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RECYCLING ALL-SOLID-STATE LITHIUM BATTERIES

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by

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ABSTRACT

All-solid-state lithium batteries (ASSBs) have emerged as a promising alternative to conventional lithium-ion batteries, offering the potential for improved safety, higher energy density, and longer cycle life. Unlike traditional lithium-ion batteries that use liquid electrolytes, ASSBs employ solid-state electrolytes, which eliminate the risk of electrolyte leakage and flammability. The development of ASSBs has gained significant attention in recent years, driven by the increasing demand for safer and more efficient energy storage solutions in applications ranging from portable electronics to electric vehicles.

Despite the growing interest in ASSBs as a next-generation energy storage technology, the development of effective recycling methods for these batteries has received relatively little attention. As ASSBs near widespread commercialization, the lack of established recycling processes poses a significant challenge in terms of environmental sustainability and resource conservation. ASSBs present unique complexities due to their diverse materials and intricate architectures, which complicates the recycling process and requires the development of novel separation and recovery techniques. Moreover, the absence of standardized designs and the use of scarce materials further emphasize the urgent need for efficient recycling strategies. Addressing the lack of recycling methods becomes crucial to ensure the sustainable development of this promising technology and to minimize its environmental impact.

The cold sintering process (CSP) has emerged as a promising technique for the fabrication of dense ceramic materials at remarkably low temperatures ($< 300\text{ }^{\circ}\text{C}$), offering a more energy-efficient and environmentally friendly alternative to traditional high-temperature sintering methods. By applying the principles of CSP, it is possible to effectively repair and densify fragmented solid-state electrolytes, which often undergo severe mechanical degradation during cycling. The low-temperature nature of CSP allows for the reintegration of composite electrolytes

without causing significant changes to the chemical composition or structure, thereby preserving their electrochemical properties.

Designing recyclable ASSBs is a vital step towards promoting sustainability and minimizing the environmental impact of energy storage technologies. By incorporating design principles that facilitate the separation process and allow for direct recycling of spent batteries, we can greatly improve the sustainability of ASSB. A promising approach involves introducing polymer interfacial layers between the electrodes and the solid-state electrolyte. These flexible polymer-salt layers serve a dual purpose: they bridge the solid-solid interfaces, enabling lithium-ion conduction across the interfaces, and they act as sacrificial layers that can be easily removed to facilitate the separation process during recycling.

While lithium metal anodes in all-solid-state batteries offer enhanced energy density, they introduce challenges related to unstable interfaces. The introduction of fluorine-containing lithium salts in the polymer-salt layers on the anode interfaces leads to the formation of a LiF-rich solid electrolyte interphase (SEI) layer, which serves as a protective barrier. This LiF-rich SEI passivates the Li metal surface, prevents side reactions, minimizes resistive secondary phases, and suppresses lithium dendrite growth, thereby enhancing cycling stability and longevity. This stable SEI also simplifies the recycling process by reducing interfacial chemistry complexity, and its effective removal allows for efficient recovery of valuable electrolyte materials without extensive purification, ultimately improving the battery performance, durability, and recyclability.

The occurrence of incongruent dissolution during the cold sintering process can potentially alter the stoichiometric composition and affect the electrochemical properties of the ceramic materials. By replacing liquid water with water vapor as the transient solvent, the extent of incongruent dissolution can be minimized while maintaining effective densification of the fragmented composite electrolytes. Through careful control of the transient solvent amount, it is

possible to tailor the intergranular properties of LATP–LiTFSI electrolytes, promoting lithium-ion transport within the water-in-salt structures formed at the grain boundaries.

To improve the cycling performance and recyclability of all-solid-state lithium batteries, optimizing the polymer interfacial layer is crucial. Enhancing the mechanical strength of this layer can prolong battery longevity and facilitate efficient separation during recycling. Adopting green solvents during recycling can contribute to a safer environment and better human health. Further research is necessary to solidify the understanding of intergranular properties and their impact on battery performance, validating the concept and guiding future developments.

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Chapter 1

Introduction

1.1 Motivation

All-solid-state batteries mark a significant leap forward in energy storage technology, offering distinct advantages over conventional lithium-ion batteries. These batteries utilize solid electrolytes, eliminating the safety hazards associated with flammable liquid electrolytes, thus enhancing overall safety.^[1] Moreover, when combined with lithium metal anodes, solid-state batteries exhibit higher energy densities, enabling greater energy storage capacity in a smaller volume, particularly beneficial for electric vehicles and portable electronics.^[2] Furthermore, solid electrolytes demonstrate superior mechanical strength and enhanced chemical stability against lithium metal, resulting in extended cycle life.^[3] While still in the early phases of commercialization, all-solid-state batteries hold immense promise for transforming the energy storage landscape, driving progress towards a more sustainable and efficient future.

As technological advancements bring ASSBs nearer to commercialization, the pressing necessity to address their recycling and end-of-life management becomes more apparent. However, despite the growing recognition of this issue, ASSB recycling remains in its early stages, with inadequate research and infrastructure to effectively address this challenge. The inherent complexity of ASSBs, characterized by their composition of ceramic electrolytes, polymers, and diverse electrode materials, poses unique challenges in the recycling process, differentiating them from the well-established methods employed for traditional lithium-ion batteries.^[4] Furthermore, the intimate contacts between battery components, which facilitate efficient lithium-ion transport, introduce additional difficulties in component separation during recycling.^[5] Consequently,

developing efficient and eco-friendly recycling techniques specifically designed for ASSBs is crucial for their widespread adoption and long-term environmental sustainability, ensuring the viability of this promising energy storage technology.

The thesis focuses on addressing the critical challenge of recycling ASSBs through several innovative approaches. Firstly, it explores the use of the cold sintering process to re-densify fragmented composite electrolytes, aiming to restore their structural integrity and functionality. Additionally, it investigates the design and fabrication of recyclable all-solid-state lithium batteries, highlighting the importance of the design of the battery configuration to promote their recycling capabilities. Furthermore, the thesis delves into using interfacial engineering methods to enhance both the cycling performance and recyclability of all-solid-state batteries. Finally, it examines the intergranular properties of reprocessed composite electrolytes, seeking to optimize their structural characteristics for improved electrochemical performance.

1.2 All-Solid-State Lithium Batteries

Since their commercial introduction in the early 1990s, lithium-ion batteries have revolutionized the field of portable energy storage.^[6] These rechargeable batteries have become ubiquitous in our daily lives, powering a wide range of devices, from small portable electronics such as smartphones and laptops to larger-scale applications like electric vehicles and energy storage systems. Compared to other battery technologies, lithium-ion batteries offer several distinct advantages, such as high energy density, low self-discharge rates, and long cycle life, making them the preferred choice for many modern energy storage needs.^[7]

The basic working mechanism of lithium-ion batteries relies on the movement of lithium ions between the cathode and anode during charging and discharging processes. The cathode is typically made of lithium-containing compounds, include lithium cobalt oxide (LiCoO_2), lithium

manganese oxide (LiMn_2O_4), lithium iron phosphate (LiFePO_4 , LFP), and lithium nickel manganese cobalt oxide (LiNiMnCoO_2 , NMC), while the anode is usually composed of graphite.^[8] During charging, lithium ions migrate from the cathode to the anode through the electrolyte, which is commonly a solution of lithium salt in organic solvents. This electrolyte facilitates the efficient transfer of ions between the electrodes. Conversely, during discharging, the lithium ions travel back from the anode to the cathode, releasing electrons to power the connected device. This shuttling of lithium ions between the electrodes forms the foundation of energy storage and delivery in lithium-ion batteries.^[7, 9]

Notwithstanding their widespread adoption, lithium-ion batteries encounter several challenges that restrict their performance and safety. One significant challenge is the flammability of the organic electrolytes used in these batteries, which poses potential safety hazards. Moreover, the inclusion of liquid electrolyte restricts the energy density of lithium-ion batteries, hindering their ability to meet the ever-increasing energy storage demands of modern applications.^[7a, 10] Another urgent concern revolves around the demand for accelerated charging rates to improve user convenience and satisfaction. In response to these challenges and the increasing need for energy storage solutions that are both high-performing, safe, and environmentally friendly, researchers and engineers are dedicatedly pushing the limits of lithium-ion battery technology.

All-solid-state lithium batteries have emerged as a promising next-generation energy storage solution, aiming to overcome the drawbacks associated with conventional lithium-ion batteries.^[1b] While lithium-ion batteries employ liquid electrolytes, all-solid-state lithium batteries utilize solid-state electrolytes, which are commonly made from ceramic, glass, or polymer materials. The incorporation of solid-state electrolytes brings about several remarkable advantages. Firstly, the non-flammable nature and high mechanical strength of solid-state electrolytes significantly enhance the safety of all-solid-state lithium batteries. Moreover, these batteries exhibit higher energy densities, enabling more compact and lightweight designs. Additionally, solid-state

electrolytes offer the potential for faster charging and discharging rates, a crucial feature for applications demanding rapid energy transfer.^[3a, 11]

One of the major benefits of all-solid-state lithium batteries is that they allow for the use of lithium metal anodes, which have a much higher theoretical capacity of 3860 mAh g^{-1} compared to the 372 mAh g^{-1} of graphite anodes used in lithium-ion batteries.^[1b, 12] As depicted in Figure 1-1, the progression of energy storage technology has advanced from lithium-ion batteries to high-energy-density all-solid-state batteries.^[5a] Pairing solid-state electrolytes with lithium metal anodes in all-solid-state lithium batteries presents new prospects for developing batteries with high energy densities, bolstering the potential to address the rigorous requirements of applications necessitating significant energy storage capacities

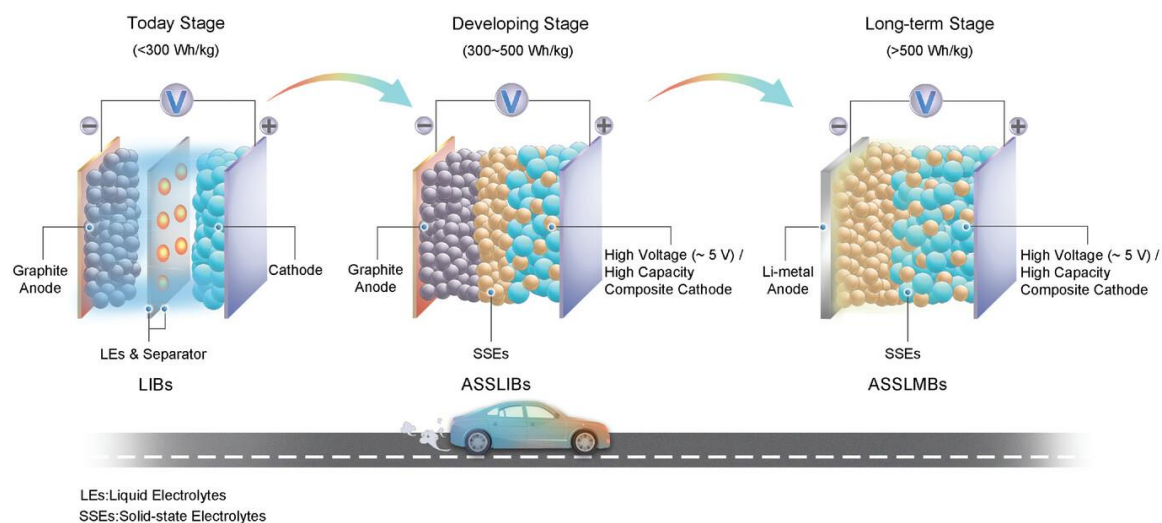


Figure 1-1: Schematic illustration of the transition from lithium-ion batteries to all-solid-state battery incorporated with lithium metal anodes.^[5a]

1.3 Solid-State Electrolytes

Solid-state electrolytes are considered a game-changing component in the development of next-generation lithium batteries, providing enhanced safety, increased energy density, and a broader operational temperature range compared to conventional liquid electrolytes. These electrolytes can be broadly classified into two main categories: organic (polymer) electrolytes and inorganic electrolytes.^[3b, 13] Each type of solid-state electrolyte exhibits unique characteristics, which are summarized as follows:

Polymer Electrolytes

Polymer electrolytes are usually composed of a polymer matrix, commonly polyethylene oxide (PEO) or its derivatives, where lithium salts are dissolved or dispersed.^[14] The transport of lithium ions is facilitated by the segmental motion of the polymer chains above the glass transition temperature.^[15] This segmental motion creates transient free volumes, enabling the hopping of lithium ions coordinated with the polar groups of the polymer chains. The number of free lithium ions available for transport depends on the extent of lithium salt dissociation within the polymer matrix. Polymer electrolytes offer advantages such as flexibility and ease of processing. However, their ionic conductivity at room temperature, which show to be lower than $10^{-5} \text{ S cm}^{-1}$, is a significant challenge. To address this issue, researchers are exploring strategies like incorporating ceramic fillers or using gel polymer electrolytes (GPEs), which contain a liquid component to enhance ionic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$).^[16]

Inorganic Electrolytes

Inorganic electrolytes include a wide range of lithium-ion conductors such as LISICON, argyrodite, garnet, perovskite, and NASICON-type.^[17] In crystalline solid electrolytes, the ionic conductivity is influenced by the presence of defects such as interstitials, vacancies, and partial occupancy on lattice sites or interstitial positions. Ion diffusion can occur via various mechanisms involving point defects like vacancies and interstitials, such as the vacancy mechanism, divacancy mechanism, interstitial mechanism, and interstitial-substitutional exchange mechanism.^[17-18] Materials with high ionic conductivities typically consist of two sublattices, a crystalline framework of immobile ions and a sublattice of mobile species. For efficient ionic conduction, these structures usually satisfy three main requirements: a large number of equivalent sites available for mobile ions, low migration barrier energies between adjacent sites, and a continuous diffusion pathway formed by these available sites.^[3b] In this thesis, the focus is specifically on garnet and NASICON-type solid-state electrolytes due to their high ionic conductivity, making them promising candidates for applications.

Solid-state electrolytes with garnet structures and the general formula of $A_3B_2(XO_4)_3$, in particular cubic $Li_7La_3Zr_2O_{12}$ (LLZO) with a space group of $Ia\bar{3}d$, have garnered significant attention due to several advantages, including efficient ion transport (10^{-4} – 10^{-3} S cm⁻¹), high chemical stability against lithium metal, and a wide electrochemical stability window (up to 9 V).^[19] The garnet framework structure is composed of LaO_8 dodecahedra and ZrO_6 octahedra. Within the interstices of the framework, Li atoms occupy two distinct crystallographic sites.^[20] As depicted in Figure 1-2(a), Li1 atoms reside in the tetrahedral 24d site, while the Li2 atoms are situated in the distorted octahedral 96h site. In the ideal garnet structure, the Li2 site remains vacant. However, due to the positional disorder in the lithium distribution, the Li2 atom can be located at two equivalent positions within the distorted octahedron. The disordering and partial occupation of the

Li atoms at the Li2 site have been reported to facilitate the lithium-ion conduction in garnet materials.^[20a]

The Li-ion migration pathway in a structure is associated with the arrangement of Li atoms within the structure. In cubic LLZO, the basic unit of the lithium distribution exhibit a loop structure consisting of Li1 and Li2 sites (Figure 1-2(b)). These loops are connected to each other, with the Li1 site acting as a junction point shared by two loops, resulting in a three-dimensional Li-ion migration pathway throughout the structure (Figure 1-2(c)). As such, the high ionic conduction in cubic LLZO can be ascribed to the three-dimensional lithium-ion network composed of the loop structures with the short Li-Li distance and the occupation disordering.^[20a]

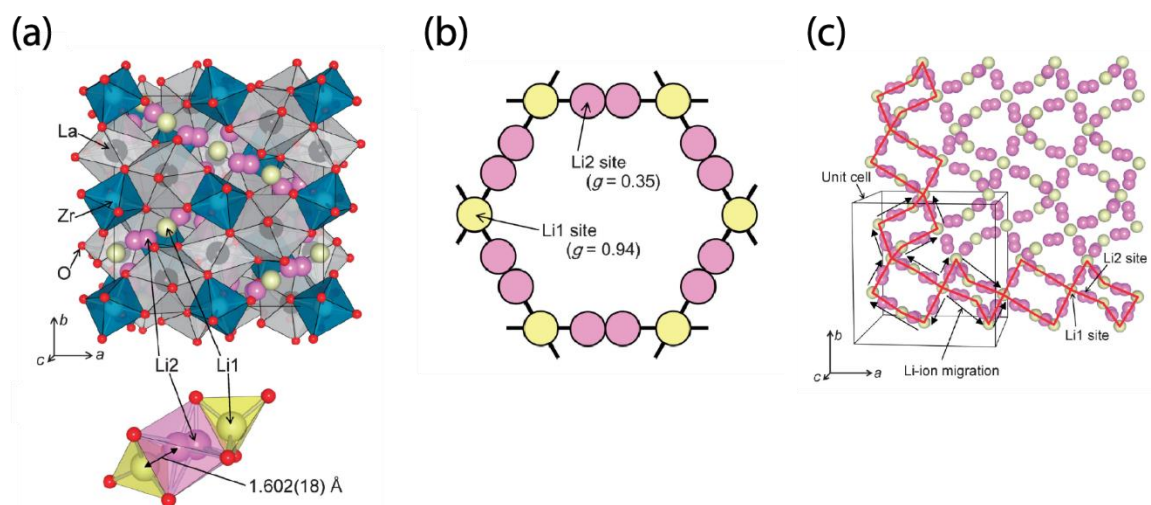


Figure 1-2: (a) Crystal structure of LLZO composed of sixfold coordinated ZrO₆ octahedral and eightfold coordinated LaO₈ dodecahedra with Li1 and Li2 occupied sites. (b) The distribution of Li atoms in cubic LLZO results in unit loop structures. g stands for occupancy. (c) The three-dimensional network of interconnected loop structures in cubic LLZO.^[20a]

NASICON-type solid electrolytes, such as $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP), and $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP), shows promising features, including air and water stability, high ionic conductivities of 10^{-4} – 10^{-3} S cm⁻¹ at room temperature, low cost and toxicity. The main phase of LATP is $\text{LiTi}_2(\text{PO}_4)_3$ (LTP), while LAGP primarily consists of $\text{LiGe}_2(\text{PO}_4)_3$ (LGP). In both materials, a portion of the Ti⁴⁺ in LATP or Ge⁴⁺ in LAGP are substituted by Al³⁺ ions.^[21] This

substitution with smaller ions reduces the size of the unit cell and enhances the ionic conductivity. The structures of LTP and LGP composed of TiO_6 (or GeO_6) octahedra and PO_4 tetrahedra, which are interconnected to create a three-dimensional network. This network creates cavities that accommodate lithium ions and bottlenecks through which lithium ions migrate. As illustrated in Figure 1-3, there are three Li sites (denoted as Li(1), Li(2), and Li(3)) in the LTP (or LGP) structure, where Li(1) site is fully occupied, while the Li(2) and Li(3) sites are partially filled with lithium ions.^[22]

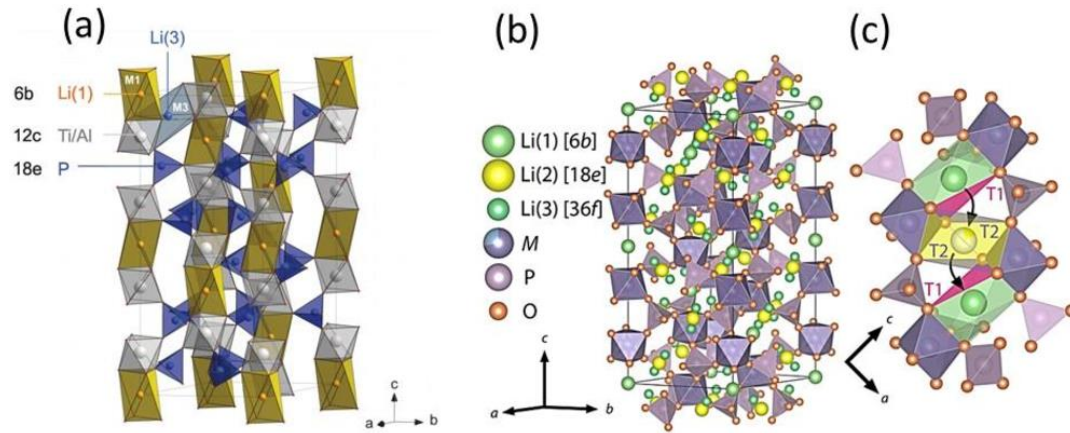


Figure 1-3: Crystal structures of (a) $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) and (b) $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (LAGP).^[22] (c) Visualization of the hopping path of lithium ions through bottlenecks (T1 and T2) in LATP.^[22b]

1.4 Failure Mechanisms of All-Solid-State Lithium Batteries

All-solid-state lithium batteries (ASSBs) have attracted considerable attention as a promising next-generation energy storage solution, owing to their potential for improved safety, increased energy density, and wider operating temperature ranges compared to conventional lithium-ion batteries using liquid electrolytes.^[23] Despite these advantages, ASSBs encounter several challenges associated with degradation mechanisms, which can compromise their performance and long-term stability. Understanding these degradation mechanisms is crucial for developing effective mitigation strategies and realizing the full potential of ASSBs. This section delves into the primary degradation mechanisms in ASSBs (Figure 1-4), with a focus on the roles of interfacial degradation, mechanical stress, lithium dendrite formation, and chemical instability in the degradation process.

