of the liquid phase increases. Therefore, when the sintering temperature reaches $160 \text{ }^{\circ}\text{C}$, the evaporation rate of water increases, and the reduction of the liquid phase adversely impacts the cold sintering mechanism.

Table 3.2. Cold sintering conditions and relative densities of the fabricated pellets.

Temperature (°C)	Pressure (MPa)	Duration (hours)	Relative Density (%)
100	500	2	84.399
120	500	2	83.217
140	500	2	81.571
160	500	2	75.066
120	500	1	78.090
120	500	3	76.058
120	500	4	73.681
120	300	2	76.807
120	400	2	76.541
120	600	2	76.137

Solvent: 30 wt.% deionized water, Initial particle size D50 < 10 μm .

The use of deionized water as a transient solvent facilitates the achievement of a relative density that exceeds 80%. However, the ionic conductivity of the cold-sintered pellets remains notably low, persisting below $10^{-9} \text{ S cm}^{-1}$ at room temperature. Figure 3.2 shows the relative densities and total ionic conductivities of cold-sintered solid electrolytes at various sintering temperatures and durations. A direct proportionality exists between the relative density and ionic conductivity values, with the latter increasing in parallel with the increase in densities. The highest density is attained when the sintering duration is 2 h. The phase purity and crystal structure of the Al-doped LLZO powder and cold-sintered pellets were examined by XRD analysis. Figure 3.3 displays the XRD patterns of the Al-doped LLZO powder and the cold-sintered LLZO solid electrolytes, which were obtained using 30 wt.% deionized water at 120 °C for 2 hours and under a pressure of 300-400 MPa. The obtained XRD peaks of the powder matched closely with the reference pattern (ICDD: 04-023-8443) of the cubic garnet-type $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, indicating the absence of any detectable impurity phases.

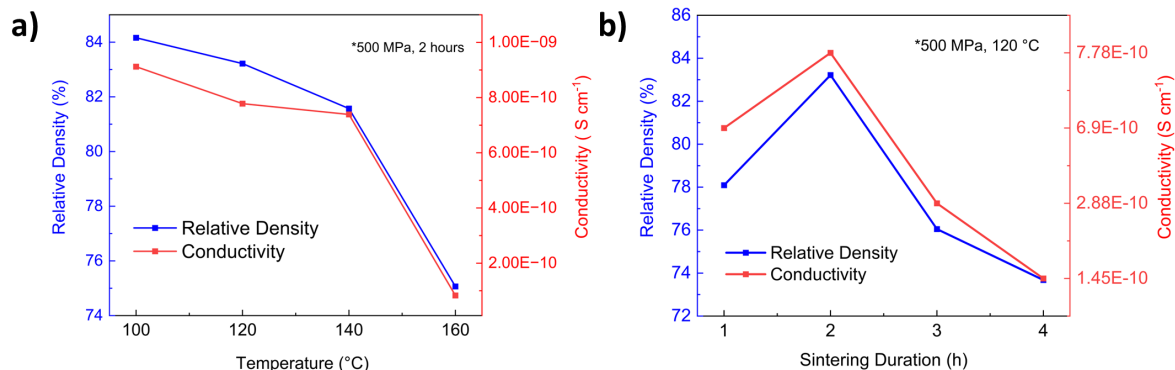


Figure 3.2. Relative densities and ionic conductivities of cold-sintered LLZO solid electrolytes at room temperature by (a) varying sintering temperatures, (b) varying sintering durations.

The cold-sintered pellets exhibit additional peaks, which correspond to the reference pattern (ICDD: 00-006-0585) of the lanthanum hydroxide $\text{La}(\text{OH})_3$. The emergence of lanthanum hydroxide is attributed to incongruent dissolution in water. It is plausible that water selectively dissolves lithium and zirconium from the grain edges of LLZO, leaving lanthanum behind and causing the formation of lanthanum hydroxide. No other impurity phases were detected in the XRD characterization of the pellets; however, the Li and Zr-containing impurity phases may have formed in an amorphous state. The formation of lanthanum hydroxide suggests the potential formation of additional impurity phases lacking lanthanum. Figure 3.2a demonstrates that increasing the temperature results in a reduction in ionic conductivity, likely due to the accelerated evaporation of water. This rapid evaporation may disrupt the dissolution–precipitation mechanism, leading to lower relative densities. Furthermore, as shown in Figure 3.2b, when the temperature is maintained at 120 °C, prolonging the sintering time beyond 2 hours further decreases the ionic conductivity, which is presumably caused by the progressive formation of the secondary phase $\text{La}(\text{OH})_3$.

Figure 3.4 presents the EDS mapping of the LLZO solid electrolyte, subjected to cold sintering conditions at 120 °C and 400 MPa for 2 hours. The distribution of La and Zr elements demonstrates incongruent dissolution in water, since lanthanum-deficient

secondary phases (Point 1) segregate and disperse within the bulk solid electrolyte (Point 2). Quantitative chemical analysis at two points confirms the formation of secondary phases deficient in lanthanum, as the weight percentage of lanthanum decreases from 40.4 wt.% to 3.4 wt.% between points 1 and 2. The formation of impurity phases adversely affects the ionic conductivity of solid electrolytes because of their constrained ion transport mechanisms in contrast to the superior bulk ionic conductivity exhibited by the LLZO phase. The minute carbon content originates from the grinding process, in which silicon carbide sandpaper is utilized to attain a polished surface before microstructural characterization.

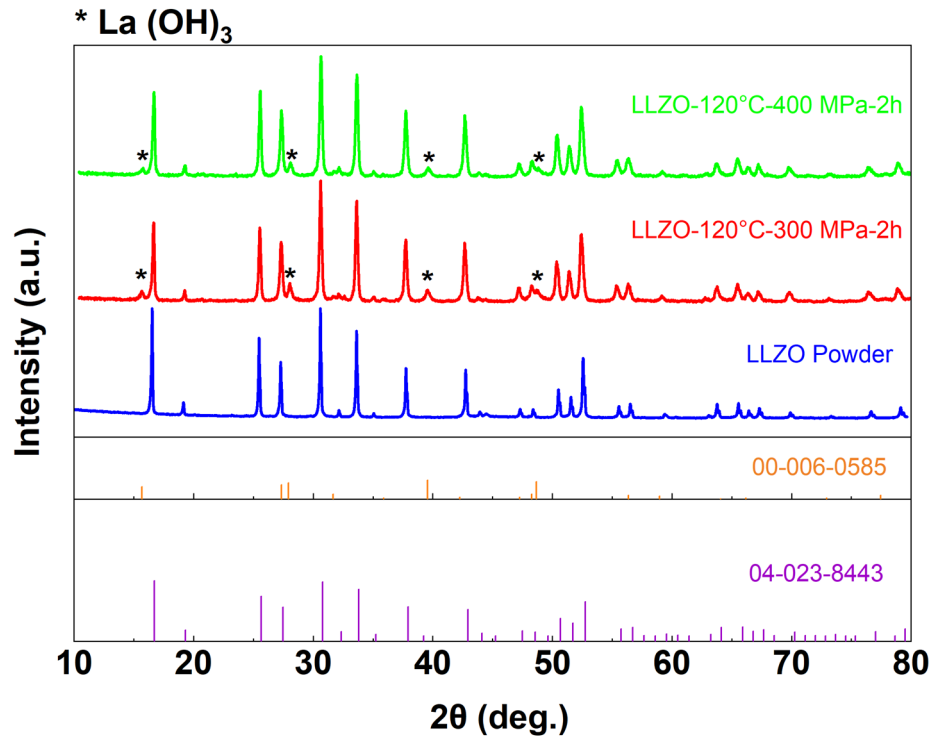


Figure 3.3. XRD patterns for LLZO powder and the cold-sintered LLZO solid electrolytes.

The exceptionally low temperature processing and the incongruent dissolution in cold sintering lead to amorphous grain boundaries characterized by low ionic conductivity [72, 111, 112]. Consequently, the primary bottleneck in the cold sintering of

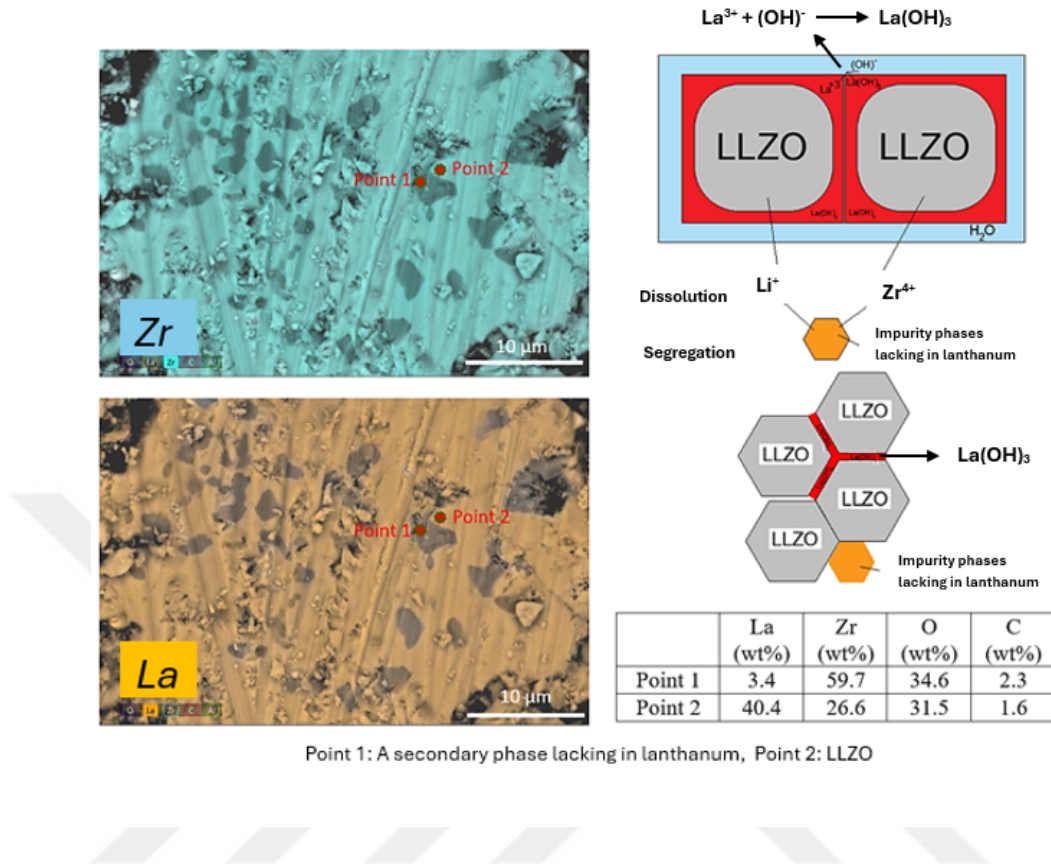


Figure 3.4. SEM images and EDS mapping results of the cold-sintered LLZO solid electrolyte fabricated at 120 °C and 400 MPa for 2 h.

solid-state electrolytes is the attainment of increased ionic conductivity at the grain boundaries. Therefore, to establish conductive pathways across grain boundaries, a polymer-salt solution was prepared with varying polymer-to-salt weight ratios (PPC: $\text{LiClO}_4 = 1, 2, 4, 8$) to fabricate ceramic-polymer composite solid electrolytes. Furthermore, the effect of initial particle size on the resulting relative density and ionic conductivity was examined using LLZO powders with different particle size distributions ($D_{50} < 10 \mu\text{m}$ and $D_{50} < 1 \mu\text{m}$) within the framework of the cold sintering process.

Figure 3.5a shows the Nyquist plots of composite electrolytes containing LLZO-PPC- LiClO_4 . The relative density of cold-sintered composite solid electrolytes decreases from 84.5% to 76.2% as the content of polypropylene carbonate in PPC- LiClO_4

increases (Figure 3.5b). As more PPC is incorporated, it can inhibit grain-to-grain contact between LLZO particles due to its lower density compared to the ceramic phase, thereby reducing the overall packing efficiency. The ionic conductivity of the cold-sintered composite electrolytes reaches a maximum value of $2.15 \times 10^{-4} \text{ S cm}^{-1}$ at a PPC: LiClO_4 weight ratio of 2. The PPC: LiClO_4 weight ratios of 1 and 4 yield moderately reduced ionic conductivities of $5.25 \times 10^{-5} \text{ S cm}^{-1}$ and $7.1 \times 10^{-5} \text{ S cm}^{-1}$, respectively, whereas the ratio of 8 exhibits a significantly lower conductivity of $5.29 \times 10^{-6} \text{ S cm}^{-1}$, nearly two orders of magnitude lower than the maximum conductivity achieved at a weight ratio of 2.

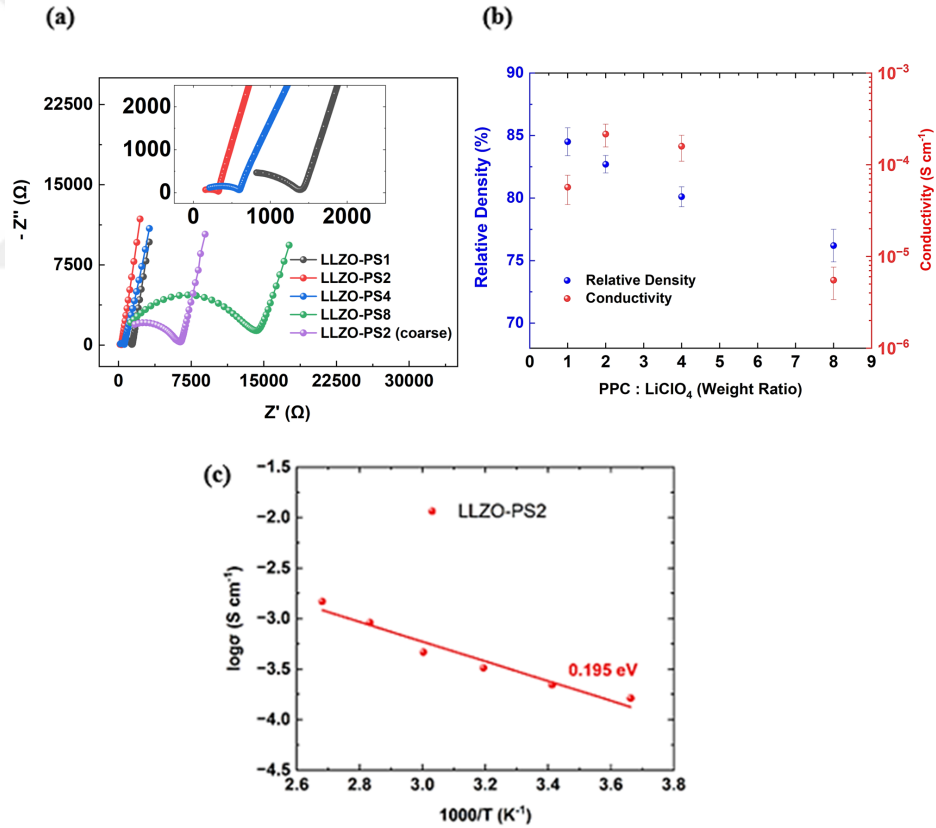


Figure 3.5. (a) Nyquist plots of cold-sintered LLZO-based composite electrolytes. (b) Relative densities and ionic conductivities of cold-sintered composite solid electrolytes at room temperature. (c) Arrhenius plot of the cold-sintered LLZO composite (LLZO-PS2).

The decline in ionic conductivity at higher PPC: LiClO_4 weight ratios can be attributed to the excess amount of PPC combined with a deficient concentration of lithium salt. At lower PPC contents, PPC- LiClO_4 effectively infiltrates grain boundaries, improving ionic transport by providing continuous Li^+ conduction pathways. However, as the PPC content increases without a proportional increase in lithium salt, the Li^+ concentration within the PPC phase becomes insufficient to sustain efficient ionic conduction. The excess PPC may accumulate at the grain boundaries, forming insulating or poorly conducting regions due to the limited availability of mobile Li^+ ions. Consequently, the imbalance between the content of PPC and LiClO_4 at high PPC loadings leads to decreased ionic conductivity and increased resistance at the grain boundaries. The equivalent circuit model for cold-sintered LLZO composites is shown in Figure 3.6.

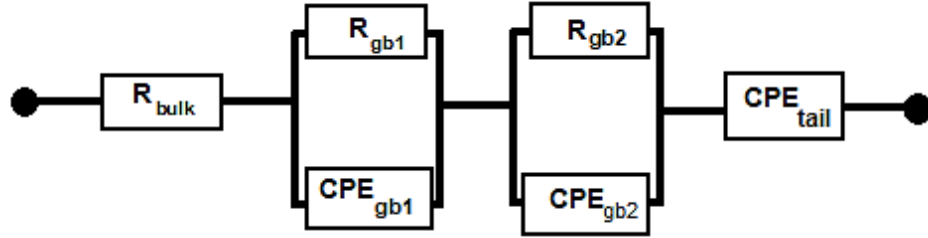


Figure 3.6. Equivalent circuit model for cold sintered LLZO composites.

R_{bulk} represents the bulk lithium-ion conductivity within the LLZO ceramic phase. In addition, parallel configurations of resistors (R_{gb1} and R_{gb2}) and constant phase elements (CPE_{gb1} and CPE_{gb2}), expressed as $R_{\text{gb1}} \parallel \text{CPE}_{\text{gb1}}$ and $R_{\text{gb2}} \parallel \text{CPE}_{\text{gb2}}$, were used to model grain boundary lithium-ion conductivities. Cold-sintered LLZO composites exhibit two distinct grain boundary resistances due to the partial filling of the grain boundaries by PPC- LiClO_4 , resulting in heterogeneous grain boundaries. The tail in the low-frequency region was modeled by adding a constant phase element (CPE_{tail}) in series with the other circuit elements, as previously described, to represent lithium-ion blocking electrodes [113].

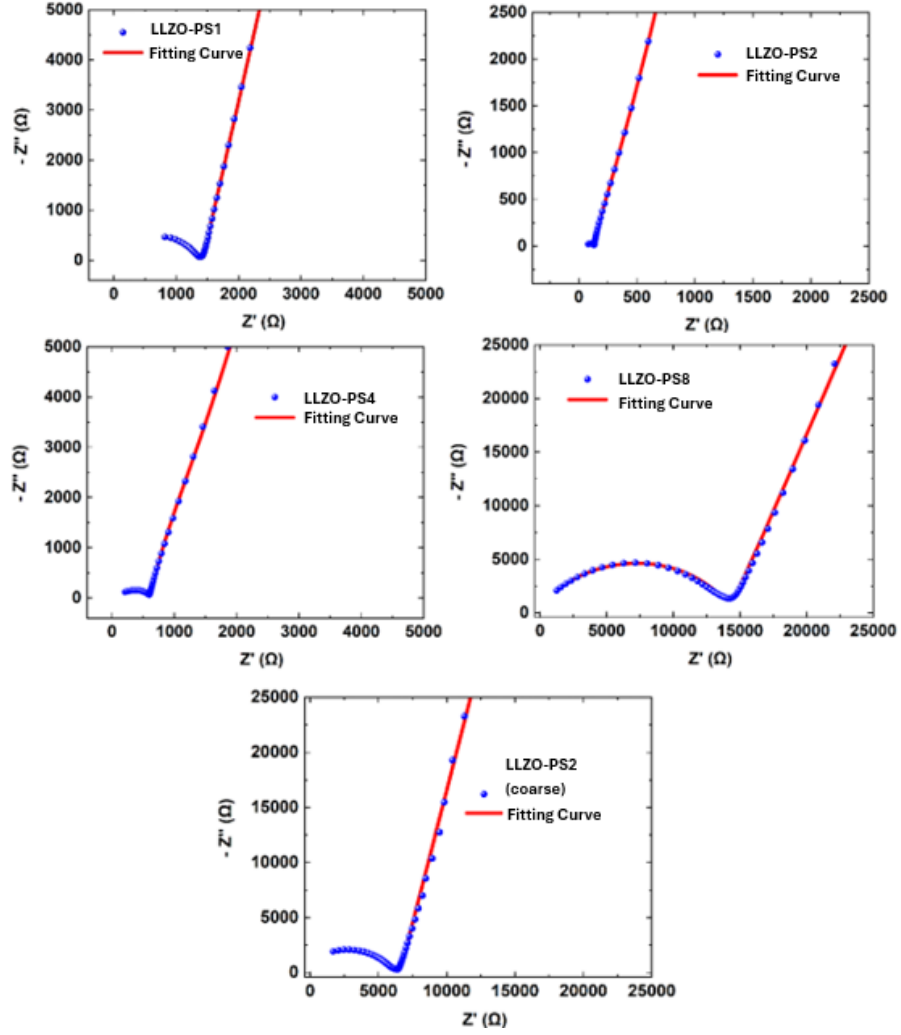


Figure 3.7. Fitting of Nyquist Plots for cold sintered LLZO composites.

The Nyquist plots of LLZO composites along with their fitted curves and the corresponding EIS fitting parameters are shown in Figure 3.7 and Table 3.3, respectively. Figure 3.5c shows the temperature dependence of ionic conductivity of cold-sintered LLZO composite electrolytes (LLZO-PS2). The temperature dependence appears of Arrhenius form for the cold-sintered solid electrolyte with an activation energy of 0.195 eV. The reported activation energy of Al-doped LLZO solid electrolytes falls within the range of 0.3 to 0.4 eV [107,108]. Incorporating an appropriate amount of PPC-LiClO₄ into the LLZO phase can substantially enhance lithium-ion transport, leading to a decrease in the activation energy.

Table 3.3. EIS fitting results for cold sintered LLZO composites.

Sample	R_{bulk} (Ω) R_{gb1} (Ω)	$\text{CPE}_{\text{gb1-T}}$ (F) $\text{CPE}_{\text{gb1-P}}$	$\text{CPE}_{\text{gb2-T}}$ (F) $\text{CPE}_{\text{gb2-P}}$	$\text{CPE}_{\text{tail-T}}$ (F) $\text{CPE}_{\text{tail-P}}$	R_{gb2} (Ω)
LLZO-PS1	75.20 470.32	1.05×10^{-10} 1.07	1.74×10^{-7} 0.55	2.61×10^{-6} 0.89	882.80
LLZO-PS2	74.50 57.00	1.48×10^{-8} 0.93	1.59×10^{-5} 0.88	2.61×10^{-6} 0.90	250.70
LLZO-PS4	100.25 511.00	9.98×10^{-8} 0.69	1.02×10^{-5} 0.92	2.37×10^{-6} 0.88	625.10
LLZO-PS8	73.15 316.40	5.85×10^{-11} 1.18	3.69×10^{-9} 0.74	1.07×10^{-6} 0.78	13857.00
LLZO-PS2 (coarse)	100.65 1546.00	1.52×10^{-6} 0.50	6.72×10^{-10} 0.84	3.76×10^{-6} 0.87	4958.00

The initial average particle size of the powder used in the cold sintering of composite electrolytes is about 1 μm , except for the sample designated LLZO-PS2 (coarse), where the initial average particle size of the powder measures around 10 μm . When using a fine powder ($\sim 1 \mu\text{m}$) in the cold sintering process, an ionic conductivity exceeding $10^{-4} \text{ S cm}^{-1}$ is attained for a PPC: LiClO_4 weight ratio of 2. However, under identical conditions, the ionic conductivity of the pellet is measured as $1.24 \times 10^{-5} \text{ S cm}^{-1}$ when the initial average particle size is 10 μm , accompanied by a relative density of approximately 76%. This represents an almost 7% reduction in relative density compared to the fine powder counterpart, highlighting the notable influence of particle size on both ionic conductivity and relative density in the cold sintering process. The establishment of a polymer-salt bridge, serving as an ionic transport channel, is plausible at the interfaces between the grains in the densely packed solid electrolytes [114]. Hence, to promote the establishment of polymer-salt bridges among ceramic particles, it is essential to achieve relative densities above 80%, characterized by intimate contact between grains and minimal porosity.

Figure 3.8 presents SEM images that capture the fracture cross sections of the cold-sintered pellets. Figure 3.8a illustrates the microstructure of the cold-sintered pellet fabricated using 30 wt.% deionized water at 120 $^\circ\text{C}$ and 500 MPa for 1 hour, with an initial particle size averaging 10 μm . SEM images reveal the presence of

large pores between the grains, with the initial particle size of approximately 10 μm hindering intimate contact between them, leading to the formation of a loosely packed microstructure. The hindrance of lithium-ion conduction by the voids between the grains leads to a notable decline in ionic conductivity, with values remaining below $10^{-9} \text{ S cm}^{-1}$.

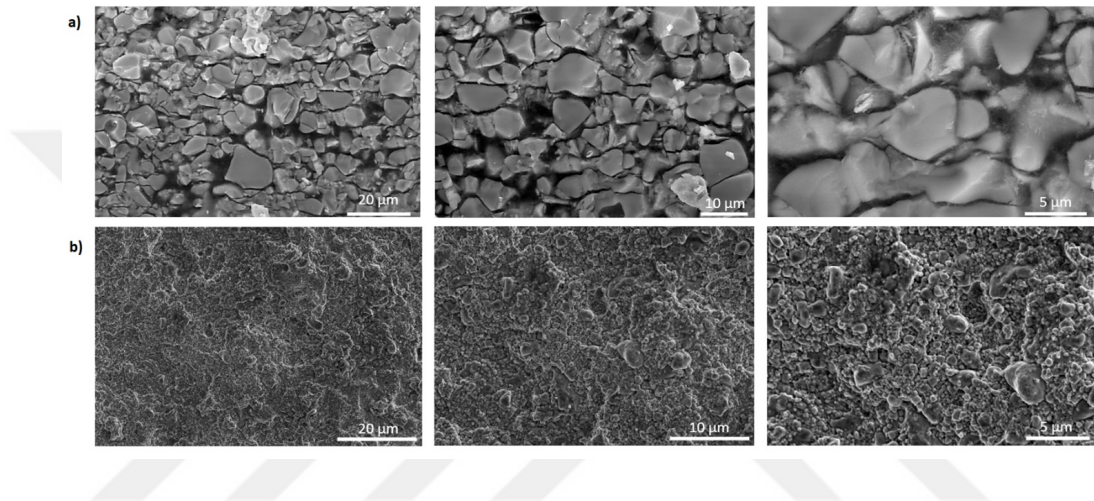


Figure 3.8. Microstructural characterization of the cold-sintered pellets: (a) at 120 °C, 500 MPa for 1 hour using 30 wt.% deionized water, (b) at 100 °C, 300 MPa for 1 hour using a binder-salt solution.

Figure 3.8b elucidates the microstructure of the cold-sintered pellet, manufactured using a binder-salt solution under conditions of 100 °C and 300 MPa for 1 hour, with an initial particle size of around 1 μm . In addition, the solid composite electrolyte comprises 95% LLZO powder by weight, with a PPC/LiClO₄ weight ratio of 2. The reduction in initial particle size results in a densely packed microstructure and a continuous framework with minimal porosity.

Figure 3.9 illustrates the EDS mapping of the cold-sintered electrolyte LLZO-PS2, which was densified at 100 °C and 300 MPa for 1 hour. In the composite solid electrolyte, the constituent elements of LLZO, namely La and Zr, exhibit a uniform distribution. The C element of the PPC and the Cl element of the LiClO₄ salt are

evenly distributed within the bulk, indicating that the lithium salt is well dissolved in the PPC matrix. A relative density above 95% is expected in conventional high-temperature sintering; however, the application of extremely low temperatures in cold sintering results in a lower relative density. In particular, polymer-salt additives are crucial in promoting lithium-ion transport across grain boundaries, forming a conductive framework that effectively fills the voids and leads to an ionic conductivity exceeding $10^{-4} \text{ S cm}^{-1}$. Figure 3.10 displays the XRD patterns of cold-sintered LLZO composite electrolytes with varying binder to salt content.

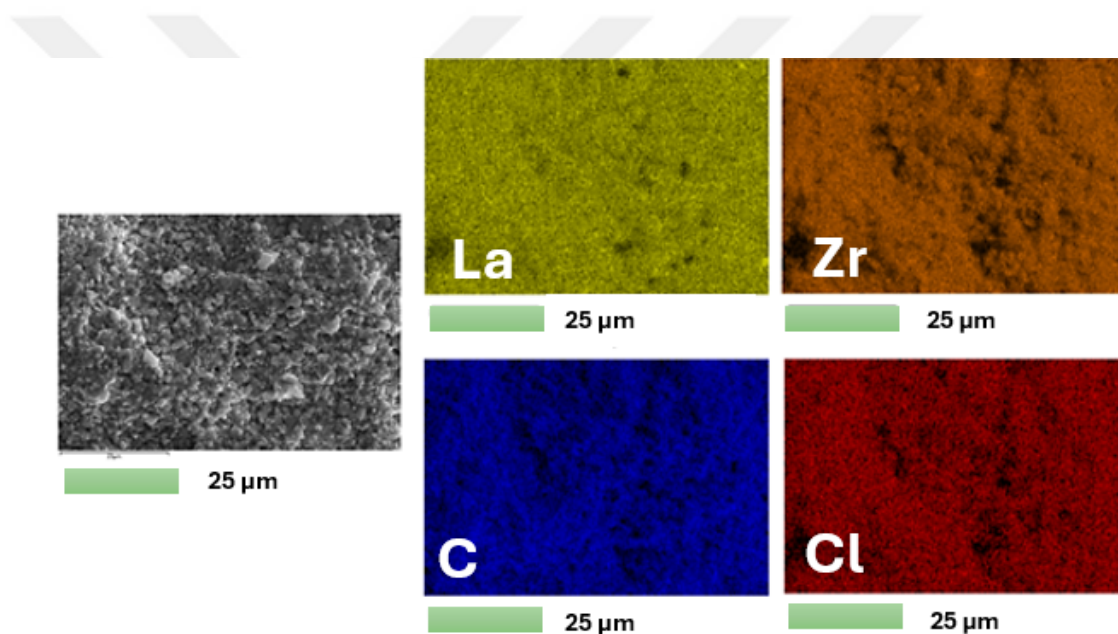


Figure 3.9. EDS mapping of the cold-sintered LLZO-PS2 solid electrolytes.

The X-ray diffraction peaks obtained from all composite solid electrolytes closely match the reference pattern (ICDD: 04-023-8443), which corresponds to the cubic garnet-type crystal structure of $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$. This alignment indicates that these composite electrolytes maintain the characteristic cubic phase with a garnet-type structure and exhibit excellent crystallinity. Therefore, the incorporation of PPC and LiClO_4 through the cold sintering process does not alter the crystal structure of the ceramic LLZO phase.

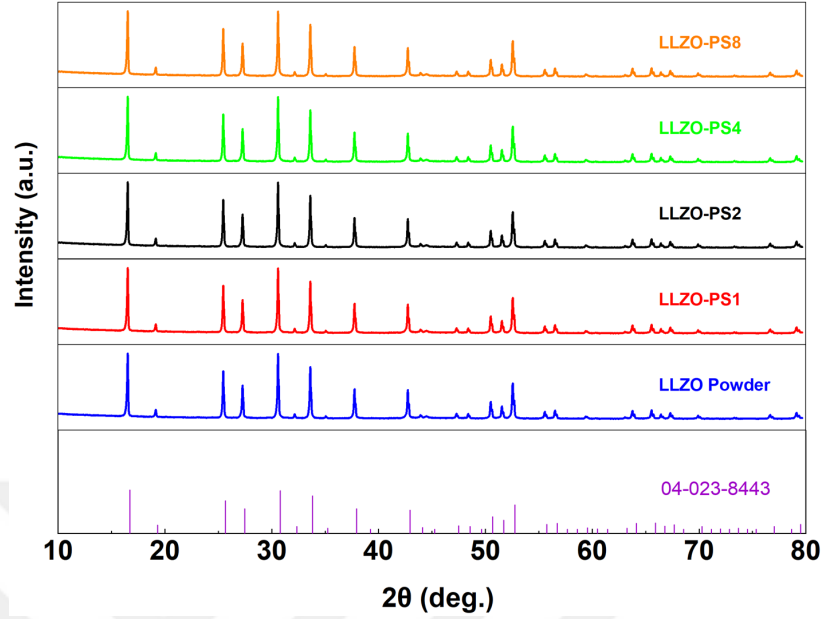


Figure 3.10. XRD Patterns of the cold-sintered LLZO composite solid electrolytes with varying PPC to LiClO_4 weight ratios.

3.2. Cold Sintering Process of LLTO Composite Solid Electrolytes

3.2.1. Introduction

Cold sintering has been successfully applied to LATP and LLZO composite electrolytes, and the obtained ionic conductivities are comparable to those of conventional sintering [60, 73]. Nevertheless, cold sintering of the perovskite LLTO remains under-explored, despite the potential to serve as a solid electrolyte within all-solid-state batteries. High grain boundary resistance is a well-documented limitation in oxide-based ceramic solid-state electrolytes, including garnet and NASICON-type materials [113]. This issue becomes particularly severe in perovskite-type lithium lanthanum titanate (LLTO), posing a critical bottleneck to ionic conductivity. Previous work has reported that the conductivity at the grain boundaries in LLTO can be 2 to 3 orders of magnitude lower than in the bulk, significantly limiting electrochemical performance [115]. The ability to co-sinter ceramic and polymer materials with cold sintering could address this limitation by providing alternative pathways for ion transport in LLTO-based

composites [60]. Here, ceramic-based composite electrolytes were manufactured by integrating polymer-salt mixtures (PPC-LiClO₄) with LLTO using cold sintering at 125 °C. Cold sintered composites exhibit high relative densities above 80% and a high ionic conductivity of $3 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature; the ionic conductivity was high for temperatures between 0 and 100 °C, leading to a low activation energy of 0.25 eV.

3.2.2. Experimental Methods

LLTO perovskites were synthesized via the solid-state reaction method without secondary phase formation. Details of the synthesis process and the XRD pattern of the synthesized perovskites are provided in Appendix B. Throughout all the cold sintering experiments, commercial-grade LLTO powder was used to avoid the additional effort of synthesizing high-purity powders required for the process, even though high-purity LLTO powders had been synthesized via the solid-state reaction method. Li_{0.29}La_{0.57}TiO₃ powders, with a particle size distribution (D50) of less than 1 µm, were purchased from Toho Titanium Co., Ltd. PPC and LiClO₄ were purchased from Sigma-Aldrich.

A binder-salt solution was prepared with a 2:1 weight ratio of PPC to LiClO₄. This ratio was fixed at 2 for LLTO composites, as it had previously provided the highest ionic conductivity in LLZO-based composites. In the preparation of the binder-salt solution, the binder and lithium salt were dissolved in acetonitrile. The resulting mixture was stirred overnight at 25 °C using a magnetic stirrer. Afterward, the LLTO powder was mixed with the binder-salt solution and DMF. Subsequently, the mixture was mixed using an agate mortar and pestle for 5 minutes. To explore the influence of the introduction of polymer-lithium salt on lithium ion conductivity and relative density, the volume fractions of PPC-LiClO₄ were systematically altered for the solid composite electrolytes, ranging from 4% to 13% by volume (designated LLTO-PS (4-13 vol%). The weight percentages of the constituents in the LLTO composites are shown in Table 3.4. 9 wt.% DMF was used as the cold sintering solvent. The resulting wetted powder was placed in a 13 mm die and sandwiched between aluminum foils, serving

as blocking electrodes for impedance measurements. The die was then surrounded by a bracelet connected to a heating element, equipped with a thermocouple, and loaded into a uniaxial press to apply pressure and heat simultaneously.

Table 3.4. The weight percentages of the constituents in the LLTO composites.

Sample	LLTO (wt.%)	PPC (wt.%)	LiClO ₄ (wt.%)
LLTO-PS (4 vol%)	98.787	0.809	0.404
LLTO-PS (7 vol%)	97.830	1.446	0.723
LLTO-PS (10 vol%)	96.830	2.113	1.056
LLTO-PS (13 vol%)	95.786	2.808	1.404

Figure 3.11 illustrates the cold sintering process of LLTO composites. The composite powder was subjected to a uniaxial pressure of 600 MPa at 125 °C for 1 h with a ramp-up rate of 10 °C/minute. The composite pellet was then assembled within a 2032-coin cell to perform EIS measurements. Both the preparation of the binder-salt solution and the cold sintering process of the composite powder were performed in an Ar-filled glovebox. PPC-LiClO₄ thin films were also manufactured. A binder-salt solution was prepared by dissolving PPC and LiClO₄ in acetonitrile at a weight ratio of 2:1, stirring for several hours to obtain a homogeneous mixture. The polymer electrolyte is fabricated by drop-casting the binder-salt solution onto a substrate and drying it in a glovebox. To determine the ionic conductivity of the polymer electrolyte, symmetric cells were assembled that incorporated the fabricated PPC-LiClO₄ film between aluminum foils.