(1) Interfacial degradation

One primary degradation mechanism in ASSBs involves the occurrence of undesired reactions at the interfaces between the solid electrolyte and the electrodes. Due to inherent chemical potential incompatibility between solid-state electrolytes and cathode or anode materials, spontaneous chemical reactions take place. These reactions lead to the formation of a resistive solid electrolyte interphase (SEI) on the anode side or a cathode electrolyte interphase (CEI) on the cathode side. The high impedance of these interfacial layers hinders both lithium-ion diffusion and charge transfer. Furthermore, the continuous growth of the SEI and CEI layers during cycling can deplete active materials, resulting in a gradual loss of capacity over time.^[24]

(2) Mechanical degradation

ASSBs face challenges related to mechanical degradation, primarily stemming from the inherent rigidity of the solid electrolyte and the volume changes experienced by the electrodes during charging and discharging cycles. As the electrodes undergo volumetric expansion and

contraction, they exert mechanical stress on the solid electrolyte, which can lead to the initiation and growth of cracks within the electrolyte, causing the loss of intimate contact between particles, increased internal resistance, and even short circuits.^[25]

(3) Lithium dendrite formation

The imperfect contact between inorganic electrolytes and the lithium metal anode can cause high contact resistances and the uneven deposition of lithium ions at the interface, leading to the initiation of lithium dendrites. These needle-like structures can propagate along grain boundaries and voids in solid electrolytes towards the cathode. As dendrites grow in defects or cracks, stress is generated, potentially extending the crack and facilitating further Li dendrite propagation. If dendrites reach the cathode, they can establish a direct electrical connection between the anode and cathode, causing a short circuit. Once the dendrites reach the cathode, they can establish a direct electrical connection between the anode and cathode, causing a short circuit.^[26]

(4) Chemical and electrochemical instability

Solid electrolytes with a limited electrochemical stability window are unable to operate across a wide voltage range of the cathode and anode materials. When in contact with electronically conductive materials such as cathode/anode materials, current collectors, or conductive additives, solid-state electrolytes can undergo oxidation at high voltages or reduction at low voltages. Insulating products resulting from this undesired reaction can accumulate at the electrode-electrolyte interfaces or within the bulk of the electrolyte, thereby increasing the overall resistance of the battery and impeding the efficient transport of lithium ions. Additionally, the electrode materials employed in ASSBs may undergo chemical decomposition during cycling, inducing structural alterations, phase transitions, and the generation of undesirable products.^[24b, 27]

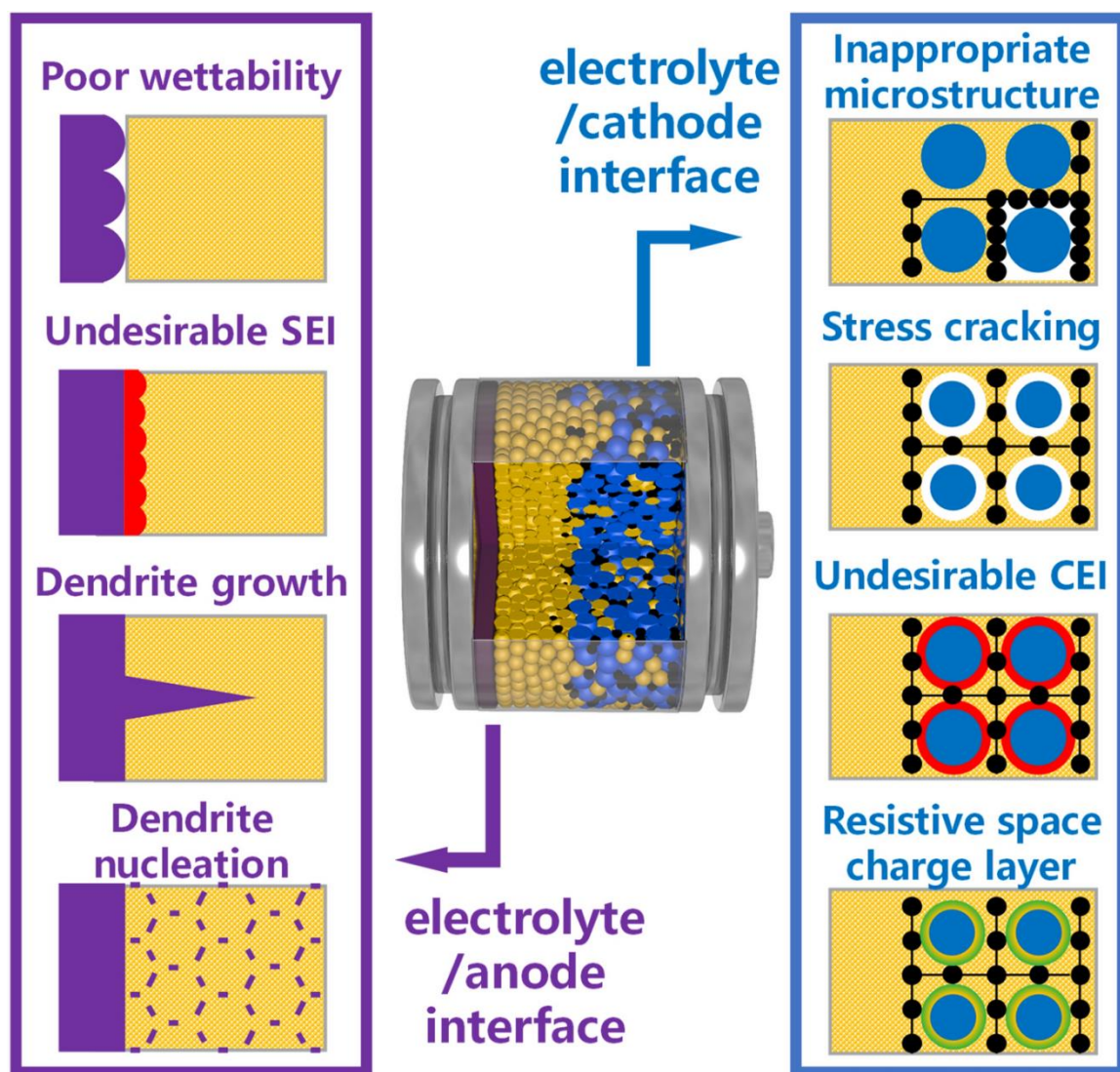


Figure 1-4: Schematic illustration of various degradation mechanisms in all-solid-state lithium batteries.^[26c]

1.5 Recycling of Spent Lithium Batteries

The recycling of spent lithium batteries is crucial for sustainable energy storage and the circular economy. As the demand for lithium-ion batteries continues to grow, particularly in the electric vehicle and consumer electronics sectors, it is essential to develop efficient and environmentally friendly recycling processes to recover valuable materials and reduce waste. The majority of current recycling methods for lithium-ion batteries employ a combination of mechanical separation, pyrometallurgical, and hydrometallurgical processes.^[28]

The recycling process of used lithium-ion batteries relies significantly on mechanical separation, serving as an initial phase for subsequent recycling methods. The primary objective of mechanical separation is to dismantle the battery packs and modules, extracting the essential components through various procedures including disassembly, shredding, crushing, and sieving. This process yields a mixture of cathode and anode powders, known as black mass, which can undergo further separation and processing. The mechanical separation phase aims to efficiently extract valuable materials from spent batteries, facilitating their recovery and recycling through subsequent processes.^[29]

The pyrometallurgical method utilizes high-temperature furnaces to extract valuable metals from spent batteries. During this process, metal oxides from the cathode material are reduced to form an alloy containing cobalt, copper, iron, or nickel, sourced from the cathode, cell casings, and current collectors. However, this approach has several drawbacks. The elevated smelting temperatures required by this technique result in considerable energy consumption, rendering it less environmentally friendly and more costly. Additionally, certain components, such as lithium and polymers, remain unrecoverable during the smelting process. Furthermore, the pyrometallurgical method generates significant quantities of CO₂, exacerbating the environmental impact of the recycling process.^[30]

Hydrometallurgy, a wet chemistry-based approach, breaks down and dissolves metal compounds into a solution via acid-base leaching. It then purifies and enriches various metals in the solution, followed by the precipitation of desired materials using appropriate counter anions such as carbonates or hydroxides. Hydrometallurgy, compared to pyrometallurgy, is more environmentally friendly and capable of recovering lithium but may involve multiple steps and generate wastewater. It can recycle most lithium-ion battery components with high recovery rates exceeding 90%, regenerate high-purity materials, accommodate different cathode chemistries, and have low energy costs and emissions. However, the process is complex, potentially expensive due to input material costs, and can generate significant hazardous waste solutions, which require proper treatment and disposal.^[31]

The increasing complexity of ASSBs, with their varied compositions, chemistries, and potential use of precious metals, poses new challenges for traditional recycling processes. Conventional methods may not be adequate or may require substantial modifications to handle ASSBs effectively. Consequently, alternative approaches like direct recycling are garnering interest as promising solutions to address these emerging challenges. Direct recycling aims to recover and reuse electrode and electrolyte materials without breaking them down into individual elements, offering several advantages over traditional recycling processes.^[5, 32] By preserving the structure and composition of the original materials, direct recycling maintains their performance characteristics, ensuring recycled materials retain functionality in new batteries. Additionally, direct recycling is less energy-intensive than other methods, avoiding high-temperature smelting or extensive chemical processing. This energy reduction enhances cost-effectiveness and environmental friendliness by minimizing the carbon footprint.^[4] However, direct recycling is sensitive to impurities and degradation in recovered materials, which may require additional regeneration steps known as direct regeneration. Despite this, direct recycling processes can be relatively straightforward, facilitating efficient conversion of materials into components for new

electrode fabrication. Figure 1-5 presents various recycling processes for spent all-solid-state lithium batteries, highlighting the key steps involved in each method.^[5a]

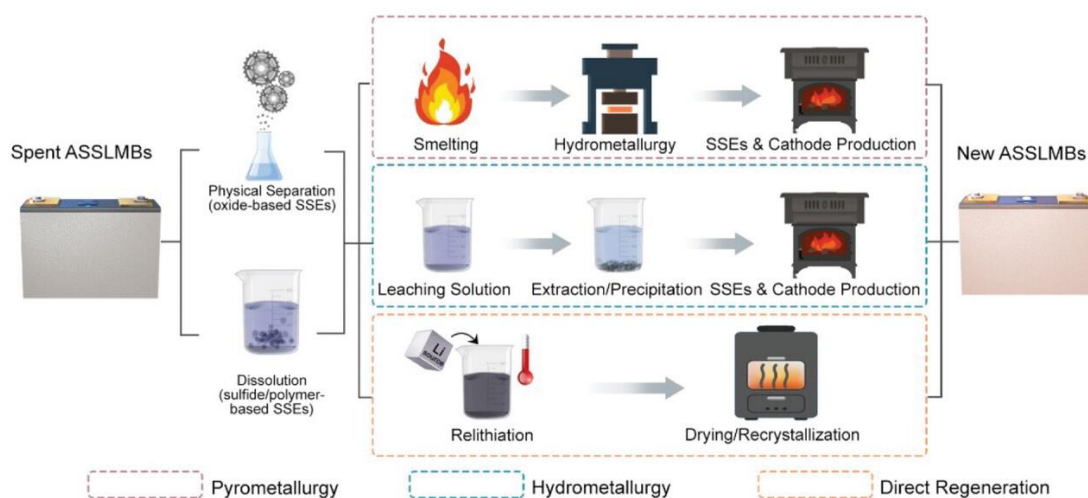


Figure 1-5: Schematic overview depicting the three primary recycling methods for spent all-solid-state lithium batteries: pyrometallurgy, hydrometallurgy, and direct regeneration.^[5a]

1.6 Cold Sintering Process

Sintering is a thermal treatment method that converts a compressed powder, referred to as a green body, into a dense and mechanically robust polycrystalline material.^[33] This process occurs at elevated temperatures, typically below the melting point of the main component, and is driven by the minimization of surface energy associated with the high surface area of the powder particles. Throughout the sintering process, particles merge together through the formation and enlargement of necks at their contact points, resulting in decreased porosity and the formation of a cohesive microstructure.^[34] By controlling various parameters such as temperature, duration of sintering, particle size, and external pressure, the sintering process can be fine-tuned to achieve the desired final density, microstructure, and properties of the sintered product.

Lowering sintering temperatures below 300°C has been a longstanding objective in materials synthesis and processing to enable integration with polymers and temperature-sensitive metals. In 2016, Randall and his research team at Penn State introduced the cold sintering process (CSP) for ceramics and ceramic-based composites. CSP, an ultra-low energy sintering method, involves mixing ceramic powder with a solvent and simultaneously applying uniaxial pressure and heat not exceeding 300°C.^[35] The cold sintering process shares some similarities with other sintering techniques, such as liquid phase sintering and hot pressing. Similar to liquid phase sintering, CSP involves the use of a transient solvent that aids in the densification process. CSP also bears resemblance to hot pressing, as both techniques involve the simultaneous application of temperature and pressure to enhance the densification of the ceramic material.

The cold sintering process (CSP) involves several stages, as illustrated in Figure 1-6.^[36] Initially, an aqueous solution is added to wet the surface of ceramic particles uniformly, creating a liquid film that facilitates local dissolution of sharp particle surfaces and acts as a lubricant for particle rearrangement and sliding. As external pressure is applied, the aqueous solution fills the interparticle spaces. The high chemical potential at particle contacts, caused by capillary pressure, drives the diffusion of ionic species and/or atomic clusters through the liquid, which then precipitate on particles away from stressed contact areas. This mass transport reduces excess surface free energy, eliminating porosity and densifying the material. During the final sintering stage, an amorphous phase may form in grain boundary regions, potentially limiting grain boundary diffusion or mobility and restricting grain growth. As the transient phase evaporates, the grain boundary phase remains, which may either crystallize or stay amorphous.^[35, 37]

CSP presents several significant advantages compared to traditional sintering techniques. Operating at temperatures well below 1000°C, CSP drastically reduces the energy required for densification, leading to cost savings and a reduced environmental impact. This low-temperature approach, complemented by pressure and solvent-assisted densification, makes CSP highly

efficient and adaptable.^[38] Its versatility allows for the fabrication of various materials, including ceramics, salts, and polymers, facilitating the fabrication of innovative composite materials tailored to specific properties.^[39] With the energy-efficient and adaptable characteristics of CSP position it as a promising alternative to conventional sintering methods, with the potential to revolutionize materials processing and manufacturing practices, leading to more sustainable and cost-effective production processes.

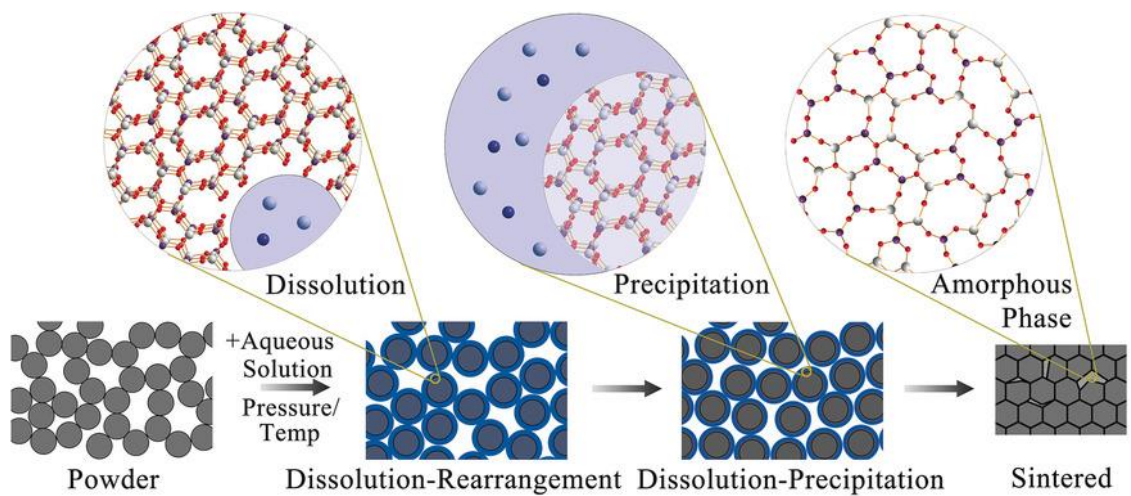


Figure 1-6: Schematic illustration of the cold sintering process densifying powders into a sintered bulk phase under pressure and temperature conditions with the incorporation of transient solvents.^[36]

1.7 Dissertation Overview

This thesis aims to provide insights and perspectives on the recycling of all-solid-state lithium batteries (ASSBs) to promote sustainability in the energy storage industry. As technological advancements propel ASSBs closer to widespread commercialization, the urgent need to address their end-of-life management and develop efficient recycling processes becomes increasingly evident.

Chapter 1 introduces various types of solid-state electrolytes, with a particular focus on the promising garnet and NASICON-type electrolytes. The failure mechanisms of ASSBs are explored in detail, shedding light on the complexities and challenges associated with their degradation. Additionally, the current state-of-the-art recycling methods for conventional lithium-ion batteries are examined, providing a foundation for understanding the potential strategies that could be adapted for ASSB recycling. Lastly, a novel sintering technique known as the cold sintering process is introduced, along with its underlying working principle.

Chapter 2 provides a comprehensive overview of the most commonly used characterization techniques and the key performance parameters employed to evaluate and benchmark all-solid-state lithium batteries. The chapter delves into the fundamental theories underpinning these techniques, enabling readers to grasp the essential principles and mechanisms that govern their operation. Moreover, the chapter introduces crucial parameters used to benchmark battery performance, equipping readers with the knowledge necessary to effectively evaluate and compare different battery systems, laying the groundwork for the subsequent chapters of this thesis.

In chapter 3, we explore the application of cold sintering as a novel approach to reprocess solid-state composite electrolytes, specifically focusing on Mg and Sr doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with polypropylene carbonate (PPC) and lithium perchlorate (LLZO-PPC- LiClO_4). It highlights the

significant potential of the cold sintering process in reprocessing fragmented electrolytes, offering a pathway toward more sustainable and eco-friendly recycling methods.

Chapter 4 introduces an innovative architectural design for recyclable all-solid-state lithium batteries that incorporates flexible lithium bis(fluorosulfonyl)imide doped polypropylene carbonate (PPC-LiFSI) interfacial layers at the electrode interfaces. This chapter showcases a novel approach to designing recyclable all-solid-state lithium batteries, facilitating the direct recycling of ASSBs and contributing to the long-term goals of developing sustainable energy storage devices.

In Chapter 5, we present an innovative strategy to address the undesired interfacial reactions at Li metal interfaces by introducing fluorine-containing lithium-salt solutions. This chapter highlights the potential of this proposed approach in tackling the challenges associated with lithium metal anodes and promoting the recyclability of all-solid-state lithium batteries.

In Chapter 6, we employ the cold-sintering process to repair fragmented LATP–LiTFSI and LAGP–LiTFSI composite electrolytes, which simulate the cycled solid-state electrolyte undergoing severe mechanical degradation. This chapter highlights the remarkable capability of the cold sintering process in modifying and optimizing the intergranular properties within reprocessed solid-state composite electrolytes.

Lastly, Chapter 7 discusses the main conclusions of this dissertation as well as future directions, including optimizing polymer interfacial layers, employing green solvents in the recovery process, and visualizing the water channel in LATP-LIFSI composite electrolytes. By addressing these key aspects, this thesis aims to contribute to the growing body of knowledge on the recycling of ASSB and inspire further research and development in this critical area.

Chapter 2

Characterization Techniques for Electrochemical Performance

This chapter lays the groundwork for comprehending the electrochemical characterization techniques employed in evaluating individual battery components and assessing the performance of assembled half-cell and full-cell configurations. It covers various electrochemical characterization methods, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), elucidating their distinct capabilities and the specific facets of battery performance they can investigate. The chapter delves into the fundamental theories underpinning these techniques, enabling readers to grasp the essential principles and mechanisms that govern their operation. Practical application examples are provided to illustrate how these techniques are implemented in real-world scenarios, helping readers appreciate their relevance in battery research and development. Moreover, the chapter introduces some key parameters used to benchmark battery performance, equipping readers with the knowledge necessary to evaluate and compare different battery systems effectively.

2.1 Electrochemical Impedance Spectroscopy

In a typical Electrochemical Impedance Spectroscopy (EIS) measurement, a potentiostat or galvanostat instrument is employed to apply a small alternating current (AC) or voltage signal to the electrochemical cell over a wide range of frequencies, usually spanning from millihertz to megahertz. When a DC voltage is applied, the relation among R , V and I satisfy Ohm's law, $R = \frac{V}{I}$; when an AC voltage is applied to an electrochemical cell, the impedance $Z(\omega)$ follows the equation

for Ohm's law in an AC circuit, $Z(\omega) = \frac{V(\omega)}{I(\omega)}$, where V_m and I_m represent the maximum values of voltage and current, ω is the angular frequency of the applied AC voltage, as shown in Figure 2-1.^[40]

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

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

$$\omega = 2\pi f$$

The impedance $Z(\omega)$ can be further simplified into real and imaginary parts,

$$Z(\omega) = Z_0 \cos(\phi) + Z_0 \sin(\phi)j$$

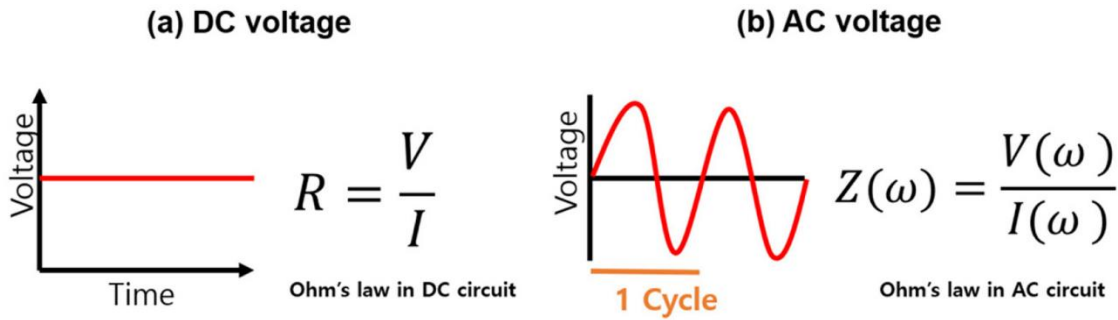


Figure 2-1: The schematic diagrams and equations of the Ohm's law for direct current (DC) and alternating current (AC) circuits.^[40]

Figure 2-2 depicts two ways to plot the impedance spectra: (1) The Bode plot, which displays the phase shift and magnitude changes across the applied frequency ranges, and (2) The Nyquist plot, which depicts the imaginary part of the impedance versus the real part of impedance on Cartesian coordinates.^[40-41] The Bode plot offers advantages for observing phase margins, where the system, such as sensors, filters, and transistors, exhibits significant phase or magnitude changes. The Nyquist plot provides insights into the possible mechanisms or governing phenomena within an equivalent circuit model system. For instance, Nyquist plots are frequently used to analyze the characteristics of lithium-ion batteries to elucidate the active reaction mechanisms.^[42] The

impedance can be interpreted by various circuit elements, such as resistors, inductors, and capacitors, which collectively constitute the overall impedance in the circuit model.

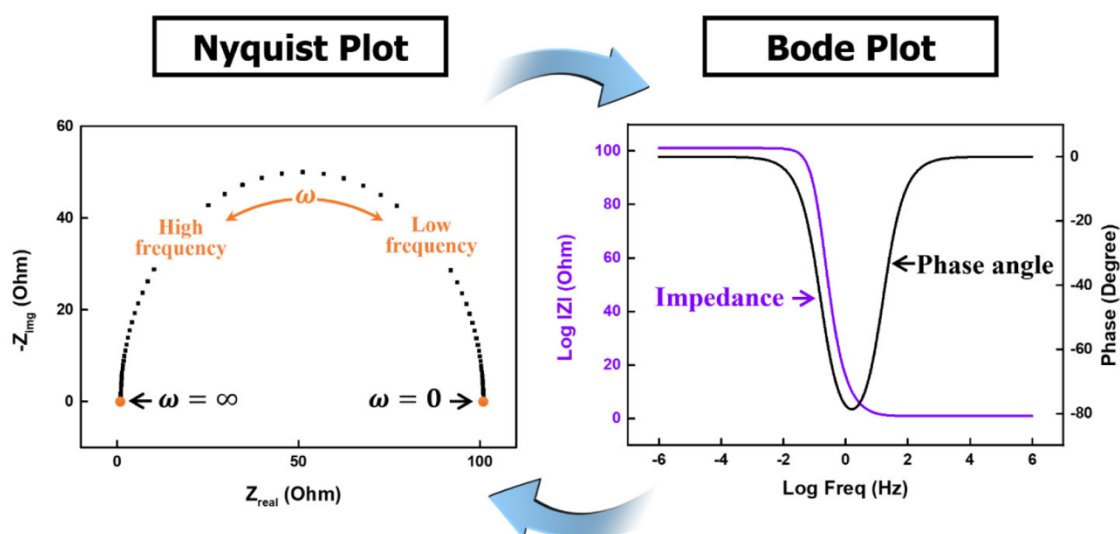


Figure 2-2: Representation of Electrochemical Impedance Spectroscopy through by Nyquist plot and Bode plot.^[40]

Circuit Model

A major strength of electrochemical impedance spectroscopy (EIS) lies in its capability to simulate the measured impedance spectra by fitting the data to an equivalent electrical circuit model. This process allows for the extraction of numerical values corresponding to the various components represented in the equivalent circuit. To perform this simulation and fitting, researchers can utilize specialized software tools designed specifically for this purpose, such as Zview, Zplot, and others.^[43]

To gain a comprehensive understanding of the overall electrochemical system, the designated circuit model is constructed to represent the entire system of the electrochemical cell. Fundamental electrochemical elements and corresponding formula utilized in constructing the equivalent circuit model are listed in Table 1-1.^[40] Example circuit models consist of electrical circuit elements, such as resistors (R), capacitors (C), and inductors (L), and the corresponding Nyquist plots are shown in Figure 2-3.^[41] The constant phase element (CPE) is used to account for non-ideal capacitive behavior, which often occurs at electrode-electrolyte interfaces, forming an electrical double layer. The Warburg impedance (W) is incorporated to simulate under semi-infinite conditions, where the one-dimensional lithium diffusion process occurs within the bulk phase bounded by the planar electrode surface.

Table 1-1: Circuit elements used in the equivalent circuit model.^[40]

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

When a circuit consists of a resistance R_1 in parallel with a double-layer capacitance C_1 , denoted as (R_1C_1) , the corresponding Nyquist plot depicts a semicircle. The real part of the impedance contributes to the resistance R_1 . This capacitance value can be determined from the maximum point of the semicircle in the Nyquist plot, where ω , R_1 and C_1 satisfy the equation, $\omega = \frac{1}{R_1C_1}$. If a resistor R_0 is connected in series with the (R_1C_1) circuit, denoted as $R_0(R_1C_1)$, the semicircle shifted along the real axis to a value equal to the ohmic resistance of R_0 , as shown in Figure 2-4.^[41] When a second parallel (R_2C_2) circuit is connected to $R_0(R_1C_1)$, forming $R_0(R_1C_1)(R_2C_2)$ circuit, the Nyquist plot shows two semicircles.