Another sample was produced in air using deionized water as the transient solvent without adding polymer and lithium salt to investigate the effect of a binder-salt solution between ceramic grains (designated as CS LLTO). 20 wt.% deionized water was added to the LLTO powder and mixed in a mortar and pestle for 5 minutes. The powder was then subjected to a uniaxial pressure of 600 MPa at 125 °C for 2 hours with a ramp-up rate of 10 °C/minute, and the solid electrolyte was assembled within a 2032

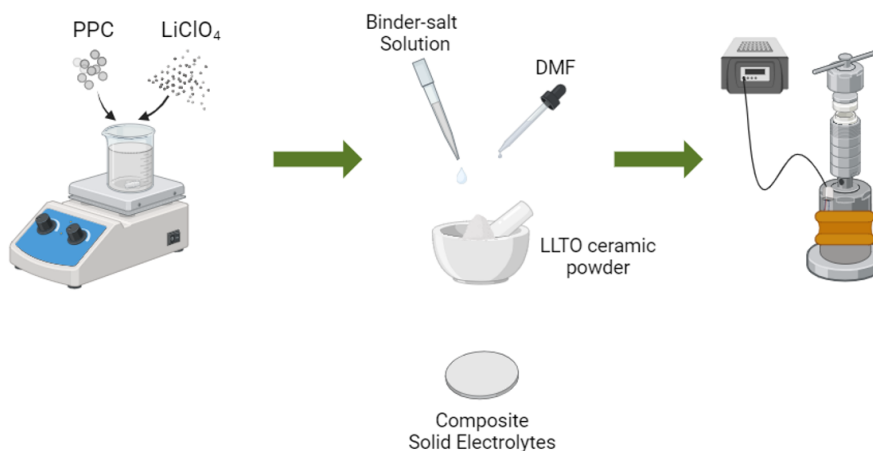


Figure 3.11. Cold sintering process of LLTO composite solid electrolytes.

coin cell for EIS measurements. In addition, a sample was fabricated for comparative analysis using the conventional high-temperature sintering technique (designated as HTS LLTO). To fabricate LLTO solid electrolytes measuring 12.7 mm in diameter and 1 mm in thickness, a uniaxial force of 75 kN was applied to the powder for 5 minutes. In the subsequent step, the samples were buried in LLTO powder within an alumina crucible to mitigate the potential loss of lithium. The sintering step was performed at 1200 °C for 10 hours with ramp-up and ramp-down rates of 5 °C per minute.

3.2.3. Results and Discussion

Cold sintering enables the densification of ceramic-based composites at modest temperatures (under 300 °C) by employing a transient solvent to facilitate mass transport [69]. This approach not only reduces energy consumption but also minimizes damage to temperature-sensitive materials, making it promising for the fabrication of solid-state batteries. A crucial challenge in cold sintering of solid electrolytes is to achieve high ionic conductivity across grain boundaries. Exposure to the transient solvent can lead to incongruent dissolution if elements dissolve to different degrees. Re-precipitation can then result in amorphous or secondary phases with disrupted composition and incomplete densification. Thus, incongruent dissolution often limits

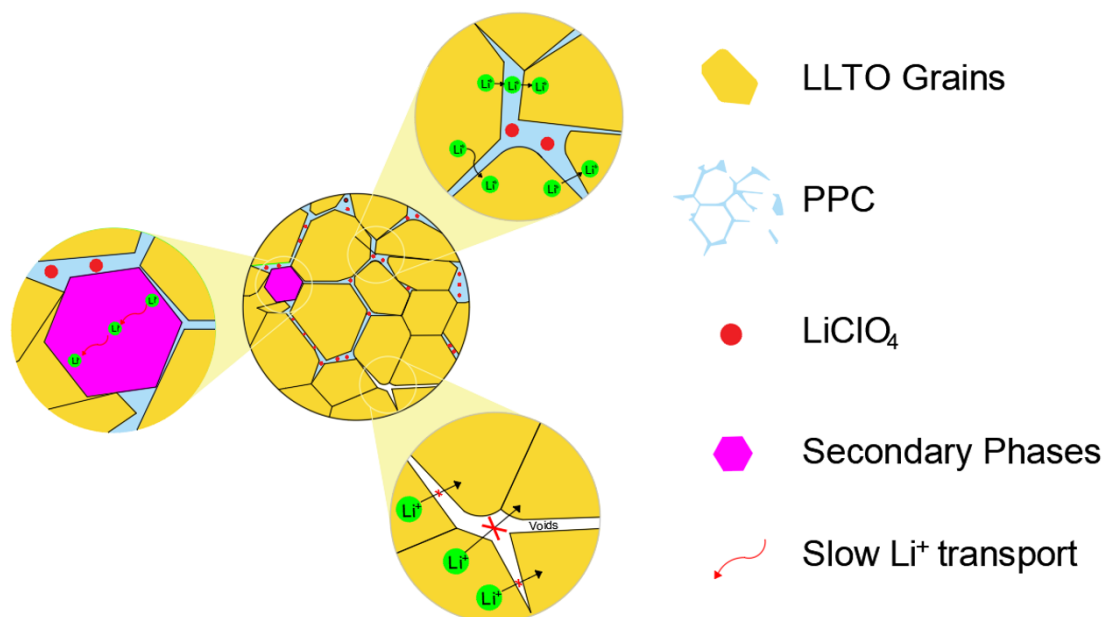


Figure 3.12. Schematic illustrating LLTO ceramic grains with grain boundaries filled with a binder-salt mixture, which effectively enhances the conductivity at the grain boundaries.

the ionic conductivity of cold-sintered electrolytes [71]. Co-sintering with polymers or lithium salts can help bypass these phases and form continuous lithium-ion transport pathways. Incorporation of PPC-LiClO₄ into the LLTO structure results in the infiltration of the binder salt solution into the grain boundaries, effectively reducing interfacial resistance and enhancing ionic transport pathways. This improved grain boundary connectivity facilitates the movement of lithium ions, as shown in Figure 3.12, leading to a significant increase in overall ionic conductivity [116].

To explore the influence of the introduction of polymer-lithium salt on lithium ion conductivity and relative density, the volume fractions of PPC-LiClO₄ were systematically altered for solid composite electrolytes, ranging from 4% to 13% by volume (designated LLTO-PS (4-13 vol%). The drop-casted PPC-LiClO₄ film is shown in Figure 3.13a. The Nyquist plot of the polymer electrolyte is provided in Figure 3.13b. The ionic conductivity of the drop-cast films of PPC-LiClO₄ is $7.8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature.

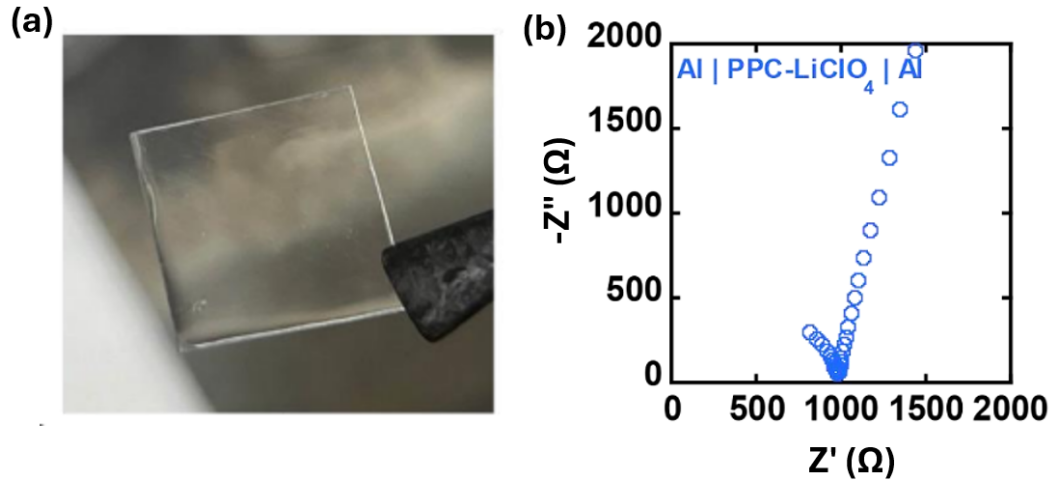


Figure 3.13. (a) The fabricated PPC-LiClO₄ film. (b) Nyquist plot of the PPC-LiClO₄ polymer electrolyte.

9 wt.% DMF is used as a sintering aid in the cold sintering process, which outperforms other solvents, such as acetone and dimethylsulfoxide (DMSO), in promoting densification and optimizing interface design [73]. Figure 3.14 shows the thermogravimetric analysis (TGA) of the cold-sintered solid composite electrolyte at 400 MPa and 125 °C for 30 min. The temperature was equilibrated at 50 °C for 10 minutes to remove trapped moisture near the surface (~ 1.7 wt.%). The weight loss observed up to 100 °C is attributed to the evaporation of residual moisture, estimated at approximately 1 wt.%. The weight loss between 100 and 180 °C is attributed to the evaporation of DMF (~ 1.5 wt.%). The presence of residual DMF improves ionic conductivity [73]. PPC has a relatively low onset temperature for decomposition, which likely contributes to weight loss above 180 °C (~ 2 wt.%) [117]. Another sample was fabricated under identical sintering conditions, using 9 wt.% DMF and omitting the binder-salt solution (LLTO-PS (0 vol%)), to elucidate the role of the PPC-LiClO₄ ionic transport pathways. A sample was fabricated in air using deionized water as transient solvent as previously reported [60,72], without adding polymer or lithium salt (CS LLTO). For comparison, LLTO powder was densified at 1200 °C using conventional high temperature sintering (HTS LLTO).

Figure 3.15 shows the density and relative density of cold-sintered composites and how they vary with composition. The density of the composites decreases from 4.07 g/cm³ to 3.69 g/cm³, corresponding to an increase in the volume percentage of PPC-LiClO₄ from 4% to 13%. The relative density also decreases with higher PPC-LiClO₄ content. LLTO-PS (0 vol%) exhibits a density of 3.88 g/cm³. The density is slightly lower than that of LLTO-PS (4 vol%), which can be attributed to the absence of acetonitrile in LLTO-PS (0 vol%). Acetonitrile functions as a co-solvent alongside DMF, facilitating enhanced densification during processing. LLTO-PS (4 vol%) exhibits the highest density among the composite solid electrolytes, as increasing the PPC-LiClO₄ content reduces the density due to both materials having densities lower than those of the ceramic phase. HTS LLTO achieves the highest density at 4.54 g/cm³, and relative density at 89.2%. LLTO cold sintered with 20 wt.% deionized water has the lowest relative density, approximately 74%.

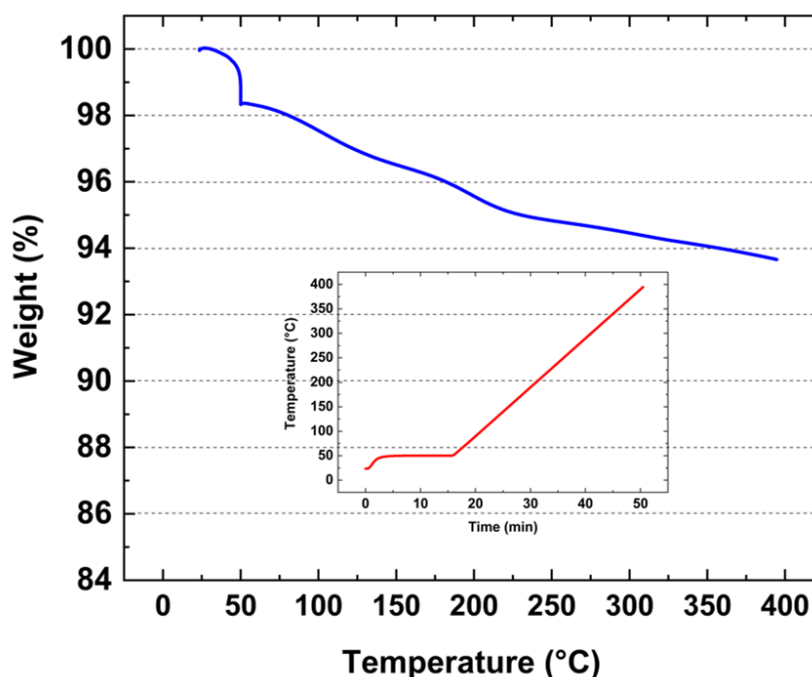


Figure 3.14. Thermogravimetric analysis of the cold sintered LLTO-PS (13 vol%) showing the weight loss as a function of temperature.

Figure 3.16 shows the electrochemical impedance spectra of LLTO-PS (4–13 vol%), CS LLTO, and HTS LLTO. The equivalent circuit used to fit the complex impedance spectra of HTS LLTO is shown in Figure 3.17. The equivalent circuit consists of $(R_{\text{bulk}} \parallel \text{CPE}_{\text{bulk}}) - (R_{\text{gb}} \parallel \text{CPE}_{\text{gb}}) - \text{CPE}_{\text{tail}}$, where R and CPE denote the resistance and constant phase element, respectively. A parallel combination of a resistor (R_{bulk}) and a constant phase element (CPE_{bulk}), denoted $R_{\text{bulk}} \parallel \text{CPE}_{\text{bulk}}$, was used to represent the bulk lithium-ion conductivity in LLTO. In addition, a parallel arrangement of a resistor R_{gb} and a constant phase element CPE_{gb} , expressed as $R_{\text{gb}} \parallel \text{CPE}_{\text{gb}}$, was used to characterize the lithium-ion conductivity at the grain boundaries. The tail in the low-frequency region was represented by incorporating an additional constant phase element (CPE_{tail}) in series with the other circuit elements, as previously reported, to model lithium-ion blocking electrodes [118].

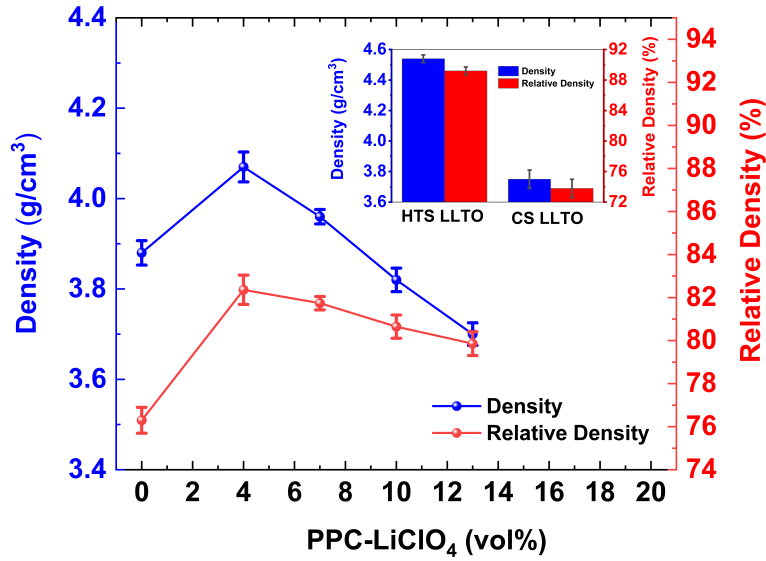


Figure 3.15. Density and relative density of composites as a function of volume percentage of PPC-LiClO₄.

The high-frequency semicircle, associated with a capacitance of 3×10^{-11} F, can be attributed to ion transport in the bulk. In contrast, the medium-frequency semicircle

exhibits a capacitance of 2.93×10^{-7} F, which can be attributed to the transport of ions at the grain boundaries. The EIS fitting parameters for conventionally sintered LLTO are provided in Table 3.5. In the cold-sintered composite samples, the equivalent circuit presents slight variations (Figure 3.18); the capacitances linked to the high-frequency and medium-frequency semicircles are on the order of 10^{-8} F and 10^{-6} F, respectively, both corresponding to ion transport across the grain boundaries. The increase in PPC-LiClO₄ content correlates with a decrease in grain boundary resistances (Table 3.6).

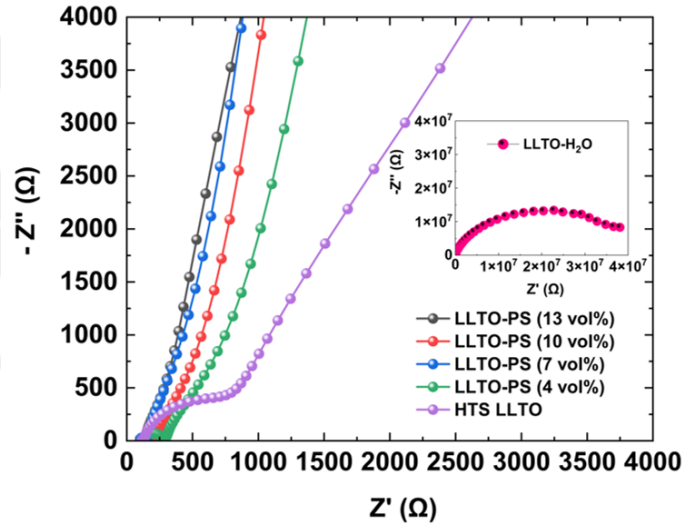


Figure 3.16. Nyquist plots of CS LLTO, LLTO-PS (4-13 vol%), and HTS LLTO solid electrolytes.

Cold-sintered composite solid electrolytes, incorporating 4–13 vol% PPC-LiClO₄ additives, demonstrate low total resistances ($R_{\text{total}} = R_{\text{bulk}} + R_{\text{gb1}} + R_{\text{gb2}}$). The total resistance decreases from $810 \, \Omega$ (4 vol% PPC-LiClO₄) to $308 \, \Omega$ (13 vol% PPC-LiClO₄), correlating with the increasing content of polymer-lithium salts. The bulk and grain boundary conductivity values for HTS LLTO and LLTO-PS (4–13 vol%) are summarized in Table 3.7. All samples exhibit similar bulk conductivities of approximately $1 \times 10^{-3} \, \text{S cm}^{-1}$, consistent with previously reported values for bulk lithium-ion conduction in LLTO [50]. The grain boundary conductivity increases from $1.04 \times 10^{-4} \, \text{S cm}^{-1}$ to $4.38 \times 10^{-4} \, \text{S cm}^{-1}$ as the PPC-LiClO₄ volume fraction increases from 4% to 13%.

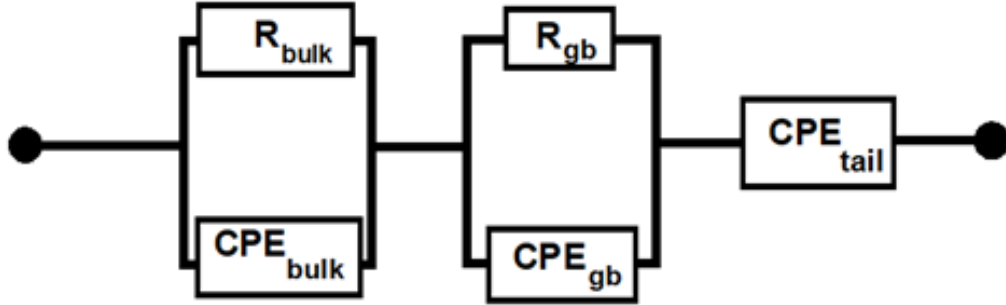


Figure 3.17. Equivalent circuit model for conventionally sintered LLTO.

Table 3.5. EIS fitting results for conventionally sintered LLTO.

Sample	R_{bulk} (Ω)	$\text{CPE}_{\text{bulk-T}}$ (F)	R_{gb} (Ω)	$\text{CPE}_{\text{gb-T}}$ (F)	$\text{CPE}_{\text{tail-T}}$ (F)
		$\text{CPE}_{\text{bulk-P}}$		$\text{CPE}_{\text{gb-P}}$	$\text{CPE}_{\text{tail-P}}$
HTS LLTO	90.60	3.00×10^{-11} 1.03	549.40	2.93×10^{-7} 0.92	8.02×10^{-6} 0.73

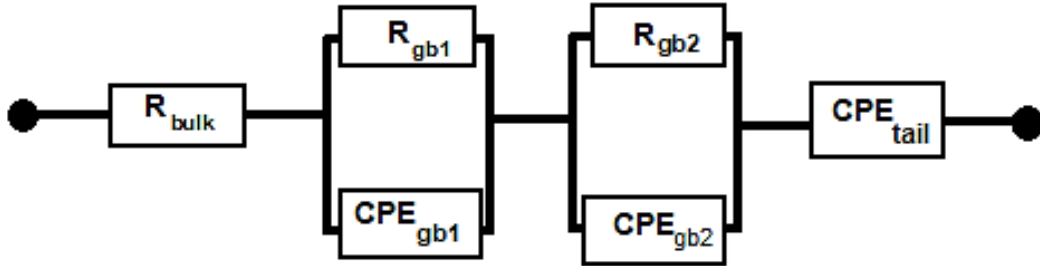


Figure 3.18. Equivalent circuit model for cold sintered LLTO composites.

The fitting of Nyquist plots for LLTO solid electrolytes is shown in Figure 3.19. Figure 3.20 compares the total ionic conductivities of cold-sintered composite electrolytes, which incorporate varying contents of PPC-LiClO₄, with the total ionic conductivity of HTS LLTO. Conductivities are obtained from Nyquist plots of symmetric cells (Al/LLTO-PS (4–13 vol%)/Al and Ag/HTS LLTO/Ag) at room temperature. Varying the volume percentage of PPC-LiClO₄ in the solid composite electrolyte from

4% to 13% significantly enhances ionic conductivity, increasing from $9.43 \times 10^{-5} \text{ S cm}^{-1}$ to $3.08 \times 10^{-4} \text{ S cm}^{-1}$. LLTO-PS (0 vol%) exhibits extremely low ionic conductivity, approximately $3 \times 10^{-11} \text{ S cm}^{-1}$. Similarly, using 20 wt.% deionized water as a transient solvent (CS LLTO) results in exceptionally high resistance on the order of $10^7 \Omega$. The ionic conductivity of CS LLTO is low, near $6 \times 10^{-9} \text{ S cm}^{-1}$. Limited grain growth, porosity, and poor contact between grains - induced by the low temperature sintering process - lead to poor ionic conductivity in the absence of binder-salt ionic pathways [119]. On the other hand, HTS LLTO shows an ionic conductivity of $1.34 \times 10^{-4} \text{ S cm}^{-1}$.

Table 3.6. EIS fitting results for cold sintered LLTO composites.

Sample	$R_{\text{bulk}} (\Omega)$	$R_{\text{gb1}} (\Omega)$	$\text{CPE}_{\text{gb1-T}} (\text{F})$ $\text{CPE}_{\text{gb1-P}}$	$R_{\text{gb2}} (\Omega)$	$\text{CPE}_{\text{gb2-T}} (\text{F})$ $\text{CPE}_{\text{gb2-P}}$	$\text{CPE}_{\text{tail-T}} (\text{F})$ $\text{CPE}_{\text{tail-P}}$
LLTO-PS (4 vol%)	81.20	213.50	4.86×10^{-8} 0.72	552.20	5.07×10^{-6} 0.80	2.26×10^{-6} 0.91
LLTO-PS (7 vol%)	89.70	103.40	8.44×10^{-8} 0.75	437.00	4.50×10^{-6} 0.85	3.11×10^{-6} 0.91
LLTO-PS (10 vol%)	75.75	144.40	1.05×10^{-7} 0.71	418.00	6.35×10^{-6} 0.81	1.88×10^{-6} 0.93
LLTO-PS (13 vol%)	81.00	56.45	6.34×10^{-8} 0.81	125.50	5.12×10^{-6} 0.93	2.33×10^{-6} 0.91

Table 3.7. Bulk and grain boundary conductivity of HTS LLTO and cold sintered LLTO-PS at varying PPC-LiClO₄ volume percentages.

PPC-LiClO ₄ (vol%)	Bulk Conductivity (S cm ⁻¹)	Grain Boundary Conductivity (S cm ⁻¹)
HTS LLTO	$1.14 \times 10^{-3} \pm 0.8 \times 10^{-5}$	$1.52 \times 10^{-4} \pm 0.6 \times 10^{-5}$
LLTO-PS (4%)	$1.01 \times 10^{-3} \pm 2.5 \times 10^{-5}$	$1.04 \times 10^{-4} \pm 1.6 \times 10^{-5}$
LLTO-PS (7%)	$1.02 \times 10^{-3} \pm 2.4 \times 10^{-5}$	$2.17 \times 10^{-4} \pm 7.6 \times 10^{-5}$
LLTO-PS (10%)	$1.05 \times 10^{-3} \pm 5.1 \times 10^{-6}$	$1.78 \times 10^{-4} \pm 3.8 \times 10^{-5}$
LLTO-PS (13%)	$1.04 \times 10^{-3} \pm 1.8 \times 10^{-5}$	$4.38 \times 10^{-4} \pm 1.0 \times 10^{-4}$

Although the ionic conductivity increases with PPC-LiClO₄ content, mechanical properties begin to degrade below the relative density of 80%, and samples containing more than 13% PPC-LiClO₄ tend to fracture easily. The inset of Figure 3.20 presents

the ionic conductivities reported for oxide-based electrolytes fabricated by cold sintering. The ionic conductivity of the cold-sintered composite electrolyte $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ remains below that of the composite electrolyte $\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$, indicating that LLTO exhibits the second highest conductivity among oxide-based solid electrolytes produced using the same sintering technique.

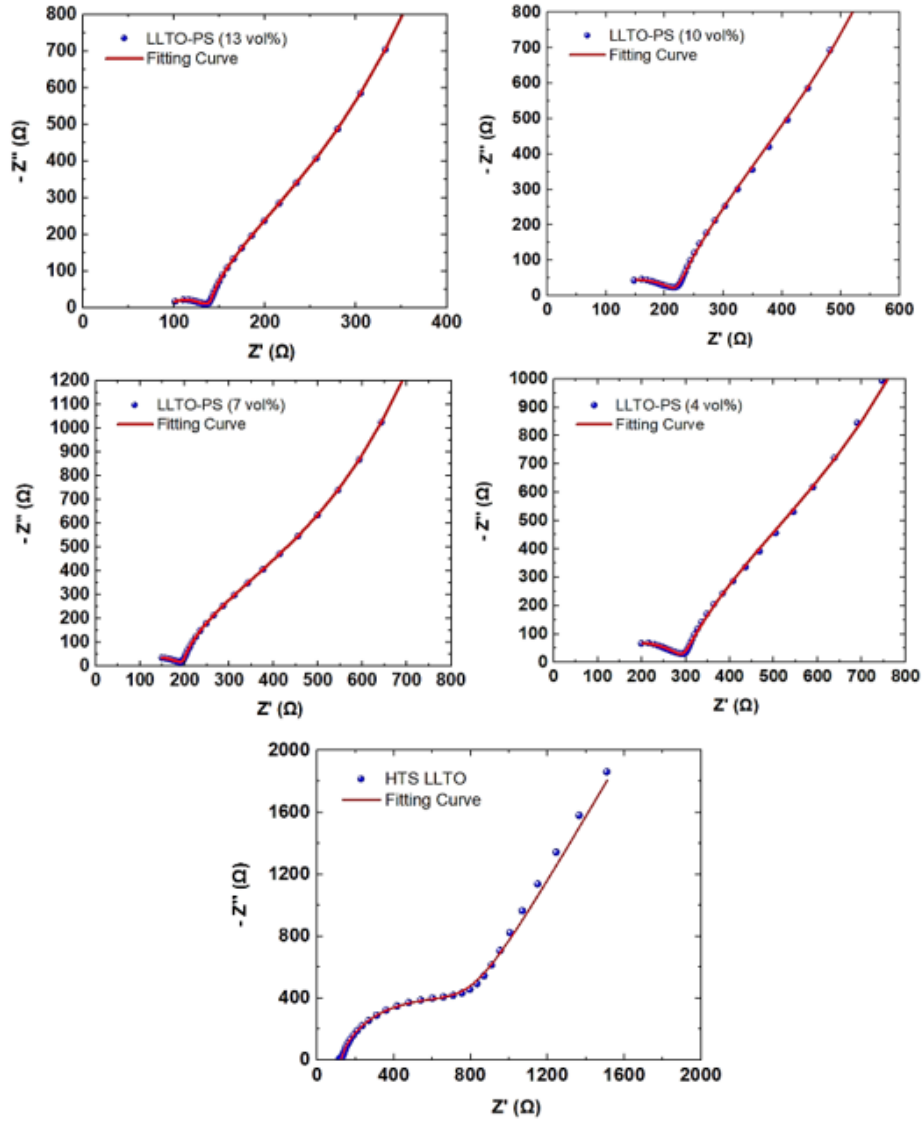


Figure 3.19. Fitting of Nyquist Plots for LLTO-PS (4-13 vol%) and HTS LLTO.

Figure 3.21 shows the temperature dependence of the ionic conductivity for cold-sintered composite oxide solid electrolytes. The temperature dependence follows an

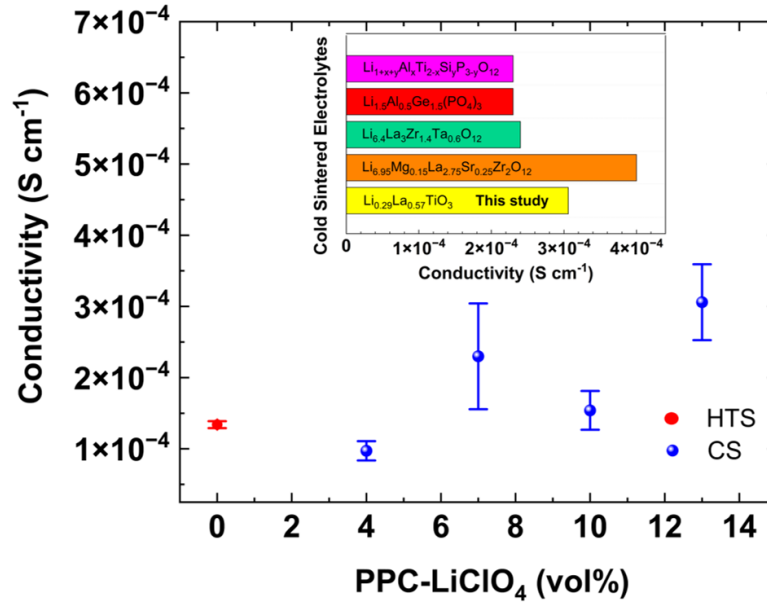


Figure 3.20. The ionic conductivity of LLTO-PS (4-13 vol%) and HTS LLTO at room temperature and comparison of the ionic conductivity of the cold sintered composite oxide solid electrolytes: Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ [60], Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O₁₂ [60], Li_{6.95}Mg_{0.15}La_{2.75}Sr_{0.25}Zr₂O₁₂ [73], Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ [74].

Arrhenius-type behavior for all cold-sintered oxide composites, with activation energies ranging from 0.25 eV to 0.37 eV. LLTO composite electrolytes exhibit high ionic conductivities in the temperature range of 0 to 100 °C, exceeding all previously reported materials except Li_{6.95}Mg_{0.15}La_{2.75}Sr_{0.25}Zr₂O₁₂. In particular, the activation energy of LLTO composites is at the lower end of this range, around 0.25 eV. The perovskite LLTO typically exhibits an activation energy between 0.3 and 0.4 eV [120]. Incorporating an appropriate amount of PPC-LiClO₄ into the perovskite LLTO phase substantially enhances lithium-ion transport, thereby lowering the activation energy.

LLTO-PS (13 vol%) exhibits the highest ionic conductivity and a relative density of around 80%; therefore, this sample was selected for further characterization. Figure 3.22 displays the XRD patterns of pristine LLTO powder and LLTO-PS (13 vol%). Compared with the reported data for LLTO (01-090-2573), it is observed that both the cold-sintered composite solid electrolyte and the pristine powder exhibit a perovskite-

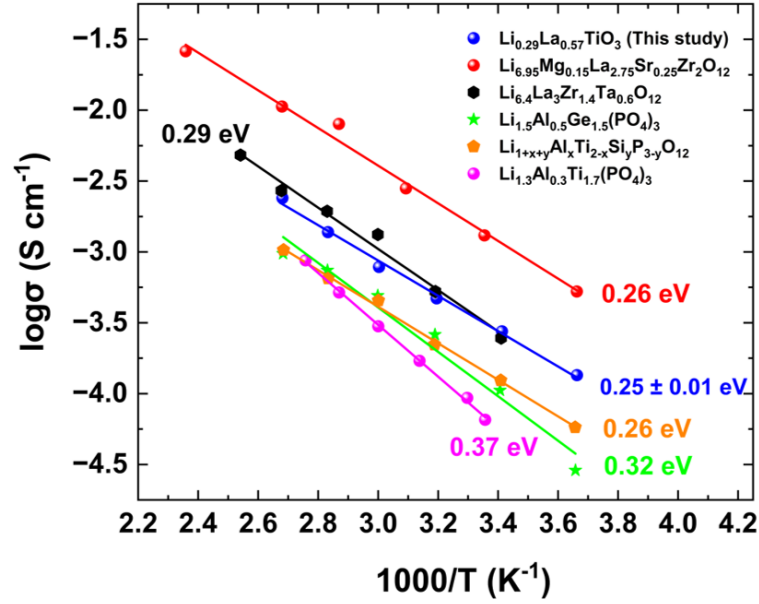


Figure 3.21. Arrhenius plots of the cold sintered composite oxide solid electrolytes:

LLTO-PS (13 vol%) (This Thesis), $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ [60],
 $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ [60], $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [72],
 $\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$ [73], $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ [74].

type tetragonal crystal structure and a high degree of crystallinity. The sole impurity phase in the pristine LLTO powder is $\text{La}_2\text{Ti}_2\text{O}_7$ (04-021-8682), and it is present in small amounts, approximately 2 wt.%. Similarly, $\text{La}_2\text{Ti}_2\text{O}_7$ is the only impurity phase observed in the cold-sintered solid electrolyte, with no change in its weight percentage. The impurities in composites are therefore attributed to the pristine LLTO powder rather than the cold sintering process. The crystal structure of the ceramic LLTO phase remains unchanged with the addition of PPC and LiClO_4 after cold sintering. Moreover, it is speculated that the lack of secondary phase formation after the cold sintering process indicates congruent dissolution during exposure to the transient solvent.

Figure 3.23 shows SEM images that capture the fracture cross sections of cold-sintered and conventionally sintered solid electrolytes, along with an image of commer-

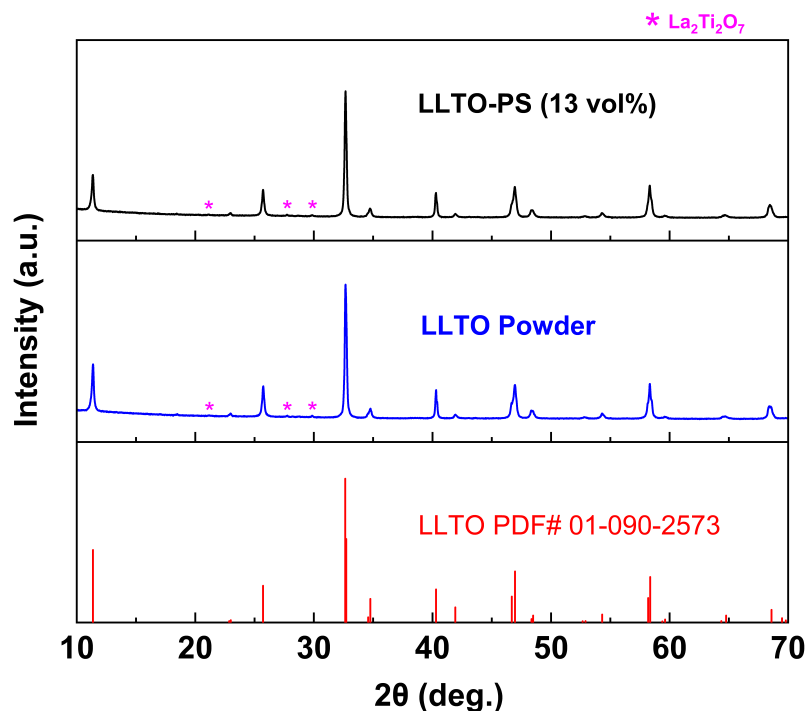


Figure 3.22. XRD patterns of LLTO powder and LLTO-PS (13 vol%).

cial grade LLTO powder. The cross-sectional images were acquired without polishing; a 5 nm-thick iridium layer was sputtered on the fractured surfaces to prevent charging issues. The powder has an average particle size of 1–2 μm . High-temperature sintering conducted at 1200 °C for 10 hours substantially increases the average grain size, reaching 5 μm . High-temperature sintering of LLTO promotes significant grain growth and results in a well-established intimate contact between the grains. The increased sintering temperature enhances the diffusion of ions and atoms at the grain boundaries, facilitating the formation of larger grains and reducing grain boundary resistance. This improved microstructure contributes to enhanced ionic conductivity by creating more continuous and less resistive ion transport pathways.