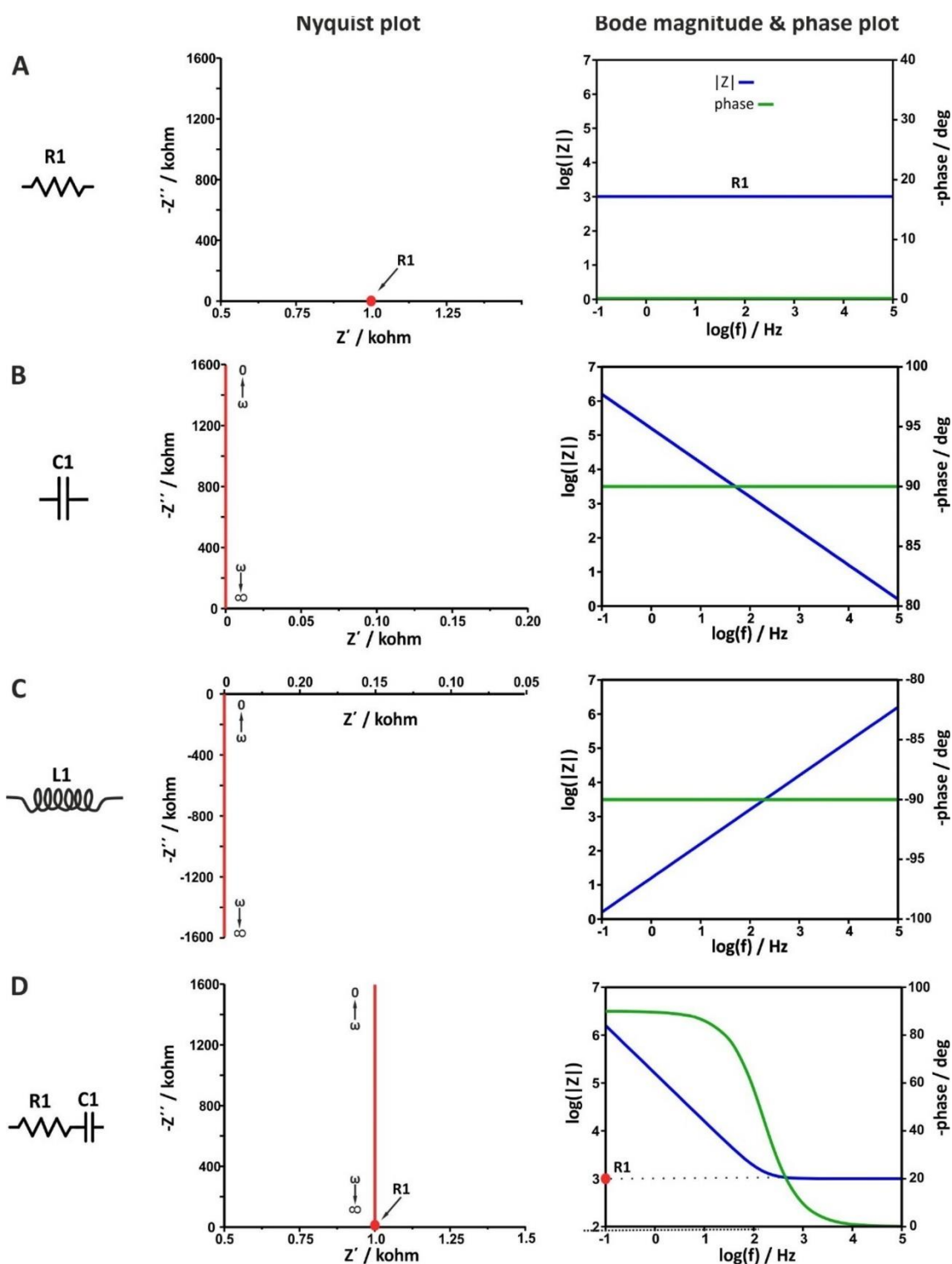


Figure 2-3: Nyquist and Bode plots of circuit models consist of electrical circuit elements and a R_1C_1 circuit, separately, with $R_1 = 1000$ ohm.^[41]

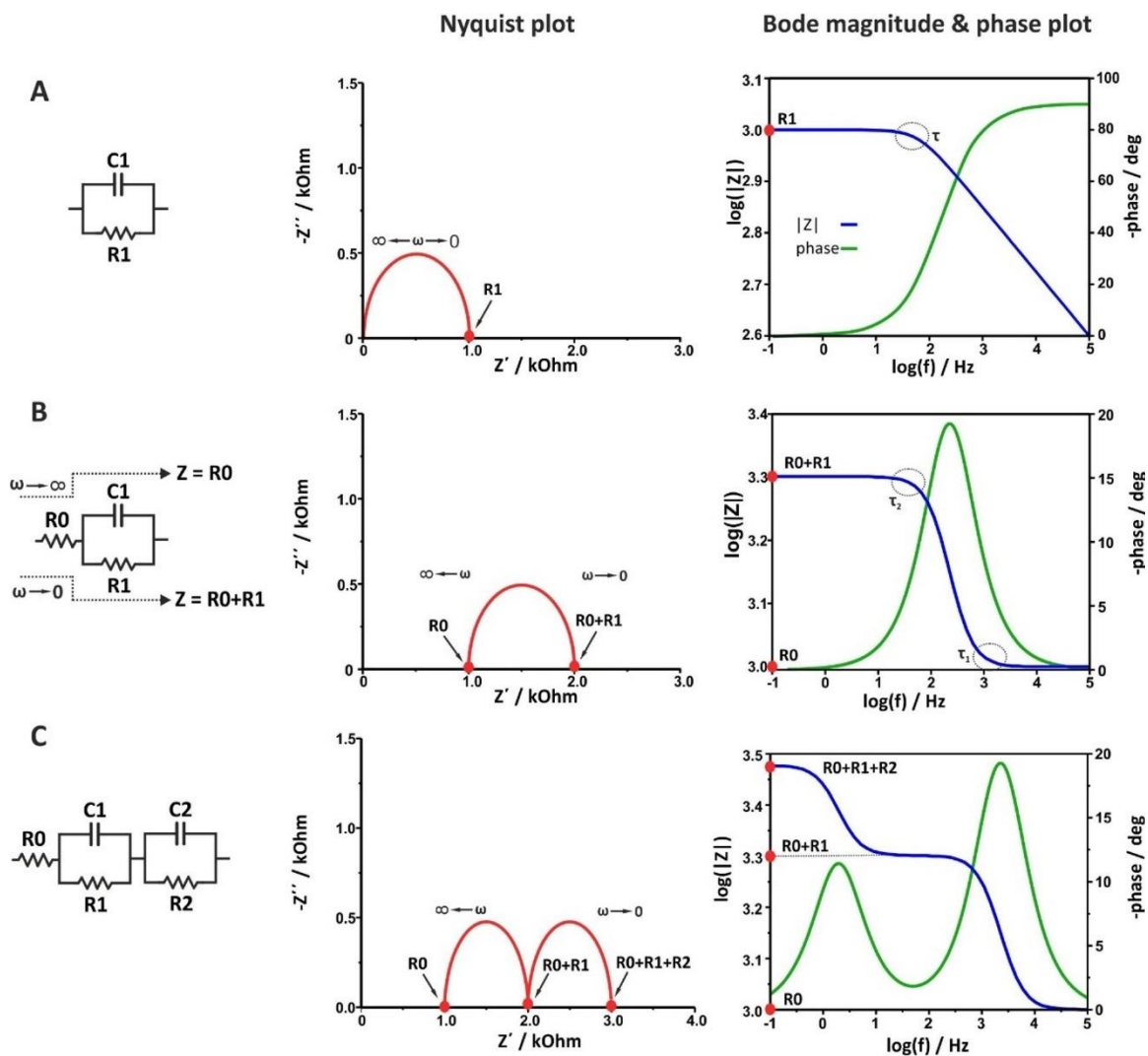


Figure 2-4: Nyquist and Bode plots of circuit models consist of the combination of electrical circuit elements with $R_0=R_1=R_2=1000 \text{ ohm}$.^[41]

Ionic Conductivity

Electrochemical impedance spectroscopy (EIS) serves as a tool for investigating complex electrochemical systems to unravel the properties of bulk electrolytes/electrodes, interfacial

reactions, and the behavior of full cell devices. EIS measurements with two-electrode configurations, where samples are sandwiched between two electrodes, are commonly used because of their simplicity and wide applicability to various material. Ion-blocking electrodes, like platinum, stainless steel, and gold, allow electron flow while inhibiting the transfer of lithium ions. They are commonly employed in constructing symmetric cells, which facilitates the investigation of the ionic conductivity of solid-state electrolytes (σ_{Li+}).

The ionic conductivity can be described as the following equation,

$$\sigma_{Li+} = \frac{h}{R_{total}A}$$

where, R_{total} is the total resistance of the electrolytes, h relates to the sample thickness and A is the contacting area.^[43] The total resistance (R_{total}) encompasses different resistance contributions, including the resistance from the bulk phase of grains, grain and phase boundaries, as well as impedances associated with any physical or chemical changes occurring at the electrode interfaces.^[44]

Ionic conductivity is a temperature dependent process that follows Arrhenius behavior,

$$\sigma T = A \exp \left(-\frac{E_a}{k_B T} \right)$$

where A is the Arrhenius prefactor, E_a is the activation energy of lithium ion transport, and k_B is the Boltzmann constant.^[45] The Arrhenius plot represents the logarithmic values of ionic conductivities as a function of the inverse temperature ($1000/T$), covering a wide range of temperatures. In this study, EIS data were acquired using a Modulab XM from Solartron AMETEK, and the resulting spectra were analyzed with the EIS software, ZView, provided by Solartron AMETEK.

2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is a fundamental analytical technique within the realm of electrochemical methods, widely employed to investigate and characterize the electrochemical processes occurring in lithium battery systems. In comparison to other electrochemical techniques, CV offers several advantages, including: (1) the ability to determine the reversibility of chemical reactions, (2) the identification of potentials at which oxidation or reduction reactions take place, (3) enabling quantitative analysis for substances with unknown concentrations, and (4) the flexibility to vary test conditions, such as scan rate and temperature, to facilitate a comprehensive understanding of the system.^[46]

CV is established based on the principle of linear sweep voltammetry, which measures the current while the applied potential is swept linearly as a function of time (Figure 2-5). The voltage is swept from an initial value E_1 to a final value E_2 at a defined scan rate (v), which represents the rate of linear voltage change during the measurement. Additional information can be obtained regarding the redox reaction potentials, reversibility, and cyclability when repeating multiple cycles under the same conditions.^[47]

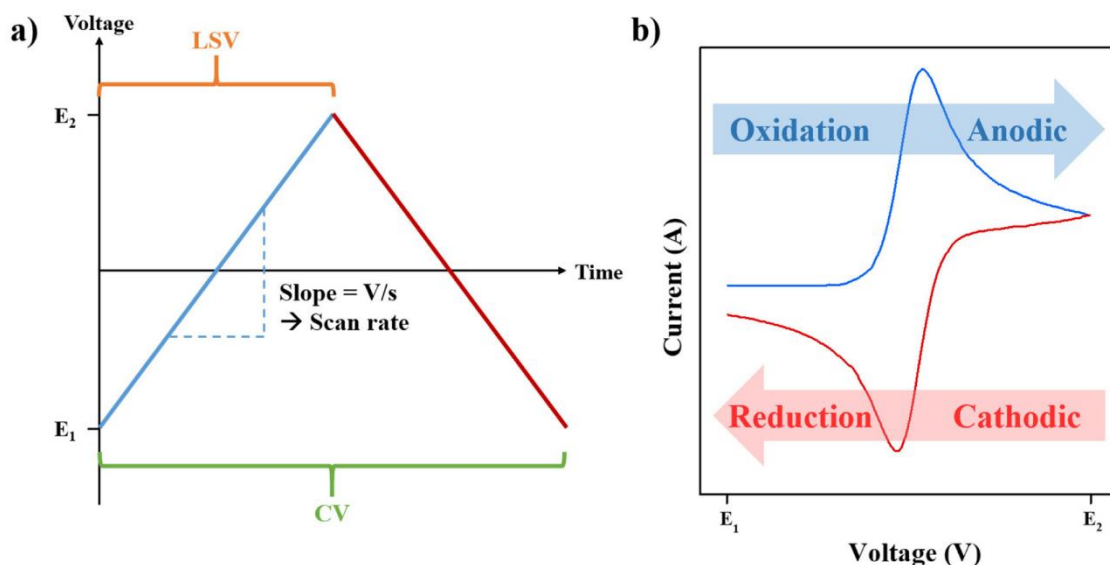


Figure 2-5: (a) The voltage-time profile of the linear sweep and cyclic voltammetry. (b) The cyclic voltammogram plot displays current versus applied potential and features distinctive cathodic and anodic peaks.^[47]

By varying the scan rate, we are able to distinguish the reversibility of the process, depending on the rate of charge transfer. Figure 2-6 illustrates a cyclic voltammogram for cases of reversible, quasi-reversible and irreversible electron transfer process. In reversible processes, the rate of electron transfer at the surface of electrode is rapid enough, thus the peak potential (E_p) is independent with the scan rate. The anodic and cathodic peaks satisfy the following equation,

$$|E_{p,a} - E_{p,c}| = \frac{59.0}{n} \text{ mV at } 298 \text{ K}$$

$$\frac{i_{p,a}}{i_{p,c}} = 1$$

$$|E_p - E_{p/2}| = 2.2 \frac{RT}{nF} = \frac{56.5}{n} \text{ mV at } 298 \text{ K}$$

where R is the universal gas constant, n is the number of electrons transferred in the reaction, and F is the Faraday constant.^[48]

In general, the lithium-ion intercalation in lithium batteries shows a quasi-reversible process, where cathodic and anodic peaks are a function of scan rate. The CV curve of a quasi-reversible process shows gradual peak shifts to a higher potential value with the increase of scan rate. With the use of CV, we are able to determine the redox reaction potential and understand the thermodynamics and kinetics of the electrochemical system. Several factors, including the particle size of active materials, electrode thickness, electrolyte concentration, operating temperature, and scan rate, may influence the shape of the CV curves. In this study, CV was employed to investigate the redox reaction potential and the chemical reversibility of all-solid-state batteries using a potentiostat system (Reference 600, Gamry Instrument).

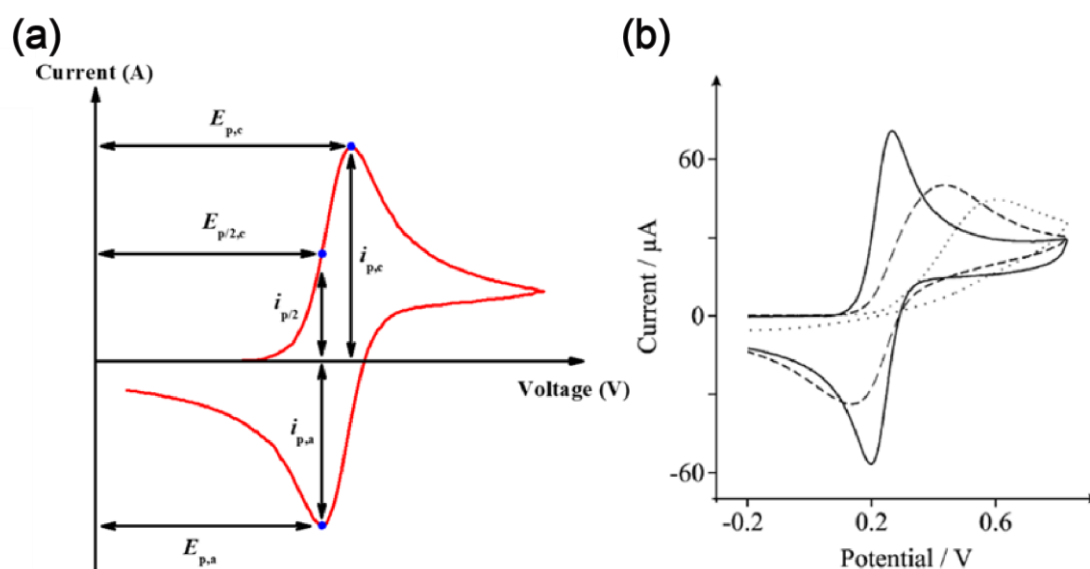


Figure 2-6: (a) The CV curve with key parameters. (b) CV curves represent the reversible (solid line), quasi-reversible (dashed line), and irreversible (dotted line) behavior in electrochemical systems.^[47]

2.3 Critical Current Density

In all-solid-state batteries employing lithium metal anodes, the penetration of lithium dendrites is the primary cause of battery short circuits.^[49] To elucidate the interfacial lithium chemistry, most measurements aimed at evaluating the anodic behavior in solid-state batteries are conducted in symmetric cells. This approach allows researchers to focus specifically on the interactions occurring at the interface between the lithium electrode and the solid-state electrolyte, providing valuable insights into the fundamental factors governing battery performance and stability.

The maximum current density that a solid-state battery can withstand without experiencing short-circuiting is defined as the critical current density (CCD).^[50] The CCD serves as an important indicator, revealing a series of reactions occurring at the Li metal anode-solid electrolyte interfaces. These include: (1) mass transport of lithium ions, (2) interfacial physical and chemical properties, (3) the lithium-ion stripping and plating kinetics, and (4) interfacial morphology evolution. Consequently, a comprehensive understanding of the CCD can provide insights into interfacial behaviors, failure mechanisms, and other factors influencing the electrochemical performance of all-solid-state batteries.^[51]

With the advancement of solid-state battery research, various measurement protocols have been established to evaluate the critical current density (CCD). In contrast to EIS measurements conducted with the AC current, direct current (DC) is applied on the electrochemical system, and the resulting voltage response is measured. Figure 2-7 illustrates schematic representations of the microstructural evolution in the cells associated with these different measurement protocols, along with their corresponding charge and discharge profiles.^[50] The protocols for assessing CCD can be categorized into four approaches, which are described as follows.

(1) Time control

The time-control test involves incrementally increasing the current density in each cycle for a fixed time duration, for instance, 10 minutes, 30 minutes, 1 hour, or longer. The time-voltage profiles associated with the time-control measurement (Figure 2-7(c)) demonstrate that polarization increases continuously until a voltage drop is observed, indicating the occurrence of a short circuit. This method offers insights into evaluating the cell endurance with simultaneously increased current density and capacity.

(2) Capacity control

The capacity control method involves applying increasing current density while maintaining a constant areal capacity, for instance, 0.2, 0.5, 1 mAh cm⁻² or more, in each cycle. The cycling time in each cycle decreases in order to maintain constant capacity (Figure 2-7(d)). This protocol is effective for assessing the impact of capacity during cycling.

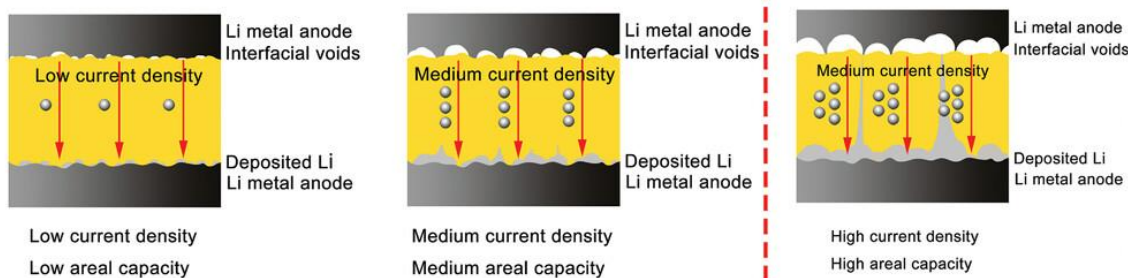
(3) Endurable time control

The measurement is conducted in the time-control test, where the procedure at each current density is repeated for several cycles (Figure 2-7(e)). This method considers both the effects of current density and cycling number.

(4) Long-term cycling

This protocol is frequently employed to gain insights into the stability of Li metal-solid-state electrolyte (SSE) interfaces in symmetric cells. By subjecting the cells to prolonged cycling, this enables the observation of any changes or degradation occurs at the interfaces between the lithium metal anode and the solid-state electrolyte.

(a) Time Control



(b) Capacity control

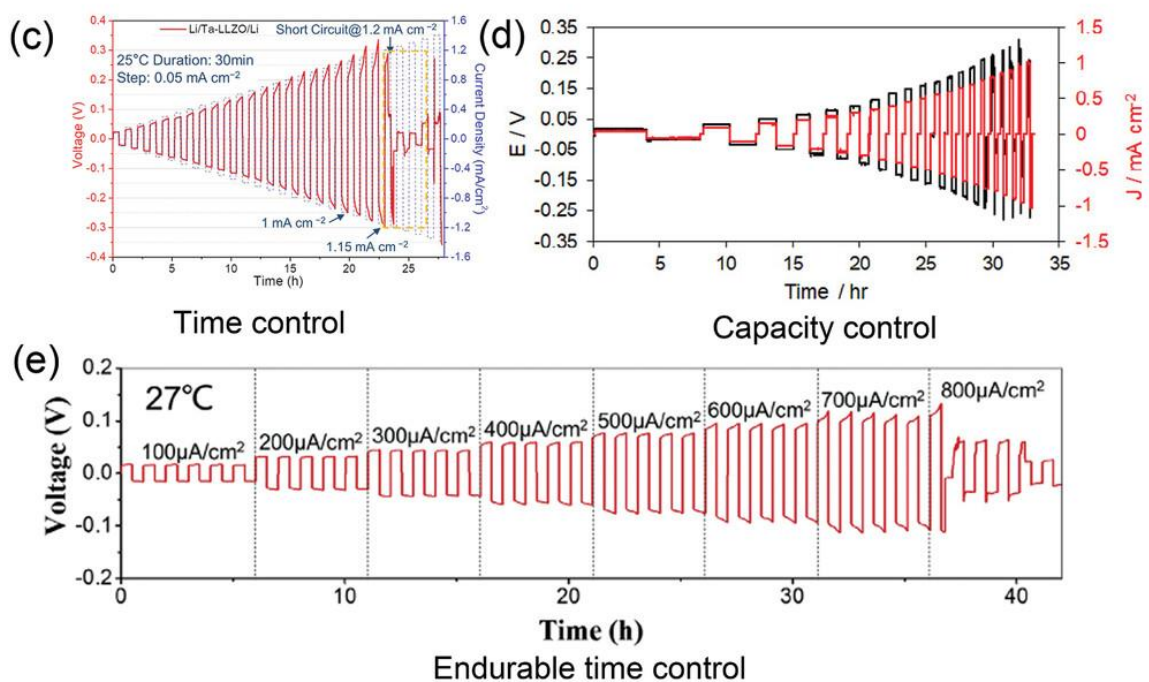
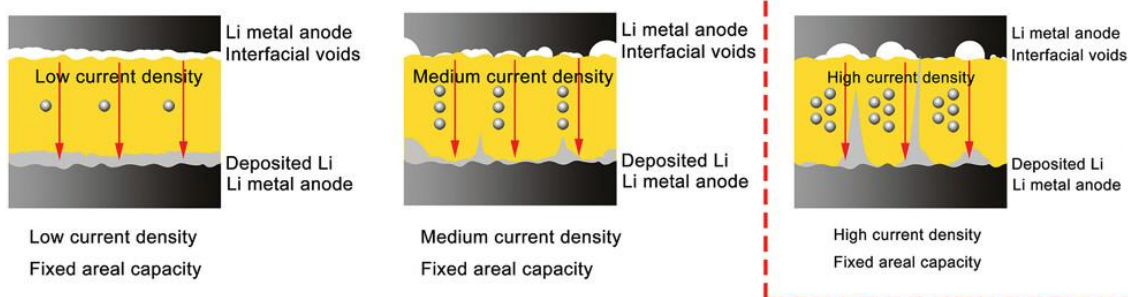


Figure 2-7: Schematic illustration of the microstructural evolution in the cells associated with different measurement protocols along with their corresponding charge and discharge profiles in (a) (c) time control, (b) (d) capacity control, and (e) endurable time control.^[50]

The critical current density (CCD) value can be determined when the anodic failure occurs. Different failure modes would exhibit distinct voltage profiles, providing insights into the mechanisms underlying the formation of lithium dendrites. Figure 2-8 depicts the different modes of lithium dendrite growth, along with the associated charge profiles and equivalent circuit models representing each growth mechanism.^[50] In all-solid-state lithium metal batteries, there are roughly four types of failure mechanisms, which are explained as follows:

(1) Sudden death

The rapid growth of thick lithium dendrites leads to contact of anode and cathode resulting in an irreversible short circuit. These dendrites can be represented as a parallel resistance with extremely low resistance (R_{short}) in the equivalent circuit model. In galvanostatic measurements, a sudden and drastic voltage drop indicates the occurrence of a short circuit. This type of hard short circuit typically occurs in stiff inorganic-based solid-state electrolytes. Areas with lower mechanical strength, such as grain boundaries and defects, makes them preferred sites for the propagation of dendrite.^[49, 52]

(2) Partly short circuit

A partial short circuit represents the initial stage of a complete short circuit, but the short-circuiting process may pause or terminate before the directly contact of electrodes. In this case, the lithium filaments penetrate only the interfacial regions rather than the entire bulk of the solid-state electrolyte. Consequently, the observation of a slight drop in the polarization voltage suggests a partial reduction in the bulk impedance. However, due to the presence of the remaining bulk impedance of electrolytes, a partial short circuit cannot be considered a complete failure of the solid-state battery.^[53]

(3) Soft short circuit

Soft short circuit occurs in batteries, particularly incorporated with polymer electrolytes or solid-liquid hybrid electrolytes, causing a slight voltage drop along with severe fluctuation of

charging curves during operation. The soft short circuit is caused by the formation and dissolution of tiny dendrites, which are limited in size due to the high viscosity of the polymer or partial liquid components. These small dendrites can easily fuse, allowing for battery recovery. However, the soft short circuit can lead to severe overcharging, resulting in energy waste.^[54]

(4) Contact loss

The loss of contact between the electrode and electrolyte is primarily caused by two factors: the accumulation of vacancies at the interface and the volume changes that occur during the continuous stripping process. When lithium atoms convert into lithium ions during the stripping process, vacant sites form. The accumulation of these vacancies results in the development of pores and defects at the interfaces. Consequently, the effective contact area between the electrode and electrolyte diminishes, leading to a localized concentration of lithium-ion flux. This concentrated flux further aggravates the contact loss, causing an increase in both polarization and interfacial impedance.^[55]

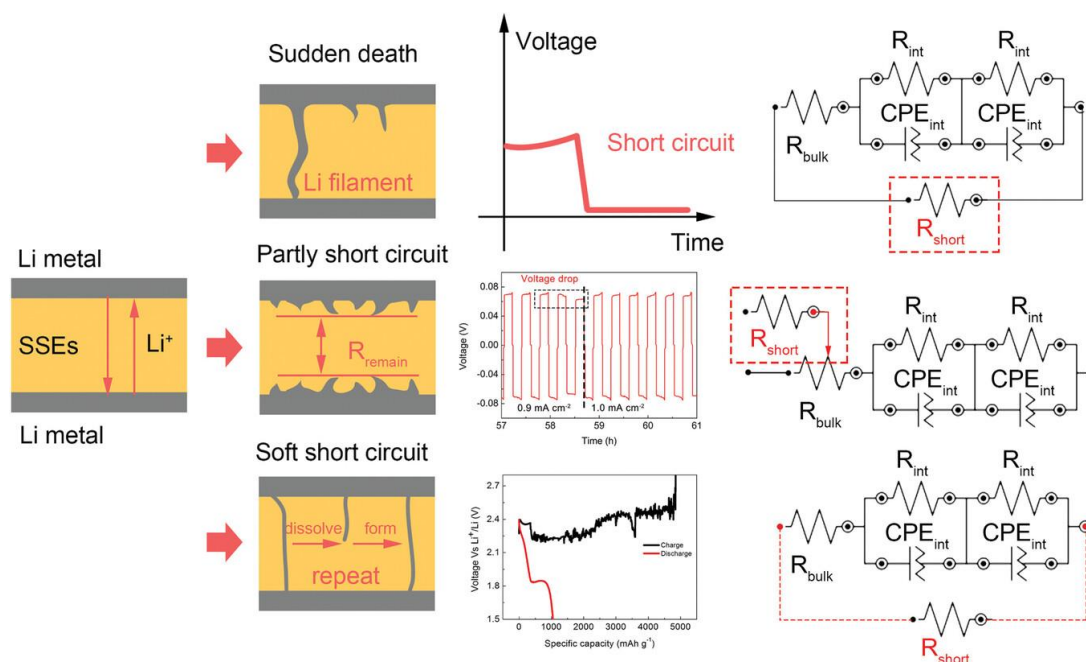
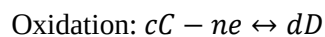
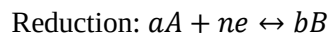


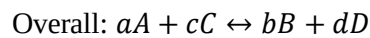
Figure 2-8: Schematic illustration of the mechanism of dendrite formation along with the associated charge profiles and equivalent circuit models.^[50]

2.4 Battery Characteristics

Batteries are devices that store energy by converting chemical energy into electrical energy and vice versa. The design of these electrochemical power sources is governed by several crucial parameters related to their operation. The electrochemical potential is a thermodynamic measure that includes the concepts of energy stored in the form of chemical potential and electrostatics. In an electrochemical cell, the overall chemical reactions can be divided into two half-reactions: reduction and oxidation. Reduction occurs at one electrode when "a" molecules of substance A gain "n" electrons (e) to form "b" molecules of substance B. Conversely, oxidation takes place at the other electrode when molecules of substance C lose electrons to form molecules of substance D.