Figure 3.23c shows the microstructure of the cold-sintered composite electrolyte incorporating 13 vol% PPC-LiClO₄ (LLTO-PS(13 vol%)), while Figure 3.23d illustrates the cold-sintered LLTO sample using deionized water as the transient solvent without any polymer or lithium salt (CS LLTO). Both samples exhibit a similar microstructure,

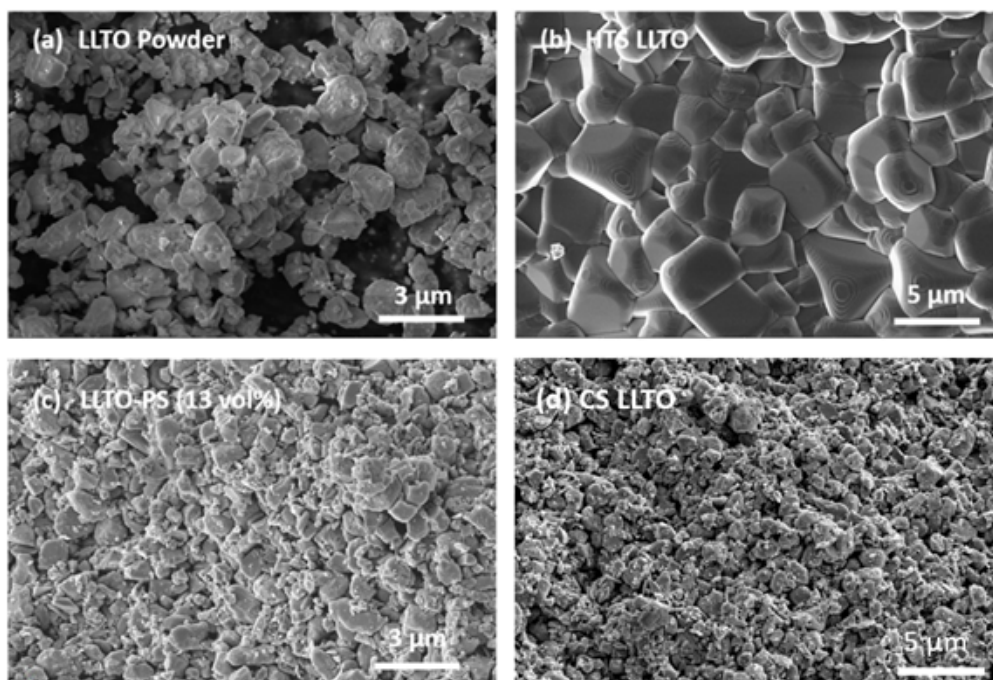


Figure 3.23. SEM images of (a) LLTO powder, (b) HTS LLTO, (c) LLTO-PS (13 vol%), and (d) CS LLTO.

with no apparent grain growth and comparable grain sizes ($\sim 1\text{--}2\text{ }\mu\text{m}$), indicating that the presence of the binder-salt solution does not significantly affect grain morphology during cold sintering. Although the composite sample (LLTO-PS (13 vol%)) has a density lower than that of the conventionally sintered solid electrolyte, the introduction of a binder-salt solution effectively establishes conductive pathways by filling the voids between the ceramic grains. This leads to high ionic conductivities in the composite samples despite sintering at temperatures approximately $1000\text{ }^{\circ}\text{C}$ lower than those sintered through high-temperature sintering.

3.2.4. Conclusions

The effect of various parameters on the cold sintering performance has been investigated, including sintering temperature, solvent selection, particle size, the weight ratio of the binder-salt and the weight percentage of the binder-salt content, to de-

termine the optimum conditions for achieving high ionic conductivity. Among these factors, solvent selection plays a crucial role in the cold sintering process, as it is based on the dissolution-precipitation mechanism of the constituent elements. Water, a commonly used transient solvent, has been found to cause incongruent dissolution in the garnet solid electrolyte, leading to the formation of low-conductivity phases. However, the use of acetonitrile and DMF leads to the congruent dissolution of the main ceramic phases, which retain their phase purity and high degree of crystallinity after processing. In addition, the use of fine particles has been identified as a key factor in achieving dense microstructures. Coarse particles tend to pack less efficiently, leading to porous structures with incomplete grain boundary contact, which increases resistance. Fine particles, on the other hand, ensure better interparticle contact and promote effective densification, ultimately improving mechanical integrity and lithium-ion transport.

Incorporation of PPC-LiClO₄ as a binder salt has also been crucial in enhancing the ionic conductivity of cold-sintered solid electrolytes. By filling the grain boundaries, the polymer-lithium salt phase significantly reduces grain boundary resistance and facilitates lithium-ion conduction. In LLTO, where grain boundary resistance is inherently high, the presence of PPC-LiClO₄ leads to a notable improvement in total conductivity. Similarly, in LLZO, despite its high bulk conductivity, the inclusion of PPC-LiClO₄ further improves intergranular lithium-ion transport. However, optimizing the weight ratio of PPC-LiClO₄ is essential, as excessive polymer content with a fixed lithium-ion concentration can lead to insufficient lithium-ion availability, resulting in lower ionic conductivity. In addition, excess PPC can cause aggregation at the grain boundaries, forming insulating layers that hinder ion transport. The ideal PPC-LiClO₄ weight ratio was determined to be 2, as this composition effectively fills the grain boundaries while maintaining a sufficient concentration of lithium ions for high conductivity.

Overall, both LLZO and LLTO-based composites demonstrated high ionic conductivities and low activation energies, highlighting the effectiveness of the cold sintering process combined with binder salt incorporation. This thesis confirms that op-

timizing the sintering parameters, solvent choice, particle size, and binder salt content is critical to maximizing the performance of cold-sintered lithium-ion conductors. The ability to co-sinter temperature sensitive materials with the main ceramic phase in cold sintering holds the potential to replace large grains and intimate contact grain boundary microstructures, typically achieved only after extremely high sintering temperatures, with binder-salt ionic pathways along the grain boundaries. These findings reinforce the notion that cold sintering, when carefully optimized, is a viable and efficient method for producing high-performance solid-state electrolytes for next-generation energy storage applications.



4. DESIGN, FABRICATION, AND PERFORMANCE OF LLTO-BASED LITHIUM-METAL CELLS

4.1. Introduction

Wenzel et al. [51] investigated the chemical stability of the Li/LLTO interface using an in situ X-ray photoelectron spectroscopy (XPS) technique. $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ was synthesized using the solid-state reaction route from the precursor powders of Li_2CO_3 , La_2O_3 and TiO_2 . The conventionally sintered LLTO pellet was transferred into the XPS chamber under the protection of an inert gas atmosphere (Ar) using a specialized transfer vessel. The lithium metal was placed on the target holder within the XPS chamber. Using the argon-ion gun component, the lithium metal was deposited onto the surface of the LLTO solid electrolyte. Next, XPS spectra were collected as a function of the deposition time. For the as-received sample, only two peaks appear in the Ti 2p spectra, confirming that titanium exhibits only the oxidation state of +4, as shown in Figure 4.1a. After contact with lithium metal, the sample exhibits new peaks on the low-binding energy side of the Ti 2p spectra. These peaks correspond to the lower oxidation states of +3 and +2 and metallic titanium as shown in Figure 4.1b.

To measure electronic conductivity, the samples were sputtered with two blocking gold electrodes before and after contact with the lithium metal. As expected, the electronic conductivity of the samples increased dramatically from $1.32 \times 10^{-11} \text{ S cm}^{-1}$ to 0.12 S cm^{-1} after lithiation, attributed to the formation of reduced titanium species. These findings demonstrate the formation of a mixed-conducting interphase at the Li/LLTO interface, facilitating electron transport across the solid electrolyte and ultimately leading to complete electrolyte failure. Due to the chemical instability at the Li/LLTO interface, research on LLTO-based Li metal batteries remains relatively limited. In the remainder of this section, proposed strategies to mitigate the chemical reactivity at the Li/LLTO interface, along with the performance of LLTO-based Li metal batteries, are presented.

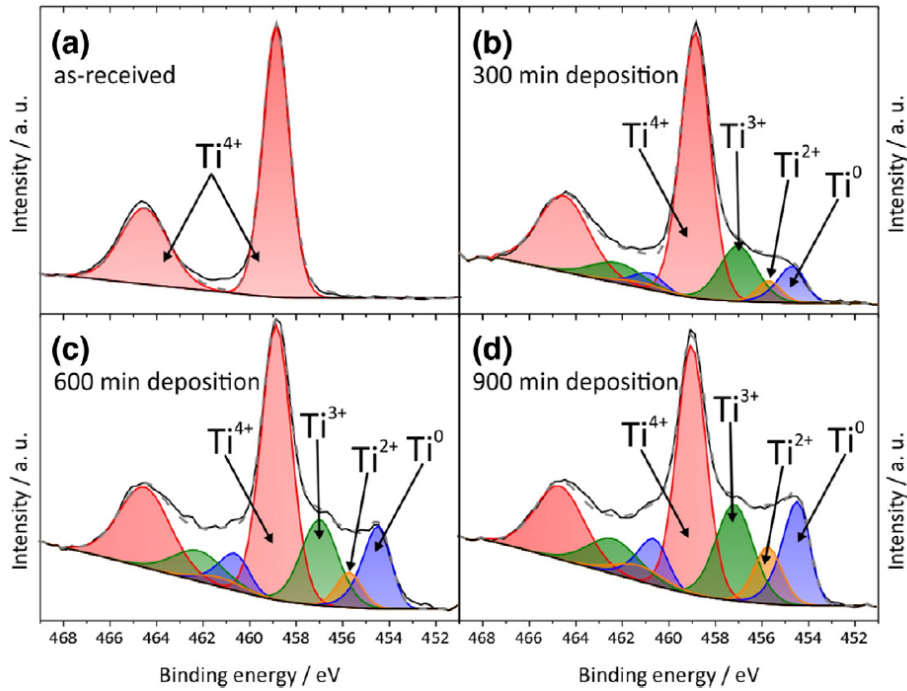


Figure 4.1. XPS spectra of (a) the as-received sample and the samples with lithium deposited for (b) 300 minutes, (c) 600 minutes, and (d) 900 minutes [51].

Jiang et al. [121] fabricated thin-film $\text{Li}_{0.34}\text{La}_{0.56}\text{TiO}_3$ solid electrolytes using the tape-casting method. The slurry was prepared using LLTO, triethanolamine, polyvinyl butyral, benzyl butyl phthalate, and ethanol, with weight percentages of 51.2%, 1.3%, 10.7%, 6.1%, and 30.7%, respectively. Polyethylene terephthalate (PET) release film was used as the substrate. The prepared slurry was poured onto the substrate, and a height-adjustable scraper was employed to produce freestanding thin-film solid electrolytes. The decomposition of organic components within the casting film was achieved by thermal treatment at 500 °C for 2 hours. Subsequently, a two-step sintering process was used: initial sintering at 1050 °C for 2 hours, followed by a further sintering step at 1260 °C for 12 hours. The total ionic conductivity of 41 μm thick solid electrolytes is $2 \times 10^{-5} \text{ S cm}^{-1}$. To prevent the reduction of Ti^{4+} in LLTO upon contact with the Li metal, a protective thin film layer comprising polyethylene oxide (PEO) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in acetonitrile was interposed between the solid electrolyte and the lithium metal anode.

XPS analysis of the Li/PEO/LLTO interface showed that the Ti 2p spectrum of the film exhibited two main peaks at 464 and 458.1 eV, respectively, corresponding to the peaks $p_{1/2}$ and $p_{3/2}$ of Ti^{4+} . Hence, the inclusion of a polymer thin film between the LLTO electrolyte and the lithium metal prevents the reduction of titanium. A Li/PEO/LLTO/PEO/LFP cell was fabricated, and its electrochemical performance is shown in Figure 4.2. Incorporation of PEO-based films results in high interfacial resistance, with the total cell resistance measured at $\approx 2400 \Omega$ at 65°C . The full cell demonstrated an initial discharge capacity of 145 mAh g^{-1} and retained 86.2% of its capacity after 50 cycles. In addition, the full cell exhibited a maximum discharge capacity of 120 mAh g^{-1} at 0.2 C and 55 mAh g^{-1} at 0.5 C .

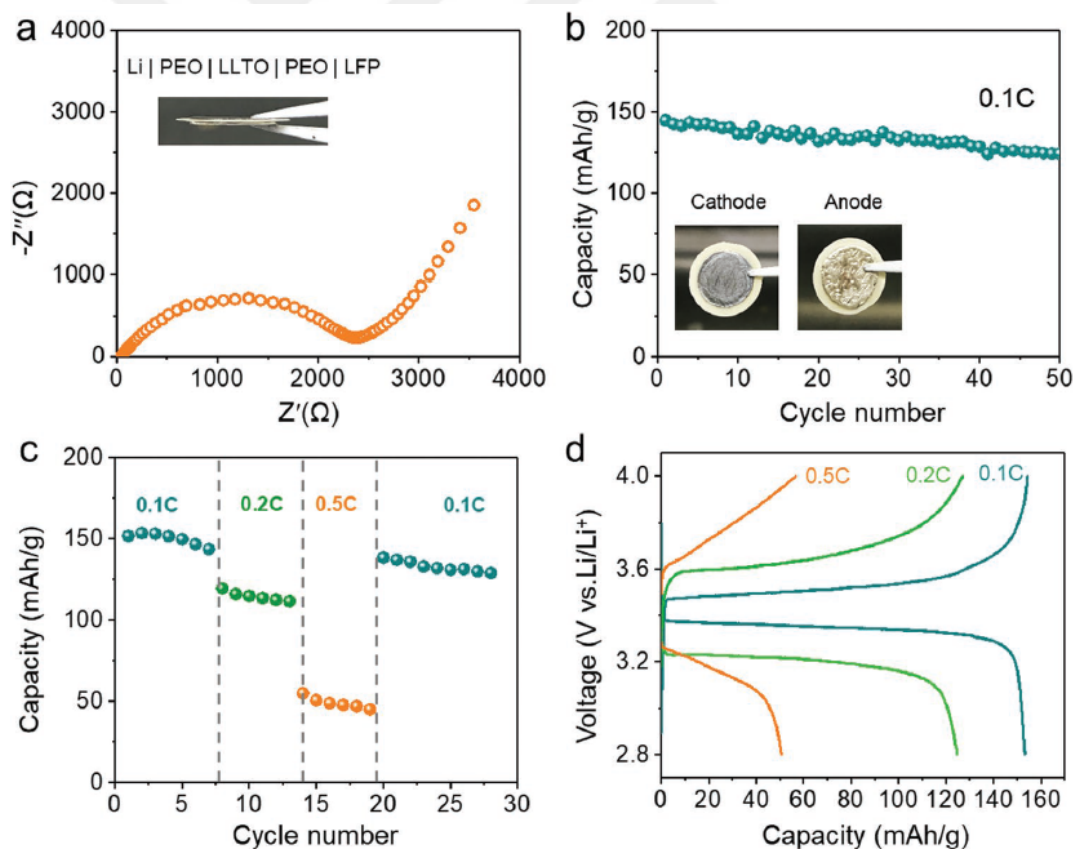


Figure 4.2. (a) The impedance spectra, (b) Cycling performance at 0.1 C , (c) Rate performance, and (d) Galvanostatic charge/discharge curves of Li/LLTO/LFP cell with PEO interlayers at 65°C [121].

Wu et al. [122] synthesized $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ composite electrolytes containing varying amounts of Bi_2O_3 (1, 2, 3, and 4 wt.%) via a solid-state sintering method. The LiFePO_4 (LFP) cathode slurry was prepared by mixing LFP, PVDF binder, and Super P conductive additive in an 8:1:1 weight ratio using N-methyl-2-pyrrolidone (NMP) as the solvent, and was directly coated onto the LLTO composite electrolytes. To mitigate chemical instability at the Li/LLTO interface, a porous polypropylene (PP) membrane was introduced. Additionally, a small amount of 1 M LiClO_4 in propylene carbonate was applied onto the PP membrane before cell assembly to improve interfacial contact. The critical current density of the $\text{Li/PP/Li}_{0.33}\text{La}_{0.557}\text{TiO}_3 + 1 \text{ wt.}\% \text{ Bi}_2\text{O}_3/\text{PP/Li}$ symmetric cell reached 0.7 mA cm^{-2} , and stable cycling was maintained at 0.1 mA cm^{-2} for 300 hours. Furthermore, the Li/PP/LLTO/LFP full cell delivered a discharge capacity of 133.1 mAh g^{-1} at 0.1 C and room temperature.

Le et al. [123] prepared aluminum-doped LLTO (A-LLTO) pellets using a citrate gel synthesis method, followed by high-temperature sintering at 1350°C for 6 hours. To optimize the ionic conductivity, 20 wt.% excess Li_2O was introduced, resulting in a total conductivity of $3.17 \times 10^{-4} \text{ S cm}^{-1}$. For cathode integration, a composite electrode was fabricated by casting a slurry of Ketjen Black and PVDF binder onto a nickel foam substrate. To address the poor wettability and high interfacial resistance between lithium metal and the LLTO solid electrolyte, a porous Whatman glass fiber separator soaked with 1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) was placed between the lithium and A-LLTO surfaces. Symmetric $\text{Li/Separator/A-LLTO/Separator/Li}$ cells demonstrated stable cycling at current densities up to 0.3 mA cm^{-2} , confirming good interfacial stability. In Li-O_2 full cell testing, the A-LLTO pellet successfully protected the lithium metal anode from oxygen crossover and degradation, enabling stable galvanostatic cycling for over 100 cycles at a capacity of 300 mAh g^{-1} .

Reported studies on LLTO-based Li metal batteries demonstrate that introducing a polymer-based interlayer can effectively mitigate the chemical reactivity at the Li/LLTO interface. However, despite these advanced interfacial designs, the fabrication of LLTO pellets in previous work relied on conventional sintering processes

(1200–1350 °C for 6–16 hours), posing a significant bottleneck for large-scale production [121–123]. This thesis investigates the cold sintering of LLTO-based composites, achieving densification at 125 °C within 30 minutes, which substantially reduces energy consumption and processing time, offering a cost-effective pathway for solid-state battery manufacturing. A PVDF membrane soaked in a LiPF_6 -based liquid electrolyte was employed as an interfacial buffer layer, successfully suppressing reduction reactions at the Li/LLTO interface, stabilizing interfacial resistance, and preventing degradation of the LLTO. As a result, the Li/PVDF/LLTO-PS (13 vol%)/LFP full cell demonstrated high discharge capacities of 151 mAh g^{-1} and 135 mAh g^{-1} at 0.1 C and 0.2 C, respectively, at room temperature.

4.2. Experimental Methods

To demonstrate the practical functionality of LLTO-based electrolytes, solid-state lithium metal batteries were fabricated using cold-sintered LLTO-PPC- LiClO_4 composite electrolytes. An 8 mm punch was used to cut lithium discs from lithium foil (MSE Supplies, the thickness of lithium and copper is $\approx 40 \text{ }\mu\text{m}$ and $11 \text{ }\mu\text{m}$, respectively). LFP-based cathode sheets (MTI Corporation, the thickness of LFP and aluminum is $\approx 68 \text{ }\mu\text{m}$ and $16 \text{ }\mu\text{m}$, respectively) were dried in a vacuum oven at 100 °C for 6 h and stored in an argon-filled glovebox to ensure the best performance. A 6 mm punch was used to cut the LFP discs from the stored sheets.

The prepared PPC- LiClO_4 solution was mixed with LLTO powder, followed by the addition of 9 wt.% DMF. The composite powder was then ground with an agate mortar and pestle for 5 minutes. Subsequently, the wet powder was placed into a 13 mm die, with a 6 mm LFP disc centered on top of it. The composite powder and the LFP disc were co-sintered under a uniaxial pressure of 400 MPa at 125 °C for 30 minutes. This process facilitates intimate contact between the $\sim 0.4 \text{ mm}$ thick solid electrolyte and the positive electrode. To prevent interfacial reactions between the lithium metal anode and the LLTO-based composite solid electrolyte, an electrolyte solution-soaked ($\approx 20 \text{ }\mu\text{L cm}^{-2}$ of LiPF_6 , 1 M, EC/DMC (v/v ratio 50/50), Sigma-

Aldrich, CA) PVDF membrane (0.45 μm , Amersham, Germany) was placed between the solid electrolyte and the anode. The battery cell was then assembled within a CR2032 coin cell, galvanostatically charged and discharged between 2.6 V and 4.0 V vs. Li^+/Li at room temperature using a battery testing device (BTS3000, Neware). The charging and discharging current densities were determined from the theoretical capacity of the LFP cathode, 170 mAh g^{-1} .

4.3. Results and Discussion

Direct contact between lithium metal and the LLTO solid electrolyte induces the reduction of Ti^{4+} to lower oxidation states. As a result, the electronic conductivity of the solid electrolyte increases significantly, ultimately leading to battery self-discharge [51]. To prevent the reduction of Ti^{4+} within the LLTO solid electrolyte by the Li metal and to reduce interfacial resistance, a 4 M lithium bis(fluorosulfonyl)imide (LiFSI) solution in dimethoxyethane (DME) ($5 \mu\text{L cm}^{-2}$) was incorporated at the Li/LLTO interface. Nevertheless, the Li/LLTO-PS (13 vol%)/LFP cell voltage rapidly declines to nearly 0 V even before galvanostatic charge and discharge tests.

A Li/LLTO-PS (13 vol%)/Li symmetric cell was assembled by introducing the trace amount of solution at the interfaces. The cell was subjected to a current density of 0.2 mA cm^{-2} for a few hours before being disassembled to measure the electronic conductivity of the LLTO solid electrolyte. The electronic conductivity of the LLTO solid electrolyte was less than $2 \times 10^{-9} \text{ S cm}^{-1}$ before contact with the Li metal. After disassembly, the electronic conductivity of the LLTO solid electrolyte increased to approximately $6 \times 10^{-5} \text{ S cm}^{-1}$, and the color of the solid electrolyte changed from white to black. To evaluate the evolution of interfacial resistance, time-resolved impedance spectroscopy experiments were performed [124]. The Li/LLTO-PS (13 vol%)/Li symmetric cells were fabricated using the trace amount of solution at the electrode contacts. The Nyquist plots of the cells at 30 min, 5 h, 30 h, and 54 h after cell assembly are shown in Figure 4.3a.

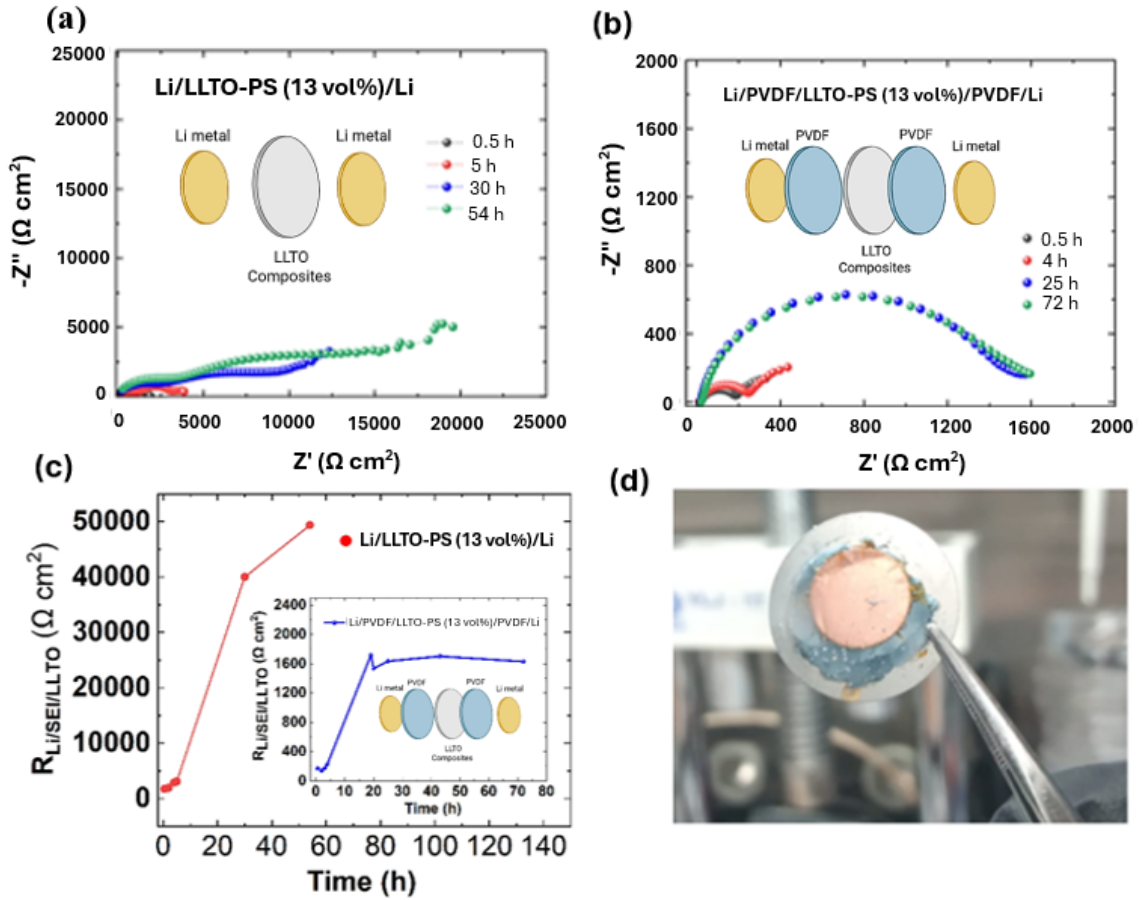


Figure 4.3. (a) Time-dependent impedance spectra without PVDF interlayers. (b) Time-dependent impedance spectra with PVDF interlayers. (c) Evolution of $R_{Li/SEI/LLTO}$ for Li/LLTO-PS (13 vol%)/Li and Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells. (d) Degradation observed in Li/LLTO-PS (13 vol%)/Li cells 54 h after cell assembly.

For comparison, a PVDF membrane soaked in a liquid electrolyte (LiPF_6 , 1 M in ethylene carbonate and dimethyl carbonate) was added as an interfacial layer between the Li anode and the solid electrolyte. When PVDF is used, the electrical conductivity of the solid electrolyte remains unaffected. A similar approach was used to prevent the reduction of Ti^{4+} in LLTO when in contact with lithium metal by adding a PEO layer at the LLTO/Li interface [121]. This strategy effectively inhibits electron conduction across the solid electrolyte, eliminating the risk of failure. Time-dependent Nyquist plots of symmetric cells with PVDF interlayers are shown in Figure 4.3b. The equiva-

lent circuit model for the symmetric cell without PVDF interlayers includes resistances arising from the solid electrolyte (R_{SE}), the solid electrolyte interphase (R_{SEI}), and the Li/LLTO interface ($R_{Li/LLTO}$), as shown in Figure 4.4. To track changes at the interface, the evolution of $R_{Li/SEI/LLTO}$ —defined as the sum of R_{SEI} and $R_{Li/LLTO}$ —is presented as a function of time after cell assembly in Figure 4.3c.

The $R_{Li/SEI/LLTO}$ resistance increases steadily over time, exhibiting a sharp rise from $1742 \, \Omega \, \text{cm}^2$ to $49,365 \, \Omega \, \text{cm}^2$, with no indication of stabilization. This suggests the formation of a steadily growing interphase between the lithium metal and the LLTO-based composite solid electrolyte. The EIS fitting results of the Li/LLTO-PS (13 vol%)/Li symmetric cells are shown in Table 4.1 after 0.5 h and 54 h of cell assembly, respectively. After the time-resolved impedance measurements, the symmetric cell was disassembled, revealing significant degradation in the solid electrolyte. This degradation was characterized by a color change, with the appearance of dark and gray regions, along with a yellow hue at the interface (Figure 4.3d).

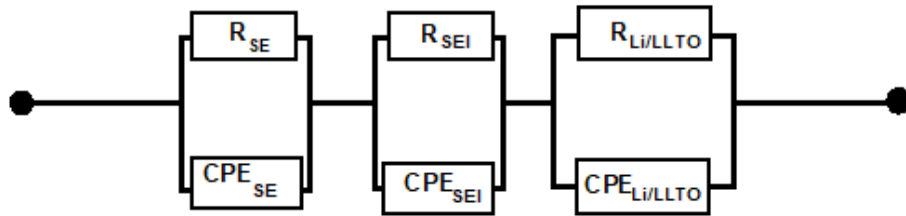


Figure 4.4. Equivalent circuit model for the Li/LLTO-PS (13 vol%)/Li symmetric cells.

Figure 4.3b shows the Nyquist plot of the Li symmetric cells with PVDF interlayers at 30 min, 4 h, 25 h, and 72 h after cell assembly. The evolution of $R_{Li/SEI/LLTO}$ as a function of time after cell assembly is presented in the inset of Figure 4.3c for Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells. The $R_{Li/SEI/LLTO}$ resistance of the cell stabilizes after approximately 20 hours and remains unchanged at around $1625 \, \Omega \, \text{cm}^2$, even after more than 72 hours. It is speculated that interfacial reactions

Table 4.1. EIS fitting results for Li/LLTO-PS (13 vol%)/Li symmetric cells at different resting times.

Time	$R_{SE} (\Omega)$	$CPE_{SE-T} (F)$ CPE_{SE-P}	$R_{SEI} (\Omega)$	$CPE_{SEI-T} (F)$ CPE_{SEI-P}	$R_{Li/LLTO} (\Omega)$	$CPE_{Li/LLTO-T} (F)$ $CPE_{Li/LLTO-P}$
0.5 h	277.8	2.69×10^{-9} 0.949	1302	1.74×10^{-7} 0.637	2165	1.10×10^{-6} 0.716
54 h	5117	3.67×10^{-9} 0.803	21281	9.61×10^{-7} 0.523	76979	1.96×10^{-5} 0.468

are complete approximately 20 hours after cell assembly, such that any interphases that formed do not grow further. The inclusion of PVDF in the symmetric cell promotes the formation of a stable interphase and effectively prevents the degradation of LLTO-based solid electrolytes. The low-frequency semicircle in the equivalent circuit model for Li symmetric cells with PVDF interlayers is attributed to electrochemical reactions at the Li metal anode interfaces, with an associated capacitance of on the order of 10^{-4} F [125] (Figure 4.5). This resistive contribution does not appear in the Li symmetric cell without PVDF interlayers, which may be attributed to the formation of a mixed conducting zone, as the increased electronic conductivity at the Li/LLTO interface can reduce the charge transfer resistance. The EIS fitting results of the Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells are shown in Table 4.2. The fitting of Nyquist plots of the symmetric cells (Li/LLTO-PS (13 vol%)/Li and Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li) is shown in Figure 4.6 - 4.7 at different resting times.

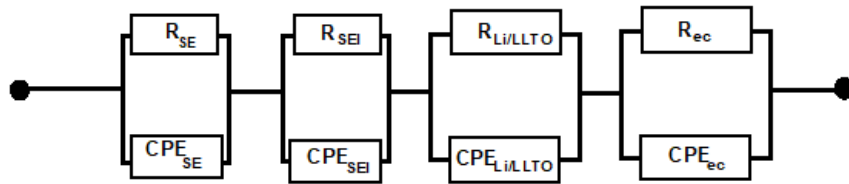


Figure 4.5. Equivalent circuit model for the Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells.

Table 4.2. EIS fitting results for Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells at different resting times.

Time	$R_{SE} (\Omega)$	$CPE_{SE-T} (F)$	CPE_{SE-P}	$R_{SEI} (\Omega)$	$CPE_{SEI-T} (F)$	CPE_{SEI-P}
0.5 h	29.74	3.78×10^{-6}	0.489	25.73	5.99×10^{-5}	0.654
72 h	46.35	2.16×10^{-5}	0.367	1139	4.45×10^{-5}	0.687
Time	$R_{Li/LLTO} (\Omega)$	$CPE_{Li/LLTO-T} (F)$	$CPE_{Li/LLTO-P}$	$R_{ec} (\Omega)$	$CPE_{ec-T} (F)$	CPE_{ec-P}
0.5 h	312.9	4.88×10^{-6}	0.904	733.1	3.82×10^{-4}	0.834
72 h	2101	1.41×10^{-6}	0.968	200	9.84×10^{-4}	1.013

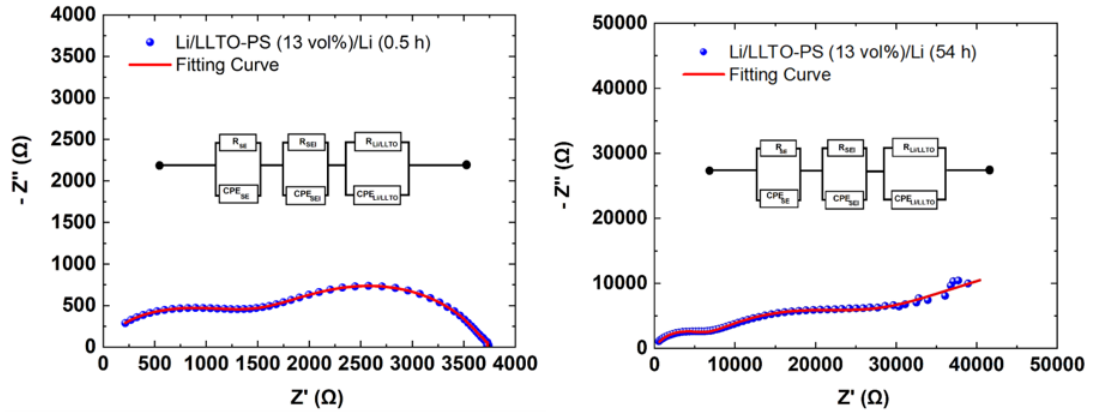


Figure 4.6. Fitting of the Nyquist Plot for Li/LLTO-PS (13 vol%)/Li symmetric cell at 0.5 h and 54 h.

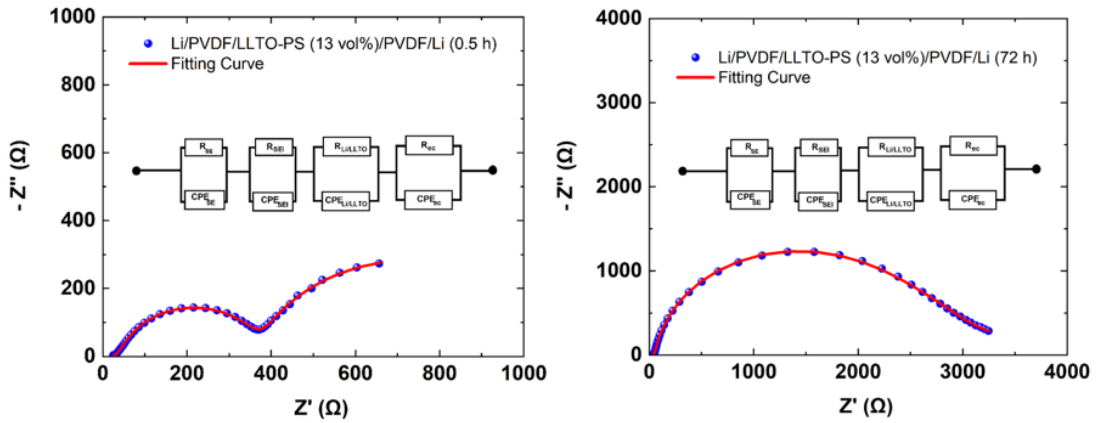


Figure 4.7. Fitting of the Nyquist Plot for Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cell at 0.5 h and 72 h.