The overall reaction in the electrochemical cell is the combination of above-mentioned two half-reactions.



The chemical driving force in an electrochemical cell arises from the difference in chemical potentials between the two electrodes. This difference is determined by the change in the standard Gibbs free energy (ΔG°) of the overall reaction, which is calculated by combining the sum of the standard Gibbs free energies of the reactants with the sum of the standard Gibbs free energies of the products. The change in the standard free energy (ΔG^0), of this reaction is

$$\Delta G^0 = -nFE^0$$

, where F is Faraday's constant ($F=eN_A=96485 \text{ C mol}^{-1}$) and E_0 is the standard electromotive force (emf).^[56]

The electrode potential (E) depends on the activities of the reactants and products involved in the redox reaction and is governed by the Nernst equation.

$$E = E^0 - \frac{RT}{nF} \ln \frac{u_B^i u_D^i}{u_A^i u_C^i}$$

where μ_i is the activity of relevant species, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature, respectively.^[57]

Open Circuit Voltage

The open circuit potential (OCP, V_{oc}) is voltage measured across the terminals of a battery when no potential or electric current is applied to the electrochemical cell.

$$V_{oc} = -\frac{1}{nF} (\mu_A^i - \mu_C^i)$$

, where $\mu_A^i - \mu_C^i$ is the difference in the chemical potential of the anode (A) and the cathode (C), n is the number of electronic charges involved in the chemical reaction of the cell. In other words, it is the potential difference between the cathode and anode when the battery is in a state of equilibrium and not being charged or discharged.^[56]

The voltage-time curve of a battery contains information about its aging process, which is influenced by the increase in internal impedance over time. When a current flows through the battery encounters resistance from various sources, such as the electrolyte, electrode materials, and interfacial layers, the electrode potential deviates from its equilibrium potential. This phenomenon is known as polarization, which results in the generation of overpotential.^[58] The effects of polarization on the cell voltage are current-dependent, with a more pronounced impact observed as the output current increases. Figure 2-9 depicts the polarization curve reflects the contributions of

three main factors that cause voltage drops in the battery: activation polarization, ohmic polarization, and concentration polarization, explained as follows.^[59]

(1) Activation polarization

The activation losses cause a sharp initial drop in the cell's open-circuit voltage as the current load increases, which is directly related to the energy barrier associated with the oxidation and reduction reactions at the electrodes.

(2) Ohmic polarization

This voltage drop is caused by the resistance to the flow of ions through the electrolyte and electrons through the electrodes and current collectors. It is directly proportional to the current and follows Ohm's law.

(3) Concentration polarization

Concentration polarization occurs when reactants are depleted at the electrode surface during high current discharge, as diffusion from the bulk electrolyte can't keep up with the consumption rate, creating concentration gradients that limit the reaction rate and cause a voltage drop.

During discharging, the voltage is reduced from its open-circuit value V_{oc} ($I_{dis}=0$) by the voltage drop ($I_{dis}R$), resulting from the internal resistance (R) of the battery and the polarization losses occur at each electrode. This causes a decrease in cell potential during discharge (V_{dis}) and conversely, an increase in cell potential (V_{ch}) during charging. As a result, the terminal voltage of a battery to be lower than the equilibrium potential during discharging and higher than the equilibrium potential during charging.^[59]

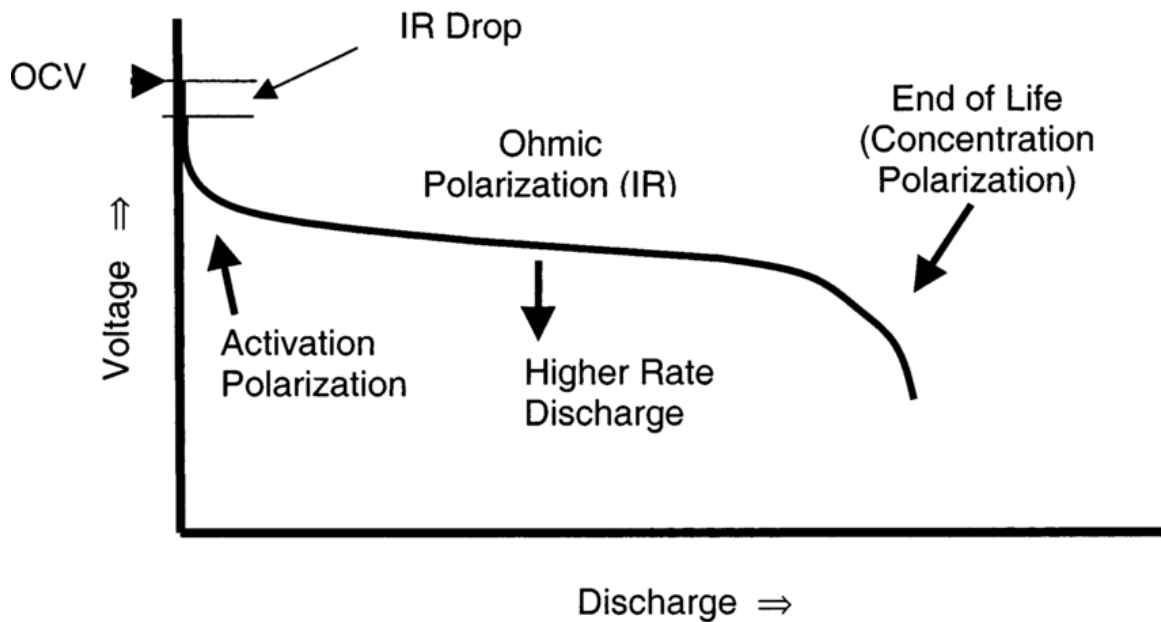


Figure 2-9: The discharge curve of a battery shows the influence of the various types of polarization.^[59]

C-rate

The C-rate is a standardized measure that describes the rate at which a battery is being discharged or charged relative to its maximum capacity. It is used to normalize battery performance data and compare different batteries, regardless of their actual capacities. In general, for a given C-rate of nC , the discharge or charge time can be calculated as $1/n$ hours. For instance, a 5 Ah battery discharging at a $C/10$ rate (0.5 A) would last for 10 hours. The C-rate is an important parameter in battery design and selection, as it affects the performance, efficiency, and longevity of a battery. High C-rates generally lead to lower capacity and increased heat generation due to internal resistance, while low C-rates result in slower charging and discharging times but offer better capacity retention and longer battery life.^[60]

Energy Density

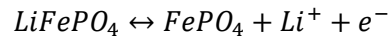
The specific energy and specific power (energy and power per unit weight) are crucial factors in applications in public transport systems such as buses, while the energy density (amount of energy stored per unit volume) is often more critical for batteries powering portable electronic devices like smart phones and laptops. Specific energy stored (in Wh kg⁻¹) in a battery is measured by discharging a battery at a current:

$$E = V_{oc} Q_{dis}$$

, where V_{oc} is the operating potential (V) and Q_{dis} is the specific capacity (Ah kg⁻¹).^[56] The theoretical capacity can be calculated as below,

$$Q_{th} = \frac{1000 \times nF}{3600 \times M_w} = \frac{26.8}{M_w} n$$

, where M_w is the molecular mass of the limiting electrode material, which has lower aerial capacity.^[61] For example, the reversible process of intercalation and deintercalation of lithium-ions into olivine structure of lithium iron phosphate (LFP, LiFePO₄) can be described as follows.



The molecular weight of LFP is around 157.7 g mol⁻¹. As such the theoretical capacity of LFP as limiting electrodes is around 170 mAh g⁻¹.

Power Density

The power output (P_{out}) of a battery can be calculated by multiplying the current (I_{dis}) delivered by the battery during discharge and the average operating voltage (V_{avg}). This relationship is expressed by the following equation:^[56]

$$P_{out} = I_{dis} V_{avg}$$

Cycle Life

As rechargeable batteries become increasingly common in various consumer products, cycle life emerges as a crucial factor to consider. Cycle life refers to the total number of complete charge-discharge cycles a battery can undergo before its capacity diminishes to a level that is no longer considered acceptable for its intended application. Typically, the end of a battery's useful life is marked by a 20-30% reduction in its original capacity.^[60]

Coulombic Efficiency

The coulombic efficiency (CE) is a measure of the reversibility of the charge and discharge processes in a battery. It is calculated by dividing the amount of charge that a battery can deliver during discharge (discharge capacity, Q_{Dch}) by the amount of charge that was initially supplied to the battery during charging (charge capacity, Q_{ch}) for a single charge-discharge cycle. The coulombic efficiency can be expressed as:^[56]

$$CE (\%) = \frac{Q_{Dch}}{Q_{ch}} \times 100\%$$

A coulombic efficiency of 100% suggests that the total charge supplied to the battery during charging is completely available for use during discharging, without any energy losses. However, in real-world scenarios, the coulombic efficiency typically falls below 100% due to several factors, including self-discharge, irreversible side reactions, and capacity fade. Regularly monitoring the coulombic efficiency across numerous charge-discharge cycles offers crucial insights into the performance, stability, and overall health of a battery, thus helping to identify potential issues and opportunities for improvement.

Chapter 3

Cold Sintering Enables the Reprocessing of LLZO-based Composites

3.1 Overview

All-solid-state batteries have the potential for enhanced safety and capacity over conventional lithium-ion batteries, and are anticipated to dominate the energy storage industry. As such, strategies to enable recycling of the individual components are crucial to minimize waste and prevent health and environmental harm. Here, we use cold sintering to reprocess solid state composite electrolytes, specifically Mg and Sr doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with polypropylene carbonate (PPC) and lithium perchlorate (LLZO–PPC– LiClO_4). The low sintering temperature allows co-sintering of ceramics, polymers and lithium salts, leading to re-densification of the composite structures with reprocessing. Reprocessed LLZO–PPC– LiClO_4 exhibits densified microstructures with ionic conductivities exceeding 10^{-4} S/cm at room temperature after 5 recycling cycles. All-solid-state lithium batteries fabricated with reprocessed electrolytes exhibit a high discharge capacity of 168 mAh g^{-1} at 0.1 C, and retention of performance at 0.2 C for over 100 cycles. Life cycle assessment (LCA) suggests that the recycled electrolyte outperforms the pristine electrolyte process in all environmental impact categories, highlighting cold sintering is a promising technology for recycling electrolytes.

3.2 Introduction

Since their commercialization in 1991, lithium-ion batteries have become a key component in electric vehicles and personal electronic devices.^[62] Growing market needs continue to drive

battery development, such as in improved electrochemical performance and extended lifetimes.^[6, 63] All-solid-state batteries, which employ solid-state electrolytes as opposed to flammable organic liquid electrolytes, can provide greater energy density, durability, and safety.^[11b, 63] The anticipated growth, both of Li-ion and solid-state batteries^[64], is expected to accelerate the depletion of mineral deposits, and potentially limit lithium battery production.^[65] Developing strategies to handle the increasing amount of battery waste is crucial, not only for resource recovery but also to prevent deleterious effects to health and the environment.

Current recycling strategies are designed to deal with spent lithium-ion batteries and to recover valuable elements from cathodes and current collectors.^[29a, 66] Because of the complexities of battery compositions and the chemistry of components, current recycling processes involve high temperature or solvents to chemically break materials down into recoverable compounds.^[65, 66h, 67] This current recycling strategy is limited in sustainability, as pyrometallurgical recovery is energy-consuming with low recovery rates, and hydrometallurgy recovery can be complicated and generate hazardous liquid wastes.^[5b] Furthermore, strategies for recycling of all-solid-state batteries remain underdeveloped.^[5b]

Given that chemical and mechanical reactions are usually coupled with each other in the failure mechanisms of solid-state electrolytes, mechanical stress is the key factor leading to failure of solid-state electrolytes, despite the modest breakdown at interfaces.^[19a, 68] As solid-state electrolytes are in contact with lithium metal, interphases with restricted electron conductivity form. This hinders electron transport and limits the propagation of side reactions; hence, the interfacial layer is usually localized.^[19a, 24a, 69] In addition, cracks generated during charging and discharging cycles may propagate through the bulk phase, resulting in battery failure.^[24a, 49] The growth of lithium dendrites and the accumulation of isolated dead lithium causes a volume fluctuation of the cell, which induces internal stress and the formation of cracks and fractures in the microstructures of solid-state electrolytes. These structural defects block lithium-ion transport

pathways, leading to a high total impedance or eventually battery short-circuits.^[70] In spite of the presence of these localized defects and fragmented microstructures, the vast majority of solid-state electrolytes remain active after cycling. Thus, once localized interfaces are eliminated, it is plausible that spent solid-state electrolytes may be recycled without undergoing sophisticated processes.^[68c]

Low energy consumption and minimal greenhouse gas production are important criteria in the selection of sustainable recycling processes. Among different reprocessing approaches, direct recycling by regenerating materials, without chemical break down and resynthesis of active components, has shown remarkable potential in meeting the aforementioned criteria.^[5b] Here, we directly reprocessed LLZO-PPC-LiClO₄ composite electrolytes using cold sintering, and demonstrate recyclability with modest loss in ionic conductivity. Cold sintering, a low-temperature sintering technology (25–300 °C), is a process that enables the densification of composites comprised of ceramics, polymers, and salts.^[71] Driven by pressure and heat, densification happens with the assistance of a transient liquid phase, which functions as a medium to aid in the dissolution and regulate the precipitation and nucleation processes.^[36, 72] We show that cold sintering enables the direct reprocessing of composite electrolytes by reintegrating ceramics with polymers and lithium salts. All-solid-state batteries with reprocessed electrolytes demonstrate a comparable cycling performance to batteries comprised of pristine electrolytes. Life cycle assessment (LCA) calculations reveal a lower energy consumption and less environmental impact of utilizing reprocessed electrolytes versus pristine materials, by avoiding the use of raw materials and eliminating the need of complicated synthetic processes. Our work provides a strategy for the direct reprocessing and reuse of spent composite electrolytes, which in turn promotes the sustainability and viability of all-solid-state batteries.

3.3 Experimental Methods

Materials

$\text{Li}_{7-2x+y}\text{Mg}_x\text{La}_{3-y}\text{Sr}_y\text{Zr}_2\text{O}_{12}$, (LLZO, $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.5$) powders with particle sizes around $1 \mu\text{m}$ were supplied by NGK Spark Plug Co., Ltd. Polypropylene carbonate (PPC), lithium perchlorate (LiClO_4), anhydrous acetonitrile (ACN), and N, N-Dimethylformamide (DMF) were purchased from Sigma Aldrich without further treatment. Cathode sheets ($241 \text{ mm} \times 200 \text{ mm} \times 83 \mu\text{m}$ thickness) with a single side coated with LiFePO_4 (LFP) were purchased from MTI Corporation. Single-sided $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) sheets ($127 \text{ mm} \times 254 \text{ mm} \times 83 \mu\text{m}$ thickness, excluding the current collector) were purchased from NEI corporation.

Fabrication of LLZO-PPC- LiClO_4 Composite Electrolytes

The composite electrolyte was prepared by cold sintering LLZO powders with polymer-salt solutions and DMF. Polymer-salt solutions were found to form a polymer-salt bridge between LLZO grains and reduce the grain boundary resistance after cold sintering.^[73] ACN and DMF were applied as non-aqueous transient solvents to promote densification by mediating the dissolution-precipitation process. DMF also acted as a plasticizer to reduce the glass transition temperature of polymers, enhancing the segmental movement of polymer chains for lithium-ion transport. A polymer-salt solution was prepared by dissolving PPC and lithium perchlorate in ACN with a ratio of 2:1:12 (wt%). The solution was stirred for several hours until the solution became homogeneous. LLZO powder was mixed with polymer-salt solution and DMF (12:2.5:1 by wt%) using a mortar and a pestle. The wetted mixture was delivered into a die with a diameter of 13 mm and sandwiched between aluminum foils as blocking electrodes for conductivity measurement. The mixture

underwent the cold sintering process by being pressed and sintered under a uniaxial pressure of 80 bar at 100 °C for 1 hour. The sintering temperature was controlled by two heating platens and a band heater wrapping around the die to prevent any temperature gradient. After cooling below 50 °C, the cold sintered composite electrolyte pellet with a thickness of around 1 mm was assembled in a CR2032 coin cell for further characterization. All the preparation processes were performed in a glovebox under an argon atmosphere.

Material Characterization

Relative densities of pristine and reprocessed LLZO–PPC–LiClO₄ are the ratios of the measured densities to the theoretical densities of the composite (4.59 g cm⁻³). The theoretical density of a composite can be calculated based on the volume fraction and theoretical densities of each constituent (LLZO=5.02 g cm⁻³, PPC=1.26 g cm⁻³, LiClO₄=2.42 g cm⁻³). Crystal structures and phase purities were determined by X-ray diffraction (Malvern Panalytical Empyrean) with Cu K α radiation. *In situ* XRD was performed in a furnace filled with argon at temperatures from ambient to 973K. Collected spectra were analyzed using MDI JADE software. Field emission scanning electron microscope and energy dispersive spectrometer (FE-SEM and EDS, Verios G4, Thermo Scientific) were used to characterize the surface morphology, cross-sections, and elemental compositions of pristine, reprocessed composite electrolytes, and all-solid-state full cells. For the determination of dissolution rates of metal elements in LLZO, inductively coupled plasma emission spectrometry (ICP-AES, Thermo iCAP 7400) was used.

Electrochemical Characterization

The ionic conductivity of the composite electrolytes is considered a critical property to estimate the conduction of ionic carriers. Electrochemical impedance spectroscopy (EIS, ModuLab XM MTS) measurements of symmetric Al|LLZO–PPC–LiClO₄|Al cells were carried out in a frequency range of 0.1 to 10⁶ Hz with a 10-mV amplitude. Conductivities were calculated using $\sigma = \frac{h}{Z_{re} \times A}$, where Z is the impedance for the real axis in the Nyquist plot, h is the thickness of the cold sintered composite electrolyte, and A is the contacting area of blocking electrodes. The activation energies were determined from the conductivities as a function of temperature ranging from –20 to 120 °C using the Arrhenius equation, $\sigma = A \times e^{-\frac{E_a}{k_B T}}$, where A is the pre-exponential factor, k_B is the Boltzmann constant, and E_a is the activation energy for lithium-ion conduction.

Cell Fabrication and Evaluation

To test the applicability of reprocessed electrolytes, all-solid-state full cells of LTO|LLZO–PPC–LiClO₄|LFP are fabricated using the cold sintering process to obtain compact layered structures. Anode and cathode discs are cut from LTO and LFP sheets, vacuum dried at 100 °C and stored in the glovebox filled with argon for further use. The composite slurry was first prepared by mixing an as-prepared polymer-salt solution with LLZO powders and DMF with a mass weight ratio of 1:4.8:4. The slurry was drop-casted on LTO discs and dried at room temperature overnight with a mass weight of around 80 mg. 9 wt% of LiClO₄/DMF solution was introduced on the LTO|LLZO–PPC–LiClO₄ discs, and a LFP circle was placed on top of it to form a three-layered structure. The cold sintering process was carried out at 100 °C under 20 bar for an hour. As the temperature drop below 50°C, the LTO|LLZO–PPC–LiClO₄ full cell was taken out and sealed into a coin cell. The cells were galvanostatically charged and discharged between 0.6 and 2.7 V vs.

Li^+/Li . The charging and discharging current densities were determined from the theoretical capacity of the LFP cathode, 170 mAh g^{-1} .

Life Cycle Assessment

The goal of the life cycle assessment (LCA) is to compare the environmental impacts of producing LLZO composite batteries using pristine or recycled materials. The results of the study will be made publicly available to allow for informed decisions regarding recycling of composite batteries. The impact assessment method used was U.S. EPA TRACI 2.1.^[74] TRACI mid-point indicators include acidification, carcinogenics, ecotoxicity, eutrophication, global warming potential, noncarcinogenics, respiratory effects, ozone depletion, and smog formation. The openLCA2.0 software was used for quantifying the potential environmental impacts. Inventory inputs were modeled throughout all life cycle stages including raw materials acquisition, annealing process, and sintering process. During the sintering process, LiClO_4 , LLZO, and PPC are recycled. The emissions and raw materials associated with all materials, processes, and wastes are quantified using the ecoinvent database accessed via OpenLCA.^[75] Literature data and patents were also used to model the production of PPC, LLZO, and LiClO_4 .^{[76],[77],[78]} The estimated energy consumption calculation can be found in the Supporting Information.

3.4 Results and Discussion

In spent solid-state composite electrolytes, defects such as voids and cracks may block lithium-ion transport pathways and thereby impede ionic conductivity. To recycle electrolytes that have undergone mechanical degradation, we use cold sintering to re-densify microstructures. The low sintering temperature during cold sintering enables co-sintering of ceramics, lithium salts, and

polymers without compromising their active properties. We mimic an extreme extent of mechanical degradation, one of the main degradation channels in all-solid-state electrolyte batteries, by breaking electrolytes into pieces through grinding.

Figure 3-1 depicts the four steps of the recycling process for solid-state composite electrolytes: coin cell disassembly, component separation, cold sintering, and reuse of reprocessed electrolytes. Composite electrolytes were taken out from coin cells using a plier and a diagonal cutter. Aluminum blocking electrodes were manually taken off using tweezers. Any obvious surface contamination was sanded away with 2500 grit sandpapers. With a mortar and a pestle, the composite powders were crushed into powder and thoroughly mixed with acetonitrile (ACN) and N, N-Dimethylformamide (DMF). These transient solvents were introduced to promote mass transport and regulate the dissolution-precipitation during cold sintering.