The critical current density (CCD) is considered to be the highest current density that a solid-state electrolyte can withstand without experiencing short circuits due to the penetration of Li dendrites [126]. The electrochemical performance of LLTO-PS (13 vol%) was evaluated in symmetric Li metal cells (Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li) to investigate the stability of the solid electrolyte and its ability to suppress lithium dendrite growth. The applied current density was incrementally increased to determine the cell CCD, starting at 0.1 mA cm^{-2} , with a fixed Li plating/stripping duration of 1 hour, following the time-controlled test method discussed in Section 2.2.1. This widely adopted protocol is the most commonly used approach in reported studies, as it simultaneously increases both current density and capacity, providing valuable insights into the cell's endurance under progressively harsher conditions and enabling assessment of its long-term stability and reliability [82].

As shown in Figure 4.8a, the symmetric cell exhibits stable cycling under various current densities. A sharp voltage increase was observed at a current density of 2 mA cm^{-2} . The Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li cell demonstrates a high CCD exceeding 1.8 mA cm^{-2} , surpassing the values reported in numerous studies on oxide-based ceramic electrolytes, as illustrated in Figure 4.9. The CCD of the symmetric cells using PVDF and PPC-LiClO₄ as the separator, Li/PVDF/PPC-LiClO₄/PVDF/Li, was also measured. In these cells, the PVDF layers were soaked in the same amount of liquid electrolyte as in the LLTO-based symmetric cells. The Li/PVDF/PPC-LiClO₄/PVDF/Li cell exhibits a CCD of 2.6 mA cm^{-2} , which is slightly higher - but in general comparable - to that of the LLTO-PS (13 vol%) symmetric cells, as shown in Figure 4.10a.

Long-term galvanostatic stripping and plating tests were performed at various current densities to assess the stability of the symmetric cell. Figure 4.8b shows the galvanostatic cycling voltage profiles of the Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li cell at different current densities. The cell shows good cycling performance, maintaining stability for more than 400 hours with low voltages of approximately 80 mV, 120 mV, and 140 mV at current densities of 0.1 mA cm^{-2} , 0.2 mA cm^{-2} , and 0.3 mA cm^{-2} ,

respectively. The initial voltage of 200 mV decreased to 80 mV after 24 hours of cycling, and the cell maintained stable cycling at this voltage until the current density increased to 0.2 mA cm^{-2} . This behavior is attributed to the formation and stabilization of the solid electrolyte interphase (SEI) layer, since LiPF_6 , ethylene carbonate (EC) and dimethyl carbonate (DMC) contribute to the formation of a SEI layer when exposed to lithium metal anodes [127]. When the current density is reduced from 0.3 mA cm^{-2} to 0.1 mA cm^{-2} , the polarization decreases to approximately 50 mV, significantly less than the initial polarization at 0.1 mA cm^{-2} .

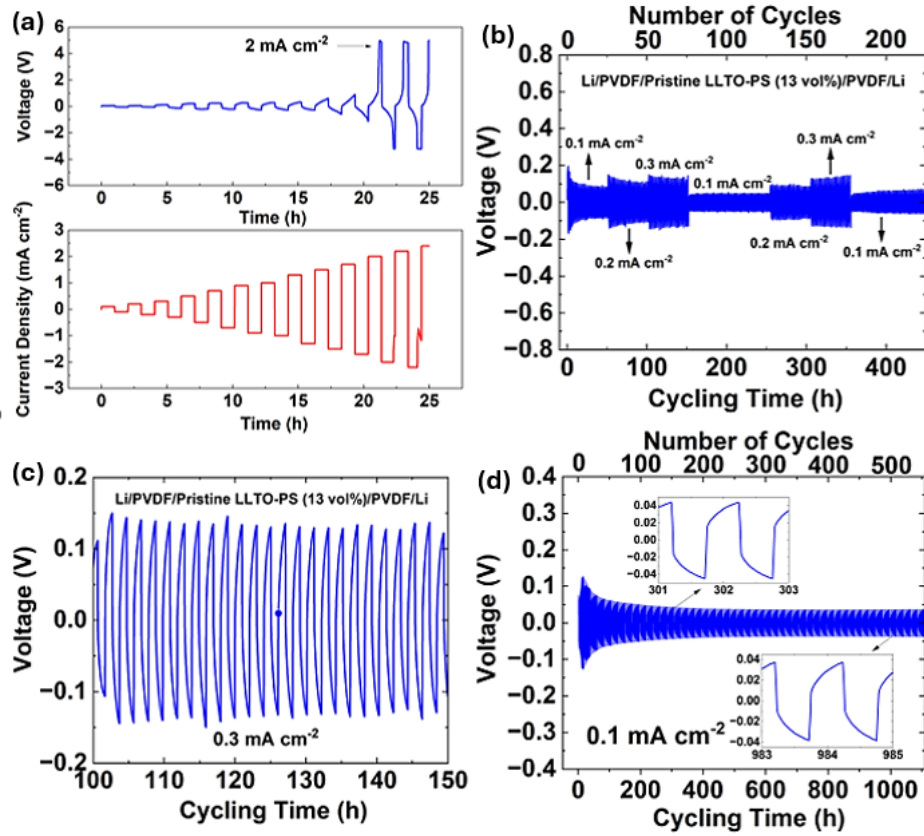


Figure 4.8. (a) Critical current density test of the Li/LLTO-PS (13 vol%)/Li cell with PVDF interlayers by galvanostatic cycling. (b) Cycling performance of the Li/LLTO-PS (13 vol%)/Li cell with PVDF interlayers under different current densities. (c) Voltage profile at 0.3 mA cm^{-2} , and d) Cycling performance of the Li/LLTO-PS (13 vol%)/Li cell with PVDF interlayers at 0.1 mA cm^{-2} .

To investigate the cause of the reduction in polarization, the cycling performance of the Li/PVDF/PPC-LiClO₄/PVDF/Li cell was presented at current densities of 0.1 mA cm⁻², 0.2 mA cm⁻², and 0.3 mA cm⁻² in Figure 4.10b. The cycling behavior of this cell is similar to that of the symmetric cell with LLTO-PS; a decrease in polarization is observed both after the initial cycling at 0.1 mA cm⁻² and when the current density is switched back to 0.1 mA cm⁻² following cycling at 0.3 mA cm⁻². This behavior suggests that the voltage drop observed after cycling at 0.3 mA cm⁻² originates from changes in the interfacial layers, rather than from degradation of the LLTO-PS solid electrolyte. It is anticipated that increasing current densities may induce interfacial changes, enhance the contact area, and facilitate ionic conduction, thereby reducing impedance.

Furthermore, cycling could alter the morphology of the SEI, potentially affecting the interfacial resistance. In particular, the voltage of the symmetric Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li cell remains unchanged when the current density is switched back to 0.1 mA cm⁻² for the third time, in contrast to the decrease in voltage observed during the second cycle at the same current density. This behavior indicates the stabilization of the interface. The cell was disassembled after the cycling test and no color change was observed in the cold-sintered composite electrolyte, as shown in Figure 4.10c. The detailed voltage profile at a current density of 0.3 mA cm⁻² is shown in Figure 4.8c. Figure 4.8d illustrates the cycling performance of the Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li cell at 0.1 mA cm⁻². The cell demonstrates excellent cycling stability at this current density for over 1000 hours.

A solid-state Li/LFP cell was manufactured by integrating LLTO-PS (13 vol%) solid electrolyte. The cold sintering process enables the co-sintering of solid electrolyte and cathode materials, promoting intimate physical contact and minimizing interfacial resistance. Cold sintering also avoids elemental mixing across the interface, thereby retaining the integrity of the assembled components [114]. LLTO solid electrolytes and LFP electrodes were co-sintered at 400 MPa and 125 °C for 30 minutes. Reducing the thickness of the composite pellet to ~ 0.4 mm in the full cell configuration allows

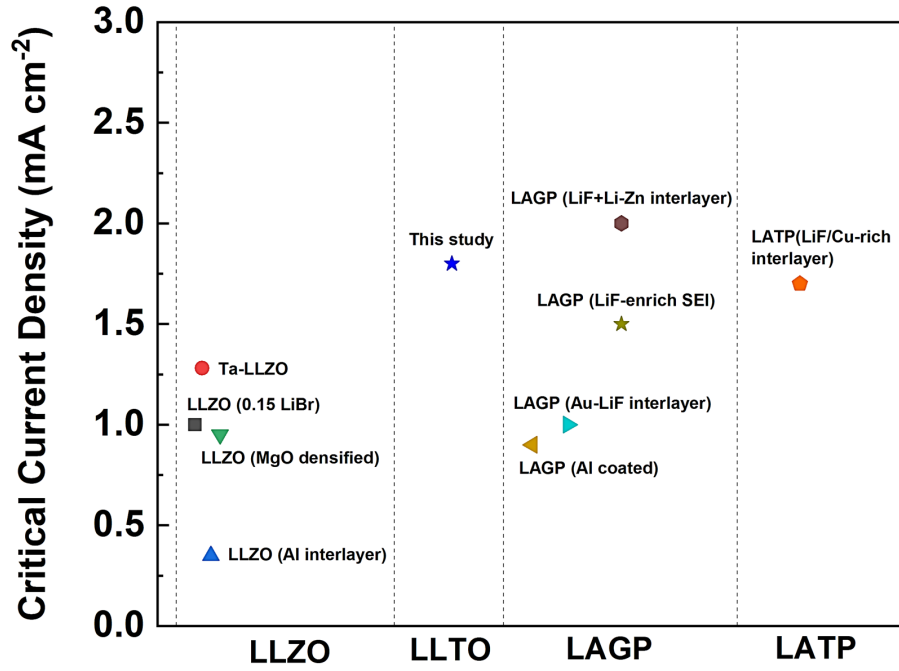


Figure 4.9. Comparison of critical current densities of oxide-based solid electrolytes.

for lower sintering pressure and shorter sintering duration. The properties of the solid composite electrolyte used in the fabrication of the full cell are listed in Table 4.3, and the Nyquist plot of the electrolyte is shown in Figure 4.11. The electrolyte exhibits an ionic conductivity of $2.86 \times 10^{-4} \text{ S cm}^{-1}$ and a relative density of 79.2%. Figure 4.12 presents the cross-sectional SEM image of the co-sintered LFP cathode and solid electrolyte, along with the corresponding EDS elemental map. The cold sintering process ensures intimate contact between the cathode and electrolyte layers. The PVDF membrane soaked with electrolyte solution was added between the solid electrolyte and the lithium foil to assemble the full cell within a 2032 coin cell, as illustrated in Figure 4.13a. Figure 4.13b shows the Nyquist plot of the Li/PVDF/LLTO-PS (13 vol%)/LFP cell at room temperature. The electrochemical impedance spectrum exhibits distinct semicircles at high and mid-frequencies, along with a low-frequency tail. The total cell resistance is estimated to be 496Ω . The low cell resistance indicates that our battery cell design, featuring co-sintering of the cathode and solid electrolyte via cold sintering, along with the use of a PVDF membrane soaked in a small amount of liquid electrolyte at the anode side, facilitates high ionic conductivity at both inter-

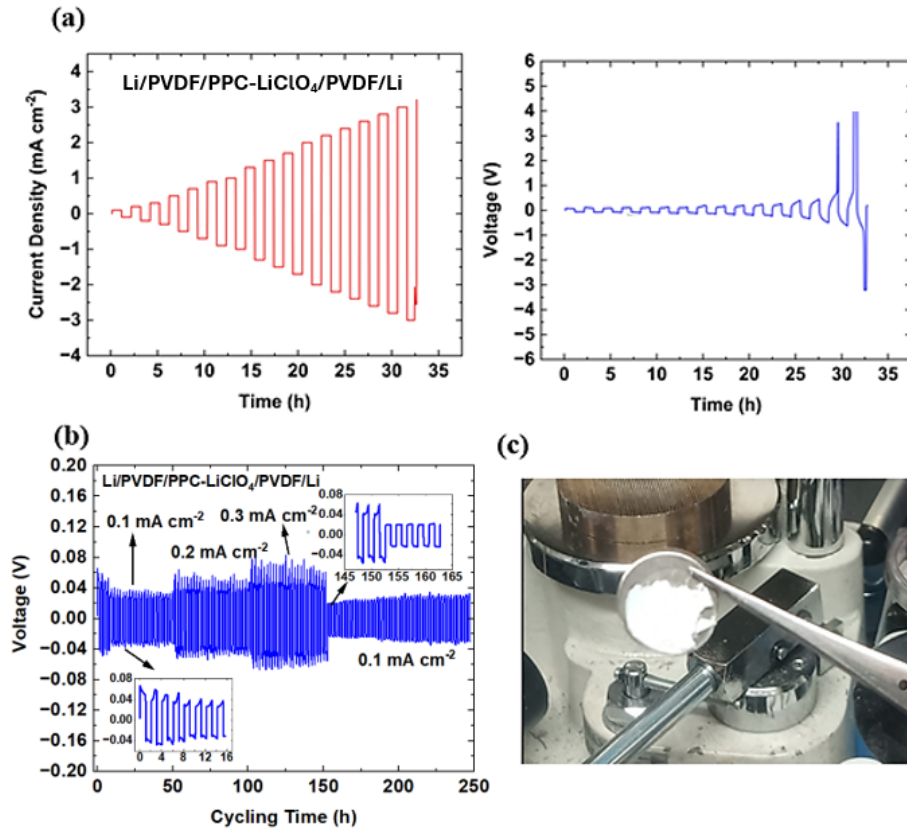


Figure 4.10. (a) Critical current density test of the Li/PPC-LiClO₄/Li cell with PVDF interlayers by galvanostatic cycling. (b) Cycling performance of the Li/PPC-LiClO₄/Li cell with PVDF interlayers under different current densities. (c) Disassembly of the Li/LLTO-PS (13 vol%)/Li cell with PVDF interlayers after cycling at varying current densities.

faces. Figure 4.13c shows the voltage profiles of the full cell at various current densities. The full cell exhibits a discharge capacity of 151 mAh g^{-1} at 0.1 C and shows a typical voltage profile of Li/LFP, featuring a flat plateau at $\sim 3.45 \text{ V}$ during galvanostatic charging and discharging. In addition, the rate performance of the cell at 0.1, 0.2, and 0.5 C is shown in Figure 4.13d. The full cell exhibits a maximum discharge capacity of 135 mAh g^{-1} at 0.2 C and 70 mAh g^{-1} at 0.5 C, respectively. The cell demonstrated a near-steady discharge capacity profile at 0.1, 0.2, and 0.5 C. The cycling stability of the Li/PVDF/LLTO-PS (13 vol%)/LFP cell at room temperature, tested at 0.1 C, 0.2 C, and 0.5 C for 30 cycles, is shown in Figure 4.14.

The cell exhibits modest cycling performance, retaining 71.3% of its initial capacity after 30 cycles, with a discharge capacity of 113 mAh g^{-1} at 0.1 C. Similarly, the cell achieves a capacity retention rate of 69.1%, with a discharge capacity of 92 mAh g^{-1} after 30 cycles at 0.2 C. At 0.5 C, the capacity decay becomes increasingly pronounced, leading to a capacity retention rate of 46.7% after 30 cycles, with a discharge capacity of 59 mAh g^{-1} . The post-mortem analysis revealed that the capacity decay was driven by the degradation of the PVDF membrane and carbonate-based organic solvents (EC:DMC) at the anode/solid electrolyte interface (Figure 4.15 - 4.22).

Table 4.3. Relative density and ionic conductivity of the composite electrolyte used in the full-cell fabrication.

Property	Value
Relative Density (%)	79.2 ± 0.3
Average Conductivity (S cm^{-1})	$(2.86 \pm 0.25) \times 10^{-4}$
Bulk Conductivity (S cm^{-1})	$(1.07 \pm 0.052) \times 10^{-3}$
Grain Boundary Conductivity (S cm^{-1})	$(3.9 \pm 0.38) \times 10^{-4}$

The battery cells exhibit a gradual capacity loss during cycling, despite their initial high discharge capacities. Post-mortem analysis was performed on cycled battery cells to elucidate the origin of the capacity decay. The Li/PVDF/Pristine LLTO-PS (13 vol%)/LFP battery cell was cycled at 0.1 C for 100 cycles (Figure 4.15a). The cell exhibits modest cycling performance during the first 30 cycles, maintaining 72% of its initial capacity with a discharge capacity of 111 mAh g^{-1} at 0.1 C. However, at the end of 100 cycles, the cell retains only 10% of its initial capacity, indicating significant degradation. Figure 4.15b shows the XRD patterns of the LLTO composites before cycling and after 30 cycles at 0.1 C. The cycled LLTO composite electrolytes maintain their phase purity. Figure 4.15c presents a cross-sectional SEM image of the co-sintered LFP cathode and the LLTO solid electrolyte after 30 cycles at 0.1 C. The LFP cathode and LLTO solid electrolyte maintain their structural integrity, with a stable interface that ensures intimate layer contact.

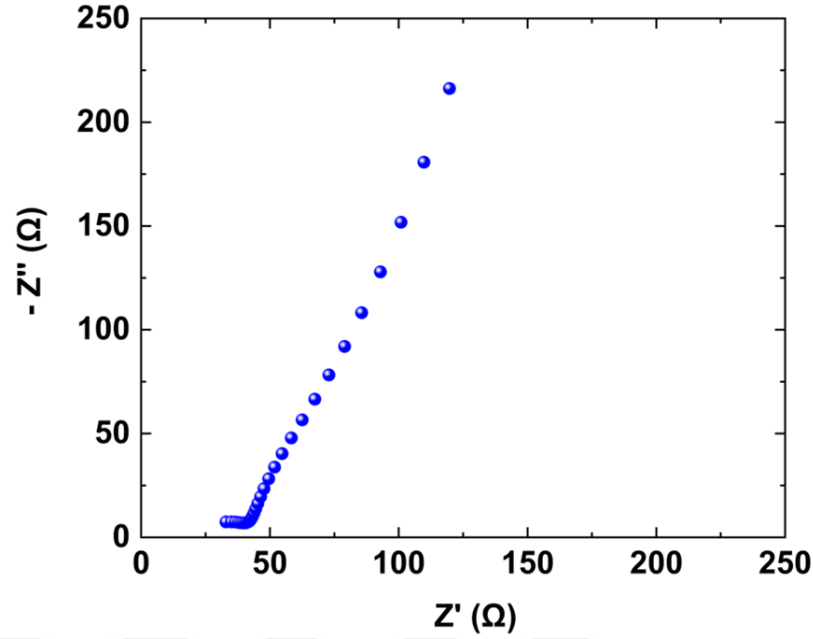


Figure 4.11. The Nyquist plot of the composite electrolyte used in the full-cell fabrication.

Figure 4.16 shows the Nyquist plots of the pristine and cycled Li/PVDF/LLTO-PS (13 vol%)/LFP cell, measured after 30 cycles at 0.1 C. The equivalent circuit model of the Li/PVDF/LLTO-PS (13 vol%)/LFP cell is shown in Figure 4.17. A parallel combination of a resistor (R_{SE}) and a constant phase element (CPE_{SE}), denoted as $R_{SE} \parallel CPE_{SE}$, was used to represent the lithium-ion conductivity in the LLTO solid electrolyte. Additionally, a parallel arrangement of a resistor ($R_{Cathode}$) and a constant phase element ($CPE_{Cathode}$), expressed as $R_{Cathode} \parallel CPE_{Cathode}$, was used to characterize the lithium-ion transport at the Li/LFP interface. Similarly, $R_{Anode} \parallel CPE_{Anode}$ was included to model the lithium-ion conductivity at the Li/LLTO interface. The tail observed in the low-frequency region was modeled by incorporating an additional constant phase element (CPE_{tail}) in series with the other circuit elements, representing the effect of lithium-ion blocking electrodes. The fitted capacitance values for the cathode|SE interface and anode|SE interface are consistent with previously reported values [128]. The EIS fitting results for the Li/PVDF/LLTO-PS (13 vol%)/LFP cell before and after cycling (30 cycles at 0.1 C) are shown in Table 4.4. The fitting of

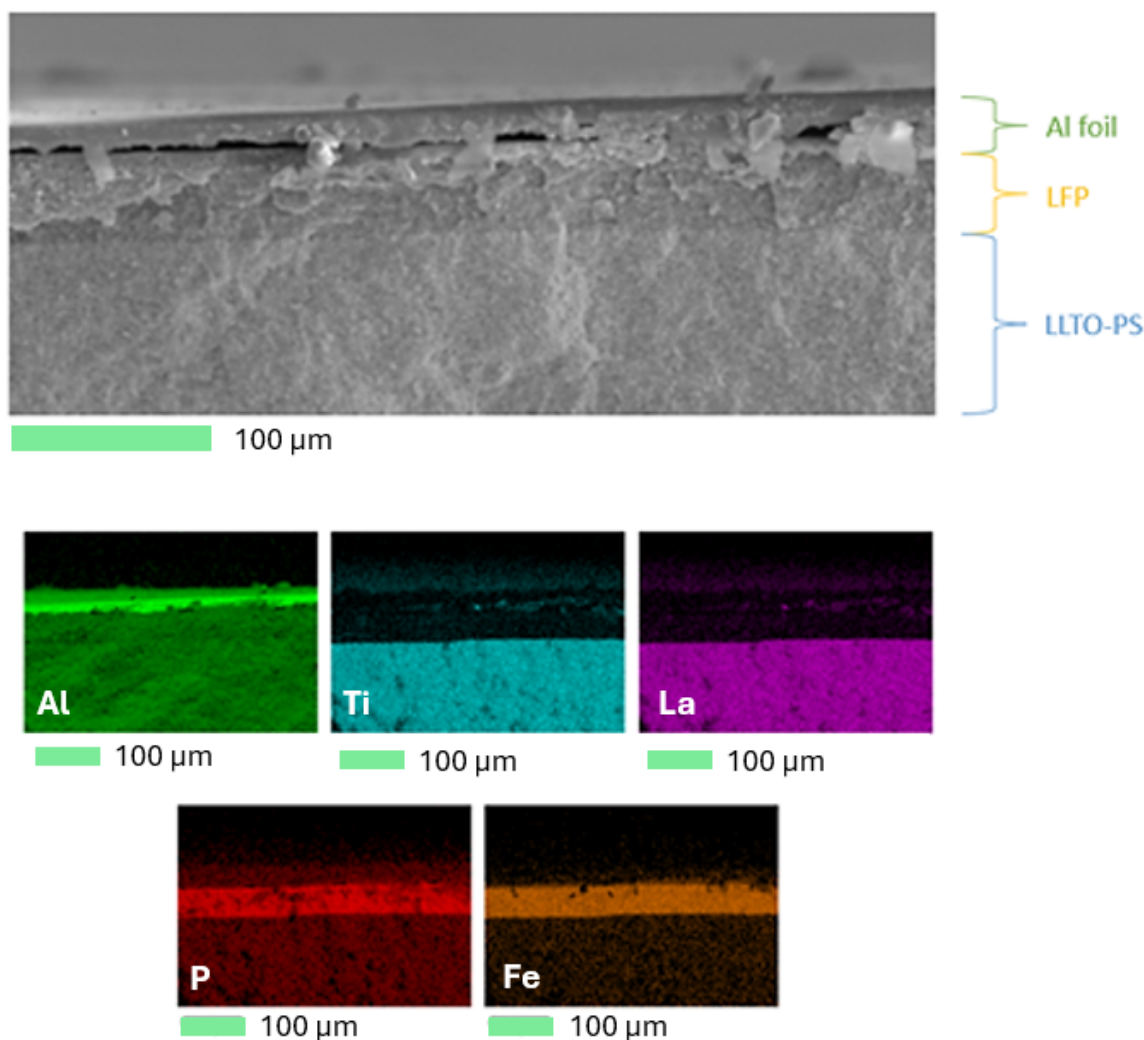


Figure 4.12. Cross-sectional SEM image of the co-sintered LFP cathode and LLTO-PS solid electrolyte, along with the corresponding EDS mapping.

Nyquist plots for the Li/PVDF/LLTO-PS (13 vol%)/LFP cell before and after cycling (30 cycles at 0.1 C) is provided in Figure 4.18. After 30 cycles at 0.1 C, the Li/LLTO interfacial resistance (R_{Anode}) increases from 258 Ω to 2350 Ω . The significant increase in interfacial resistance at the Li/LLTO interface, while other resistances remain stable, indicates degradation specific to that interface.

To evaluate the surface chemistry of the PVDF membrane soaked in liquid electrolytes, X-ray photoelectron spectroscopy (XPS) was performed on the pristine and

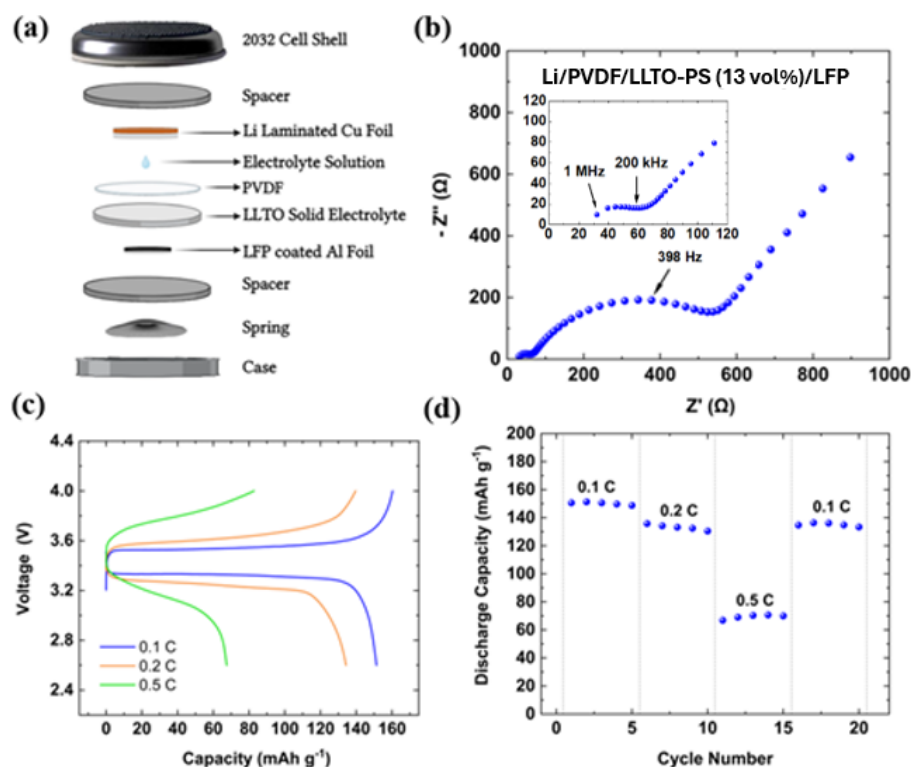


Figure 4.13. (a) Schematic illustration of the components of our batteries. (b) Nyquist plot (inset: data at high frequency). (c) Galvanostatic charge/discharge curves, and (d) Rate performance of the Li/LLTO-PS (13 vol%)/LFP cell with the PVDF interlayer at room temperature.

cycled membranes after 30 cycles at 0.1 C. In the C 1s XPS spectra, the peak at 284.8 eV, attributed to the C–H bond, shows an increased atomic concentration after cycling (Figure 4.19(a–b)). This increase may be attributed to the partial decomposition of the ethylene carbonate (EC) and dimethyl carbonate (DMC) solvents, which are prone to degradation under cycling conditions [129].

The binding energy at 290.8 eV in the C 1s spectrum corresponds to the $\text{CF}_2\text{--CH}_2$ functional group, while the F 1s peak at 688 eV is attributed to the F – C bond. Both peaks show a decrease in intensity after cycling. This decrease could be attributed to the partial decomposition of the PVDF membrane. In addition, it is speculated that the near-surface region becomes enriched with decomposition products and surface

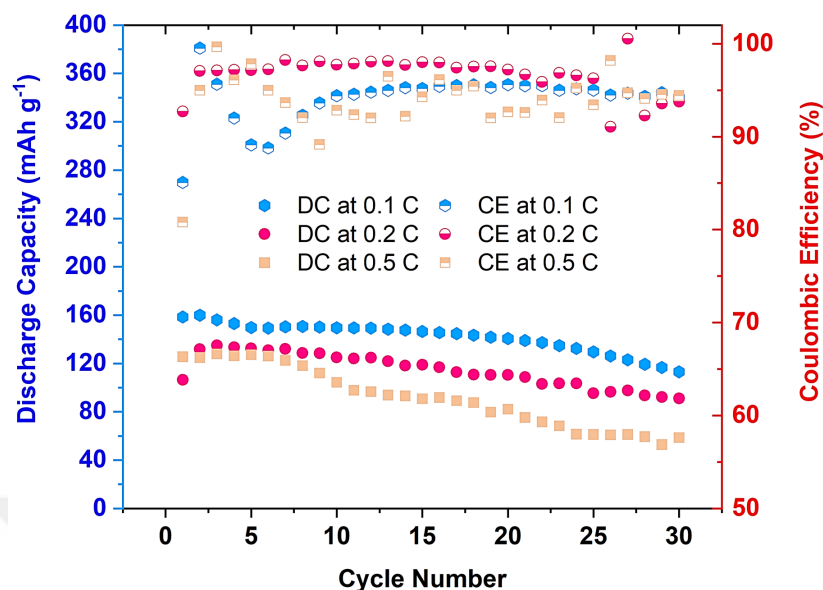


Figure 4.14. Cycling stability of the Li/PVDF/LLTO-PS (13 vol%)/LFP cell at room temperature at 0.1 C, 0.2 C, and 0.5 C.

impurities after cycling, as the increased O/Li atomic ratio (Figure 4.19e) suggests the formation of LiOH and Li₂O, two phases known to form at the lithium metal interface [127]. To investigate the stability of the liquid electrolyte-soaked PVDF membrane and examine the degradation mechanism at the interfacial layer, FTIR spectra were collected for pristine PVDF soaked in 1 M LiPF₆ in EC:DMC (50:50 v/v), cycled PVDF soaked in 1 M LiPF₆ in EC:DMC (50:50 v/v) after 30 cycles at 0.1 C, and cycled PVDF soaked in 1 M LiPF₆ in EC:DMC (50:50 v/v) after 100 cycles at 0.1 C (Figure 4.20).

Table 4.4. EIS fitting results for the Li/PVDF/LLTO-PS (13 vol%)/LFP cell before and after cycling (30 cycles at 0.1 C).

State	$R_{SE} (\Omega)$	$CPE_{SE-T} (F)$	CPE_{SE-P}	$R_{Cathode} (\Omega)$	$CPE_{Cathode-T} (F)$	$CPE_{Cathode-P}$
Pristine	73	1.10×10^{-6}	0.596	165	1.80×10^{-6}	1.048
Cycled	130	5.38×10^{-5}	0.92	140.4	1.36×10^{-6}	0.559
State	$R_{Anode} (\Omega)$	$CPE_{Anode-T} (F)$	$CPE_{Anode-P}$	$CPE_{tail-T} (F)$	CPE_{tail-P}	
Pristine	258	2.16×10^{-6}	0.84	1.30×10^{-4}	0.68	
Cycled	2350	2.99×10^{-5}	0.9441	2.67×10^{-5}	0.79	

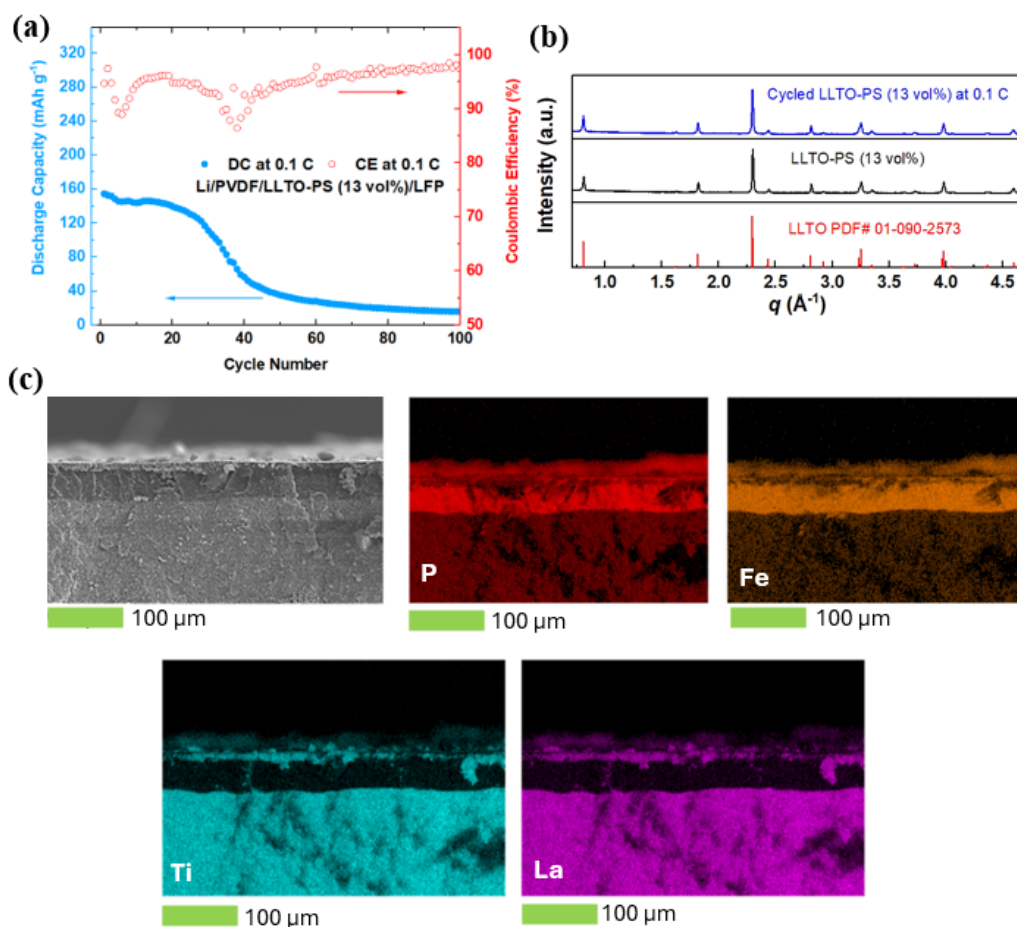


Figure 4.15. (a) Long-term cycling stability of Li/PVDF/Pristine LLTO-PS (13 vol%)/LFP cells at 0.1 C. (b) XRD patterns of LLTO composites before cycling and after 30 cycles at 0.1 C. (c) Cross-sectional SEM image of the LFP cathode and LLTO solid electrolyte after 30 cycles at 0.1 C, along with the corresponding EDS mapping.

After 30 cycles, the intensity of all DMC-related peaks decreased compared to the pristine PVDF soaked in the liquid electrolyte. The spectra were normalized based on the EC peaks at 1804 cm⁻¹ and 1775 cm⁻¹ (Figure 4.21). A newly emerged peak at 1664 cm⁻¹ is attributed to the C=O stretching vibration, likely originating from the decomposition by-products of the organic solvent DMC. After 100 cycles, the peaks associated with the EC solvent at 1804 cm⁻¹ and 1775 cm⁻¹ disappeared, and the intensity of the newly appeared C=O stretching peak increased, confirming that both the EC and DMC solvents had decomposed at the end of 100 cycles. In addition, after

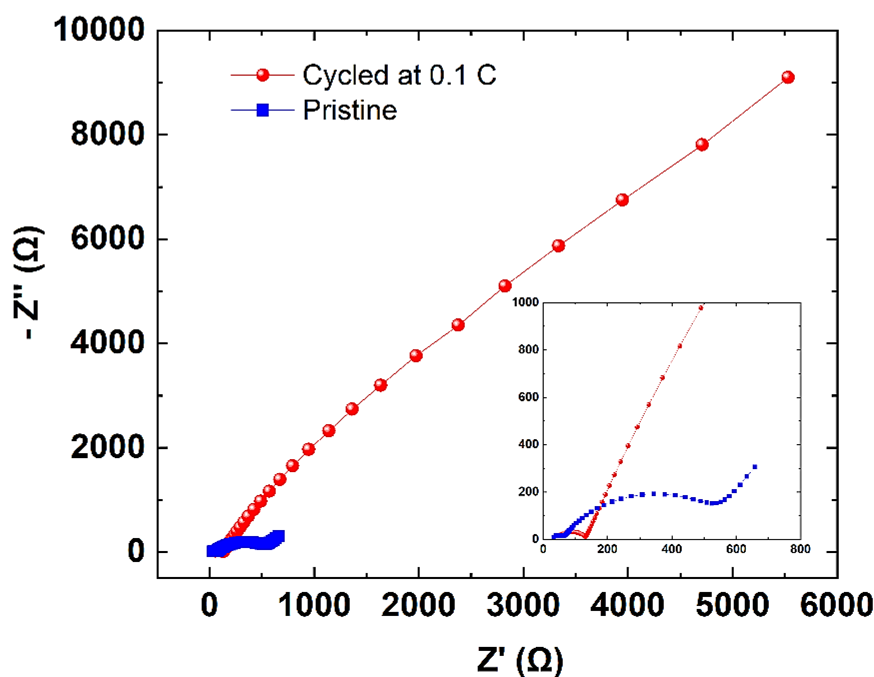


Figure 4.16. Nyquist plots of the pristine and cycled Li/PVDF/LLTO-PS (13 vol%)/LFP cell after 30 cycles at 0.1 C (inset: high-frequency region).

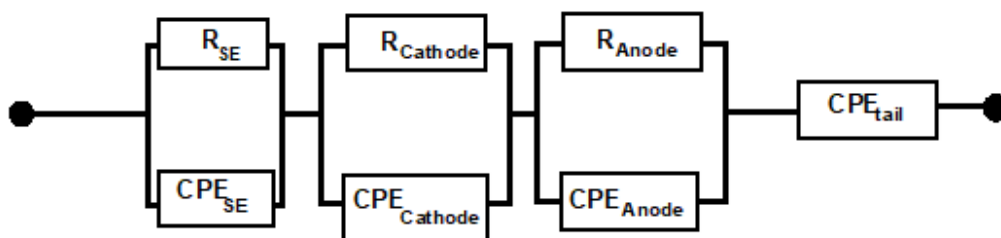


Figure 4.17. Equivalent circuit model for the pristine and cycled (30 cycles at 0.1 C) Li/PVDF/LLTO-PS (13 vol%)/LFP battery cells.

100 cycles, the peak at 1170 cm^{-1} disappeared, which is associated with symmetric stretching of the $-\text{CF}_2$ groups in the PVDF [130]. This confirms significant structural changes in the PVDF membrane after cycling. The peaks that appeared at 2946 cm^{-1} and 2837 cm^{-1} after 100 cycles are attributed to the asymmetric and symmetric CH_2 stretching vibrations [131], respectively. These peaks are likely formed as a result of the decomposition of CH_2 groups in the PVDF membrane. The broad peak near 3000--

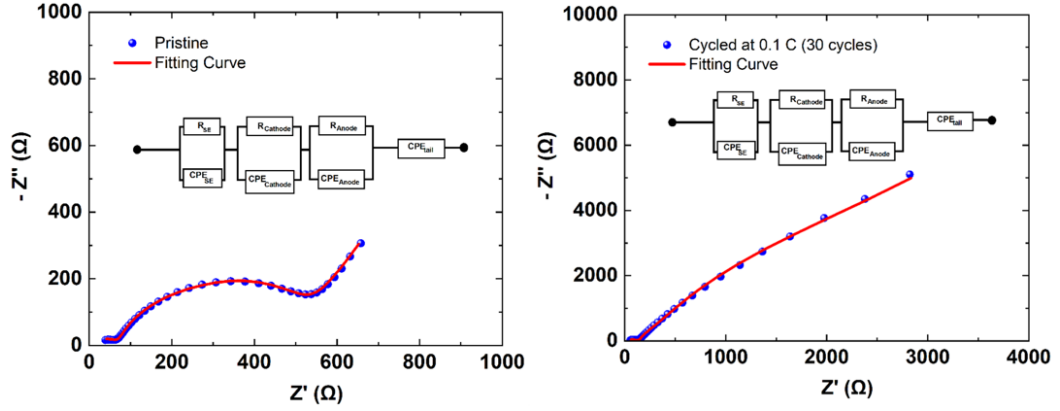


Figure 4.18. Fitting of the Nyquist Plots for Li/PVDF/LLTO-PS (13 vol%)/LFP cell before and after cycling (30 cycles at 0.1 C).

3500 cm^{-1} originates from the stretching vibrations of the -OH group [132], which can be attributed to the formation of hydroxyl groups as decomposition by-products of the organic solvents. The sharp peak at 3565 cm^{-1} that appeared after 100 cycles could be attributed to the OH stretching vibration of LiOH [133], a conclusion further supported by the XPS data.

The XPS and FTIR data confirm the degradation of the organic solvents and PVDF membrane during cycling, which is the primary cause of the capacity decay in the battery cells. In the battery cells, the PVDF membrane is placed at the Li/LLTO interface to prevent the reduction of Ti^{4+} . Figure 4.22 shows the Ti 2p XPS spectra of the pristine and cycled LLTO-PS (13 vol%) composite electrolytes after 100 cycles at 0.1 C. Ti 2p XPS spectra show two main peaks at 464 and 458.3 eV, which correspond to the $p_{1/2}$ and $p_{3/2}$ peaks of Ti^{4+} . The XPS spectra confirm that the inclusion of PVDF effectively prevents the reduction of Ti^{4+} , and even after 100 cycles at 0.1 C, Ti^{4+} maintains its oxidation state. To ensure the long-term stability and high performance of LLTO-based Li metal batteries, it is essential to prevent the reduction of Ti^{4+} during extended cycling. It was found that the degradation mechanism arises primarily from the interfacial layers, rather than from the solid electrolyte itself. Although the PVDF membrane effectively prevents Ti^{4+} reduction in LLTO, it degrades over time,

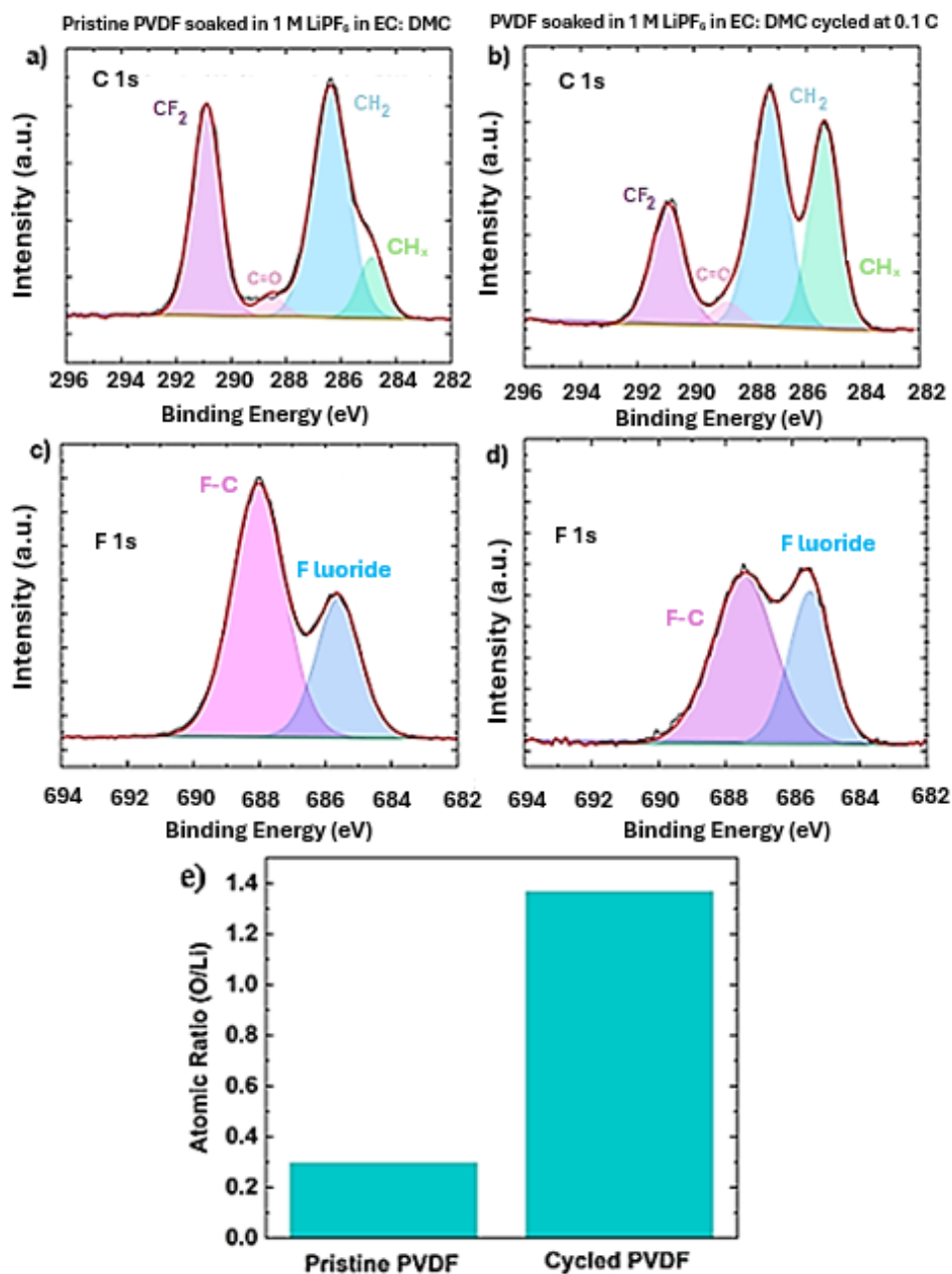


Figure 4.19. XPS analysis of (a) C 1s spectra of pristine PVDF soaked in 1 M LiPF₆ in EC: DMC. (b) C 1s spectra of PVDF soaked in 1 M LiPF₆ in EC: DMC cycled at 0.1 C for 30 cycles. (c) F 1s spectra of pristine PVDF soaked in 1 M LiPF₆ in EC: DMC. (d) F 1s spectra of PVDF soaked in 1 M LiPF₆ in EC: DMC cycled at 0.1 C for 30 cycles. (e) O/Li atomic ratio in the pristine and cycled interlayer.

emphasizing the need for further engineering of the interfacial layers to enhance cycling stability. Nevertheless, our design offers a promising approach for utilizing LLTO solid electrolytes in Li-metal batteries. The long-term performance of these batteries will ultimately depend on optimizing and protecting these interfacial layers.

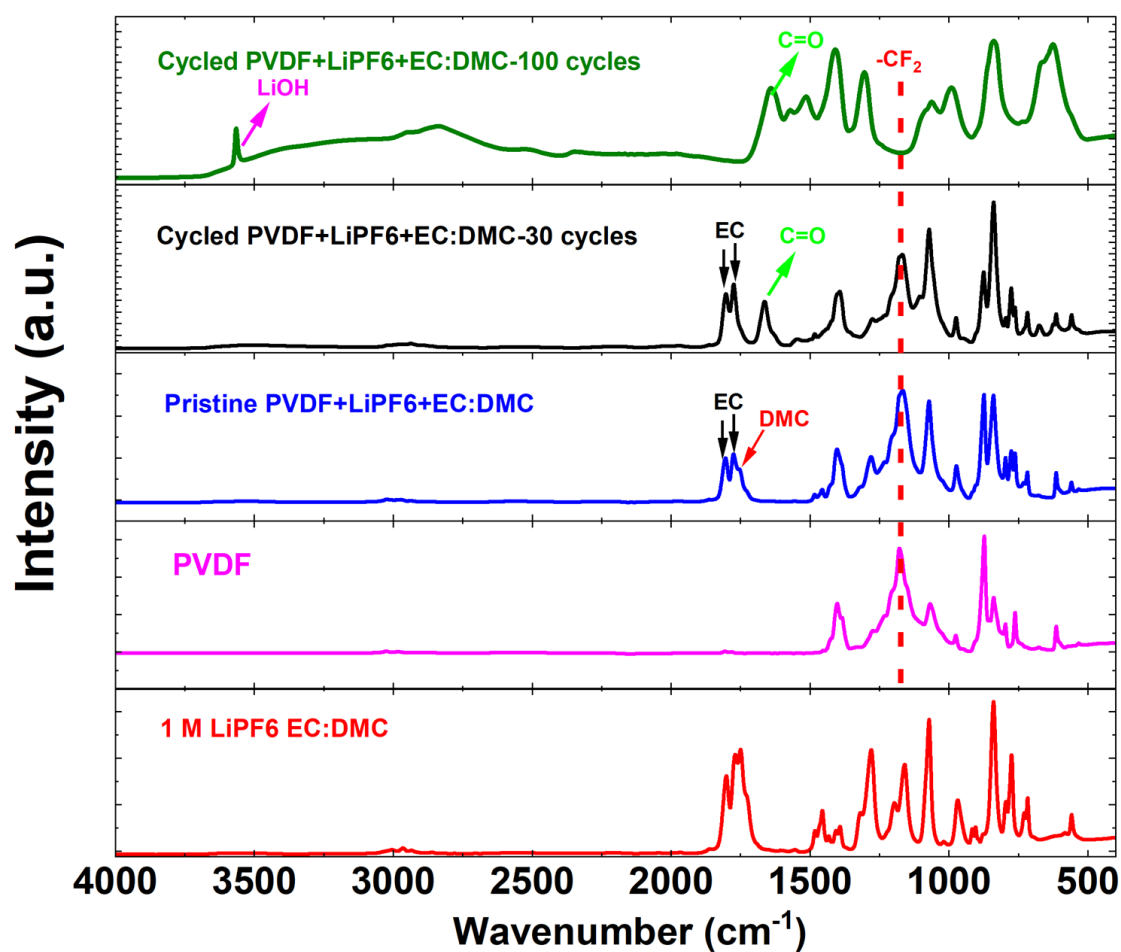


Figure 4.20. FTIR spectra of pristine 1 M LiPF_6 in EC: DMC, pristine PVDF, pristine PVDF soaked in 1 M LiPF_6 in EC: DMC, cycled PVDF soaked in 1 M LiPF_6 in EC: DMC after 30 cycles at 0.1 C, and cycled PVDF soaked in 1 M LiPF_6 in EC: DMC after 100 cycles at 0.1 C.

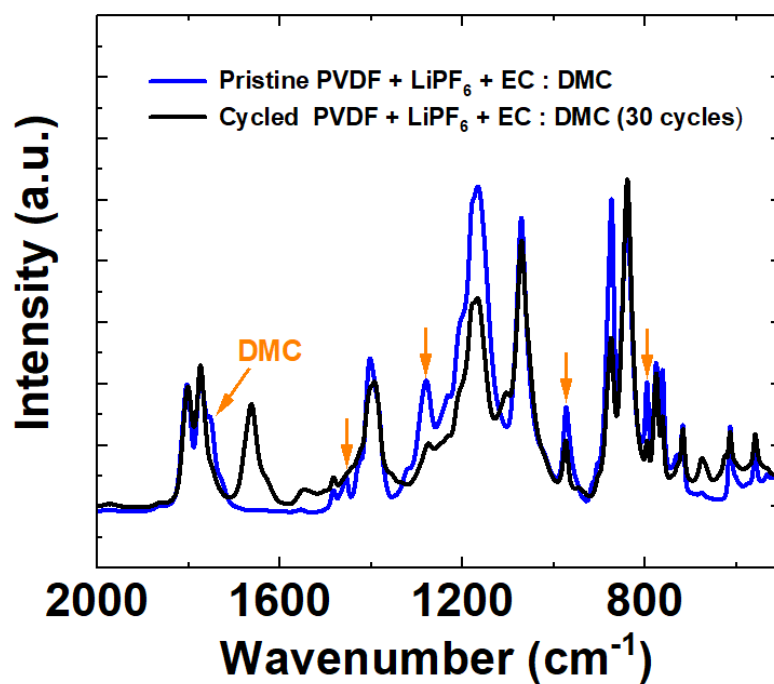


Figure 4.21. Comparison of DMC-related peaks in the FTIR spectra of pristine PVDF soaked in 1 M LiPF_6 in EC: DMC and cycled PVDF soaked in 1 M LiPF_6 in EC: DMC after 30 cycles at 0.1 C.

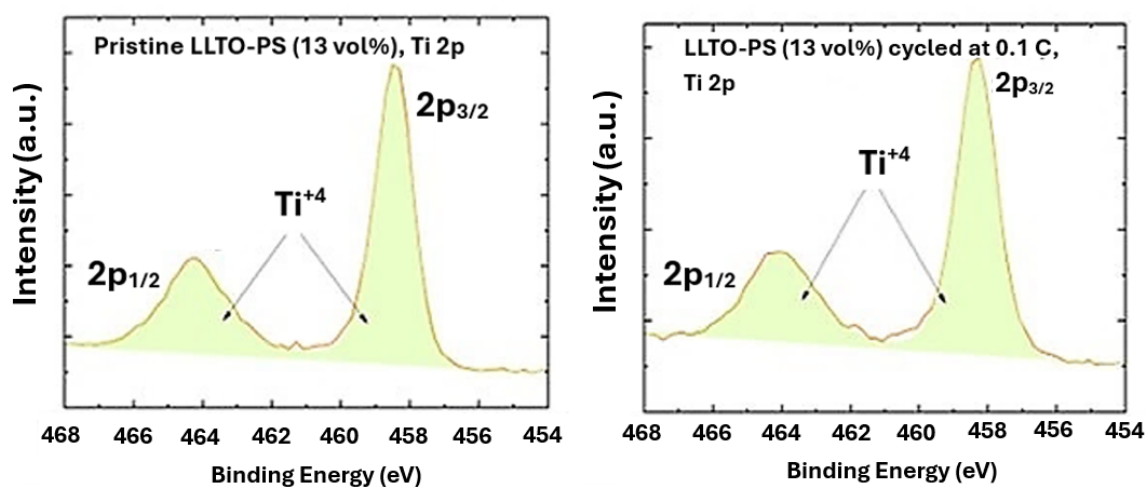


Figure 4.22. (a) Ti 2p spectra of pristine LLTO-PS (13 vol%). (b) Ti 2p spectra of LLTO-PS (13 vol%) cycled at 0.1 C for 100 cycles.

4.4. Conclusions

In this section, the interfacial compatibility between lithium metal and LLTO-based composite solid electrolytes was investigated, emphasizing the effect of interlayer strategies on electrochemical stability. Direct contact between lithium and LLTO was shown to trigger the reduction of Ti^{4+} , leading to increased electronic conductivity and rapid cell failure. Even trace amounts of LiFSI-based liquid electrolyte at the interface failed to prevent this degradation, as evidenced by substantial changes in the color and electronic conductivity of LLTO, along with continuously increasing interfacial resistance. In contrast, the use of a PVDF membrane soaked in LiPF_6 -based electrolyte as an interfacial buffer layer successfully suppressed the reduction reaction, stabilized the interfacial resistance, and prevented visible degradation of the LLTO, thereby significantly improving the chemical and electrochemical stability of the interface.

The Li/PVDF/LLTO-PS (13 vol%)/PVDF/Li symmetric cells exhibit a high CCD of 1.8 mA cm^{-2} and maintain excellent stability at 0.1 mA cm^{-2} for over 1000 hours. Moreover, the cell demonstrates stable operation under varying current densities of 0.1, 0.2, and 0.3 mA cm^{-2} , with low voltage responses for 400 hours. The LFP cathode and LLTO composite electrolyte were co-sintered under 400 MPa at 125°C for 30 minutes via cold sintering, achieving intimate interfacial contact without inducing any structural changes. This result highlights cold sintering as a promising technique for co-sintering oxide-based electrolytes and cathode materials at extremely low temperatures without compromising phase integrity. The Li/PVDF/LLTO-PS (13 vol%)/LFP full cell delivers high discharge capacities of 151 mAh g^{-1} and 135 mAh g^{-1} at 0.1 C and 0.2 C, respectively, at room temperature. Despite degradation of the liquid electrolyte-soaked PVDF membrane upon cycling, it effectively prevented any change in the oxidation state of Ti^{4+} in LLTO, even after 100 cycles at 0.1 C, providing a promising interfacial strategy for LLTO-based solid-state Li metal batteries. This battery design marks a promising LLTO-based Li-metal solid-state battery that achieves high performance at room temperature. Overall, this thesis demonstrates the viability

of cold sintering for fabricating high-performance oxide-based solid-state batteries and paves the way for future scalable processing of solid-state cells.



5. DESIGN, FABRICATION, AND PERFORMANCE OF LLZO-BASED LITHIUM-METAL CELLS

5.1. Introduction

The garnet-type cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is one of the most promising solid electrolytes for use in next-generation energy storage devices due to its high ionic conductivity, wide electrochemical stability window, and chemical stability against lithium metal [134]. However, the garnet solid electrolyte/Li interface presents significant challenges as shown in Figure 5.1, such as poor physical contact, poor wettability, and chemical instability, restricting the practical application of LLZO-based lithium metal batteries.

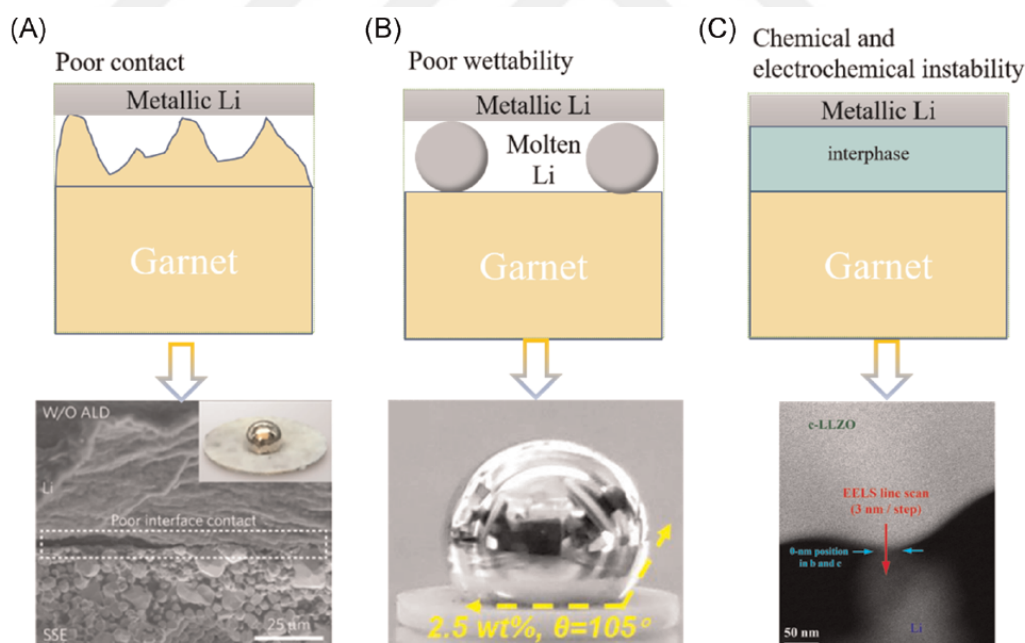


Figure 5.1. (A) Poor physical contact, (B) Poor wettability, and (C) Chemical instability between Li and LLZO [135].

Physical contact between pure lithium and LLZO solid electrolytes is poor, blocking lithium ions at the interface, leading to high interfacial resistance [136]. Poor wet-

tability at the Li/LLZO interface presents a significant challenge, attributed to the formation of impurity phases such as Li_2CO_3 . This phenomenon raises the contact angle from 95° to 146° , leading to high interfacial resistance [135]. In addition, the chemical instability of the LLZO electrolyte in contact with lithium metal induces a transition in its crystal structure from cubic to tetragonal, which has significantly lower ionic conductivity compared to the cubic LLZO phase [137].

Krauskopt et al. [138] studied the electrochemical performance of the symmetric cells ($\text{Li}/\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}/\text{Li}$). The galvanostatic cycling voltage profile of the symmetric cells demonstrates an increasing overpotential at a current density of 0.1 mA cm^{-2} . During the charging process, the formation of voids near the interface leads to contact loss between the solid electrolyte and the anode, resulting in a significant increase in the interfacial resistance. Several approaches have been adopted to address the interfacial problems that arise at the LLZO/Li interface. The use of an interlayer at the Li/LLZO interface is a promising approach to improve the wettability of the surface and achieves good physical contact at the interface, as the introduced layer fills the spaces at the contact points, as shown in Figure 5.2a. Han et al. [139] introduced an ultra-thin layer of aluminum oxide (Al_2O_3) at the garnet/Li interface using atomic layer deposition (ALD). SEM images (Figure 5.2b) demonstrate that the introduction of the ultra-thin Al_2O_3 layer facilitates intimate physical contact at the garnet/Li interface, effectively filling the voids. The addition of the interlayer led to a significant reduction in the total impedance of the symmetric Li/LLZO/Li cells, dropping from $3528 \Omega \text{ cm}^2$ to $176 \Omega \text{ cm}^2$ as shown in Figure 5.2c. This decrease is attributed to improved interfacial contact. In addition, Li plating and stripping tests reveal that symmetric cells with the interlayer exhibit stable cycling performance with minimal voltage polarization, as shown in Figure 5.2d.

Liu et al. [140] developed a gel interlayer to reduce interfacial resistance at the cathode/LLZO and anode/LLZO interfaces. The gel electrolyte comprises a PVDF-HFP polymer matrix soaked in a liquid electrolyte of 1 M LiPF_6 in a 1:1 mixture of ethylene carbonate and diethyl carbonate (EC/DEC). The fabricated gel electrolyte

demonstrates high ionic conductivity of $5 \times 10^{-4} \text{ S cm}^{-1}$ and a wide electrochemical stability window from 0 to 4.5 V vs. Li^+/Li . Introducing the gel electrolyte at the interfaces significantly reduces the interfacial resistance, decreasing from 6.5×10^4 to $248 \text{ } \Omega \text{ cm}^2$ at the cathode/LLZO interface and from 1.4×10^3 to $214 \text{ } \Omega \text{ cm}^2$ at the Li/LLZO interface.

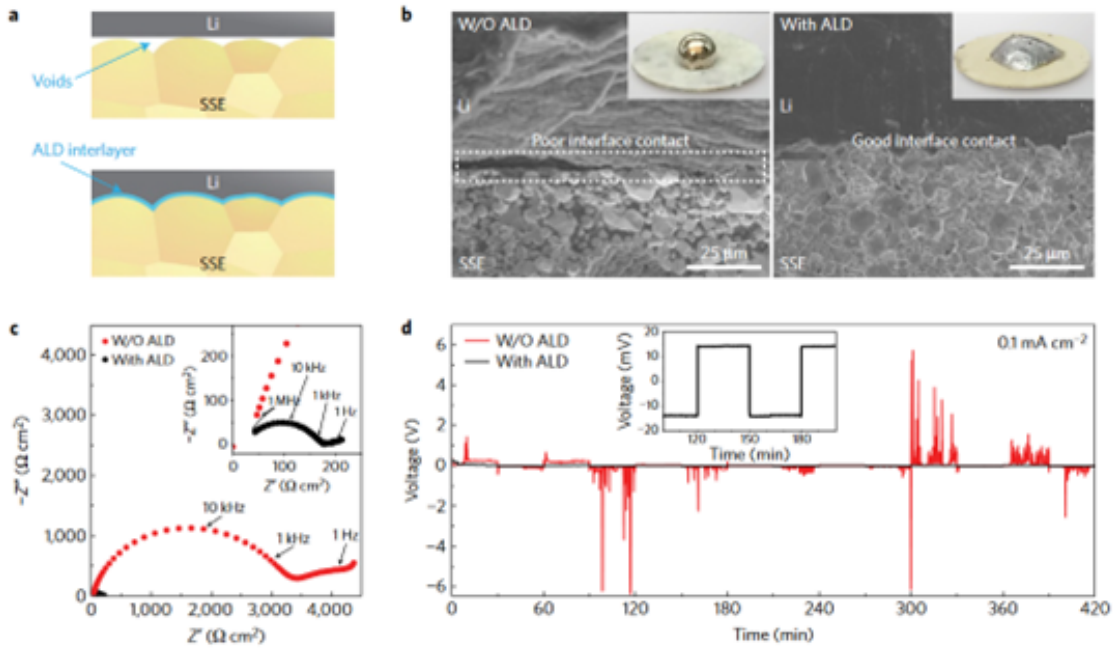


Figure 5.2. (a) Introduction of the atomic layer deposition interlayer. (b) SEM images of the Li/LLZO interface with and without an interlayer. (c) The impedance spectra of Li/LLZO/Li symmetric cells. (d) Galvanostatic cycling profile of the symmetric cells at 0.1 mA cm^{-2} [139].

A schematic illustration of the hybrid battery cell with gel electrolytes is shown in Figure 5.3a. The Li/Gel/LLZO/Gel/LFP battery cell exhibits a total impedance of $650 \text{ } \Omega \text{ cm}^2$ (Fig 5.3b), indicating excellent interfacial contact on the anode and cathode sides. Furthermore, symmetric Li/Gel/LLZO/Gel/Li cells demonstrate a stable galvanostatic cycling voltage profile with a low overpotential at a current density of 0.125 mA cm^{-2} over 15 hours as shown in Fig 5.3c, indicating a stable interface between the solid electrolyte and lithium metal. The full battery cell demonstrates a high discharge

capacity of 140 mAh g^{-1} and excellent capacity retention over 70 cycles at 1 C, as shown in Fig 5.3d.

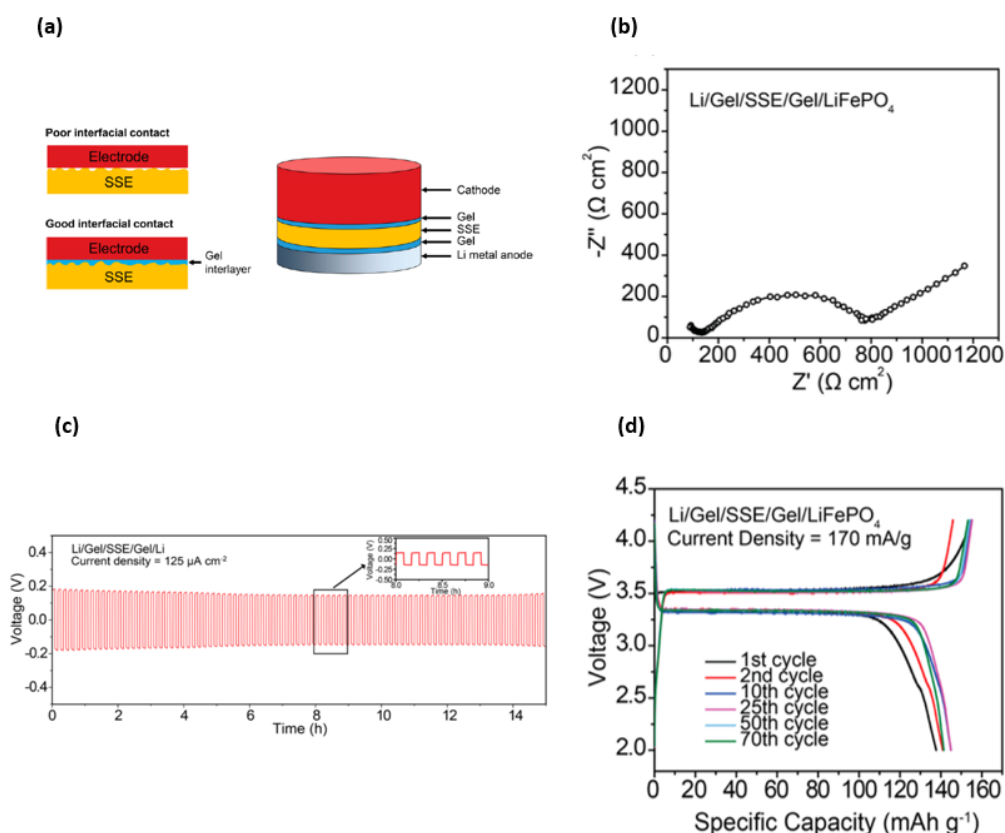


Figure 5.3. (a) Schematic illustration of the gel interfaces. (b) The impedance spectra of the Li/LLZO/LFP cell with gel interlayers. (c) Voltage profile of the symmetric cells. (d) Galvanostatic charging and discharging voltage profile at 1 C [140].

Liu et al. [141] melted commercial lithium foils at 250°C on a stainless-steel substrate and then rubbed the surface of the $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) solid electrolyte with the molten lithium until it was fully coated. To assemble Li/LLZTO/LCO full cells, a small amount ($\sim 2 \mu\text{L}$) of 1 M lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was added at the solid electrolyte/cathode interface. The assembled cells exhibited a total resistance of 421Ω and delivered discharge capacities of 157.5, 154.7, 145.8, and 130.2 mAh g^{-1} at 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively.

Cheng et al. [142] synthesized LCO powder using a sol-gel method and synthesized Li_3BO_3 (LBO) powder via a solid-state reaction. The LBO and LCO powders were mixed in a 3:7 mass ratio and ball milled at 400 rpm for 30 minutes, followed by calcination at 800°C for 2 hours in air. The resulting LBO-coated LCO was deposited onto the LLZO solid electrolyte using an aerosol deposition technique and subsequently annealed at 750°C for 2 hours in air to improve interfacial contact at the garnet/cathode interface. Additionally, a thin gold (Au) interlayer was introduced at the Li/solid electrolyte interface, and Li-Au/LLZO/LCO-LBO cells were assembled for performance evaluation. The total resistance of the cell was measured to be $115\ \Omega$ at 65°C . The cell exhibited an initial discharge capacity of $128\ \text{mAh g}^{-1}$ at 0.2 C and 60°C . $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) garnet electrolytes suffer from interfacial reactions with LiCoO_2 (LCO), which block Li ion transport and degrade cell performance. To mitigate this, Ren et al. [143] introduced a thin 5 nm aluminum oxide (Al_2O_3) interlayer between LCO and LLZO, effectively suppressing harmful interphase formation. Li/LLZO/LCO cells with this interlayer showed significantly improved performance, achieving stable discharge capacities up to $90\ \text{mAh g}^{-1}$ at 0.1 C. The diffusion of aluminum in LCO after annealing was found to maintain the protective effect without the need for a permanent physical barrier. Table 5.1 and Table 5.2 summarize the total cell resistances and discharge capacities, respectively, by comparing the findings of this thesis with the previous studies.

Table 5.1. LLZO-based full cell configurations and total cell resistances.

Full Cell	Resistance
Li/Gel/LLZO/Gel/LFP [140]	$650\ \Omega\ \text{cm}^2$
Molten Li/LLZTO/LCO [141]	$421\ \Omega$
Li-Au/LLZO/LCO-LBO [142]	$115\ \Omega$ at 65°C
Li/LLZO/LCO, Al_2O_3 interlayer [143]	$260\ \Omega\ \text{cm}^2$
Li/PPC-LiFSI/LLZO/LCO (This Thesis)	$452\ \Omega$ ($128\ \Omega\ \text{cm}^2$)

Table 5.2. LLZO-based full cell configurations and discharge capacities.

Full Cell	Discharge Capacity
Li/LLZO/Li ₂ FeMn ₃ O ₈ [139]	110 mAh g ⁻¹ , 0.1 C
Li/LLZO/LiFePO ₄ [140]	140 mAh g ⁻¹ , 1 C
Li/LLZO/LCO [141]	157.5 mAh g ⁻¹ at 0.1 C
Li/LLZO/LCO [142]	128 mAh g ⁻¹ at 0.2 C
Li/LLZO/LCO [143]	90 mAh g ⁻¹ at 0.1 C
Li/LLZO/LCO (This Thesis)	158, 141, 52 mAh g ⁻¹ at 0.1, 0.2, 0.5 C

The reported cell configurations in the literature typically utilize conventionally sintered LLZO solid electrolytes, which are fabricated at temperatures above 1000 °C for 12–20 hours [140, 141, 143]. These processes are time-consuming, energy-intensive, and often require the introduction of interlayers at the cathode/solid electrolyte interface to achieve high performance. In contrast, this thesis successfully addresses the challenges associated with the solid electrolyte/electrode interface by employing a scalable cold sintering approach. LLZO pellets are fabricated at 100 °C for 30 minutes and co-sintered directly with the electrode materials, thereby eliminating the need for conventional high-temperature sintering and additional interlayers. The battery configuration demonstrated in this thesis represents a significant step toward the development of high-energy-density, safer solid-state batteries based on garnet electrolytes. The proposed method ensures intimate physical contact at the cathode/LLZO interface, achieving low interfacial resistances comparable to those obtained with gel interlayers, but through a much simpler and more energy-efficient process.