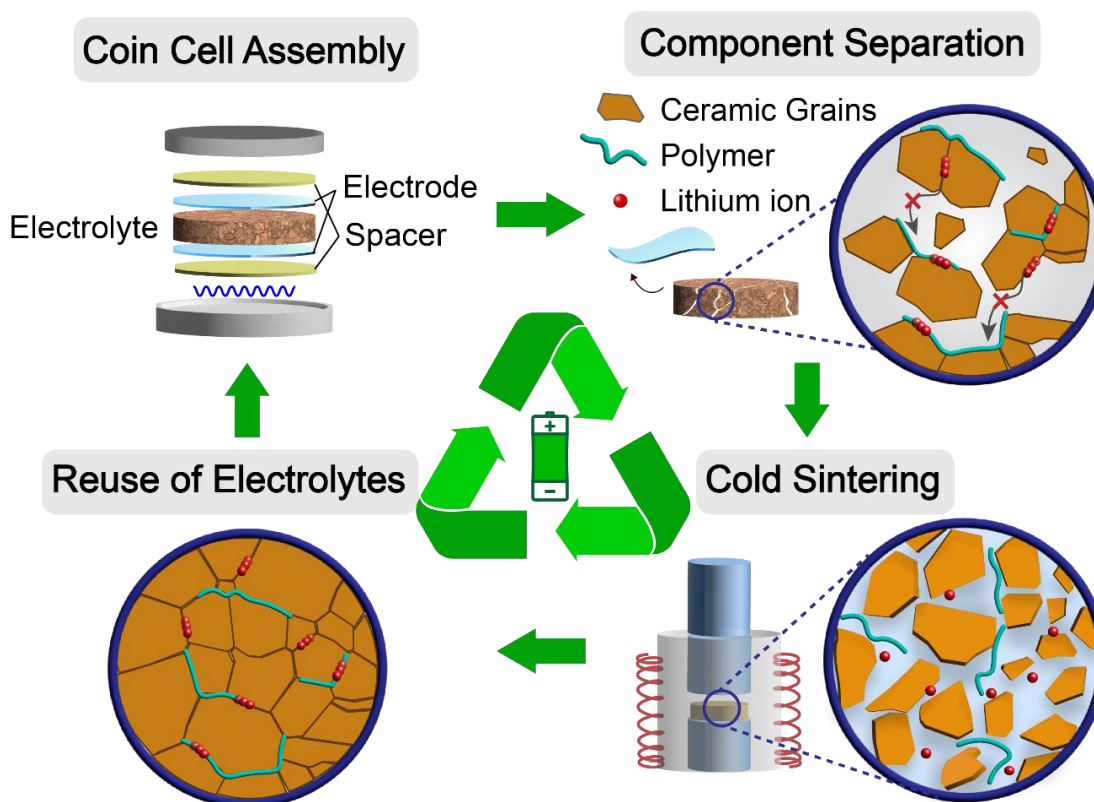


Figure 3-1: Schematic illustration of different stages during reprocessing.

To elucidate the effects of the recycling process on the functionality of reprocessed electrolytes, several cycles of reprocessing were performed on as-synthesized electrolytes and we tracked the density and ionic conductivity. Figure 3-2(a) displays the ionic conductivities and relative densities of composite electrolytes comprised of $\text{Li}_{7-2x+y}\text{Mg}_x\text{La}_{3-y}\text{Sr}_y\text{Zr}_2\text{O}_{12}$ ($0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.5$), polypropylene carbonate (PPC), and lithium perchlorate (LLZO-PPC-LiClO_4) as a function of reprocessing cycles. One-time reprocessed electrolytes demonstrate a slight increase in relative densities. The particle size of pristine LLZO was estimated to be less than 1 μm . After break up by mortar and pestle, reprocessed composite powders show variations in particle size distribution (Figure S3-1 and Figure S3-2, Supporting Information). This variation in particle size is associated with the incorporation of polymers, which binds nanocrystallites to produce sub-micrometer-sized grains.

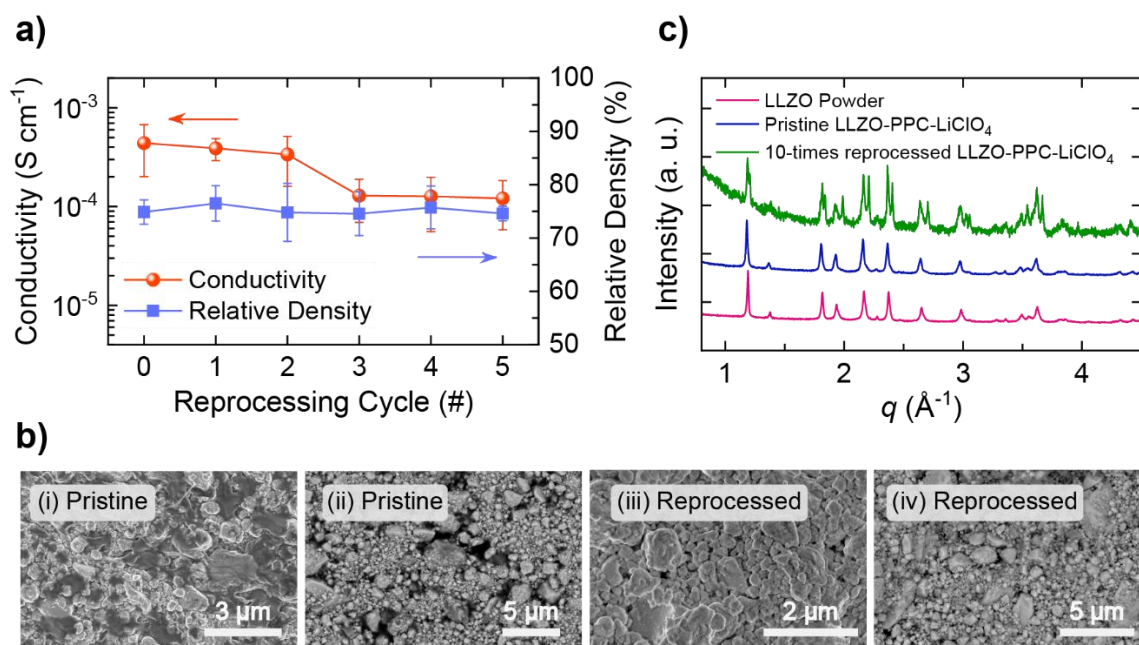


Figure 3-2: (a) Ionic conductivities and relative densities of LLZO-PPC-LiClO_4 composite electrolytes after various reprocessing cycles. (b) Secondary electron ((i), (iii)) and backscattered electron ((ii), (iv)) SEM images of pristine and one-time reprocessed composite electrolytes. (c) X-ray diffraction (XRD) spectra of composite electrolytes at the pristine and reprocessed states.

After undergoing five times reprocessing, the relative densities of reprocessed electrolytes remain constant at approximately 75 %, suggesting that cold sintering is effective in densification. The microstructures of pristine and reprocessed electrolytes were examined by secondary electron and backscattered scanning electron microscope (SEM), as shown in Figure 3-2(b). Densely packed microstructures through cold sintering are apparent in pristine and once reprocessed electrolytes.

Ionic conductivities were obtained from Nyquist plots of symmetric cells with blocking electrodes (Al/electrolyte/Al) at room temperature (Figure S3-3, Supporting Information). Once reprocessed composite electrolytes possess high average ionic conductivities of $\sim 3.9 \times 10^{-4} \text{ S cm}^{-1}$, which is approximately 88.6 % of their pristine states. The constant relative density and high ionic conductivities imply that cold sintering is capable of densifying composite electrolytes and that each component remains active after reprocessing. After five reprocessing cycles, the conductivity of reprocessed electrolytes dropped to 27.6 % of the pristine state, whereas the relative density remained constant. This implies that even though the cold sintering process remains efficacious in densifying, lithium-ion transport is hampered.

We examined the consequences of reprocessing through cold sintering using X-ray diffraction (XRD). LLZO often exhibits two crystal structures that are either tetragonal (space group $I4_1/acd$) or cubic (space group $Ia\bar{3}d$), with ionic conductivities that vary by two orders of magnitude (tetragonal: $\sim 10^{-6} \text{ S cm}^{-1}$, cubic: $\sim 10^{-4} \text{ S cm}^{-1}$).^[79] Figure 3-2(c) compares pristine and ten-time reprocessed composites. Cubic phases comprise the primary crystalline structure of pure LLZO powders and the composite electrolyte. Amorphous PPC and amorphous or crystalline LiClO_4 are not apparent due to their small quantity within composites. In ten-time reprocessed electrolytes, a combination of cubic and tetragonal phases is apparent. The lower signal-to-noise in the diffraction data from the ten-time reprocessed sample is likely due to accumulation of amorphous phases. We thus associate the reduction in ionic conductivity with the formation of tetragonal phases during reprocessing.

To identify factors driving phase changes, we applied components of our reprocessing approach in isolation, including grinding, transient solvent exposure, and heating. We examined LLZO powders that were either dry-milled, heated (without solvent), heated in ACN, heated in DMF, and heated in both ACN and DMF for 30 hours. As can be seen in Figure S3-4, powders treated by dry-milling, dry heating, and heating in DMF preserved their cubic crystalline structure. The additional peaks observed in XRD data of ACN-treated LLZO can be assigned to secondary phases, such as $\text{Li}_6\text{Zr}_2\text{O}_7$ and $\text{LiLa}(\text{CO}_3)_2$. When LLZO powders were heated in mixtures of ACN and DMF, however, the tetragonal phase emerges. Thus, transient solvents appear to drive phase transformations in LLZO composites.

In cold sintering, congruent dissolution in transient solvents at modest temperatures enables the fast dissolution-precipitation process.^[38] For many compounds, however, incongruent dissolution may occur as elements dissolve at grain surfaces with variable kinetic rates. The shift in stoichiometry can result in the formation of amorphous or unwanted phases. We hypothesize that the occurrence of incongruent dissolution leads to a phase transition from cubic to tetragonal phases. As such, dissolution rates of elements in LLZO were investigated by inductively coupled plasma emission spectrometry (ICP-AES) when heated and agitated in transient solvents. Lithium exhibited a significantly higher dissolution concentration ($\sim 11 \mu\text{mol mL}^{-1}$) than other elements ($\sim 10^{-4} \mu\text{mol mL}^{-1}$) in LLZO, as illustrated in Figure 3-3(a). The preferential dissolution of lithium ion has been widely reported in lithium-based oxide systems.^[71, 80] This can lead to secondary phases that are detrimental to ionic conduction.^[81] In our case, we propose that incongruent dissolution results in a phase transition for LLZO. Cubic and tetragonal phases of LLZO have the same lattice framework structure but differ in lithium distribution.^[82] In cubic phases, lithium ions partially occupy sites, whereas, in tetragonal phases, lithium ions fully occupy the sites. Because of the well-ordered configuration, tetragonal phases are thermodynamically stable at room temperature.^[82] During cold sintering, incongruent dissolution perturbs the stoichiometry and the

lithium content of LLZO. We speculate that reprecipitation favors crystallization into energetically-favored tetragonal phases.

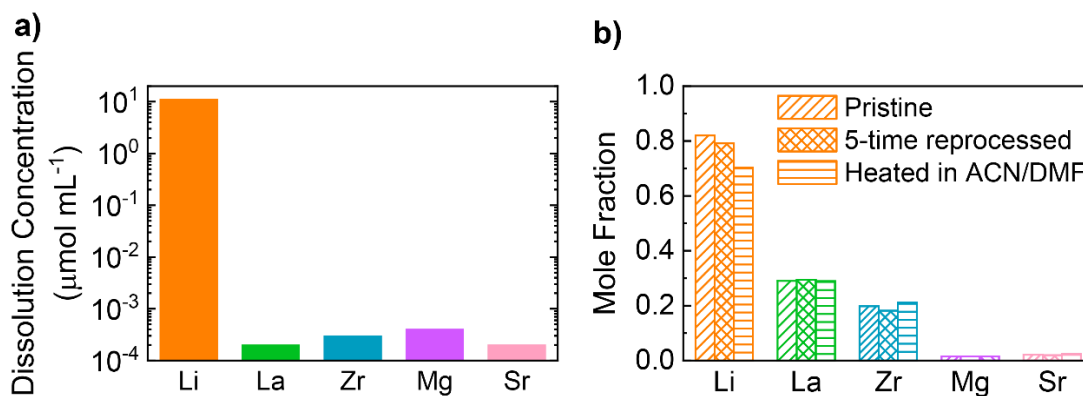


Figure 3-3: (a) Dissolution concentration of elements in LLZO suggest that lithium dissolves preferentially in acetonitrile and dimethylformamide solution at 100 °C for 1 hour. (b) ICP analysis results show that LLZO powders being heated in transient solvents for a longer time possess lower lithium contents. (5-time reprocessed: LLZO powders experienced 5-time reprocessing by cold sintering process, Heated in ACN/DMF: LLZO powders heated in transient solvents for 30 hours.)

We also explored methods to stabilize cubic phases despite reprocessing. The depletion of lithium along with the increase in lithium vacancy concentration was reported to cause a reduction in the tetragonal-to-cubic phase transition temperature of LLZO, and thus energetically favor the cubic structure.^[83] We used thermal annealing to drive our samples towards the cubic phase. We simulate the solvent exposure step of the cold sintering process by exposing LLZO powders to transient solvents for 30 hours to form tetragonal phases. Compared to pristine LLZO powders, solvent-exposed LLZO has much lower lithium content but comparable content of all other elements (Figure 3-3(b)). Solvent-exposed powders were then heat-treated at elevated temperatures under an argon environment. XRD patterns at room temperature show the presence of tetragonal and cubic phases in solvent-exposed LLZO (Figure 3-4(a)), and only the cubic structure in pristine LLZO (Figure 3-4(b)). When annealed *in-situ* above 373 K, the merging of the (211) and (112) peaks of solvent-exposed LLZO indicates a phase transition to the cubic allomorph. As temperature

risers further, the increase in intensity along with the decrease in peak width of the (211) reflection suggests cubic crystals grow in size. After annealing and cooling down to room temperature, the cubic phase in LLZO persists, as shown in Figure S3-5.

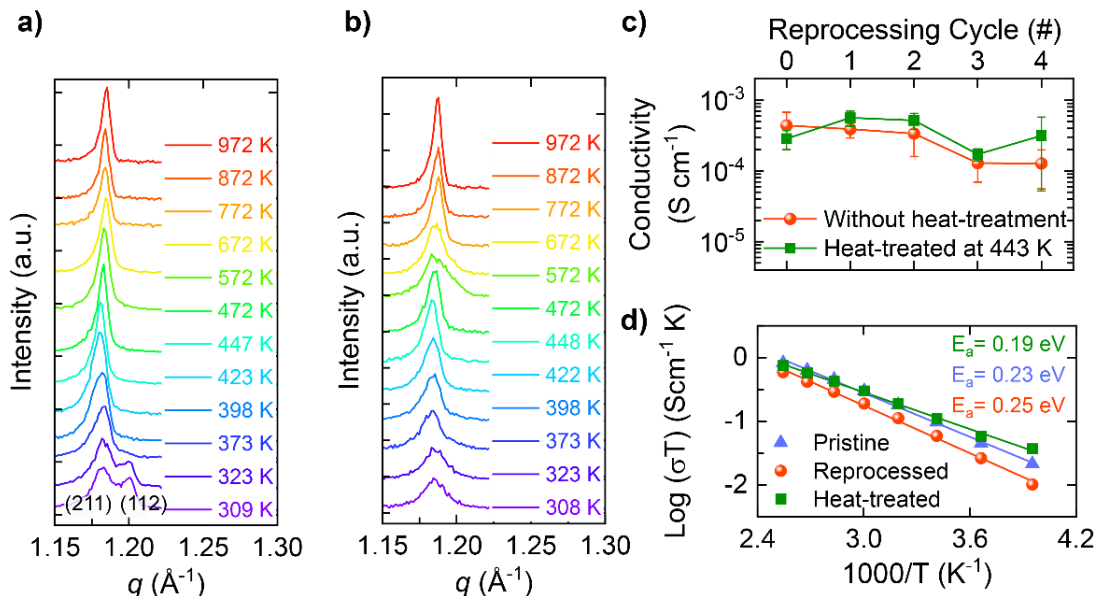


Figure 3-4: In-situ X-ray diffraction spectra of (a) solvent-exposed and (b) pristine LLZO powders in an argon environment at temperatures from 308 K to 972 K. (c) Ionic conductivities and relative densities of reprocessed LLZO–PPC–LiClO₄ composite electrolytes with and without thermal annealing at different reprocessing cycles. (d) Temperature dependence of ionic conductivity for reprocessed and thermally annealed composite electrolytes; for comparison, data of reprocessed and pristine electrolytes are included. The solid lines show Arrhenius fits with activation energies given in the inset.

The increase in lithium vacancy resulting from incongruent dissolution was found to reduce the transition temperature. Reprocessed electrolytes were annealed at different temperatures, and we found that 170 °C prevents the loss of ionic conductivity upon reprocessing (Figure S3-6). To stabilize cubic phases, we heat-treated electrolytes at 170 °C for one hour and subsequently cold sintered the electrolytes.

Figure 3-4(c) shows ionic conductivities and relative densities of reprocessed electrolytes with and without thermal annealing. Thermally annealed reprocessed composites demonstrate

improved conductivities, with an average of $3.1 \times 10^{-4} \text{ S cm}^{-1}$ after four times of reprocessing. This is similar to conductivities of pristine LLZO ($\sim 2.9 \times 10^{-4} \text{ S cm}^{-1}$). For electrolytes that are not thermally annealed, conductivities decrease substantially with reprocessing cycle. We measured temperature-dependent ionic conductivities between 20 and 120 °C to obtain the activation energy for lithium-ion conduction, as shown in Figure 3-4(d). The Arrhenius temperature dependence implies an activation energy of pristine electrolytes of 0.228 eV (95 % CI 0.215-0.241). The activation energy of reprocessed electrolyte without annealing is 0.248 eV (95 % CI 0.232-0.263), while with annealing it is lower, at 0.191 eV (95 % CI 0.180-0.202). We speculate that promoting the cubic phase in LLZO with annealing enables fast lithium-ion transport despite the formation of poorly ion-conducting phases during reprocessing.

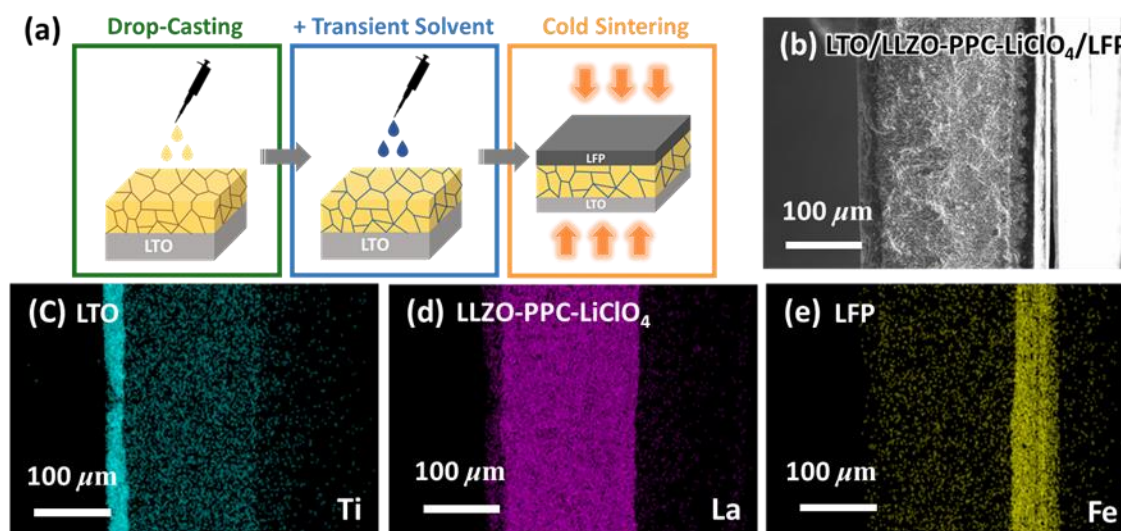


Figure 3-5: (a) Schematic illustration of fabrication of LFP/ LLZO–PPC–LiClO₄/LTO all solid-state batteries using cold sintering process. (b) SEM image and (c-e) the corresponding EDS mapping of microstructures of LTO/LLZO–PPC–LiClO₄/LFP full cell.

We fabricated all-solid-state batteries based on pristine and reprocessed electrolytes using lithium titanate (LTO) anodes and lithium iron phosphate (LFP) cathodes to evaluate electrochemical performance. The fabrication procedures are shown in Figure 3-5(a), and the

details are described in the Materials and Methods sections. Figure 3-5(b-e) show SEM and corresponding element mapping images of LFP/ LLZO–PPC–LiClO₄/LTO. The full cell with a thickness of ~200 μm shows a layered structure with intimate contacts between each layer.

The electrochemical performances of all solid-state batteries with pristine and reprocessed composite electrolytes are presented in Figure 3-6. The total impedance of LFP/reprocessed LLZO–PPC–LiClO₄/LTO is estimated to be around 11 ohm cm^2 at room temperature. Figure 3-6(b) shows the charge/discharge voltage profiles of the full cell with reprocessed LLZO–PPC–LiClO₄ at various current densities in the range of 0.1–1 C. The charge and discharge plateaus were observed around 1.9 V with limited overpotentials, which are in good agreement with previous work.^[73] The rate performance at different current densities at room temperature is shown in Figure 3-6(c). All-solid-state batteries at room temperature with reprocessed and heat-treated electrolytes have high discharge capacity of 168, 160, 144, and 125 mA h g^{-1} at 0.1, 0.2, 0.5, and 1 C, respectively. Thus, cold sintering enables the direct reprocessing of spent composite electrolytes, which are compatible with high capacity and rate performance at room temperature. Full cells with annealed reprocessed electrolytes show a modest decrease in discharge capacity with cycling. In contrast, solid-state batteries with reprocessed electrolytes that are not annealed show capacity loss at a high charge and discharge rates. Figure 3-6(d) shows the capacity retention and Coulombic efficiencies at 0.2 C for approximately one hundred cycles. The gradual decay in the capacity of LFP/reprocessed LLZO–PPC–LiClO₄/LTO can be ascribed to the drop in ionic conductivity with reprocessing. The loss of pathways for lithium-ion transport may lead to contact losses between the solid state electrolyte and the cathode. For full cells with pristine and thermally annealed reprocessed electrolytes, the high ionic conductivity and excellent stability against LTO and LFP electrodes leads to a steady discharge capacity profile. Both cells demonstrate excellent cycling retention with an average Coulombic efficiency of over 99% after the 10th cycle.

To demonstrate stability against Li metal electrodes, we fabricated all-solid-state batteries that incorporate reprocessed LLZO electrolytes (LFP/reprocessed+heat-treated LLZO-PPC-LiClO₄/Li). All-solid-state lithium metal batteries show discharge capacity of 150, 130, 107, and 53 mA h g⁻¹ at 0.1, 0.2, 0.5, and 1 C, respectively (Figure S3-7). These results demonstrate the effectiveness of directly reprocessing LLZO-PPC-LiClO₄ using the cold sintering process coupled with modest thermal annealing.

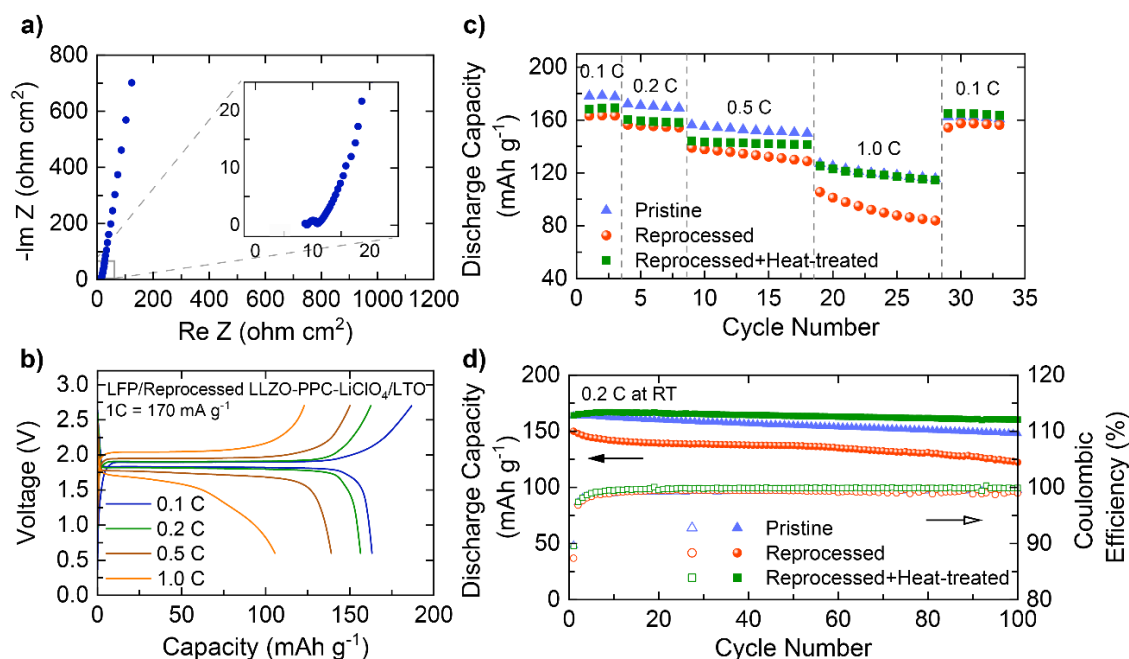


Figure 3-6: Electrochemical performance of all-solid-state batteries with pristine and reprocessed composite electrolytes at room temperature. (a) Nyquist plot of LFP/reprocessed LLZO-PPC-LiClO₄/LTO cell; Inset: data at high frequency. (b) Voltage profile and (c) rate performance at different current densities. (d) Discharge capacity retention and coulombic efficiency cycled at 0.2 C.