5.2. Experimental Methods

To demonstrate the practical functionality of LLZO-based electrolytes, a solid-state lithium-metal battery was fabricated using cold-sintered LLZO-PPC-LiClO₄ composite electrolytes. An 8 mm punch was used to cut lithium discs from lithium foil

(MSE Supplies, the thickness of lithium and copper is $\approx 40\ \mu\text{m}$ and $11\ \mu\text{m}$, respectively). LCO-based cathode sheets (MSE Supplies, the thickness of LCO and aluminum is $\approx 50\ \mu\text{m}$ and $16\ \mu\text{m}$, respectively) were dried in a vacuum oven at $100\ ^\circ\text{C}$ for 6 h and stored in an argon-filled glovebox to ensure the best performance. A 6 mm punch was used to cut the LCO discs from the stored sheets. The as-prepared PPC-LiClO₄ solution was mixed with LLZO powder, followed by the addition of 9 wt.% DMF. The composite powder was then ground with an agate mortar and pestle for 5 minutes.

Afterward, the wetted powder was placed in a 13 mm die with a 6 mm LCO disc centered on top of it. The composite powder and the LCO disc were co-sintered under a uniaxial pressure of 300 MPa at $100\ ^\circ\text{C}$ for 30 minutes. This process facilitates intimate contact between the $\approx 0.4\ \text{mm}$ thick solid electrolyte and the positive electrode. An interfacial layer composed of PPC and LiFSI was fabricated to reduce the interfacial resistance at the Li/LLZO interface. Lithium bis(fluorosulfonyl)imide (LiFSI) (Sigma Aldrich, ultra-dry, 99.9% trace metal basis; battery grade) and polypropylene carbonate (Sigma Aldrich, average $M_n \sim 50,000\ \text{Da}$) were dissolved in anhydrous acetonitrile (ACN, Sigma Aldrich) in a mass ratio of 1:2:12 under an argon atmosphere with oxygen and moisture levels maintained below 0.1 ppm. The resulting polymer-salt solution was deposited onto Aclar sheets at a volume of $46.5\ \mu\text{L}/\text{cm}^2$, followed by drying and storage at room temperature. The resulting thin polymer-salt films were easily detached from the substrate for further use. The prepared interlayer was placed between the solid electrolyte and the anode. The battery cell was then assembled within a CR2032 coin cell and galvanostatically charged and discharged between 3 V and 4.3 V vs Li⁺ / Li at room temperature using a battery testing device (BTS3000, Neware). The charging and discharging current densities were determined from the practical capacity of the LCO cathode, $150\ \text{mAh g}^{-1}$.

5.3. Results and Discussion

Physical contact between pure lithium and the LLZO solid electrolyte is poor, as voids that block lithium ions form at the interface, leading to high interfacial re-

sistance [136]. To reduce interfacial resistance at the Li/solid electrolyte interface, PPC-LiFSI thin films were fabricated, as reported elsewhere [144]. The polymer-based ion conductor exhibits an ionic conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature [144]. The electrochemical characteristics of the LLZO-based composite electrolyte, fabricated through cold sintering, were evaluated in symmetric Li metal cells (Li/i/LLZO/i/Li, i: PPC-LiFSI interlayer) to investigate the stability of the solid electrolyte and its ability to suppress lithium dendrite growth. The applied current density was incrementally increased to determine the cell CCD, starting at 0.1 mA cm^{-2} , with a fixed Li plating/stripping duration of 30 minutes, following the time-controlled test method discussed in Section 2.2.1.

As shown in Figure 5.4a, the symmetric cell exhibits stable cycling under various current densities. A sharp voltage increase was observed at a current density of 1.1 mA cm^{-2} . When the current density reached 1.25 mA cm^{-2} , the voltage response exceeded the instrument's safety limit. The Li/i/LLZO/i/Li cell demonstrates a CCD exceeding 1 mA cm^{-2} . Long-term galvanostatic stripping and plating tests were performed at 0.1 mA cm^{-2} to assess the symmetric cell's interface stability. Figure 5.4b illustrates the galvanostatic cycling voltage profiles of the symmetric cell at 0.1 mA cm^{-2} . The symmetric cell demonstrates good cycling performance, maintaining stability for 300 hours with a low polarization of approximately 100 mV at 0.1 mA cm^{-2} . Figure 5.4c provides detailed information on the last few cycles at 0.1 mA cm^{-2} . Figure 5.5 presents the cross-sectional SEM image of the co-sintered LCO cathode and solid electrolyte, along with the corresponding EDS elemental map. The cold sintering process ensures intimate contact between the cathode and electrolyte layers without structural changes. This technique offers a novel approach for co-sintering cathodes and solid electrolytes at remarkably low temperatures and within short time frames.

The PPC-LiFSI thin film was placed between the solid electrolyte and lithium foil to assemble the full device within a 2032-coin cell, as illustrated in Figure 5.6a. Although the LLZO solid electrolyte is chemically stable, direct contact between Li and LLZO resulted in a very high interfacial resistance of approximately $350,000 \Omega$ (Inset

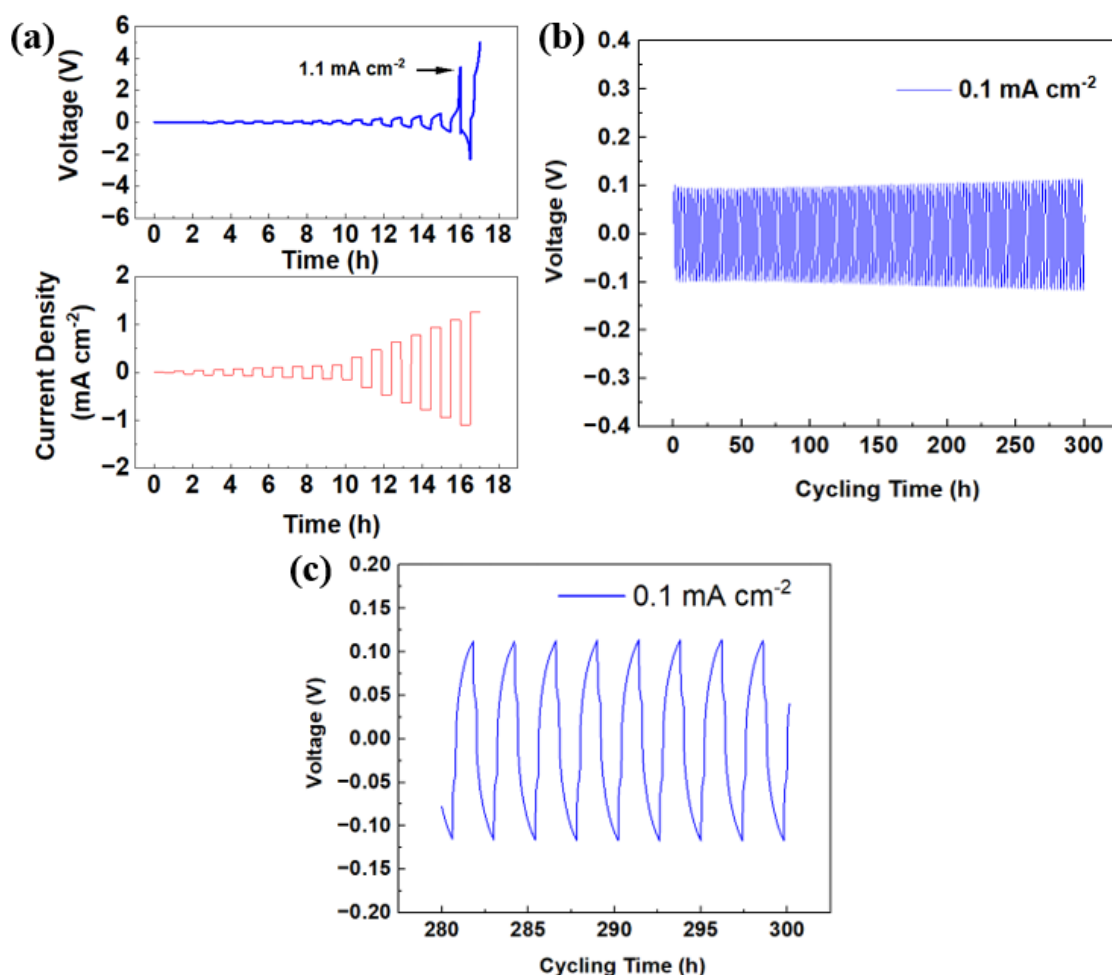


Figure 5.4. (a) Critical current density test of the Li/PPC-LiFSI/LLZO/PPC-LiFSI/Li cell by galvanostatic cycling. (b) Cyclic performance of the Li/PPC-LiFSI/LLZO/PPC-LiFSI/Li cell at 0.1 mA cm^{-2} . (c) Last few cycles at 0.1 mA cm^{-2} .

of Figure 5.6b). The fabricated PPC-LiFSI polymer thin films effectively reduced the interfacial resistance by providing intimate contact between the solid electrolyte and the lithium anode, decreasing the total cell resistance to 452Ω , as shown in Figure 5.6b. Figure 5.6c shows the voltage profiles of the full cell at various current densities. The full cell exhibits a discharge capacity of 158 mAh g^{-1} at 0.1 C . In addition, the rate performance of the cell at 0.1 , 0.2 , and 0.5 C is shown in Figure 5.6d. The full cell exhibits a maximum discharge capacity of 141 mAh g^{-1} at 0.2 C and 52 mAh g^{-1} at

0.5 C, respectively. The cell exhibited a stable discharge capacity profile at 0.1, 0.2, and 0.5 C, with a slight capacity decay observed at 0.2 C.

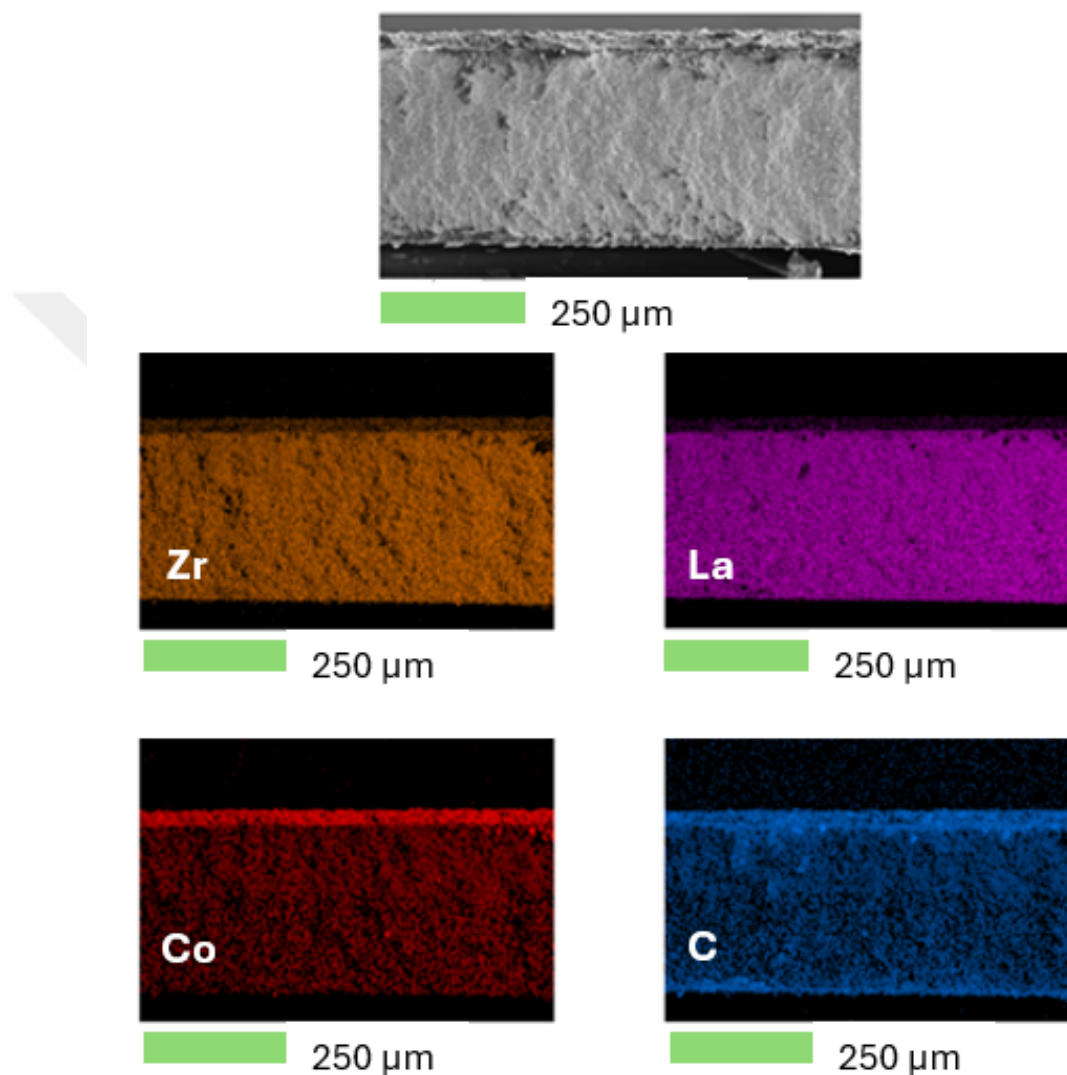


Figure 5.5. Cross-sectional SEM image of the co-sintered LCO cathode and LLZO solid electrolyte, along with the corresponding EDS mapping.

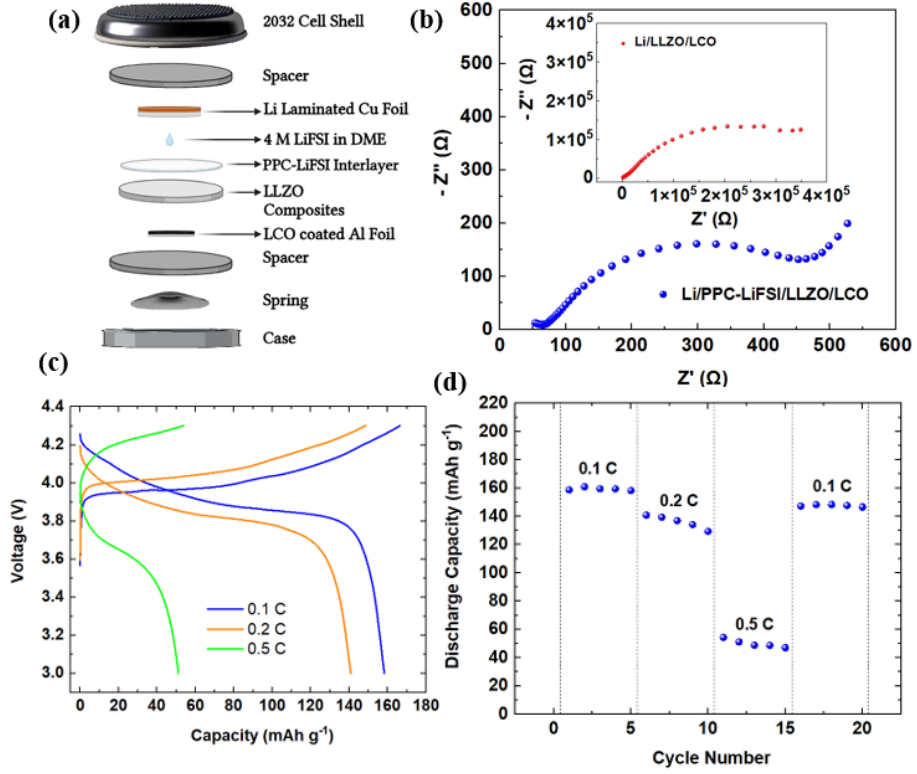


Figure 5.6. (a) Schematic illustration of the components of our batteries. (b) Nyquist plot (c) Galvanostatic charge/discharge curves, and (d) Rate performance of a Li/i/LLZO/LCO cell at room temperature.

5.4. Conclusions

A solid-state lithium-metal battery utilizing a cold-sintered LLZO-PPC-LiClO₄ composite electrolyte was successfully fabricated and demonstrated excellent electrochemical performance. The co-sintering approach enabled strong interfacial contact between the solid electrolyte and the LCO cathode at low temperatures, while the incorporation of a thin PPC-LiFSI interfacial layer at the anode significantly reduced the total cell resistance from $\sim 350,000 \Omega$ to 452Ω . Symmetric cell tests confirmed the stability of the composite electrolyte under long-term cycling, with a low polarization of $\sim 100 \text{ mV}$ and a critical current density exceeding 1 mA cm^{-2} . Furthermore, the full cell exhibited a high initial discharge capacity of 158 mAh g^{-1} at 0.1 C and retained good rate performance up to 0.5 C . These findings highlight the potential of

cold-sintered LLZO-based composite electrolytes and tailored interfacial engineering to enable high-performance solid-state lithium-metal batteries.



6. REPROCESSING LLTO COMPOSITE ELECTROLYTES VIA COLD SINTERING

6.1. Introduction

Lithium-ion batteries (LIBs) are the dominant energy storage technology, known for their high performance in portable electronics and electric vehicles. However, the use of flammable liquid electrolytes presents significant safety risks, including fire and explosion hazards [145]. Solid-state batteries, which replace volatile liquid electrolytes with solid-state electrolytes (SSEs), offer substantial advantages, including higher energy density, improved thermal stability, and improved safety [146, 147]. Solid-state lithium-ion batteries are complex structures composed of cathodes, anodes, solid electrolytes, and current collectors, containing valuable and scarce elements such as lithium and cobalt. As global demand for electric vehicles (EVs) continues to increase, addressing the sustainability of battery technologies is becoming increasingly critical. The International Energy Agency projects that by 2040, the growth of EVs could generate up to 8 million tons of battery waste, highlighting the urgent need for effective recycling techniques [148].

Recycling strategies for LIBs are generally classified into indirect and direct methods. Indirect recycling focuses on recovering valuable elements and re-synthesizing them into battery materials, while direct recycling preserves chemical bonds and crystal structures, avoiding breakdown processes [149]. Current indirect recycling techniques struggle with low lithium recovery rates, although up to 90% recovery is achievable for nickel, cobalt, and copper [150]. Pyrometallurgy and hydrometallurgy are the primary indirect recycling methods. However, both face significant drawbacks: pyrometallurgy is energy intensive, leads to substantial material losses, and produces considerable CO₂ emissions, while hydrometallurgy generates hazardous waste, involves high equipment costs, and requires complex processing [151, 152].

Direct recycling strategies offer great potential for the reusing of spent battery materials with relatively low energy consumption and significantly fewer greenhouse gas emissions than indirect recycling methods. They present a more sustainable alternative by bypassing the energy-intensive chemical decomposition processes and complex procedures inherent to indirect recycling [153–155]. However, direct recycling techniques are still in the laboratory stage and require further development to broaden their applicability beyond cathode and anode materials [156].

In solid-state batteries, degradation processes are often concentrated at the interface between the solid-state electrolyte (SSE) and the lithium metal anode, rather than affecting the entire bulk of the electrolyte. This distinction is critical for recycling strategies: if the degraded interfacial layers can be eliminated, then the bulk of the SSE, which largely retains its electrochemical properties, can be recovered and reused [144]. A clear understanding of chemo-mechanical degradation at the interface is therefore essential for designing effective reprocessing methods. Chemo-mechanical degradation is recognized as the primary cause of failure in ceramic-based solid-state electrolytes [157]. Most SSEs reported in the literature are thermodynamically unstable when in direct contact with lithium metal. As a result, secondary phases are likely to form at the interface, which can exhibit distinct ionic and electronic transport properties [158–160]. The characteristics of the interphase layer that develops between the lithium metal and the SSE largely govern the failure mechanisms. If the reaction products forming the interphase exhibit negligible electronic conductivity and remain stable during cycling, lithium dendrite growth along grain boundaries and structural defects becomes the dominant degradation pathway. These dendrites generate localized mechanical stress at crack tips, accelerating crack propagation and facilitating the formation of dendritic pathways through the SSE, which ultimately leads to cell short-circuiting [161–163].

However, if the interphase products exhibit mixed ionic and electronic conductivity, the situation becomes more complex. In such cases, the interphase layer continuously grows during electrochemical cycling, causing volume expansion and inducing

mechanical stress within the SSE. At higher current densities, non-uniform interphase growth exacerbates this effect, leading to deeper penetration into the SSE and creating highly localized, uneven stress distributions. These stresses ultimately result in fractures and a significant increase in interfacial impedance [164]. Nevertheless, even after such degradation, solid-state electrolytes largely preserve their bulk properties. Therefore, strategies that eliminate the degraded interphase and restore the mechanical integrity of the SSE, such as cold-sintering-based direct recycling, are highly promising. These approaches enable the healing of microcracks and the re-densification of the electrolyte, allowing spent SSEs to be reprocessed and reused across multiple cycles with minimal performance loss [165].

Cold sintering is a low temperature technique that employs modest pressure and a transient liquid phase to densify materials below 300 °C [69]. It enables the sintering of ceramics, polymers, and salts into composites while preserving their structural and chemical properties [73]. Beyond its potential for composite fabrication, cold sintering could also enable the recycling of spent battery materials. Lan et al. [165] proposed a direct reprocessing route using cold sintering for solid composite electrolytes comprised of Mg and Sr-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), polypropylene carbonate (PPC) and lithium perchlorate (LiClO_4). The pristine composite pellet was crushed to powder and mixed with acetonitrile (ACN)/*N,N*-Dimethylformamide (DMF) solution, where the liquid phase regulates the dissolution-precipitation process during cold sintering. The wetted powder was reprocessed at 100 °C for 1 h under a uniaxial pressure of 250 MPa to restore densified microstructures. After each of the five reprocessing cycles, the relative density of the electrolyte remained about 75%, similar to that of the pristine state, demonstrating that cold sintering effectively re-densifies composite electrolytes.

The ionic conductivity of the reprocessed pellets gradually decreases with each cycle; however, it remains above $1 \times 10^{-4} \text{ S cm}^{-1}$ even after five cycles. The gradual decline in ionic conductivity is attributed to the cubic to tetragonal phase transformation of LLZO and the formation of amorphous secondary phases due to the incongruent dissolution of constituent elements in the ACN/DMF mixture. The composite

powders were heat-treated at 170 °C before each reprocessing cycle to restore the pure cubic phase of LLZO and prevent any decay in ionic conductivity. As a result, the ionic conductivity averages $3.1 \times 10^{-4} \text{ S cm}^{-1}$ after four reprocessing cycles. In addition, batteries with reprocessed electrolytes ($\text{LiFePO}_4/\text{Reprocessed LLZO-PPC-LiClO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$) exhibit a high discharge capacity of 168 mA h g^{-1} at 0.1 C and excellent capacity retention at 0.2 C for over 100 cycles.

Lan et al. [144] introduced a direct recycling strategy for all solid state batteries (ASSBs) that uses flexible interfacial layers of lithium bis(fluorosulfonyl)imide-doped polypropylene carbonate (PPC-LiFSI) at electrode contacts. The interfacial layers facilitate intimate physical contact at the anode/SSE and cathode/SSE interfaces while enabling the easy separation of battery components with minimal intermixing. The drop-casted interfacial layers exhibit a high ionic conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, and the pristine $\text{LiFePO}_4/\text{LLZO-PPC-LiClO}_4/\text{Li}$ battery cell, fabricated with polymer-based layers at electrode contacts, demonstrates a low interfacial resistance of 338Ω . The spent battery cells were disassembled and immersed in DMF, dissolved in polymer-salt layers to separate the battery components. The recovered battery components retained their bulk crystal structures without forming secondary phases. The pristine battery cells deliver 160 and 154 mA h g^{-1} discharge capacities at 0.1 and 0.2 C, respectively. In comparison, fully recycled $\text{LiFePO}_4/\text{LLZO-PPC-LiClO}_4/\text{Li}$ cells with polymer-salt interlayers achieve discharge capacities of 148 and 121 mA h g^{-1} , corresponding to recovery rates of 92.5% and 78.6%, respectively.

Lan et al. [144] demonstrated that polymer-based interlayers enable easy separation and reprocessing of LLZO-based solid electrolytes recovered from spent solid-state cells. In contrast, this thesis focuses on evaluating the intrinsic reprocessability of LLTO-based perovskite electrolytes by simulating repeated recycling cycles. Instead of working with spent cells, the material was subjected to multiple controlled crushing and cold sintering steps to mimic the effects of successive recycling. This approach enables a systematic study of how many reprocessing cycles can be tolerated before significant degradation of the pristine electrolyte properties occurs. Notably, the reprocessing

performance of each oxide-based electrolyte may vary significantly depending on the crystal structure and the elemental solubility of its constituent elements in the cold sintering solvents. Future work could involve the design of interfacial layers and the implementation of multiple reprocessing cycles on LLTO-based electrolytes recovered from spent solid-state batteries.

Cold sintering-based reprocessing of solid-state electrolytes is a recently introduced approach, primarily explored in the literature for cubic garnet-type LLZO solid electrolytes [165]. In this thesis, the recyclability of a promising class of ceramic electrolytes, specifically perovskite-structured $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ ($0.07 < x < 0.13$) (LLTO), is systematically investigated. Unlike previous studies that primarily focused on garnet-type solid electrolytes such as LLZO [165], this thesis explores the cold sintering-based reprocessing of LLTO–PPC– LiClO_4 composite electrolytes. LLTO perovskites were subjected to up to 10 reprocessing cycles through controlled cold sintering, achieving minimal decay in ionic conductivity compared to pristine electrolytes. Even after 10 cycles, the LLTO composites maintain a high ionic conductivity of $2 \times 10^{-4} \text{ S cm}^{-1}$, demonstrating their potential for practical applications. Furthermore, LLTO perovskites retain a high degree of crystallinity after repeated processing, with no detectable formation of secondary phases, indicating excellent structural stability. Although a minor decrease in conductivity is observed, likely due to trace amounts of amorphous secondary phases, the low solubility of LLTO’s constituent elements mitigates the detrimental effects typically associated with incongruent dissolution, ensuring robust reprocessing performance.

Solid-state lithium metal batteries utilizing the reprocessed ($\times 10$) LLTO composite solid electrolytes demonstrate cycling performance comparable to those with pristine electrolytes, further confirming their suitability for practical use. Furthermore, the inclusion of a poly(vinylidene fluoride) (PVDF) membrane effectively mitigates chemical reactivity at the Li/LLTO interface, and even after 100 cycles at 0.1 C, the Ti^{4+} in the LLTO solid electrolyte remains unchanged, preserving its electrically insulating properties. The minor capacity decay observed after 10 reprocessing cycles underscores the

potential of cold sintering as a sustainable method for recycling solid-state electrolytes, offering a promising route for the development of energy-efficient and eco-friendly battery technologies.

6.2. Experimental Methods

6.2.1. Reprocessing LLTO Composite Electrolytes

$\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ powders, exhibiting a particle size distribution (D90) of less than 1 μm , were purchased from Toho Titanium Co., Ltd. Polypropylene carbonate (average $M_n \sim 50,000$ Da) and LiClO_4 (Sigma-Aldrich, battery grade, dry, 99.99% trace metals basis) were purchased from Sigma-Aldrich. A binder-salt solution was prepared with a 2:1 weight ratio of PPC to LiClO_4 . During the preparation of the binder-salt solution, the binder and lithium salt were dissolved in acetonitrile (ACN, Sigma-Aldrich, anhydrous), with acetonitrile comprising 80% of the PPC- LiClO_4 -ACN mixture by mass. The resulting mixture was stirred overnight at 25 °C using a magnetic stirrer. The LLTO powder and polymer-salt solution were mixed in a predetermined mass ratio of 95.8: 2.8: 1.4 for LLTO, PPC and LiClO_4 , respectively, along with approximately 9 wt.% of DMF.

Figure 6.1 presents the key stages of the direct reprocessing route used for LLTO composite electrolytes. As the first stage of the process, the ceramic LLTO powder is mixed with a binder-salt solution consisting of PPC- LiClO_4 and DMF using an agate mortar and pestle. The wetted powder is transferred into a 13 mm die and sandwiched between aluminum foils, which serve as blocking electrodes for impedance analysis. To enable simultaneous heating and compression, a bracelet equipped with a heating element and a thermocouple encases the die. This assembly is then placed in a uniaxial press, where the composite powder is subjected to 400 MPa of pressure and heated to 125 °C for 30 minutes, with a ramp-up rate of 10 °C/min. The cold-sintered composite solid electrolytes are assembled into a 2032-coin cell for impedance measurements.

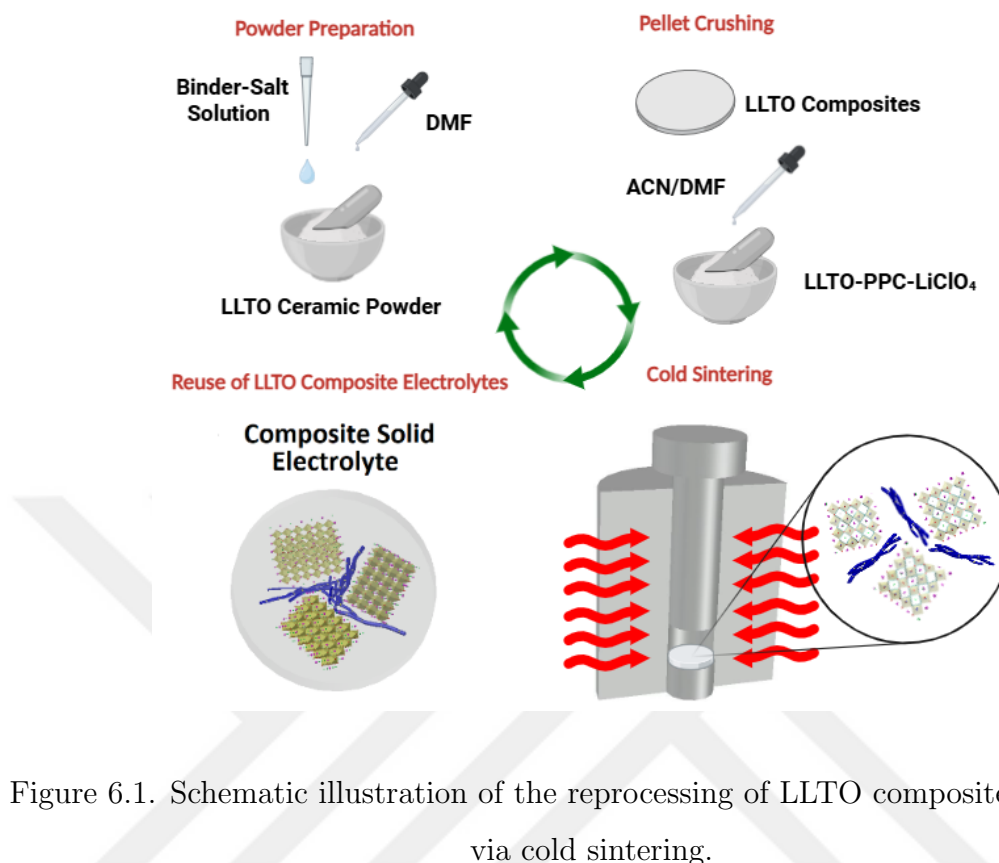


Figure 6.1. Schematic illustration of the reprocessing of LLTO composite electrolytes via cold sintering.

To reprocess composite solid electrolytes, the coin cell was disassembled using a lineman's plier and a diagonal plier. The composite electrolyte was removed from the coin cell components. The composite pellet was then crushed into powder using a mortar and pestle, and the Al foils, which served as blocking electrodes for impedance measurements, were easily removed with tweezers after the pellet was crushed. The composite powder is mixed with a solution of acetonitrile and DMF in a 2:1 w/w ratio, which regulates the dissolution-precipitation process during cold sintering. Acetonitrile did not include the binder-salt as it was already present in the crushed composite powder. The wetted powder followed the same fabrication steps as the pristine composite electrolyte and was reassembled into the coin cell for impedance measurements. All steps involved in the preparation of the binder-salt solution and cold sintering of the composite powder were carried out in an argon-filled glovebox. The wetted composite powder is reprocessed through cold sintering to restore a densified structure, simulating the recovery of cracks in spent solid-state electrolytes, using the same processing pa-

rameters applied during the fabrication of the pristine pellet. Finally, the reprocessed composite solid electrolytes are reused in both half-cell and full-cell configurations to evaluate the performance of the reprocessed electrolytes. To compare the mechanical properties, a sample was fabricated using conventional high-temperature sintering and designated as HTS LLTO. The sintering step was performed at 1200 °C for 10 hours with ramp-up and ramp-down rates of 5 °C per minute.

6.2.2. Characterization and Measurement

The density of each composite solid electrolyte was calculated by measuring the mass and thickness of the pellet and determining the mass-to-volume ratio. The relative density of the composite solid electrolytes was calculated as the ratio of the measured density to the theoretical density of the composite, which consists of the ceramic LLTO phase ($\rho_{\text{LLTO}} = 5.09 \text{ g/cm}^3$), PPC ($\rho_{\text{PPC}} = 1.26 \text{ g/cm}^3$), and LiClO_4 ($\rho_{\text{LiClO}_4} = 2.42 \text{ g/cm}^3$). The theoretical density of the composite solid electrolytes was calculated using the following equation [68]:

$$\rho_{\text{composite}} = \rho_{\text{LLTO}} f_{\text{LLTO}} + \rho_{\text{PPC}} f_{\text{PPC}} + \rho_{\text{LiClO}_4} f_{\text{LiClO}_4}, \quad (6.1)$$

where ρ_{LLTO} , ρ_{PPC} , and ρ_{LiClO_4} denote the densities of LLTO, PPC, and LiClO_4 , respectively, and f_{LLTO} , f_{PPC} , and f_{LiClO_4} represent their corresponding volume fractions. The Nyquist plots of the composite solid electrolytes were obtained using EIS with a 10 mV AC signal over a frequency range of 1–10⁶ Hz (Modulab XM, Solartron Analytical). ZView software (Scribner Associates, USA) was used to fit the EIS data using equivalent circuit modeling. The ionic conductivity (σ_{ion}) of the solid electrolytes was calculated using the following equation [78]:

$$\sigma_{\text{ion}} = \frac{t}{R_{\text{total}} \cdot A}, \quad (6.2)$$

where R_{total} and t represent the total resistance and thickness of the solid electrolyte, respectively, and A denotes the area of the ion-blocking electrodes. The ionic conductivity of the samples was measured over a temperature range of 0 to 100 °C in 20 °C increments to assess its temperature dependence. The samples were held at each target temperature for 10 minutes before measurement to ensure thermal equilibrium. The

activation energies of the sintered solid electrolytes were extracted from the slope of the Arrhenius plot using the following equation:

$$\sigma_{\text{ion}} = A \exp \left(-\frac{E_a}{k_B T} \right), \quad (6.3)$$

where A is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature.

Phase identification and crystal structure analysis were performed using an X-ray diffractometer (Empyrean, Malvern Panalytical). XRD patterns were recorded with Cu-K α radiation in a 2θ range of 10° to 70° with a step size of 0.013° . The acquired patterns were analyzed using MDI Jade software. Microstructural characterization of the specimens was performed on fractured surfaces using a Thermo Fisher Scientific Verios scanning electron microscope (SEM). Before imaging, a ~ 5 nm iridium coating was sputtered on the fractured surfaces to mitigate the charging effects.

To evaluate the dissolution behavior of elements in LLTO or LLZO powders, 1 g of pristine powder was immersed in an ACN/DMF solution and heated at 125°C for 5 and 30 hours. The resulting mixture was then extracted with a syringe and filtered through a $0.22\ \mu\text{m}$ syringe filter. The final volume after filtration was adjusted to 5000 μL . The filtered solution was subsequently dried at 120°C and redissolved in 2% (v/v) trace metal grade HNO_3 for inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES). The ICP-AES analysis was performed on a Thermo iCAP 7400 Duo ICP-OES/AES, using standards purchased from High Purity Standards (North Charleston, SC) for calibration of the measured elements.

Fourier transform infrared (FTIR) spectroscopy measurements were performed using a Bruker Vertex 70 spectrometer equipped with a diamond crystal in attenuated total reflection (ATR) mode. The Raman spectra of the cold sintered composites were recorded using a Raman spectrometer (LabRAM HR Evolution, HORIBA Scientific) with a 532 nm excitation laser and 1800 g/mm grating. X-ray Photoelectron Spectroscopy (XPS) was employed to examine the surface composition and chemical states of the samples. XPS experiments were conducted using a Physical Electronics

VersaProbe III instrument, equipped with a monochromatic Al K α X-ray source and a concentric hemispherical analyzer. Charge neutralization was achieved using low-energy electrons (below 5 eV) and argon ions. Measurements were performed at a 45° take-off angle relative to the sample surface plane, resulting in a typical sampling depth of 3–6 nm, with 95% of the signal originating from this depth or shallower. XPS data analysis was performed using CasaXPS software.

Particle size analysis of pristine powders and crushed composite powders from pellets was performed using a laser diffraction particle size analyzer (Mastersizer 3000+) with isopropanol as the dispersing agent. Before nanoindentation and microindentation measurements, conventionally sintered and cold-sintered pellets were embedded in resin and their surfaces were polished using 600, 800, 1200, and 2400 grit grinding paper to achieve desired surface flatness, without the use of any solvent. Nanoindentation measurements were made using a Hysitron TI-900 with a 10 mN load and a Berkovich-type indenter. Micro-indentation measurements were performed using a Vickers indenter on the HV-1 and HV-10 scales.

6.2.3. Fabrication of Full Cells and Performance Testing

Li/LFP battery cells were fabricated using pristine and reprocessed ($\times 10$) LLTO composite solid electrolytes. An 8 mm punch was used to cut lithium discs from lithium foil (MSE Supplies; the thicknesses of lithium and copper are approximately 40 μm and 11 μm , respectively). LFP-based cathode sheets (MTI Corporation; the thicknesses of LFP and aluminum are approximately 68 μm and 16 μm , respectively) were dried in a vacuum oven at 100 °C for 6 h and stored in an argon-filled glovebox to ensure optimal performance. A 6 mm punch was used to cut the LFP discs from the stored sheets. The as-prepared PPC–LiClO₄ solution was mixed with LLTO powder, followed by the addition of 9 wt.% DMF. The resulting composite powder was ground for 5 minutes using an agate mortar and pestle. Subsequently, the wetted powder was placed into a 13 mm die, with a 6 mm LFP disc centered on top. The composite powder and the LFP disc were co-sintered under a uniaxial pressure of 400 MPa at 125 °C for 30 minutes.

To prevent interfacial reactions between the lithium metal anode and the solid LLTO-based composite electrolyte, a PVDF membrane (0.45 μm , Amersham, Germany) soaked with an electrolyte solution ($\approx 20 \mu\text{L cm}^{-2}$ of 1 M LiPF_6 in EC:DMC, 50/50 (v/v), Sigma-Aldrich, CA) was placed between the solid electrolyte and the anode. The battery cell was then assembled within a CR2032 coin cell, galvanostatically charged and discharged between 2.6 V and 4.0 V vs. Li^+/Li at room temperature using a battery test device (BTS3000, Neware). In addition to battery cells manufactured with pristine LLTO composite solid electrolytes, full cells were also fabricated using reprocessed ($\times 10$) LLTO composite solid electrolytes to evaluate their performance. The densities of the charging and discharging currents were determined based on the theoretical capacity of the LFP cathode, 170 mAh g^{-1} .

6.3. Results and Discussion

6.3.1. The Effect of Reprocessing on Material Properties and Conductivity

The PPC- LiClO_4 volume fraction in LLTO-polymer-salt composites (LLTO-PS) is maintained at 13 vol%, referred to as LLTO-PS (13 vol%). Based on our previous study [166], the highest ionic conductivity was achieved at a PPC- LiClO_4 volume fraction of 13 vol%; therefore, this composition was selected for a further study on reprocessing. Figure 6.2a shows the Nyquist plots of pristine and multiple-times-reprocessed LLTO-PS (13 vol%) composite solid electrolytes. The equivalent circuit used to fit the complex impedance spectra of the composite solid electrolytes consists of $R_{\text{bulk}}-(R_{\text{gb1}}\parallel\text{CPE}_{\text{gb1}})-(R_{\text{gb2}}\parallel\text{CPE}_{\text{gb2}})-\text{CPE}_{\text{tail}}$, where R and CPE denote the resistance and constant phase element, respectively.

R_{bulk} represents the bulk lithium-ion conductivity within the LLTO ceramic phase. In addition, parallel configurations of resistors (R_{gb1} and R_{gb2}) and constant phase elements (CPE_{gb1} and CPE_{gb2}), expressed as $R_{\text{gb1}}\parallel\text{CPE}_{\text{gb1}}$ and $R_{\text{gb2}}\parallel\text{CPE}_{\text{gb2}}$, were used to model the grain boundary lithium-ion conductivities. Cold-sintered LLTO composites (13 vol% PPC- LiClO_4) exhibit two distinct grain boundary resistances due

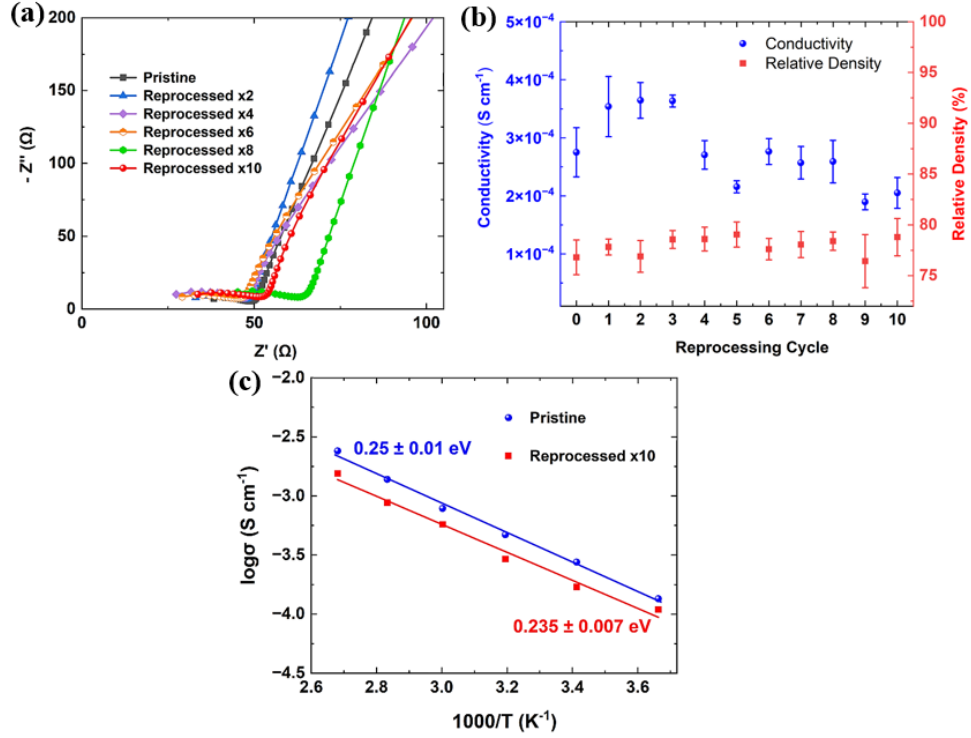


Figure 6.2. (a) Nyquist plots of pristine and multiple-times-reprocessed LLTO-PS (13 vol%). (b) Ionic conductivities and relative densities of LLTO-PS (13 vol%) composite electrolytes as a function of reprocessing cycles. (c) Arrhenius plots of the pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) electrolytes.

to the partial filling of the grain boundaries by PPC-LiClO₄, resulting in heterogeneous grain boundaries. Both resistances are more pronounced at lower PPC-LiClO₄ contents, as reported in our recent study [166]. The tail in the low-frequency region was modeled by adding a constant phase element (CPE_{tail}) in series with the other circuit elements, as previously described, to represent lithium-ion blocking electrodes [113]. The equivalent circuit model for the pristine and reprocessed ($\times 10$) composite electrolytes is shown in Appendix B.

To assess the effect of reprocessing on electrolyte performance, composite electrolytes were reprocessed up to 10 times, with their density and ionic conductivity

measured throughout the cycles. Figure 6.2b illustrates the changes in ionic conductivity and relative density of the composite electrolytes as a function of reprocessing cycles. Conductivities were obtained from Nyquist plots of symmetric cells (Al/LLTO-PPC-LiClO₄/Al) at room temperature. The ionic conductivity of the pristine LLTO composites was measured to be $2.75 \times 10^{-4} \text{ S cm}^{-1}$. After one reprocessing cycle, the ionic conductivity increased to $3.53 \times 10^{-4} \text{ S cm}^{-1}$, reaching a peak value of $3.64 \times 10^{-4} \text{ S cm}^{-1}$ after two cycles. Between the 4th and 8th cycles, the ionic conductivity fluctuated around $2.5 \times 10^{-4} \text{ S cm}^{-1}$, before stabilizing at approximately $2 \times 10^{-4} \text{ S cm}^{-1}$ in the 9th and 10th cycles. This implies that LLTO composites show excellent stability under multiple reprocessing cycles via cold sintering, despite a slight reduction in ionic conductivity after 10 reprocessing cycles. The minor decrease in ionic conductivity may be attributed to the formation of trace amounts of amorphous secondary phases.

The relative density of the pristine LLTO composites is measured at 76.8%, increasing slightly to 78.8% after 10 reprocessing cycles. On average, the relative density across all ten cycles is approximately 78%, suggesting that cold sintering effectively densifies the crushed composite powders into pellets, demonstrating the potential for mechanical recovery over extended cycling. Figure 6.2c presents the temperature dependence of the ionic conductivity of pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) composite electrolytes. The temperature dependence follows an Arrhenius behavior for both pristine and reprocessed ($\times 10$) LLTO composites, with activation energies of 0.25 eV and 0.235 eV, respectively. The slight reduction in activation energy after 10 reprocessing cycles may be attributed to the gradual formation of lithium vacancies due to the preferential dissolution of lithium [165]. The increased vacancy concentration could enhance lithium-ion mobility by facilitating vacancy-assisted conduction, thereby lowering the energy barrier for ion migration.

Figure 6.3 displays scanning electron microscopy (SEM) images of the fracture cross-sections of pristine, reprocessed, and reprocessed ($\times 10$) composite electrolytes and commercial-grade LLTO powder, acquired in secondary electron imaging mode.

The cross-sectional images were captured without polishing, with a 5 nm-thick iridium layer sputtered onto the fractured surfaces to mitigate charging issues. Pristine, reprocessed, and reprocessed ($\times 10$) LLTO composite solid electrolytes exhibit similar, dense microstructures without any noticeable grain growth typically observed in conventional sintering techniques.

The particle size of pristine LLTO powder (without binder-salt) ranges from submicron to about 1 μm . To measure the particle size distribution, the composite pellets were crushed into powder after ten reprocessing cycles, resulting in a shift towards smaller particle sizes compared to the pristine powder. This shift is likely due to the grinding process during successive reprocessing cycles. Additionally, a small fraction of particles in the 10–100 μm range was observed, which can be attributed to the binder causing submicron particles to cluster (Figure 6.4).

Figure 6.5 shows the XRD patterns of pristine LLTO powder and pristine and reprocessed ($\times 10$) LLTO composite electrolytes. The XRD pattern of pristine LLTO powder closely matches the reference pattern of perovskite tetragonal LLTO (01-090-2573), with a trace amount (~ 2 wt%) of impurity phases of $\text{La}_2\text{Ti}_2\text{O}_7$ (04-021-8682). The cold-sintered pristine LLTO-PS (13 vol%) demonstrates a high degree of crystallinity. Similarly, $\text{La}_2\text{Ti}_2\text{O}_7$ is the only impurity phase detected in the cold-sintered solid electrolyte, with no change in its weight percentage. This suggests that the impurities in our composites originate from the pristine LLTO powder rather than the cold sintering process. Even after 10 reprocessing cycles, the LLTO composites retain their perovskite-type tetragonal crystal structure with a high degree of crystallinity. The sole crystalline impurity phase, $\text{La}_2\text{Ti}_2\text{O}_7$ (~ 2 wt%), is attributed to the pristine powder.

Figure 6.6 presents the Raman spectra of pristine and reprocessed ($\times 10$) LLTO composite electrolytes. Characteristic peaks appear at 140 cm^{-1} , 238 cm^{-1} , 316 cm^{-1} , 456 cm^{-1} , and 526 cm^{-1} , corresponding to LLTO perovskite vibrations, and are in good agreement with literature data [167–169]. Within the Raman spectra, the peak at

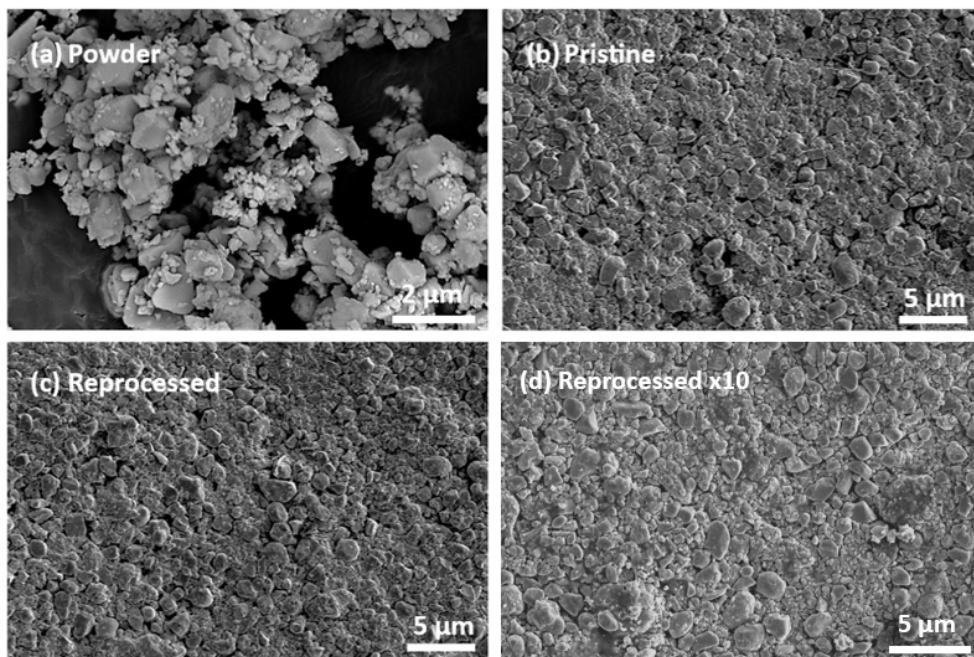


Figure 6.3. SEM images of (a) LLTO powder, (b) Pristine, (c) Reprocessed, and (d) Reprocessed ($\times 10$) composite solid electrolytes.

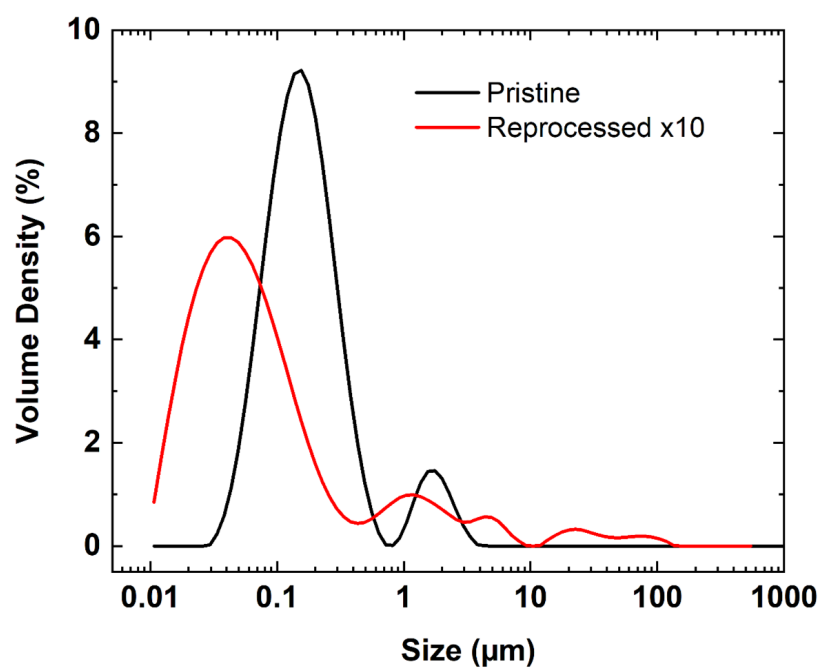


Figure 6.4. Particle size distribution of pristine LLTO powders and powders from crushed reprocessed ($\times 10$) composite pellets.

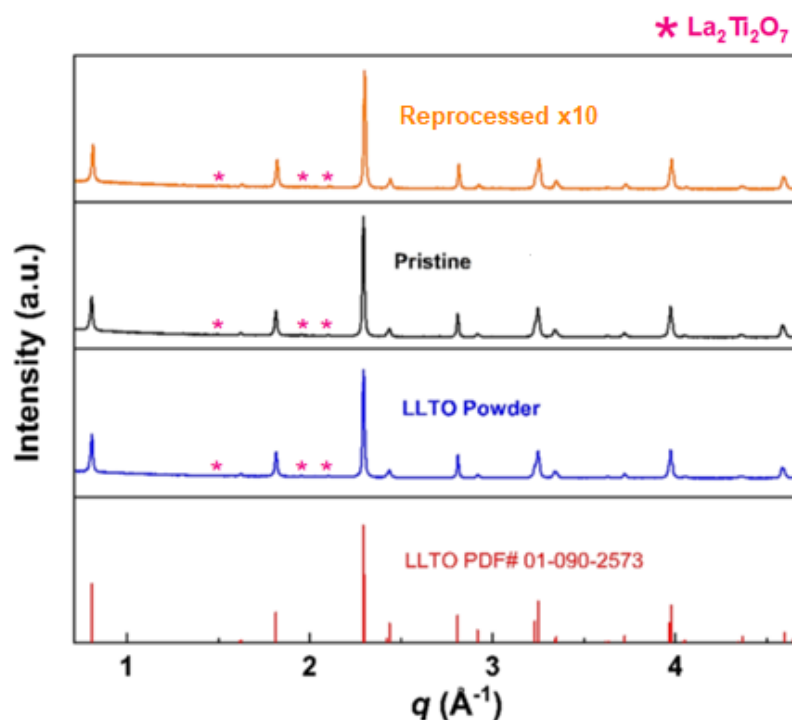


Figure 6.5. The XRD patterns of pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) composite electrolytes.

140 cm^{-1} is attributed to Ti displacements in the x - y plane, and the peaks at 238 cm^{-1} and 526 cm^{-1} correspond to TiO_6 octahedral tilting within the x - y plane. The peak at 316 cm^{-1} is assigned to Ti displacements along the z -axis. The peak at 456 cm^{-1} , along with the shoulder near 560 cm^{-1} , is ascribed to TiO_6 octahedral tilting along the z -axis of the lattice [169]. After 10 reprocessing cycles, both the peak positions and the full width at half maximum (FWHM) values for all peaks remain unchanged, without any peak broadening. This observation demonstrates that the LLTO perovskite structure retains exceptional stability throughout multiple reprocessing cycles via cold sintering. The strong Ti-O bonding, primarily driven by covalent interactions between O $2p$ and Ti $3d$ orbitals within the TiO_6 octahedra, is believed to be the key factor preserving the integrity of the local structure and ensuring the stability of the perovskite tetragonal crystal lattice [170,171]. The Raman bands observed at 860 cm^{-1} and 931 cm^{-1} are attributed to the symmetric C-N stretching vibration of DMF and the presence of free ClO_4^- ions from LiClO_4 , respectively [172,173].

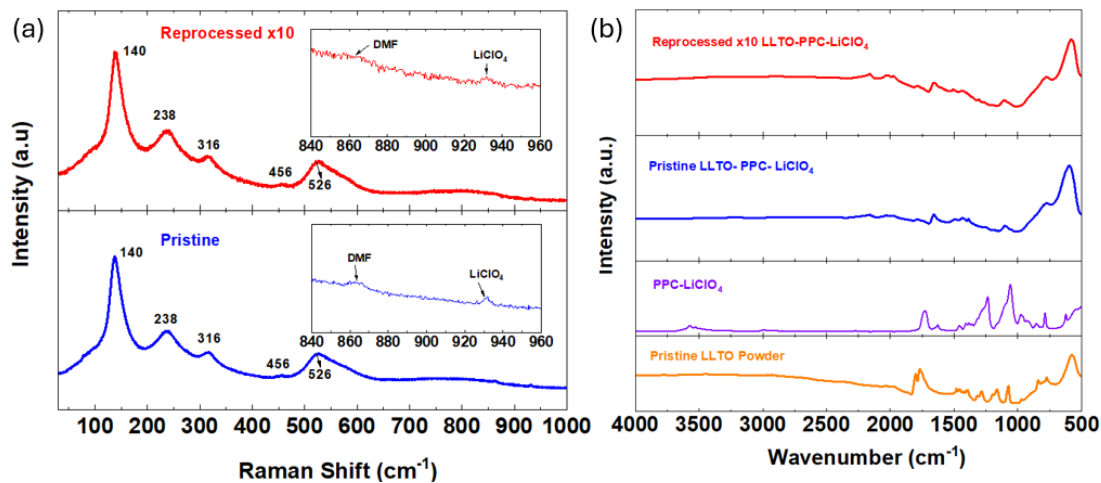


Figure 6.6. (a) Raman and (b) FTIR spectra of pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) composite electrolytes.

The pristine and reprocessed ($\times 10$) LLTO-PPC-LiClO₄ composites were characterized using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), as shown in Figure 6.6b. The FTIR spectrum of the pristine LLTO composite displayed characteristic peaks corresponding to the LLTO ceramic phase and the PPC-LiClO₄ binder-salt additives, with no additional peaks assignable to unknown phases. After ten reprocessing cycles, the LLTO composites exhibited FTIR spectra nearly identical to those of the pristine samples, indicating that the chemical structure remains unaltered despite repeated processing via cold sintering. This suggests that the reprocessing method does not induce any detectable degradation or structural perturbation at the molecular level.

6.3.2. Phase Stability and Solubility of LLTO in ACN and DMF

To further examine the stability of the LLTO ceramic phase against solvents used in the cold sintering process, pristine LLTO powders were subjected to prolonged exposure in an ACN/DMF mixture at 125 °C for 200 hours. The XRD pattern of LLTO powders heated in the ACN/DMF mixture at 125 °C for 200 h confirms that LLTO powders retain their perovskite tetragonal crystal structure without forming any un-

wanted phases. This proves that the LLTO phase exhibits excellent stability against the densification-assisting solvents used in the cold sintering process, even after prolonged exposure (Figure 6.7a). LLTO composite solid electrolytes were fabricated for impedance measurements using LLTO powders exposed to ACN/DMF for 200 h. The Nyquist plot of the fabricated composite solid electrolytes is shown in Figure 6.7b. The LLTO–PS (13 vol%) electrolytes, fabricated using the powders exposed to prolonged treatment, exhibit an ionic conductivity of $1.55 \times 10^{-4} \text{ S cm}^{-1}$.

Neither 10 reprocessing cycles via cold sintering nor prolonged exposure to solvents leads to any significant structural changes in the LLTO ceramic phase. This is of high significance, as a recent study reported that the ACN/DMF mixture induces phase transformations, and repeated cold sintering cycles lead to the accumulation of amorphous phases in the garnet solid electrolyte ($\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$) [165]. During cold sintering, congruent dissolution in transient solvents at moderate temperatures promotes a rapid dissolution–precipitation process, facilitating densification [69]. However, incongruent dissolution can occur for many compounds when elements at the grain surfaces dissolve at different kinetic rates, driven by differences in their chemical reactivity and bonding strength. This imbalance in dissolution behavior can disrupt the stoichiometry of the material, potentially leading to the formation of amorphous phases or secondary crystalline phases, which may degrade the structural integrity and functional properties of materials [165].

Figure 6.8a presents the dissolution concentrations of Li, La, and Ti after LLTO powders were heated in an ACN/DMF mixture at 125 °C for 5 hours. A 5-hour solvent exposure was chosen to approximate the cumulative conditions of 10 reprocessing cycles, assuming a 30-minute cold sintering duration per cycle. Lithium exhibits a significantly higher dissolution concentration (approximately $0.26 \mu\text{mol mL}^{-1}$) compared to La and Ti, both of which remain at much lower levels (approximately $10^{-4} \mu\text{mol mL}^{-1}$). Upon extending the exposure duration to 30 hours, the dissolution concentrations of Li, La, and Ti were measured to be $1.74 \mu\text{mol mL}^{-1}$, $7.2 \times 10^{-4} \mu\text{mol mL}^{-1}$, and $8.3 \times 10^{-4} \mu\text{mol mL}^{-1}$, respectively (Figure 6.8b).

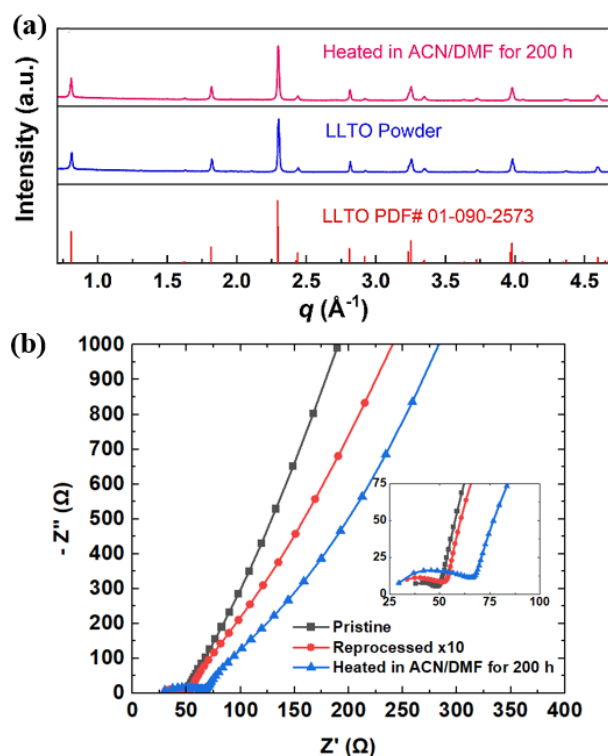


Figure 6.7. (a) XRD patterns of pristine LLTO powder and LLTO powders heated in ACN/DMF at 125 ° C for 200 hours. (b) Nyquist plots of LLTO–PS (13 vol%) fabricated using LLTO powders heated in ACN/DMF at 125 ° C for 200 hours. After prolonged heating in the ACN/DMF mixture, the ionic conductivity slightly decreased to $1.55 \times 10^{-4} \text{ S cm}^{-1}$.

Figure 6.8c presents the dissolution concentrations of Li, La, and Zr after LLZO powders were heated in an ACN/DMF mixture at 125 °C for 5 hours. The dissolution concentrations of Li, La, and Zr were initially measured as 26.87, 1.7×10^{-3} and $1 \times 10^{-2} \mu\text{mol mL}^{-1}$, respectively. Upon extending the exposure duration to 30 hours, these values increased to 57.24, 5.8×10^{-3} , and $3.4 \times 10^{-2} \mu\text{mol mL}^{-1}$, respectively (Figure 6.8d). Incongruent dissolution is observed in both LLTO and LLZO during exposure to polar organic solvents; however, the extent of dissolution differs significantly between the two materials. Despite having comparable particle sizes, the dissolution rates of the constituent elements in LLTO are significantly lower than those in LLZO. In particular, the lithium dissolution concentration in LLZO is nearly two

orders of magnitude higher than in LLTO, suggesting that LLZO is more susceptible to lithium loss during cold sintering. This pronounced lithium depletion in LLZO can promote a cubic-to-tetragonal phase transformation during reprecipitation, which is thermodynamically favored under lithium-deficient conditions [165]. In contrast, the lower elemental solubility in LLTO limits the detrimental dissolution typically associated with incongruent dissolution. Furthermore, it is speculated that LLTO possesses a more inherently stable crystal structure in polar organic environments, which contributes to its enhanced resistance to solvent-induced degradation.

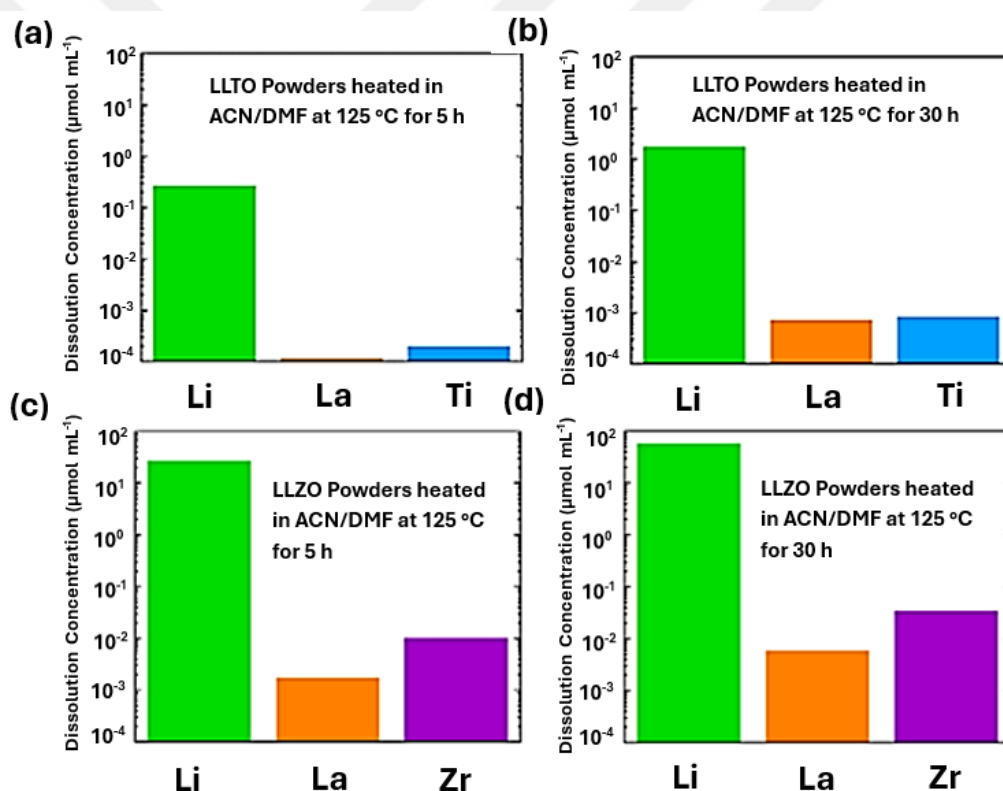


Figure 6.8. Dissolution concentrations of elements in LLTO and LLZO powders under different treatment conditions.

6.3.3. Mechanical Characterization of Cold-Sintered LLTO Composites

The mechanical properties of solid-state electrolytes are critical for the performance and longevity of solid-state batteries. To compare mechanical properties, a

sample was manufactured using conventional high-temperature sintering at 1200 °C and designated as HTS LLTO. The mechanical properties of the cold-sintered composite electrolytes and HTS LLTO were characterized using nanoindentation and micro-indentation techniques. Nanoindentation measurements were performed using Hysitron TI-900, and force-displacement curves for HTS LLTO, pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) composite electrolytes are shown in Figure 6.9. The elastic modulus of HTS LLTO was measured to be 200.82 ± 2.94 GPa, which is well aligned with the reported values [174]. In contrast, the elastic moduli of the pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) composite electrolytes were found to be 36.58 ± 2.06 GPa and 32.15 ± 2.38 GPa, respectively. These values reflect a significant reduction compared to the HTS LLTO, highlighting the impact of different processing conditions.

The inclusion of binder-salt additives, coupled with the notable difference in relative density ($\sim 78\%$ for cold-sintered composites versus $\sim 89\%$ for HTS LLTO), plays a key role in altering the elastic modulus of solid electrolytes. Similarly, the hardness values obtained from the nanoindentation measurements were 14.7 GPa, 1.13 GPa, and 0.89 GPa for HTS LLTO, pristine, and reprocessed ($\times 10$) LLTO composites, respectively. The lower relative density of the cold-sintered composites ($\sim 78\%$ for cold-sintered composites versus $\sim 89\%$ for HTS LLTO) indicates a less compact microstructure, likely contributing to the reduced stiffness and mechanical strength observed in these materials.

Micro-indentation tests were performed using a Qness Q60 A+ micro-indenter. The hardness of the pristine and reprocessed ($\times 10$) LLTO composites was measured to be 1.14 GPa and 0.88 GPa, respectively. Micro-indentation, which probes a larger volume of material compared to nanoindentation, yielded a lower hardness value of 9.45 GPa for HTS LLTO, aligning well with the reported values [174]. This difference can be attributed to variations in scale, applied forces, and probe depth between the two methods. Despite these differences, both techniques provide valuable insight into the mechanical properties of the material, reflecting the distinct probing depths and corresponding material responses at different scales.

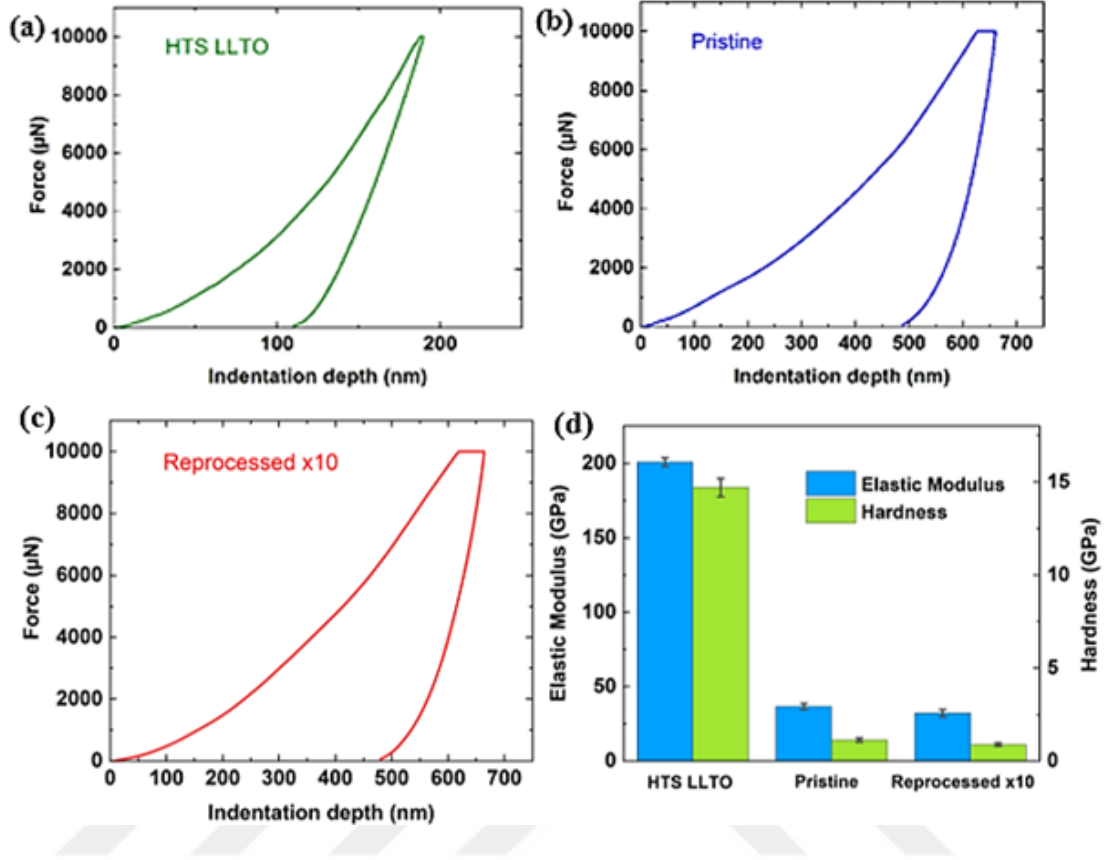


Figure 6.9. Force-displacement curves from the nanoindentation test for (a) HTS LLTO, (b) Pristine LLTO-PS (13 vol%), (c) Reprocessed ($\times 10$) LLTO-PS (13 vol%). (d) Elastic modulus and hardness values obtained from nanoindentation measurements.