In order to elucidate the environmental impacts of the recycling decisions and enable comparisons between recycled and pristine materials, we conducted life cycle assessment (LCA) calculations. Categories and characterization factors in the Tool for the Reduction and Assessment of Chemical and other Environmental Impacts (TRACI 2.1) of the U.S. EPA ^[74] were used. We

focus on global warming potential (GWP) and ecotoxicity impact, considering the chemicals and solvents used to produce battery components tend to be in waste streams released to the environment. Additionally, the net energy balance, including both indirect energy and direct energy consumption, were evaluated using the Cumulative Energy Demand (CED) method. The functional unit was based on processing 1 g of the composite electrolyte. The scope of the analysis is cradle-to-gate.

Impacts on ecotoxicity, greenhouse gas (GHG) emissions, and CED are shown in Figure 3-7. Results show that, when comparing the potential environmental impacts of using pristine materials with recycling the main components, the recycled electrolyte outperforms the pristine electrolyte process in all environmental impact categories. These LCA results further highlight cold sintering as a promising technology for recycling electrolytes.

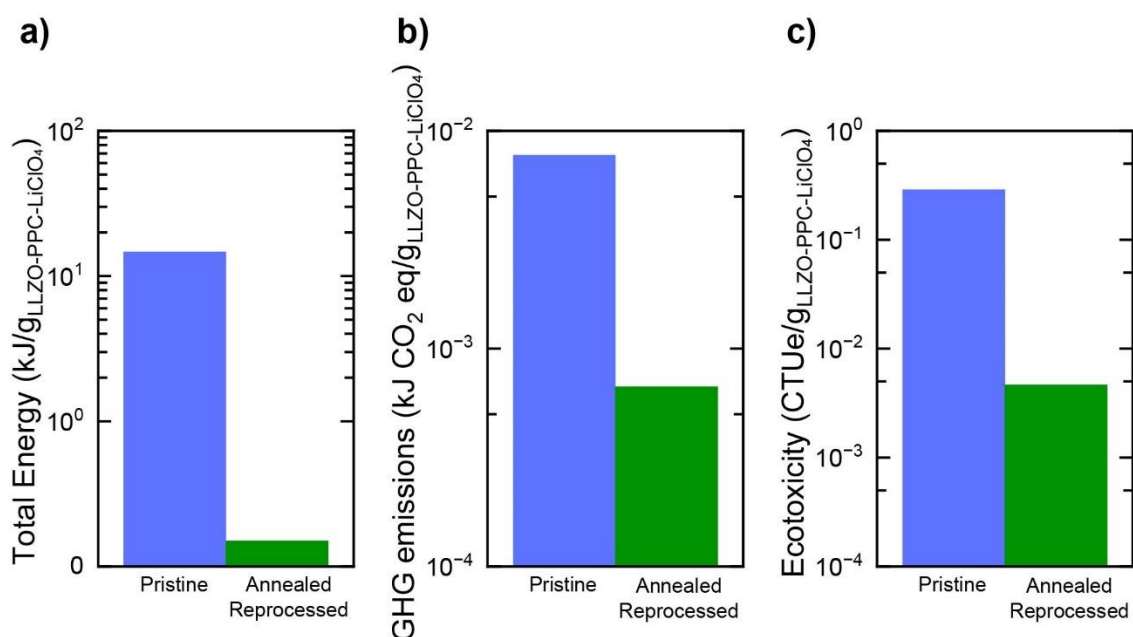


Figure 3-7: Life cycle assessment results of annealed reprocessed electrolyte versus an electrolyte made with pristine materials. (a) Cumulative energy demand. (b) Greenhouse gas (GHG) emissions. (c) Ecotoxicity.

3.5 Conclusion

We demonstrate an approach to directly reprocessed LLZO–PPC–LiClO₄ composite electrolytes using cold sintering. Reprocessed LLZO–PPC–LiClO₄ demonstrates ionic conductivities that exceed 10^{-4} S cm⁻¹ at room temperature after five reprocessing cycles. The occurrence of incongruent dissolution during cold sintering results in a partial transition from a highly conductive cubic phase into a poorly conducting tetragonal phase. Cubic phases can be promoted through thermal annealing at 170 °C, which recovers ionic conductivity after reprocessing. All-solid-state lithium batteries with thermally annealed reprocessed electrolytes deliver high discharge capacity of 168 mAh g⁻¹ at 0.1 C and excellent retention of performance at 0.2 C for over one hundred cycles. LCA reveals that the use of reprocessed electrolytes significantly reduces both energy consumption and GHG emissions by avoiding the use of raw materials and eliminating the need of complicated synthetic reprocessing. Overall, we show that cold sintering enables direct reprocessing of composite electrolytes, and provides a needed approach for sustainability of energy storage devices.

3.6 Supporting Information

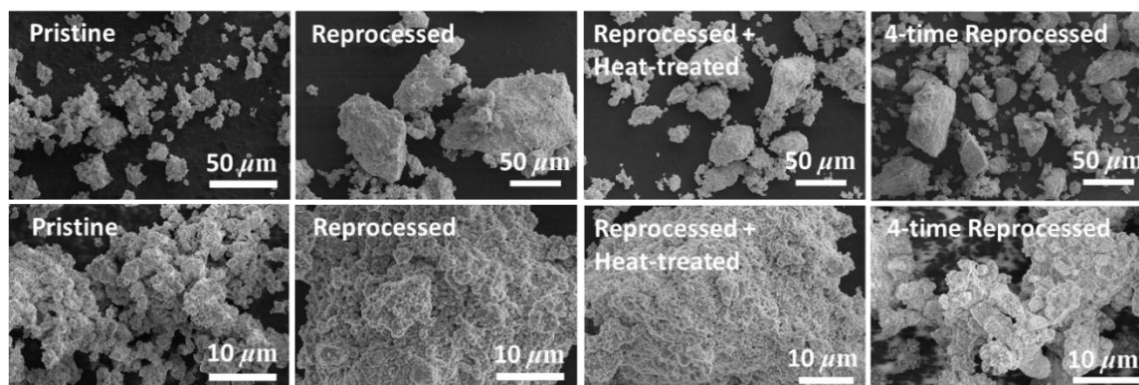


Figure S3-1: SEM images of pristine and one-time reprocessed composite electrolyte powders. Reprocessed composites powders show wide variations in particle size distribution.

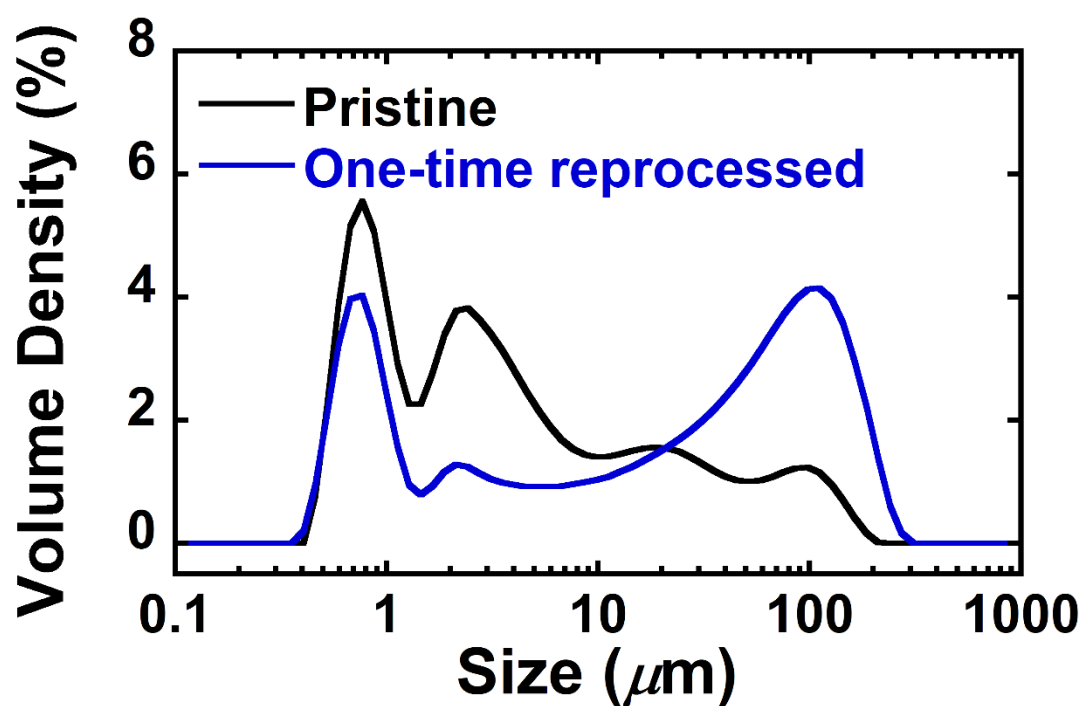


Figure S3-2: Particle size distribution of pristine and one-time reprocessed composite electrolytes powders. Reprocessed composites powders show bi-modal in particle size distribution.

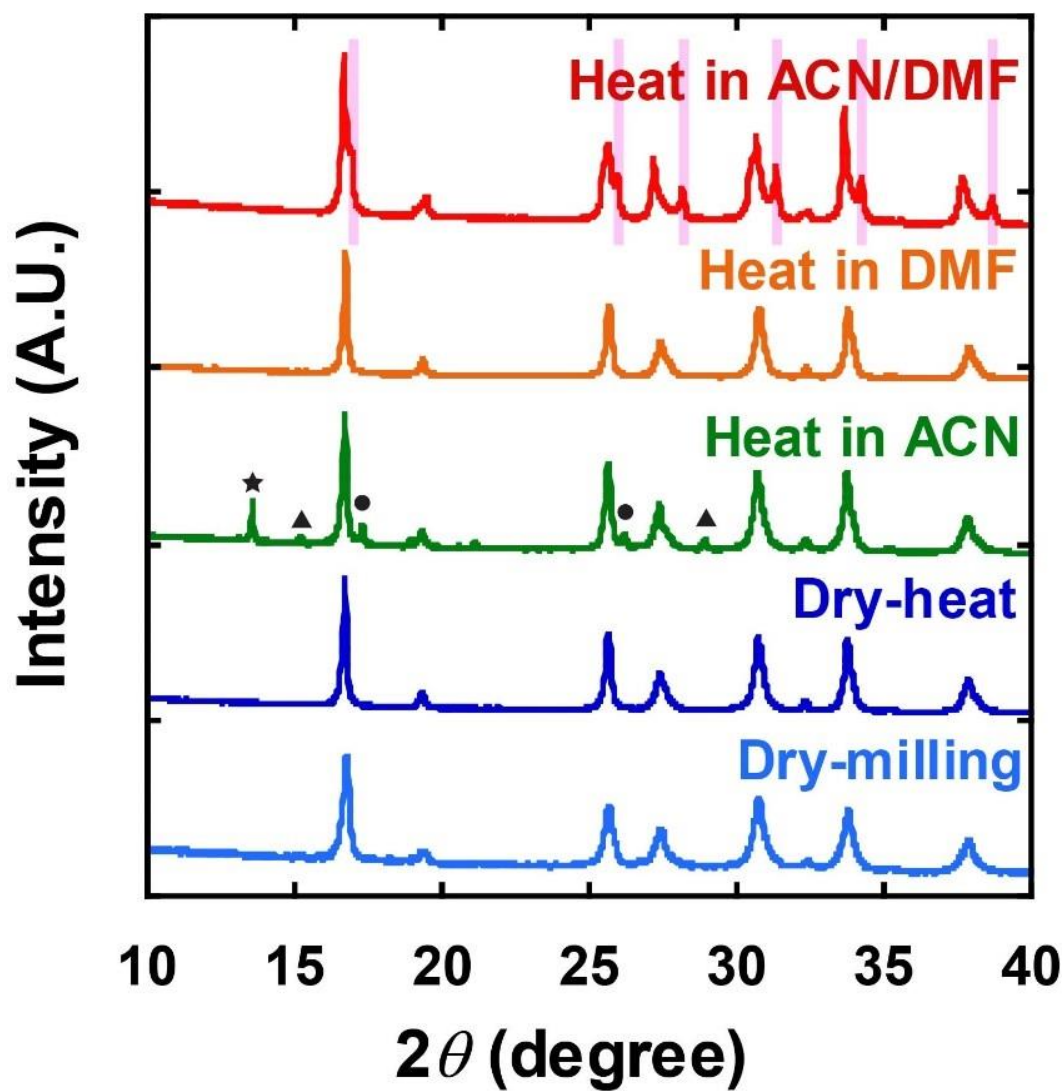


Figure S3-3: XRD patterns for LLZO powders that being dry-milled, dry-heated and heated in acetonitrile, dimethylformamide, and acetonitrile/dimethylformamide transient solutions at 100 °C for 30 hours. (shaded area for heated in ACN/DMF: tetragonal phases; ● : $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, ▲ : $\text{Li}_6\text{Zr}_2\text{O}_7$, ★ : $\text{LiLa}(\text{CO}_3)_2$).

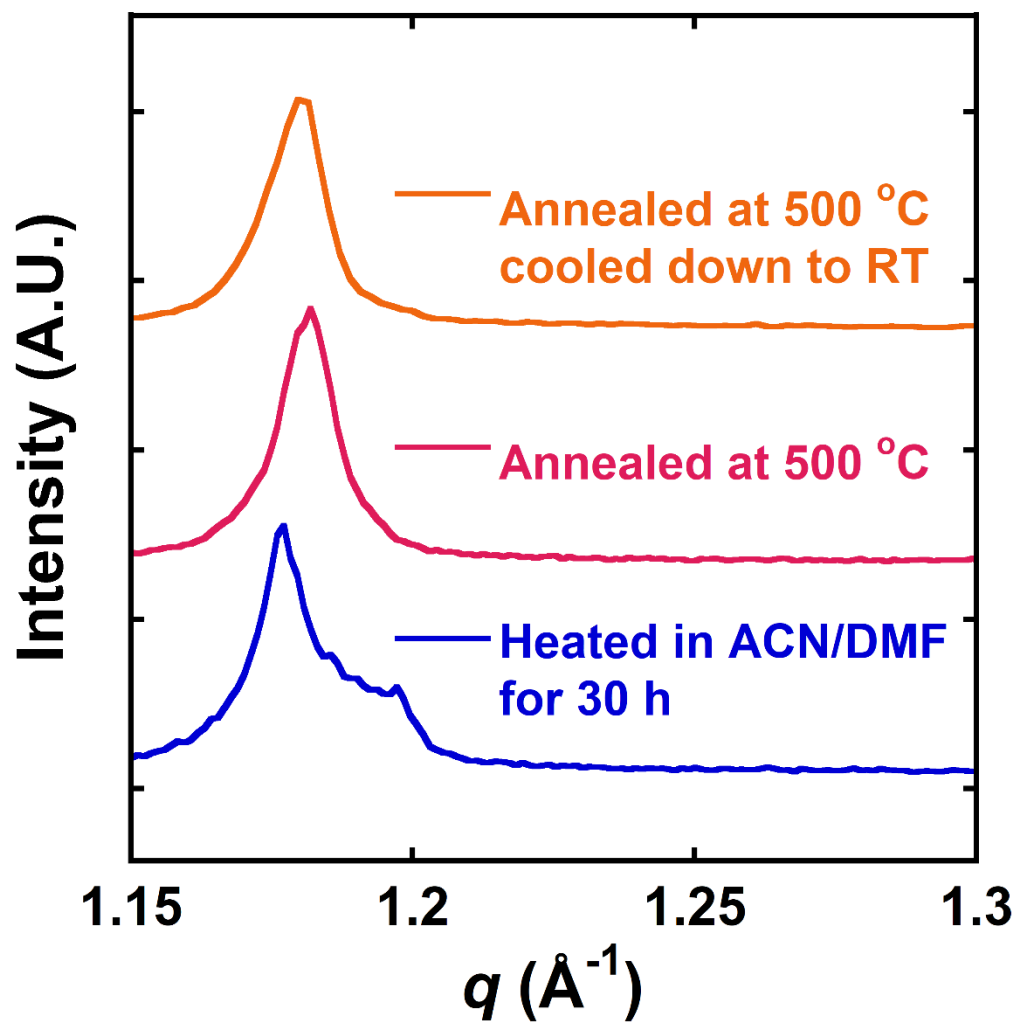


Figure S3-4: XRD patterns for pristine LLZO powders treated in ACN/DMF solutions at 100 °C for 30 h to form tetragonal crystalline phases. LLZO powders show cubic crystalline phases after being annealed at 500 °C and cooled down to room temperature, indicating the stabilization of c-LLZO.

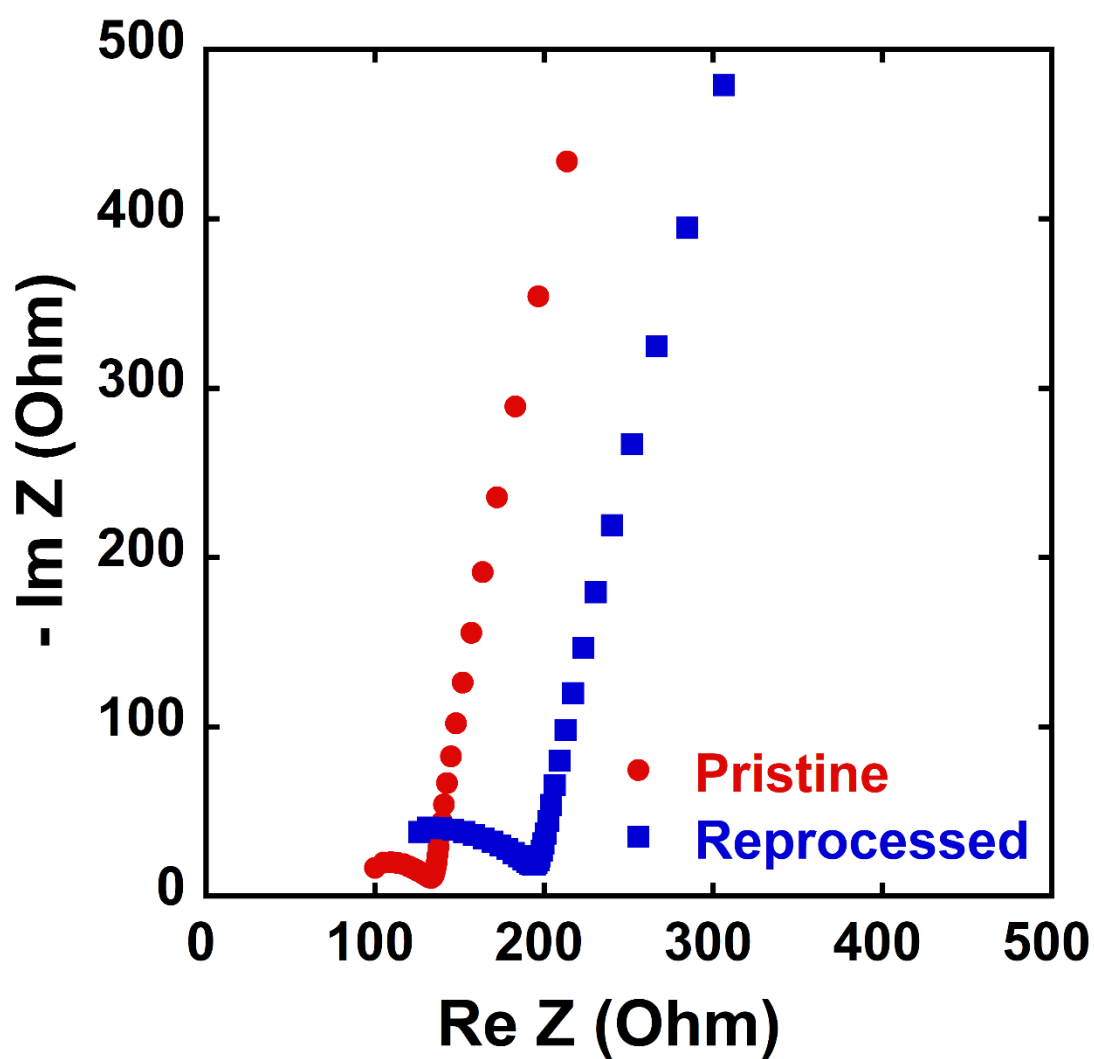


Figure S3-5: Nyquist plot from impedance measurements indicates the retention of ionic conductivity of one-time reprocessed LLZO-PPC-LiClO₄.

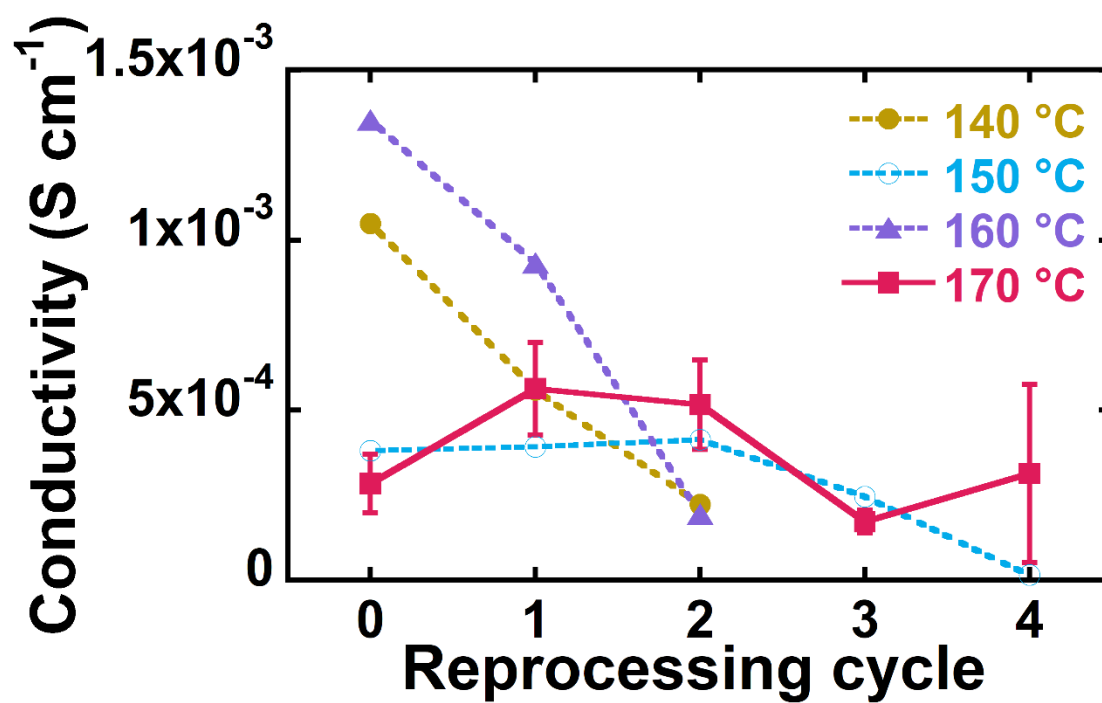


Figure S3-6: Ionic conductivities and relative densities of reprocessed LLZO-PPC-LiClO₄ composite electrolytes heat-treated at different temperatures.