Figure 6.10a presents the optical image of the Vickers indent and the resulting cracks that originate at the indent corners in HTS LLTO under HV1 load. Fracture toughness can be calculated using the following analytical equation [104]:

$$K_{IC} = 0.16 \times H \times d^2 \times C^{-1.5}, \quad (6.4)$$

where H is the Vickers hardness, d is half the diagonal of the Vickers indent, and C is the radius of the critical crack [104]. The fracture toughness of the HTS LLTO was calculated to be $1.18 \text{ MPa}\cdot\text{m}^{1/2}$, which is consistent with the reported values [174]. Figure 6.10b shows the optical image of the Vickers indent and the resulting cracks in

HTS LLTO under HV10 load. When the applied load was increased to 10 kilograms force (HV10), long cracks initiated from the corners of the indent and extended across the entire field of view captured by the 10 $\times$ objective.

Figure 6.10c shows the optical image of the Vickers indent in the pristine LLTO-PS (13 vol%) composite electrolyte under HV1 load, with no visible crack formation observed. To calculate the fracture toughness, the applied load was increased to 10 kilograms of force (HV10), which was sufficient to initiate crack formation and propagation in the composite samples (Figure 6.10d). The fracture toughness of the pristine and reprocessed ($\times 10$) LLTO composites was calculated to be 2.04 MPa $\cdot$ m^{1/2} and 1.62 MPa $\cdot$ m^{1/2}, respectively. Although they show comparable fracture toughness values, the mechanical responses of the cold-sintered and conventionally sintered LLTO samples differ markedly under mechanical loading. Under a 10-kg force load, the HTS LLTO sample demonstrates a shallower indentation depth but exhibits extensive crack propagation. In contrast, cold-sintered samples show greater penetration depths accompanied by shorter cracks.

This behavior can be attributed to the microstructural differences induced by processing. The presence of residual porosity and polymeric phases in the cold-sintered composite may allow localized deformation through pore collapse and matrix flow, thus dissipating stress and suppressing crack initiation. However, the high relative density ($\sim 89\%$) of the HTS LLTO restricts such mechanisms, leading to more brittle fracture behavior. Porosity has been reported to strongly influence the mechanical properties of composite lithium electrodes [175]. Similar trends have been observed in polymer-infiltrated ceramics, where the introduction of a polymer phase improves ductility and strain tolerance [176].

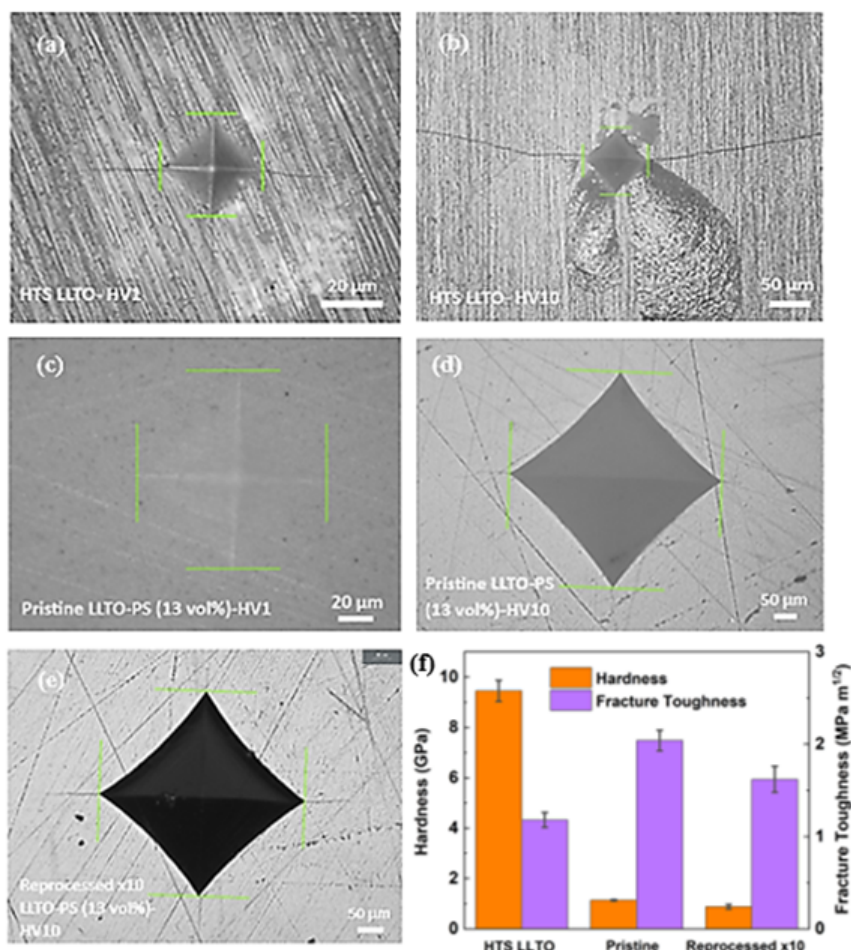


Figure 6.10. Optical images of Vickers micro-indentation tests for (a) HTS LLTO at HV1, (b) HTS LLTO at HV10, (c) Pristine LLTO-PS (13 vol%) at HV1, (d) Pristine LLTO-PS (13 vol%) at HV10, (e) Reprocessed ($\times 10$) LLTO-PS (13 vol%) at HV10, (f) Hardness and fracture toughness values obtained from micro-indentation measurements.

6.3.4. Electrochemical Performance of LLTO-Based Cells

Long-term galvanostatic stripping and plating experiments were performed to evaluate the electrochemical stability of lithium symmetric cells incorporating both pristine and reprocessed ($\times 10$) composite electrolytes. Figure 6.11a displays the galvanostatic cycling voltage profiles of the Li/LLTO-PS (13 vol%)/Li half-cell with PVDF interlayers at various current densities. The cell exhibits stable cycling performance,

maintaining its integrity for over 400 hours while demonstrating relatively low polarization overpotentials of approximately 80 mV, 120 mV, and 140 mV at current densities of 0.1, 0.2, and 0.3 mA cm⁻², respectively. Similarly, Figure 6.11b presents the voltage profiles of the Li/Reprocessed ($\times 10$) LLTO-PS (13 vol%)/Li half-cell with PVDF interlayers under identical conditions. In particular, even after ten reprocessing cycles, the half-cell maintains long-term stability, with polarization overpotentials of 70 mV, 130 mV, and 220 mV at 0.1, 0.2, and 0.3 mA cm⁻², respectively, closely matching those of the pristine cell. The slightly reduced ionic conductivity compared to that of the pristine state, combined with the consistent interfacial design, results in nearly identical galvanostatic cycling performance. These findings underscore the robustness of the LLTO-PS composites, demonstrating that multiple reprocessing cycles do not significantly degrade their electrochemical stability and reinforce their potential for long-term energy storage applications.

To assess the dendrite suppression capability of LLTO composite electrolytes with PVDF interlayers, critical current density (CCD) tests were conducted in pristine and reprocessed ($\times 10$) solid electrolytes. The applied current density was gradually increased, starting from 0.1 mA cm⁻², with a fixed Li plating/stripping duration of 1 hour, to determine the CCD for each cell. Figure 6.11c illustrates that the symmetric cells exhibited stable cycling performance under various current densities. A sharp increase in voltage was observed at a current density of 2 mA cm⁻². The Li/PVDF/Pristine LLTO-PS (13 vol%)/PVDF/Li cell demonstrated a high CCD exceeding 1.8 mA cm⁻². In contrast, the half-cells incorporating reprocessed ($\times 10$) LLTO composites experienced a sharp voltage increase at 1.7 mA cm⁻² (Figure 6.11d). The Li/PVDF/Reprocessed ($\times 10$) LLTO-PS (13 vol%)/PVDF/Li cell displayed a CCD of 1.5 mA cm⁻², slightly lower, but overall similar, than that of the pristine LLTO-PS symmetric cells.

A solid-state Li/LFP cell was assembled using pristine and reprocessed ($\times 10$) LLTO-PS (13 vol%) solid electrolytes. The cold sintering process allows the co-sintering of solid electrolytes and cathodes at relatively low temperatures ($< 150^\circ\text{C}$), improv-

ing interfacial contact and preserving the integrity of the assembled components by minimizing elemental interdiffusion [114]. LLTO composites and LFP electrodes were co-sintered at 400 MPa and 125 °C for 30 minutes.

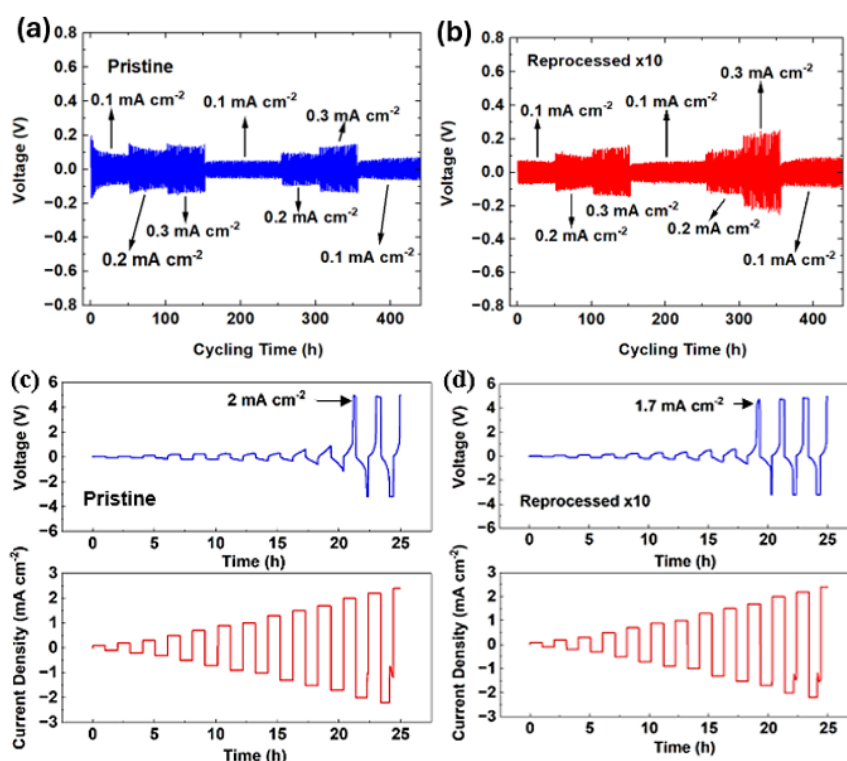


Figure 6.11. Cyclic performance of the (a) Li/PVDF/Pristine LLTO-PS/PVDF/Li and (b) Li/PVDF/Reprocessed ($\times 10$) LLTO-PS/PVDF/Li half-cells under different current densities. (c) CCD test of the Li/PVDF/Pristine LLTO-PS/PVDF/Li half-cell by galvanostatic cycling. (d) CCD test of the Li/PVDF/ Reprocessed ($\times 10$) LLTO-PS/PVDF/Li half-cell by galvanostatic cycling.

Direct contact between the lithium anode and the LLTO solid electrolyte causes the reduction of Ti^{4+} to lower oxidation states, significantly improving the electronic conductivity of the solid electrolyte and ultimately leading to battery self-discharge [51]. Our recent study demonstrates that the incorporation of a PVDF membrane, soaked in a small amount of liquid electrolyte (1 M LiPF_6 in EC:DMC, 50:50 (v/v)), effectively mitigates the chemical reactivity between lithium metal and LLTO [166]. Therefore,

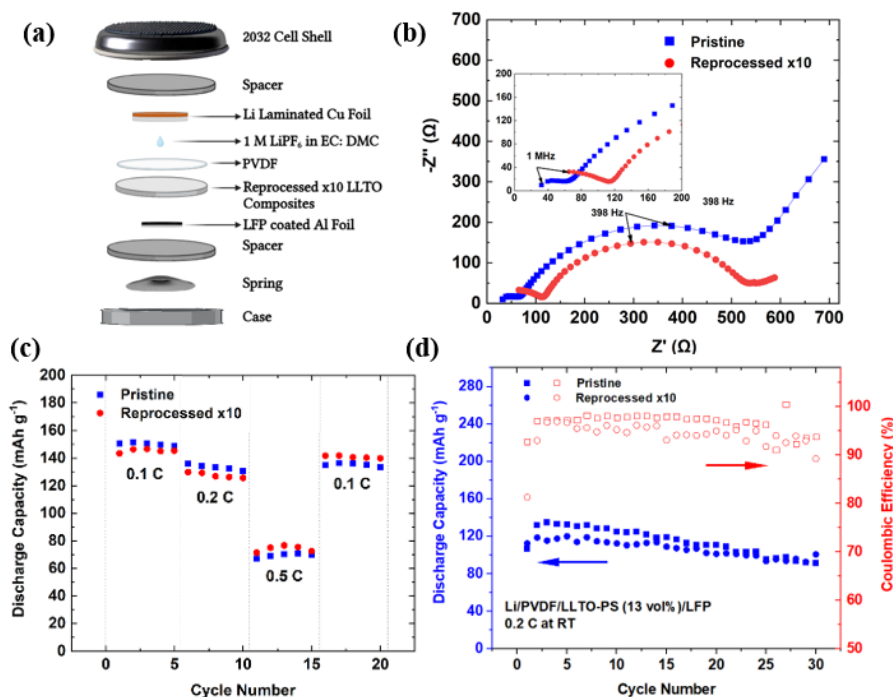


Figure 6.12. (a) Schematic of battery components. (b) Nyquist plots of Li/PVDF/LLTO-PS (13 vol%)/LFP with pristine and reprocessed ($\times 10$) electrolytes (inset: high-frequency data). (c) Rate performance and (d) cycling stability of the same cells at room temperature and 0.2 C, respectively.

the PVDF membrane soaked in the electrolyte solution was placed at the Li/solid electrolyte interface and full cells were assembled into 2032-coin cells using pristine and reprocessed ($\times 10$) LLTO composites. Figure 6.12a shows a schematic illustration of the battery components. Figure 6.12b shows the Nyquist plot of the Li/PVDF/Pristine LLTO-PS (13 vol%)/LFP and Li/PVDF/Reprocessed ($\times 10$) LLTO-PS (13 vol%)/LFP cells at room temperature. The electrochemical impedance spectra exhibit distinct semicircles at high and mid frequencies, along with a low-frequency tail. The pristine and reprocessed ($\times 10$) battery cells exhibit total resistances of 496 Ω and 502 Ω , respectively.

Figure 6.12c shows the rate performance of Li/LFP battery cells incorporating pristine and reprocessed ($\times 10$) LLTO composite solid electrolytes at 0.1, 0.2, and 0.5 C

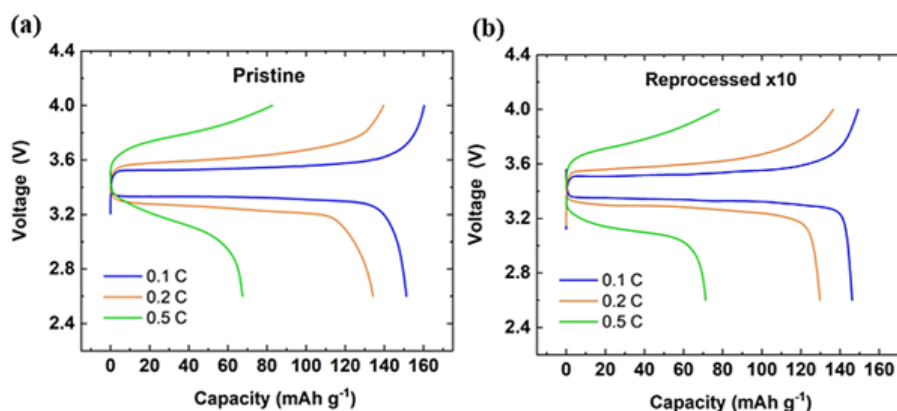


Figure 6.13. Galvanostatic charge/discharge curves of (a) Li/PVDF/Pristine LLTO-PS (13 vol%)/LFP and (b) Li/PVDF/Reprocessed ($\times 10$) LLTO-PS (13 vol%)/LFP cells.

rates. The pristine full cell exhibits maximum discharge capacities of 151 mAh g^{-1} , 135 mAh g^{-1} , and 70 mAh g^{-1} at 0.1, 0.2, and 0.5 C, respectively. The full cell assembled with the reprocessed ($\times 10$) LLTO composite solid electrolyte delivers maximum discharge capacities of 146 mAh g^{-1} , 129 mAh g^{-1} , and 75 mAh g^{-1} at the same respective C rates, showing performance comparable to the pristine cell in all tested C rates. The pristine and reprocessed ($\times 10$) battery cells exhibit a near-steady discharge capacity profile at 0.1, 0.2, and 0.5 C.

Figure 6.12d illustrates the cycling stability of pristine and reprocessed ($\times 10$) battery cells at 0.2 C, tested at room temperature. The pristine cell exhibits modest cycling performance, retaining 69.1% of its initial capacity after 30 cycles, with a discharge capacity of 92 mAh g^{-1} , while the reprocessed ($\times 10$) battery cell retains 78% of its initial capacity with the same discharge capacity. Figure 6.13 shows the voltage profiles of the pristine and reprocessed ($\times 10$) full cells at various current densities. The full cells display a typical voltage profile of Li/LFP, featuring a flat plateau at approximately 3.45 V during galvanostatic charging and discharging.

6.4. Conclusions

This study demonstrates the feasibility of repeatedly reprocessing LLTO-based composite solid electrolytes via cold sintering, offering a sustainable and low-energy recycling pathway for solid-state electrolytes. The cold-sintered LLTO perovskites retained high crystallinity and phase purity even after ten reprocessing cycles, with only a minor reduction in ionic conductivity, maintaining a practical level of $2 \times 10^{-4} \text{ S cm}^{-1}$. Despite the occurrence of incongruent dissolution driven by preferential lithium leaching, the detrimental effects were significantly suppressed due to the intrinsically low elemental solubility of LLTO. Symmetric Li metal cells using reprocessed ($\times 10$) LLTO composite solid electrolytes demonstrated good cycling performance, maintaining stability for over 400 hours at different current densities. The full cell assembled with the reprocessed ($\times 10$) LLTO composite solid electrolytes delivered maximum discharge capacities of 146 mAh g^{-1} , 129 mAh g^{-1} , and 75 mAh g^{-1} at 0.1, 0.2, and 0.5 C, respectively, showing performance comparable to the pristine cell. Overall, LLTO perovskites show excellent structural and electrochemical stability in multiple cold sintering reprocessing cycles, underscoring their strong potential for sustainable reuse in next-generation solid-state battery technologies.

7. CONCLUSIONS

This dissertation, which focuses on oxide-based LLTO and LLZO solid electrolytes, consists of four main parts. First, the cold sintering parameters for LLTO and LLZO were explored to achieve ionic conductivities greater than $10^{-4} \text{ S cm}^{-1}$. Second, co-sintering of LLTO/LFP and LLZO/LCO interfaces was successfully demonstrated via cold sintering at approximately 100°C for 30 minutes, without inducing structural or chemical degradation. Third, the interfacial reactivity between lithium metal and the LLTO solid electrolyte was mitigated by introducing a PVDF membrane soaked in a liquid electrolyte, enabling the fabrication of Li/LFP battery cells using cold-sintered LLTO composites. Fourth, interfacial resistance at the Li/LLZO interface was reduced by applying a PPC-LiFSI polymer thin film, and Li/LCO battery cells were assembled using cold-sintered LLZO composites. Finally, the reprocessing performance of LLTO composites was investigated through repeated cold sintering cycles to evaluate the material's structural and electrochemical stability under multiple reuse conditions.

The cold sintering behavior of perovskite-type tetragonal $\text{Li}_{0.29}\text{La}_{0.57}\text{TiO}_3$ (LLTO) and garnet-type cubic $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid electrolytes has been systematically investigated. Congruent dissolution plays a critical role in the cold-sintering process. If the constituent elements of a material dissolve at unequal kinetic rates in the transient solvent, it may result in non-stoichiometric precipitation and the formation of secondary phases, which can significantly degrade the ionic conductivity of the pristine material. Therefore, the selection of an appropriate solvent is of critical importance in the cold sintering process. When the LLZO powder was cold sintered using water as a transient solvent, secondary phases such as $\text{La}(\text{OH})_3$ were observed, indicating incongruent dissolution behavior in water. However, when acetonitrile was used as a transient solvent instead of water, the LLZO solid electrolyte retained its phase purity and a high degree of crystallinity, demonstrating the suitability of acetonitrile for cold sintering.

In addition, because of the governing dissolution-precipitation mechanism in cold sintering, amorphous phases can form at the grain boundaries, which significantly reduce the ionic conductivity of the material. Furthermore, the relative density of the cold-sintered samples is around 80%, which is significantly lower than that achieved by conventional sintering. As a result, the voids between the grains further impede the ionic conductivity. Therefore, cold sintering of a single ceramic phase resulted in extremely low ionic conductivities on the order of 10^{-9} S cm $^{-1}$. In this regard, a promising approach is to co-sinter the main ceramic phase with a polymeric binder and lithium salts, as the extremely low processing temperature in cold sintering facilitates the design of composite materials. The cold-sintered LLTO–PPC–LiClO $_4$ composites (96 wt.% LLTO) and LLZO–PPC–LiClO $_4$ composites (96 wt.% LLZO) exhibited high ionic conductivities of 3×10^{-4} S cm $^{-1}$ and 2.15×10^{-4} S cm $^{-1}$, respectively, after cold sintering at approximately 100 °C. These values indicate that both perovskite and garnet-type structures are compatible with low-temperature processing when combined with polymer–salt additives, offering a promising route for scalable solid-state electrolyte fabrication.

LLZO is well known for its excellent chemical and electrochemical stability against lithium metal, making it a strong candidate for use in solid-state lithium batteries with lithium metal anodes [177]. Although the LLZO solid electrolyte is chemically stable, direct contact between Li and LLZO resulted in a very high interfacial resistance of approximately 350,000 Ω . The fabricated polymer thin films effectively reduced the interfacial resistance by providing intimate contact between the solid electrolyte and lithium anode. The major difference between LLTO and LLZO is that LLTO is chemically unstable against lithium metal, and direct contact leads to a significant increase in electrical conductivity, which is detrimental to its performance as an electrolyte.

The same polymer thin films (PPC–LiFSI) were introduced by adding 5 μ L cm $^{-2}$ of 4 M LiFSI in DME to the surfaces of the films in order to mitigate the chemical reactivity between LLTO and lithium metal. However, the LLTO solid electrolyte still experienced the same failure mode, despite the presence of the polymeric interlayer.

The fabricated polymer film became softer and gel-like upon the addition of a small amount of electrolyte solution, and it could not fully prevent direct contact between the lithium metal and the LLTO solid electrolyte. However, the addition of a PVDF membrane soaked in a small amount of liquid electrolyte effectively mitigated the chemical reactivity between the lithium metal and the LLTO solid electrolyte, preventing the reduction of Ti^{4+} in LLTO. This enhancement is primarily attributed to the mechanically robust nature of the PVDF membrane, which maintains structural integrity even after electrolyte uptake, providing a more uniform and continuous physical barrier that suppresses direct contact between the lithium metal and the solid electrolyte. The symmetric $\text{Li}/i/\text{LLZO}/i/\text{Li}$ (i : PPC-LiFSI) demonstrated a critical current density (CCD) of 1.1 mA cm^{-2} , while the $\text{Li}/\text{PVDF}/\text{LLTO}/\text{PVDF}/\text{Li}$ symmetric cell exhibited a higher CCD of 1.8 mA cm^{-2} . These results show that the PVDF-introduced Li/LLTO interface has greater potential to support operation under higher current densities.

In the $\text{Li}/\text{PVDF}/\text{LLTO}/\text{LFP}$ cell, the use of a PVDF membrane soaked with liquid electrolyte and cold sintering resulted in a total cell resistance of 496Ω , and the $\text{Li}/\text{PPC-LiFSI}/\text{LLZO}/\text{LCO}$ cell achieved a slightly lower resistance of 452Ω through the incorporation of a PPC-LiFSI polymer film, providing improved interfacial contact between the lithium anode and the solid electrolyte. Regarding electrochemical performance, the $\text{Li}/\text{PVDF}/\text{LLTO}/\text{LFP}$ cell exhibited an initial discharge capacity of 151 mAh g^{-1} at 0.1 C , 135 mAh g^{-1} at 0.2 C , and 70 mAh g^{-1} at 0.5 C , while the $\text{Li}/\text{PPC-LiFSI}/\text{LLZO}/\text{LCO}$ cell delivered a discharge capacity of 158 mAh g^{-1} at 0.1 C , 141 mAh g^{-1} at 0.2 C , and 52 mAh g^{-1} at 0.5 C . These results show that cold-sintered LLTO- and LLZO-based composite solid electrolytes perform well in full-cell configurations, achieving high discharge capacities comparable to their conventionally sintered counterparts. In addition, the co-sintering of LLTO/LFP and LLZO/LCO via cold sintering at about 100°C for 30 minutes eliminates the need for energy-intensive and time-consuming sintering processes and avoids the use of buffer layers at the cathode/solid electrolyte interface.

Cold sintering is governed by a dissolution–precipitation mechanism; therefore, the solubility of the constituent elements in the selected solvent plays a critical role in determining cold sintering performance. In the experiments, acetonitrile and DMF were employed as solvents for the cold sintering of LLTO and LLZO composite electrolytes. ICP-AES results revealed that lithium exhibits a significantly higher solubility in comparison to the other elements in both LLTO and LLZO, indicating an incongruent dissolution. However, the degree of dissolution varies markedly between the two materials. Despite having comparable particle sizes, the dissolution rates of LLTO’s constituent elements are substantially lower than those of LLZO. In particular, the concentration of dissolved lithium in LLZO is nearly two orders of magnitude higher than that in LLTO, suggesting that LLZO is more prone to lithium loss during cold sintering. This severe lithium depletion in LLZO can facilitate a cubic-to-tetragonal phase transformation during reprecipitation, which is thermodynamically favored under lithium-deficient conditions. In contrast, the lower elemental solubility in LLTO mitigates the adverse effects typically associated with incongruent dissolution.

This distinction is of great importance in terms of recyclability via cold sintering. The LLTO solid electrolyte outperformed LLZO in maintaining its structural and electrochemical properties through multiple reprocessing cycles. Although LLZO exhibited a phase transformation from cubic to tetragonal and an accumulation of amorphous phases, LLTO preserved its high crystallinity and perovskite tetragonal structure without any detectable secondary phase formation, even after ten reprocessing cycles. LLZO, on the other hand, could only maintain near-pristine properties for up to five reprocessing cycles, requiring a post-sintering thermal treatment to recover the cubic phase after each cycle [165]. In this regard, LLTO shows superior recyclability and presents a more sustainable pathway for solid-state electrolyte production.

The major accomplishments and novelties of this thesis are as follows: (1) Co-sintering the LLTO solid electrolyte with PPC–LiClO₄ via cold sintering and achieving a high ionic conductivity of $3 \times 10^{-4} \text{ S cm}^{-1}$, (2) Co-sintering LLTO/LFP and LLZO/LCO interfaces via cold sintering without inducing any structural or chemi-

cal changes at the interface, (3) Mitigating the chemical reactivity between Li metal and the LLTO solid electrolyte by introducing a PVDF membrane soaked in a small amount of liquid electrolyte and achieving high discharge capacities of 151 mAh g^{-1} and 135 mAh g^{-1} from the Li/PVDF/LLTO/LFP cell at room temperature—the first demonstration of a cold-sintered LLTO-based Li metal cell, (4) Demonstrating the exceptional recyclability of the LLTO solid electrolyte via cold sintering, retaining its phase purity and near-pristine ionic conductivity even after 10 reprocessing cycles.



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APPENDIX A: SYNTHESIS OF PEROVSKITE LLTO SOLID ELECTROLYTES VIA SOLID STATE REACTION METHOD

In this study, a solid-state reaction method was employed to synthesize perovskite-type $\text{Li}_{0.305}\text{La}_{0.565}\text{TiO}_3$ powder in a multistep fashion. Starting with the precise stoichiometric quantities of precursor powders, including lanthanum oxide (La_2O_3), lithium carbonate (Li_2CO_3), and titanium dioxide (TiO_2 , anatase), the constituents were subjected to 45 minutes of grinding, utilizing an agate mortar and pestle. Next, the mixed powder was placed in an alumina crucible and subjected to calcination in a sintering furnace at 1000 °C for 12 hours, with a heating and cooling rate of 5 °C per minute. The calcination was followed by a 45-minute intermediate grinding step using an agate mortar and pestle to facilitate mixing the calcined powder—60 wt.% of the calcined powder was set aside, and the remaining powder was mixed with a thermoplastic binder additive, Polyvinyl Butyral (approximately 5 wt.%). The powders were mixed in ethanol using a mortar and pestle until the complete removal of ethanol.

To fabricate hot sintered LLTO pellets with dimensions of 10 mm in diameter and 1 mm in thickness, a uniaxial force of 50 kN was applied to the mixed precursor-binder powder for 5 minutes. In the following step, the pellets were embedded into the binder-free calcined precursor powder to mitigate the loss of lithium. The sintering step was performed at 1150 °C for 12 hours with a heating and cooling rate of 5 °C per minute. XRD analysis was conducted using a $\text{Cu-K}\alpha$ radiation source to assess the phase purity of the synthesized powder. The XRD peaks obtained matched closely with the reference pattern (ICDD: 01-070-6719) of the perovskite-type $\text{Li}_{0.305}\text{La}_{0.565}\text{TiO}_3$ as shown in Figure A.1.

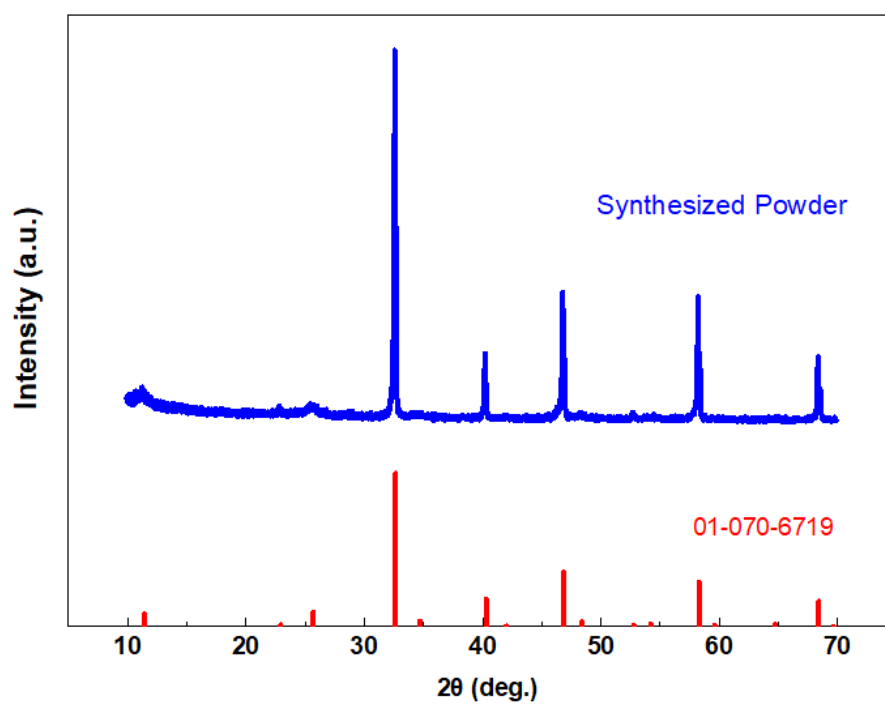


Figure A.1. X-ray diffraction pattern of the synthesized LLTO powder with Cu-K α radiation.

APPENDIX B: EQUIVALENT CIRCUIT FITTING FOR PRISTINE AND REPROCESSED ($\times 10$) LLTO COMPOSITE ELECTROLYTES

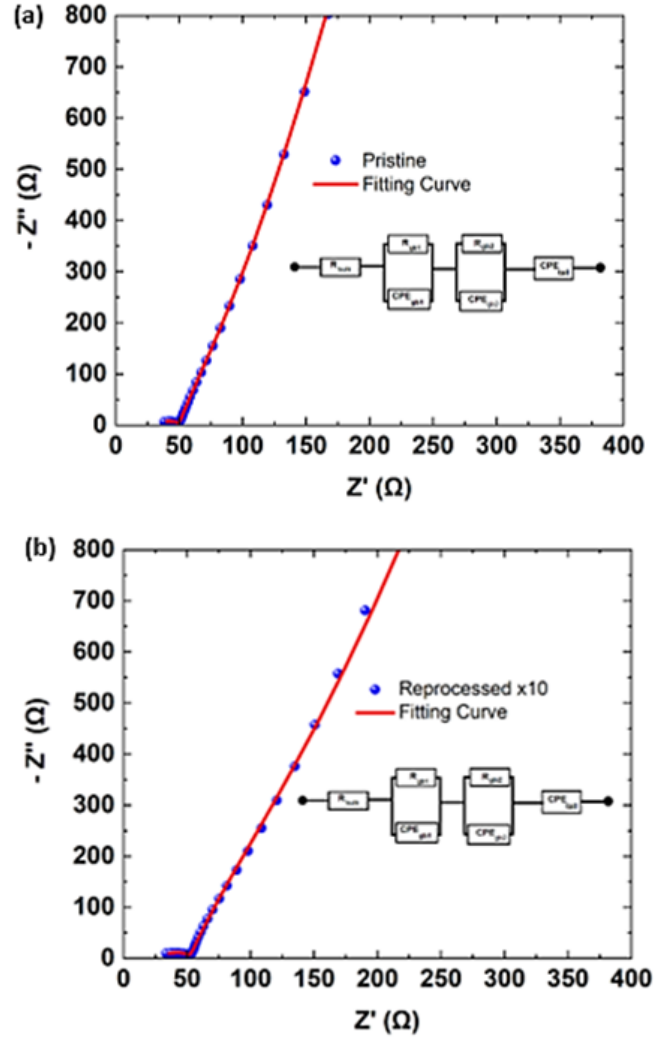


Figure B.1. Fitting Nyquist plots for (a) Pristine and (b) Reprocessed ($\times 10$) LLTO composites.

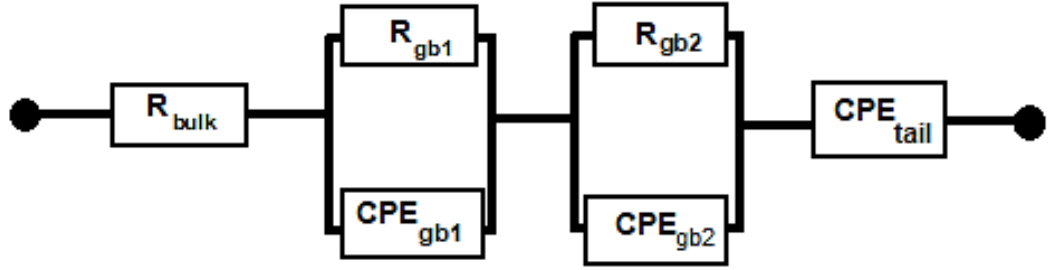


Figure B.2. Equivalent circuit model for pristine and reprocessed ($\times 10$) LLTO composites.

Table B.1. EIS fitting results for pristine and reprocessed ($\times 10$) LLTO composites.

Sample	R_{bulk} (Ω)	R_{gb1} (Ω)	$\text{CPE}_{\text{gb1-T}}$ (F) $\text{CPE}_{\text{gb1-P}}$	R_{gb2} (Ω)	$\text{CPE}_{\text{gb2-T}}$ (F) $\text{CPE}_{\text{gb2-P}}$	$\text{CPE}_{\text{tail-T}}$ (F) $\text{CPE}_{\text{tail-P}}$
Pristine	33.56	16.06	5.61×10^{-8} 0.92	50	4.88×10^{-5} 0.77	1.98×10^{-6} 0.93
Reprocessed ($\times 10$)	30.38	27.41	9.62×10^{-8} 0.86	94	1.50×10^{-5} 0.86	2.15×10^{-6} 0.92