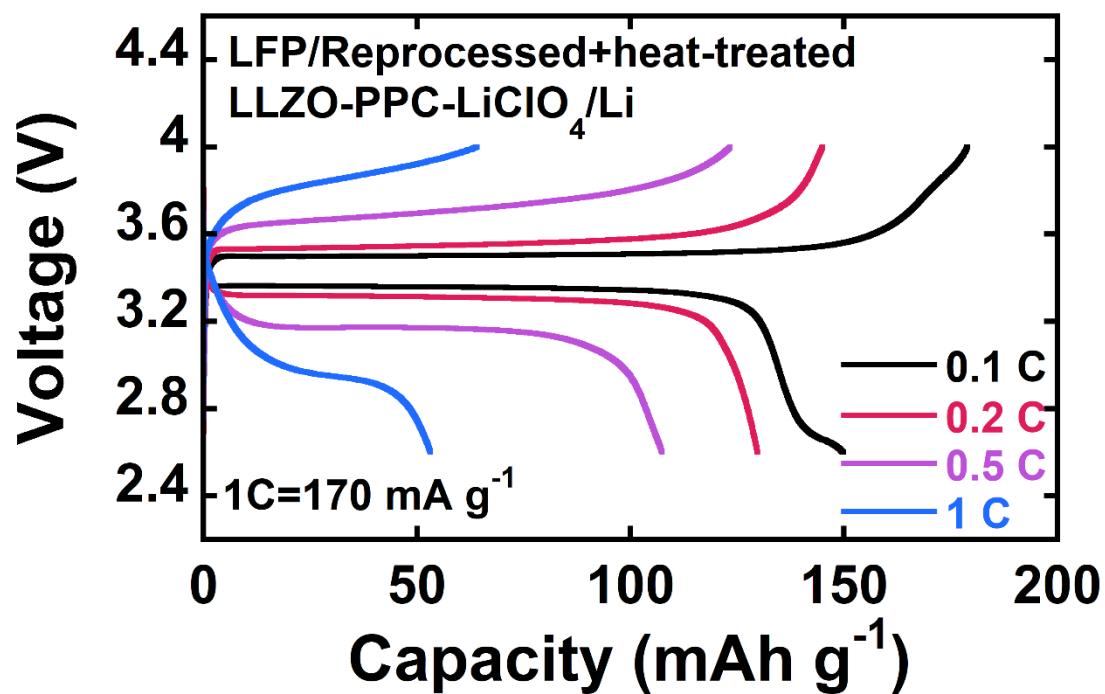


Figure S3-7: Charge and discharge profile of all-solid-state batteries, LFP/reprocessed+heat-treated LLZO-PPC-LiClO₄/Li, at room temperature.

Life Cycle Assessment (LCA)

Data for the environmental impact of acetonitrile (ACN) and dimethylformamide (DMF) was found using the process background data ecoinvent. The energy for cold sintering was calculated using the equations below. For both the pristine material and recycle calculation, the process above was modeled into OpenLCA, using the available processes in the ecoinvent database. The processes for the production of PPC, LLZO, and LiClO₄ were not available in the ecoinvent database, thus these activities were created using available literature and patents.^{[76],[77],[78]}

We define our system as the solid electrolytes whose geometry is set by the press and plates that apply heat and pressure for our cold sintering process. The plates on the top and bottom apply pressure and heat uniaxially and simultaneously. We use our control volume and calculate the energy balance as $\Delta U = Q + W$, where ΔU is the change in internal energy of our solid electrolytes, Q is the heat applied and W is the work due to the applied pressure.

We calculate the heat applied as $Q = \sum m_i C_{p,i} \Delta T + m_i \Delta h_{latent,i}$, where m_i and $C_{p,i}$ are the mass and heat capacity of the individual components of the composite electrolyte and transient solvent, respectively. The change in temperature ΔT is from room temperature to the cold sintering temperature. Any latent heats associated with phase transitions are accounted by $\Delta h_{latent,i}$.^{[77],[84],[85]} Thus, we ignore heat losses to the environment during the cold sintering process; this is a necessary assumption given the variability of processing equipment that might be used in a final manufacturing application.

The work associated with cold sintering is calculated as $-P\Delta V$, with P as the applied pressure during cold sintering and ΔV the resulting compaction from powder to sintered solid electrolyte.

Chapter 4

Interfacial Layers to Enable Recyclability of All-Solid-State Lithium Batteries

4.1 Overview

All-solid-state batteries provide opportunities for safe and robust energy storage solutions. An emerging issue is the final disposal of spent batteries due to the required production scale, limited lifetime, and lack of recycling methods. Here, we propose an architectural design for recyclable all-solid-state lithium batteries based on interfacial layers at the electrodes. Flexible lithium bis(fluorosulfonyl)imide doped polypropylene carbonate (PPC-LiFSI) interfacial layers improve physical contacts at Li metal and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)-based composite electrolytes interfaces, and serve as sacrificial layers to enable clean separation and direct recycling. Recovered components demonstrate the preservation of electrochemical properties through direct reintegration into batteries. Fully recovered full cells with Li-metal and LTO anodes show 92.5 % and 93.8% of original discharge capacity at 0.05 C and room temperature. We demonstrate an approach for the design of recyclable all-solid-state lithium batteries to fulfill long-term goals for sustainable energy storage devices.

4.2 Introduction

The development of all-solid-state batteries is driven by the need to enhance electrochemical performance, lifespan, and safety in energy storage devices.^[24b, 86] Replacing conventional liquid electrolytes with solid alternatives mitigates the risks associated with leakage and flammability. Moreover, the inherent mechanical strength and electrochemical stability of solid-state electrolytes augments the structural stability and operating voltage window.^[19b, 87] These characteristics enable the safe use of lithium metals anodes in all-solid-state batteries with improved energy density and longevity, even after long-term charge and discharge cycles.^[88]

The increasing demand for lithium-ion batteries in portable consumer electronics and sustainable transportation are pushing the limit of raw material availability and resulting in substantial growth in waste that is generated as batteries reach end-of-life.^[89] Improper disposal and inadequate recycling practices pose risks to human health and threaten ecosystems and wildlife due to hazards associated with lithium, cobalt, and other heavy metals.^[90] The development of efficient and sustainable recycling processes is essential to reduce the environmental impact of the green energy revolution and enable circularity for valuable battery materials. As the consumption of lithium-ion batteries continues to grow, the management of spent batteries must be addressed to minimize their negative environmental impact and promote a more sustainable approach to energy storage technology.

Although efforts to recycle batteries continues to grow, few recycling strategies exist for solid state batteries. Current adopted lithium-ion battery recycling focuses on the recovery of a few key materials, such as lithium, cobalt, nickel, and other metals.^[91] This recycling involves using a combination of energy intensive mechanical separation, pyrometallurgy, and hydrometallurgy processes to chemically breakdown battery components into simple precursors that can be recycled in production of new batteries.^[65, 92] Nevertheless, these traditional recycling processes may not be

sustainable when considering energy and material input costs and production of hazardous wastes.^[93] In addition, traditional recycling methods may not be suitable for all-solid-state lithium batteries, as the inclusion of solid electrolytes brings additional challenges in recycling due to their unique battery architecture and chemistries.^[5b, 94] The diversity of designs and chemistries among different all-solid-state batteries also complicates the development of a universal recycling approach. As a result, developing recycling processes that can accommodate this variability while ensuring efficient resource recovery remains a substantial obstacle.

A more sustainable way to address spent all-solid-state batteries is through direct recycling, which avoids chemically breaking down battery components and lowers processing costs by minimizing material lost and energy inputs.^[5b, 95] This approach has not been demonstrated on all-solid-state batteries, likely because of the implementation of solid electrolytes. Compact microstructures play an important role dictating cycling performance. The intimate contacts at solid–solid interfaces, however, complicate the separation process, resulting in a mixture of electrolyte and electrode powders. To achieve a balance between intimate contacts and easy separation, one approach to enable recycling could be to engineer interfaces between the electrode and electrolytes that promote separation when needed.

Interfacial engineering has been explored for many years to tune the interfacial chemistry between electrodes and electrolytes and ensure effective contacts, low interfacial resistance, and high stability.^[96] Various strategies have been employed, including using anodes with Li-containing alloys^[97], and introducing buffer layers by depositing inorganic metallic oxides^[98], non-metallic element interlayers^[99], and gel electrolytes^[100]. Batteries with engineered interfaces introduce greater complexity in battery fabrication, which could present additional challenges in recycling. Nevertheless, one approach to enable effective recycling could be to engineer interfaces between the electrode and electrolytes that promote separation on demand.

Here, we propose an architectural design for recyclable all-solid-state lithium batteries by introducing interfacial layers at electrode interfaces to allow intimate contacts while facilitate separation during recycling. To demonstrate the applicability of this strategy, flexible lithium salt doped polypropylene carbonate (polymer-salt) interfacial layers were introduced at electrode contacts in all-solid-state batteries. The flexible polymer-salt films promote interfacial contacts between LLZO composite electrolytes and Li metal. The removal of polymer-salt layers facilitates the component separation process, allowing for direct recycling. Full cells with recycled components show good cycling performances, indicating the viability in recycling spent batteries. We provide a new structural design for recyclable batteries and an approach to promote the sustainability of energy storage technologies.

4.3 Experimental Methods

Fabrication of Polymer-Salt Interfacial Layers

Lithium bis(fluorosulfonyl)imide (LiFSI) (Sigma Aldrich, ultra dry, 99.9% trace metals basis) (Sigma Aldrich, battery grade, dry, 99.99% trace metals basis) and polypropylene carbonate (Sigma Aldrich, average $M_n \sim 50,000$ Da) were dissolved in acetonitrile (ACN, Sigma Aldrich, anhydrous) with a ratio of 1:2:12 by mass under argon atmosphere ($O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm). The polymer-salt solution was deposited on Aclar sheets ($46.5 \mu L/cm^2$), dried and stored at the room temperature. Polymer-salt thin films can be easily released from the substrates for further use.

Fabrication of LLZO-PPC-LiClO₄ Solid-State Electrolyte Composites (LLZO-SE)

$\text{Li}_{7-2x+y}\text{Mg}_x\text{La}_{3-y}\text{Sr}_y\text{Zr}_2\text{O}_{12}$, (LLZO, $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.5$, NGK Spark Plug Co., Ltd, particle size $\sim 1 \mu\text{m}$) powders were mixed with polymer-salt solution and N, N-Dimethylformamide (DMF, Sigma Aldrich, anhydrous) (12:2.5:1 by mass) using a mortar and a pestle. The mixture was introduced into a hardened steel pressing die with a diameter of 13 mm and underwent the cold sintering process by being pressed and sintered under a uniaxial pressure of 100 bar at 100 °C for 1 h. To ensure uniform sintering temperature, two heating platens and a band heater were used to encircle the die to prevent any temperature variations. As the temperature dropped below 50 °C, as-prepared composite electrolytes were released. All the preparation processes were performed under an argon atmosphere.

Material Characterization

The crystal structure and secondary phases of battery components were analyzed by X-ray diffractometry (Malvern Panalytical Empyrean, Cu K α radiation, 40 kV, 40 mA). Collected spectra were analyzed using MDI JADE. Field emission scanning electron microscope and energy dispersive spectrometer (FE-SEM and EDS, Verios G4, Thermo Scientific) were performed to characterize the surface morphology, cross-sectional structures, and elemental mapping of battery components. Fourier-transform infrared spectroscopy (FTIR) was carried out using a Bruker Vertex 80 spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Physical Electronics VersaProbe III instrument equipped with a monochromatic Al K α x-ray source ($h\nu = 1486.6 \text{ eV}$) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons ($<5 \text{ eV}$) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu (Cu 2p $_{3/2} = 932.62 \text{ eV}$, Cu 3p $_{3/2} = 75.1 \text{ eV}$) and Au foils (Au 4f $_{7/2} = 83.96$

eV). Peaks were charge referenced to CH_x band in the carbon 1s spectra at 284.8 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the X-ray cross section and inelastic mean free path of the electrons. On homogeneous samples, major elements (>5 atom%) tend to have standard deviations of $<3\%$ while minor elements can be significantly higher. The analysis size was $\sim 200\ \mu\text{m}$ in diameter. Tensile properties of PPC-LiFSI were determined following ASTM D638 Type V using an Instron 5943 (100 N load cell) at $10\ \text{mm min}^{-1}$. The cross-sectional area (thickness and width) was measured with digital calipers prior to deformation. The tensile results are reported as engineering stress and strain to determine the Young's modulus, ultimate tensile stress, strain at break. The tensile properties were all tested multiple times ($n = 3$) and averages are reported.

Fabrication of All-Solid-State Batteries and Electrochemical Tests

Anode discs were punched from single side laminated lithium copper foils (MSE Supplies, thickness of lithium and copper ~ 40 and $11\ \mu\text{m}$, respectively) and single-sided $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) copper sheets (NEI corporation, tape thickness $\sim 60\ \mu\text{m} \pm 12\ \mu\text{m}$). Cathode discs were cut from single side coated LiFePO_4 (LFP) sheets (MTI Corporation, coating thickness $\sim 68\ \mu\text{m} \pm 10\ \mu\text{m}$). Before full cell assembly, surface oxides were scratched off from lithium discs by razor blades to show metallic surface. LTO and LFP electrodes are heated at $100\ ^\circ\text{C}$ for over 1 hour under argon environment. For the fabrication of Li symmetric cells, composite electrolytes were placed between two Li metal discs with and without the introduction of polymer-salt films at the interfaces. To fabricate LFP/i/LLZO-SE/i/Li and LFP/i/LLZO-SE/i/LTO full cells, polymer-salt thin films were placed on electrodes along with the addition of 4M LiFSI/dimethoxyethane (DME) solution (5.97

and $3.98 \mu\text{L}/\text{cm}^2$ on the anodes and cathodes surfaces, respectively) to wet the surfaces. LLZO-SE were sandwiched between thin-film modified LFP cathodes and Li or LTO anodes. The assembled full cells were sealed in CR2032 coin cells for further characterization. Galvanostatic cycling tests were carried out in the voltage range from 2.7 to 4.0 V vs. Li^+/Li for LFP/i/LLZO-SE/i/Li and 0.6 to 2.8 V vs. Li^+/Li for LFP/i/LLZO-SE/i/LTO cells using a Neware CT-4008 battery testing system. The charging and discharging current densities were determined from the theoretical capacity of LFP cathodes, 170 mAh g^{-1} . Electrochemical impedance spectroscopy (EIS, ModuLab XM MTS) measurements were performed in a frequency range of 0.1 to 10^6 Hz with a 10-mV amplitude. Zview was used to analyze obtained spectra and produce equivalent circuit models.

Recovery Process

Cycled full cells were opened using a lineman's plier and a diagonal plier. Stainless steel spacers and springs were removed. Full cells were delaminated by soaking in DMF to dissolve polypropylene carbonate and lithium perchlorate that doped in LLZO and polymer-salt films. Recovered components were further soaked in DMF and followed by dimethoxyethane (DME) to remove residuals and contaminants. After being dried at the room temperature overnight under argon environment, recovered components will undergo direct recycling process by assembling a new battery with the incorporation of recovered components.

4.4 Results and Discussion

All solid-state batteries that incorporate lithium iron phosphate (LFP) cathodes, $\text{Li}_{7-2x+y}\text{Mg}_x\text{La}_{3-y}\text{Sr}_y\text{Zr}_2\text{O}_{12}$ -polypropylene carbonate-lithium perchlorate solid composite electrolytes (LLZO-SE), and Li metal or lithium titanate (LTO) anodes are chosen to demonstrate

recyclability. The composite electrolyte, LLZO-SE, was fabricated using the cold sintering process, which enables densification of composites comprised of ceramics, polymers, and salts at a low temperature with the addition of applied pressure and transient solvents.^[71b, 101]

The interface between Li metal anodes and LLZO solid electrolytes plays an important role in determining the cycling performance due to the lithiophobic nature of the LLZO surface, which can lead to poor physical contacts and high interface resistance.^[96a, 102] Strategies such as surface modification and interfacial engineering have been applied to improve the wettability and interface contacts.^[103] We introduce a soft polymer-salt layer, polypropylene carbonate-Lithium bis(fluorosulfonyl)imide (PPC-LiFSI), to bridge solid-solid interfaces and enable lithium-ion transport between electrode and electrolyte.

The polymer-salt layer, PPC-LiFSI, is transparent and flexible with an average thickness of $102 \pm 2 \mu\text{m}$ (Figure S4-1). To measure the ionic conductivity of this layer, we built symmetric cells with PPC-LiFSI in between aluminum blocking electrodes and 4M LiFSI/DME at the contacts. Figure S4-2 shows a Nyquist plot from impedance spectroscopy, from which we obtain an ionic conductivity of $3.9 \times 10^{-3} \text{ S cm}^{-1}$ for PPC-LiFSI at room temperature. We also measured ionic conductivity in PPC-LiFSI from -20°C to 80°C , as shown in Figure S4-3. Temperature-dependent conductivities were fit to the Arrhenius equation, to extract the activation energy (E_a) for ionic conduction of approximately 0.31 eV. As ion transport in polymer-salt films depends strongly on polymer properties, we characterized thermal and mechanical properties of the polymer-salt layers (Figure S4-4). With the incorporation of lithium salt into polypropylene carbonate ($[\text{O}]:[\text{Li}^+]=10:1$), PPC-LiFSI shows a lower glass transition temperature (T_g) around 13.5°C , compared 19°C for pure PPC. The low T_g suggests a high segmental mobility of PPC, which can facilitate lithium-ion transport across the interfacial layer.^[104] The tensile stress-strain curve for dog bone-shaped PPC-LiFSI films, fabricated by drop-casting polymer-salt solution on the substrate and dried in the glovebox, is shown in Figure S4-5, with the corresponding properties shown in Table S4-1. PPC-

LiFSI shows plastic deformation with an ultimate tensile strength of 40 MPa, elongation at break of 113 % and Young's modulus of 1,500 MPa.

To examine the effect of incorporating PPC-LiFSI on interfacial resistance, the performance of Li metal symmetric cells with LLZO composite electrolytes was compared between cells incorporating PPC-LiFSI with 4M LiFSI/DME at interfaces and those without PPC-LiFSI. Figure **4-1(a)** shows the total area specific resistance of half cells with and without PPC-LiFSI layers. Half cells that include polymer thin films show a substantial reduction in the total resistance, which is estimated to be around 208 ohm cm²; whereas half-cells without interfacial modifications have a total resistance around 2.9×10^4 ohm cm². The impedance spectrum of the half cells with interfacial layers was fit using an equivalent circuit model, shown in Figure **4-1(b)**. The first poorly-resolved semicircle at high frequency is attributed to bulk (R_b) and grain boundary ($RCPE_{gb}$) resistances ($\sim 36.07 \Omega$ in total) of the solid electrolyte. The second semicircle has an associated capacitance of 6.21×10^{-6} F, which can be ascribed to the electrolyte-electrode interfaces ($RCPE_{in}$) with an area specific resistance of 94 ohm cm². The third semicircle in the low frequency region with a capacitance of 1.5×10^{-3} F can be attributed to the electrochemical reaction ($RCPE_{ecr}$) at Li metal anode interfaces. The addition of a small amount of 4M LiFSI/DME solution improves the wetting ability of the PPC-LiFSI layer at the Li metal and LLZO-SE interfaces, facilitating enhanced contact between the polymer layers and ceramic particles, leading to more efficient ion transport and a reduction in interfacial resistance (Figure **S4-6**).

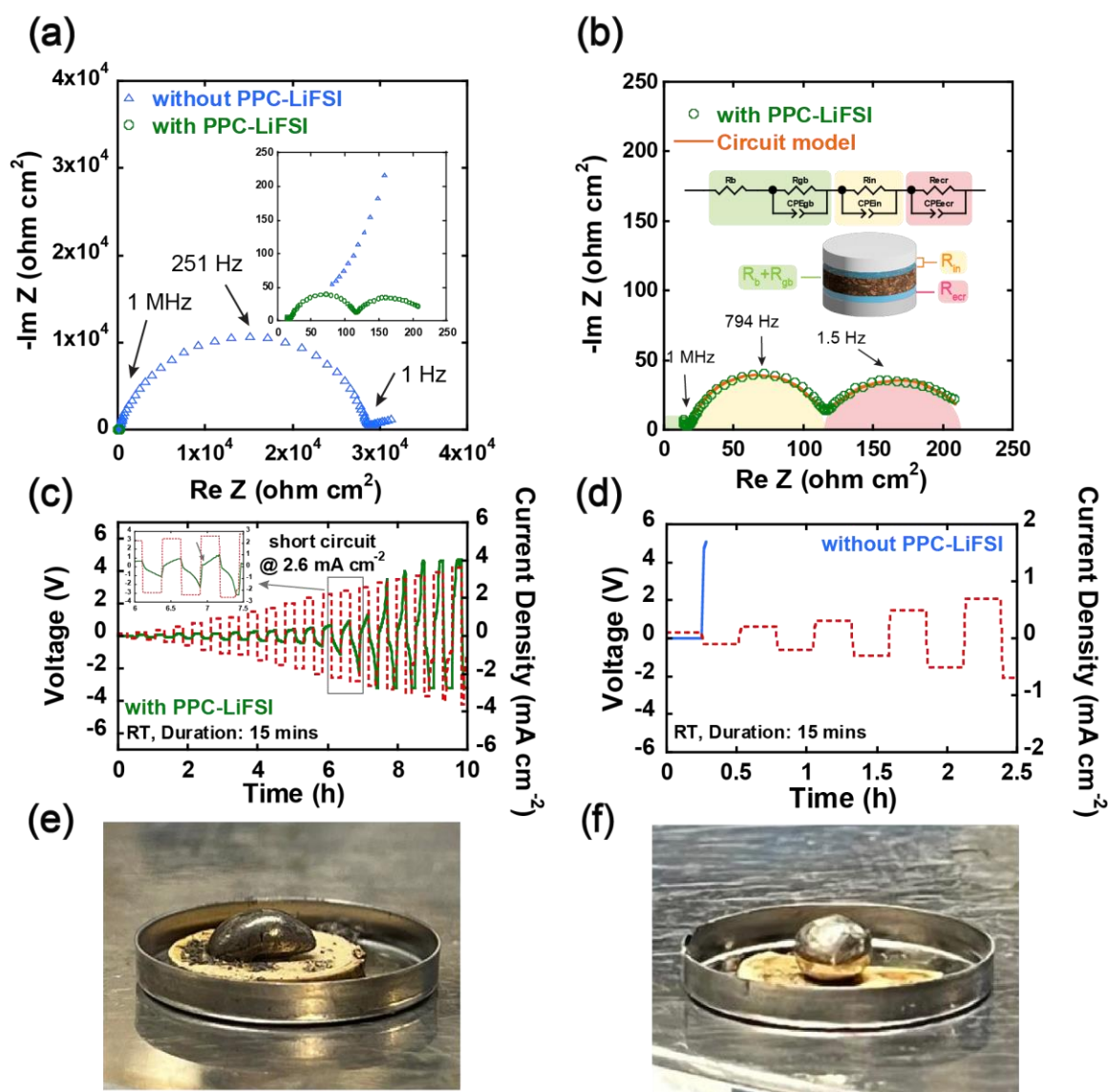


Figure 4-1: Nyquist plots (a) and equivalent circuit model (b) of Li metal symmetric cells with and without PPC-LiFSI layers. Critical current density (c, d) of Li metal symmetric cells and wettability of molten Li metal on the surface of LLZO-SE (e) with and (f) without polymer-salt layers.

The stability of electrode–electrolyte interfaces was assessed by measuring critical current densities (CCD). The rate performances of Li metal symmetric cells were examined at current densities ranging from 0.1 to 4.0 mA cm^{-2} in a time-control manner with a 15 mins duration time at room temperature, as shown in Figure 4-1(c-d). Symmetric cells without PPC-LiFSI layers failed to safely cycle at a current density of 0.1 mA cm^{-2} . The failure mechanism is due to the poor contact

between Li metal and solid electrolytes.^[105] With PPC-LiFSI, the symmetric cell demonstrate a stable polarization increase accompanied with the elevated current densities. A slightly voltage drop at 2.6 mA cm^{-2} implies the occurrence of soft short circuit due to the formation of small dendrites.^[50] The critical current density of symmetric cells with polymer-salt interfacial layers is estimated to be 2.4 mA cm^{-2} , suggesting a stable lithium-ion transport path across electrode interfaces under much higher cycling current densities. To study the effect on the performance of lithium plating/stripping, symmetric cells with PPC-LiFSI interfacial layers, which we denote as Li/i/LLZO-SE/i/Li, were cycled at a current density of 0.2 mA cm^{-2} over long cycles, where 0.1 mAh cm^{-2} capacity of lithium metal was plated/stripped during each cycle (Figure S4-7). The cycling curve shows a stable voltage-time profile with small polarization up to ~ 410 hours, followed by a sharp increase in overpotential probably due to interphase delamination.

To examine the contact between LLZO-SE and Li metal, we examined the wettability by depositing molten lithium (with the oxide layer of Li metal manually removed) on heated LLZO-SE with and without polymer-salt layers on the top. As shown in Figure 4-1(e-f), the composite electrolyte with polymer-salt layers shows a smaller contact angle compared to the one without. Color change of the sample with polymer-salt layers is due to partial degradation of polymer layers at high temperature (above the Li melting temperature $\sim 181^\circ\text{C}$). The high contact angle results from the lithiophobic nature of LLZO against Li-metal; whereas Li metal maintains adherence to the LLZO-SE surface with the presence of soft polymer-salt layers bridging the solid-solid interfaces. This supports the idea that introducing polymer-salt layer promotes intimate contact between LLZO-SE and Li metal that leads to reduced interfacial resistance.

Ion transport across electrolyte–Li metal interfaces is limited by area specific resistances and strongly governs critical current densities. We compare these values with previous results in Figure S4-8.^[54, 100, 106] The inverse correlation highlights the need to control interfacial chemistry to achieve high power density. Our results demonstrate an approach for achieving low area specific

resistance and higher critical current density compared to most of the reported data. Furthermore, our method has advantages related to the use of low-cost materials and low energy-consuming processes (Table **S4-2**).

Full cells with interfacial layers on both cathode and anode side, which we denote as LFP/i/LLZO-SE/i/Li or LFP/i/LLZO-SE/i/LTO, were assembled to test performance, and compared with recycled full cells (see next section). The cyclic voltammogram curves of LFP/i/LLZO-SE/i/Li are shown as Figure **S4-9**. Two characteristic peaks are apparent that correspond to the charge (2.95 V) and discharge (3.77 V) potential of LiFePO_4 . No other redox peak can be observed during the cycling process, which implies that no unexpected side reaction occurred. The three curves nearly overlap, except for the first cycle, which can be attributed to the formation of a solid electrolyte interphase (SEI). This indicates that the polymer-salt layers enable lithium-ion transport along the interfaces while providing excellent reversible behavior and electrochemical stability. Overall, our results demonstrate an approach for bridging the electrolyte-electrode interfaces to achieve low area specific resistance and high critical current density, and as we discuss below, recyclability with the use of low-cost material and low energy-consuming processes.

Pristine full cells were cycled at a certain C-rate until the discharge capacity reached less than 50% of its original discharge capacity (denoted as 50% DCp), after which the full cells underwent recycling (Figure **S4-10**). Nyquist plots of pristine and recycled Li metal-based full cells show a slight increase in the bulk and grain boundary resistance from 36.9 ohm to 53.12 ohm; whereas, the impedance at the interfaces increases from 338 ohm to 3710 ohm, as shown in Figure **4-2(a)**. The occurrence of lithium dendrite growth and the buildup of isolated dead lithium results in volume change within the cell, creating internal stress that leads to the formation of cracks and fractures at the interfaces of the microstructures of solid-state batteries. These structural instabilities obstruct pathways for lithium-ion transport, resulting in elevated interfacial impedance. The failure

of the full cell is dictated by evolution and degradation at interfaces, while the majority of LLZO-SE remain intact.^[107] Therefore, it is conceivable that spent battery components could be recycled without necessitating complex processes once localized interfaces are eliminated.^[108]

Spent batteries were further disassembled and underwent a delamination process where the removal of polymer-salt layers allows the separation and recovery of spent components. Recovered components were then reused and incorporated into a new battery, as illustrated in Figure 4-2(b). Dimethylformamide (DMF), an aprotic solvent, which is compatible with LLZO within a short duration,^[108] was used to dissolve the polymer-salt layer where undesired side reactions and secondary phases occur. In addition, DMF may react with Li metal,^[109] enabling the effective removal of a significant portion of lithium dendrites exposed to the surface of spent LLZO-SE, as depicted in Figure S4-11. Figure 4-2(c) shows optical images of recovered components. Recovered LLZO-SEs show an off-white color with an average recovery rate of around 85-90 wt%, while recovered LFP and recovered LTO have a blackish color with limited amount of weight loss. Although the color difference among recovered components implies an efficient separation, SEM images and elemental mapping analysis on recovered components (Figure S4-12) suggest that trace contamination of recovered electrolytes on recovered electrodes occurs, and vice versa. Even with limited mixing during recovery, we hypothesize that the incorporation and removal of polymer-salt interfacial layers is an effective recovery strategy to effectively avoid the formation of anode-cathode mixtures, otherwise known as black mass.^[5b]

We also examined cycled Li metal anodes. After cycling, Li metal anodes are not uniform (Figure S4-13) when compared to pristine Li metal electrodes with smooth surfaces and small number of defects. This non-flat surface can be attributed to uneven deposition of lithium during cycling. EDS analysis shows that white surface features primarily consist of oxygen and carbon (Figure S4-14).

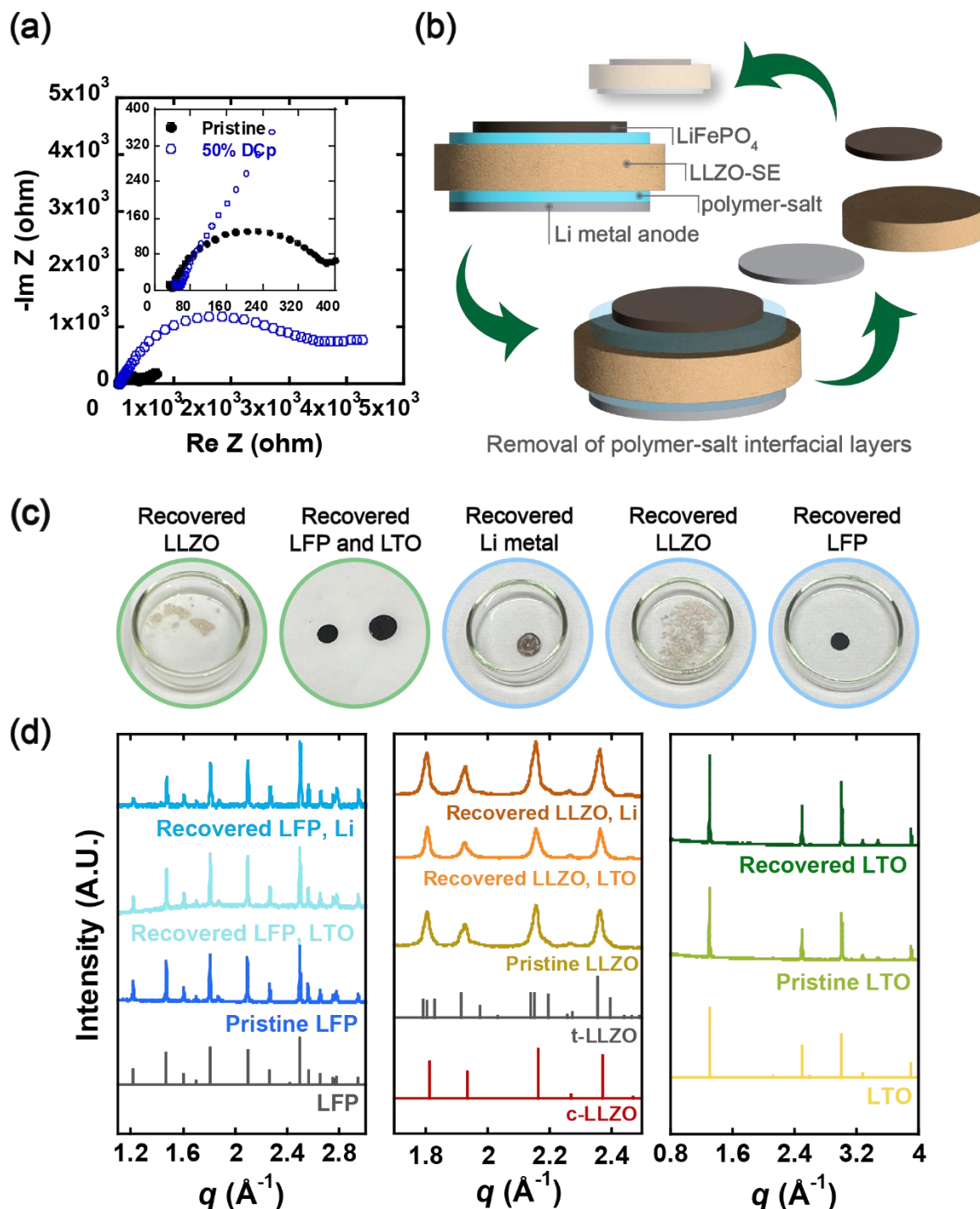


Figure 4-2: (a) Nyquist plots of pristine and cycled LFP/LLZO-SE/Li with discharge capacity lesser than 50% of its original value; Inset: data at high frequency. (b) Schematic illustration of the removal of polymer-salt interfacial layers that enables recyclability of all-solid-state lithium batteries. (c) Recovered components from LTO (highlight in green) and Li (highlight in blue) anode-based full cell. (d) XRD spectra of recovered LFP, LLZO and LTO confirmed that

components recovered from full cell with LTO and lithium Li metal anodes demonstrate a high degree of crystallinity of ceramic materials. Data are shown for pristine materials (pristine LFP; pristine LLZO; pristine LTO), recovered materials from cells containing Li anodes (Recovered LFP, Li; Recovered LLZO, Li) and recovered materials from cells containing LTO anodes (Recovered LLZO, LTO; Recovered LTO). Expected diffraction peaks from reported unit cells are also shown for LFP, LLZO with cubic and tetragonal phases (c-LLZO; t-LLZO) and LTO.

To study the purity and bulk phase of recovered components, recovered LFP, LLZO, and LTO were characterized using XRD, as shown in Figure 4-2(d). Recovered LFP from LTO and Li-based full cells possess olivine crystal structures^[110], with XRD data with larger noise than profiles from pristine LFP due to uneven surfaces after recovery. Recovered LLZO from full cells with LTO anodes demonstrates a cubic crystalline phase with a space group of $Ia-3d$, which is the same as pristine LLZO.^[79] XRD spectra of recovered LLZO from Li metal-based full cell shows a cubic crystalline (c-LLZO) bulk phase; but, minor peaks at 1.98, 2.26, and 2.40 Å⁻¹ suggest the presence of a minor quantity of tetragonal phases (t-LLZO). Although LLZO is reported to be compatible with Li metal, several previous reports proposed that c-LLZO may experience an interfacial cathodic reaction when in contact with Li metal. As the reduction process advances, along with electron transfer, lithium ions diffuse from Li metal into c-LLZO in order to maintain charge balance. The increase in Li content could energetically favor a structural transition from the cubic to the tetragonal phase.^[69] This t-LLZO interface is approximately 6 nm thick, and may not be perceptible with the use of X-ray diffraction techniques. In the case of recovered LTO, a spinel crystal structure with a space group of $Fd\bar{3}m$, which is the same as pristine LTO, is apparent.^[111] Overall, the absence of any new phases indicates that the recovery process was carried out without degrading the bulk crystal structures of cell components.

To further investigate the occurrence of undesired reactions during recovery, pristine and recovered components from Li metal and LTO anode-based full cells were characterized using FTIR in an attenuated total reflection (ATR) geometry (Figure S4-15). Successful removal of interfacial layers can be confirmed as spectra of recovered components did not show any

characteristic peaks belonging to PPC-LiFSI. Recovered electrodes displayed a similar spectra as pristine ones, implying that there is no perturbation to the chemical structure from the recovery process. Peaks at 3670 cm^{-1} in pristine and recovered LLZO may be attributed to the O–H stretching from lithium hydroxide, a common surface contaminant when LLZO reacts with ambient water.^[112] A higher intensity in the O–H stretching peak in recovered LLZO from the Li metal anode-based full cell can be apparent when comparing to pristine and reprocessed LLZO from an LTO-based full cell. This can be explained by the lithium deposited in the microstructure of recovered LLZO, as lithium metal oxidized to form lithium hydroxide.^[113] We did not detect any peaks from DMF and DME, implying that solvents were not left in the recovered components after direct recovery. Overall, the similar spectra before and after recovery suggests that the recovery process is compatible with battery components.

A post-mortem SEM image of spent LFP/LLZO-SE/i/Li (one PPC-LiFSI layer at the anode interface) reveals that the Al current collector, LFP, and LLZO electrolyte composites have thicknesses of approximately 16.5, 46.2, and $343\text{ }\mu\text{m}$, respectively, and a total thickness of $493\text{ }\mu\text{m}$ (Figure S4-16). Consequently, subtracting the thicknesses of the Li and copper foils, we can estimate the thickness of the interfacial layers in the full cell to be around $36.3\text{ }\mu\text{m}$. SEM images of pristine and recovered electrodes and electrolyte are shown in Figure S4-17. Both pristine and recovered battery components demonstrate similar surface morphologies with no significant change in particle sizes and shapes. Post-mortem X-ray photoelectron spectroscopy (XPS) was performed to study the surface chemistry on recovered LLZO from LTO and Li metal anode-based full cells. The concentrations of elements detected on as received surfaces are shown in Figure 4-3(a). Measurements were conducted at a takeoff angle of 45° relative to the sample surface plane, yielding a sampling depth of 3-6 nm, with 95% of the signal originating from this depth or shallower. The measurement confirmed that the near-surfaces were enriched in Li and O, and depleted in Zr and La for both pristine and recovered LLZO. With a minimal amount of La and Zr detected, Li

and O appearing at the near-surfaces can be ascribed to LiOH. This confirms the presence of larger amounts of oxide on surfaces of recovered LLZO from Li metal anode-based full cells, probably due to the oxidation of deposited lithium dendrites.^[114] In the C 1s XPS spectra (Figure 4-3(b)), a stronger CO₃ peak was observed in recovered LLZO from Li-based full cell than the pristine state, which can be attributed to Li₂CO₃, resulting from the reaction between LiOH and CO₂. Recovered LLZO from an LTO-based full cell shows a higher amount of C, which mostly can be attributed to C-C bonds according to the C 1s spectra. The source of carbon may come from the carbon additives in LTO anodes. Figure 4-3(c) shows the depth profile of the concentration of Li, La, Zr, O, and C as a function of sputtering depth from recovered LLZO from a Li-based full cell. Depth profiles confirmed that the near-surfaces were enriched in Li and depleted in Zr. Oxides and carbonates concentrate at 0-6 nm beneath the surface, suggesting the existence of an uppermost layer comprised of LiOH and Li₂CO₃. Carbonates decrease gradually reaching the minimum concentration at about 41 nm, indicating the native oxide/hydroxide layers of LLZO with a thickness of around 35 nm. The increase in Zr and La contents and decrease in both carbonate and Li oxide/hydroxide concentrations as sputtering depth increases suggests the bulk phase of pristine LLZO. The concentration with depth is summarized in Figure 4-3(c). These findings show the surface of recovered LLZO is covered with contaminants formed during recycling.

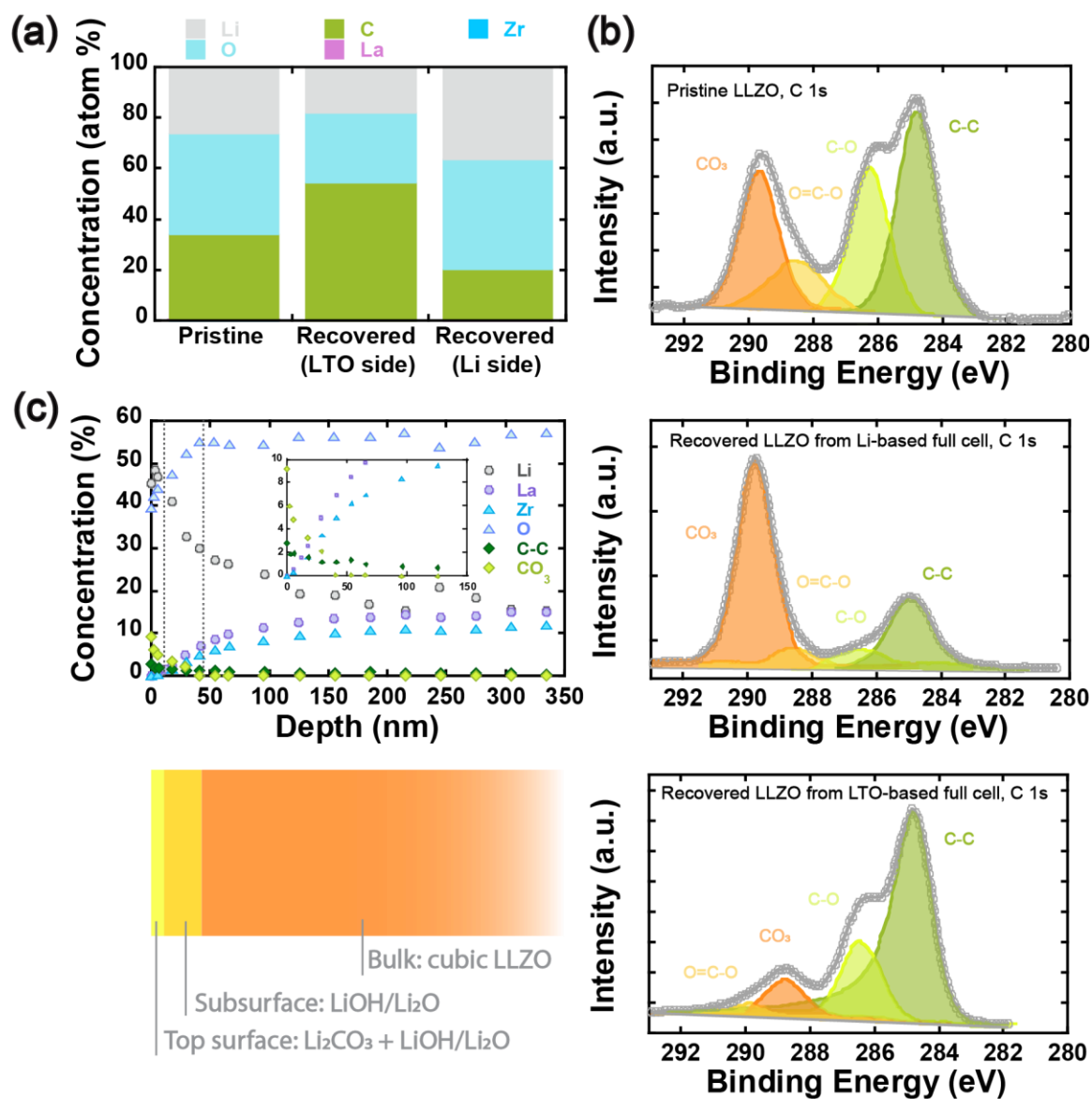


Figure 4-3: Post-mortem XPS analysis of (a) concentration of elements and (b) C 1s XPS Spectra of pristine and recovered LLZO (c) depth profile of recovered LLZO from Li-based full cell.

Recovered LLZO was reprocessed by cold-sintering, which in our previous work demonstrates the ability to fix fragmented microstructures and re-integrate LLZO with polymer and lithium salts to form a dense bulk phase.^[108] To evaluate the electrochemical performance and stability of recovered components, fully recycled all-solid-state batteries were fabricated by integrating recovered components (fully recycled LFP/i/LLZO-SE/i/Li is incorporated with recovered LFP and recovered LLZO-SE; fully recycled LFP/i/LLZO-SE/i/LTO is incorporated with recovered LFP, recovered LLZO-SE, and recovered LTO). Figure **4-4(a)** shows Nyquist plots of the pristine and fully recycled LFP/i/LLZO-SE/i/Li, where high-frequency semicircles and a low-frequency spike can be observed. Both demonstrate similar grain boundary resistances, approximately 22.5 ohm and 38.7 ohm, respectively. Fully recycled LFP/i/LLZO-SE/i/Li shows a significant decrease in the interfacial resistance around 409 ohms after recycling compared to cycled full cells (Figure **4-2(a)**). This suggests that the removal of polymer-salt layers during the separation process enables the elimination of most of electrochemical byproducts localized at interfaces. Solid-state electrodes and electrolytes remain electrochemically functional after cycling. Thus, we hypothesize that we can reuse battery components without undergoing complicated recycling processes and demonstrate recycling of full cells.

Figure **4-4(b)** illustrates the rate performance and coulombic efficiency of pristine and fully recycled LFP/i/LLZO-SE/i/Li at various C rates at room temperature. For a loading of LFP (1 C = 170 mAh/g_{LFP}) of around 0.012 g cm⁻², the current density at 1 C is 0.58 mA cm⁻². Pristine full cells show a discharge capacity of 160 and 154 mAh g⁻¹ at 0.1 and 0.2 C, while fully recycled LFP/LLZO-SE/Li cells show an average discharge capacity of 148 and 121 mAh g⁻¹, demonstrating a recovery of 92.5 and 78.6% of the original capacity, respectively (Figure **4-4(b)**).

The cycling stability of pristine and fully recycled LFP/i/LLZO-SE/i/Li at 0.1 C at room temperature is shown in Figure **S4-18**. Pristine full cell shows a stable cycling performance over 32 cycles with a discharge capacity of 109 mAh g⁻¹ with a Coulombic efficiency of 90 % and a

capacity retention rate of 74 %. Similar cycling performance is observed for the fully recycled full cell, with stable retention performance and a discharge capacity of 106 mAh g^{-1} with a Coulombic efficiency of 92 % and a capacity retention rate of 70 % after 30 cycles.

This implies retention of electrochemical properties in recovered components due to the elimination of most secondary phases at interfaces, regardless of the limited presence of contaminants. The decrease in discharge capacity may result from a surface contaminant, specifically lithium hydroxide. Although lithium hydroxide was found to be present on surfaces, recycling mixes surface and bulk layers and embeds LiOH into the bulk phase during cold sintering. Thus, the presence of lithium hydroxide with low ionic conductivity may explain the lower discharge capacity in fully recycled LFP/i/LLZO-SE/i/Li.

Charge and discharge curves of the pristine and fully recycled LFP/i/LLZO-SE/i/Li full cell at various C rates are shown in Figure 4-4(c-d). Both cells exhibit a flat discharge plateau at 0.1 and 0.2 C, while fully recycled LFP/i/LLZO-SE/i/Li shows a higher charge/discharge potential gap of 0.24 V compared to 0.22 V for pristine devices. The increase in voltage difference and loss in cycling stability can be attributed to the presence of oxides in recovered components. The non-conductive phases may hinder ion transport pathways, leading to an increase in Ohmic resistance and polarization in the full cell. This phenomenon will become more pronounced during cycling at elevated C rates or over extended cycling periods. An inhomogeneous distribution of applied current density may facilitate growth of lithium dendrites and degrade electrochemical properties.^[115]

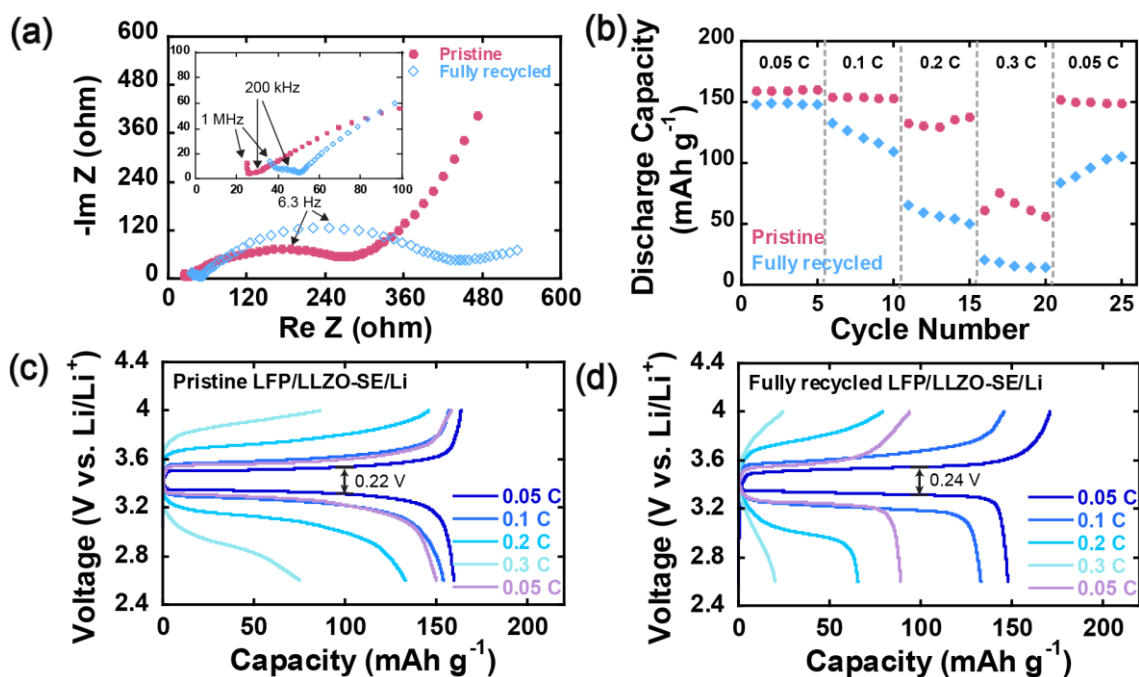


Figure 4-4: (a) Nyquist plots of pristine and fully recycled LFP/LLZO-SE/Li. The inset depicts the high-frequency region of the plots. (b) Rate performance and (c-d) galvanostatic charge and discharge curves of pristine and fully recycled LFP/LLZO-SE/Li at room temperature.

To demonstrate that the recyclability of all-solid-state lithium batteries is not limited to Li metal anodes, pristine and fully recycled LTO anode-based full cells were evaluated, as shown in Figure 4-5. Pristine LFP/i/LLZO-SE/i/LTO were cycled at a certain C-rate until the discharge capacity reached $\leq 50\%$ of its original discharge capacity. Nyquist plots of pristine and cycled LFP/i/LLZO-SE/i/LTO is shown in Figure S4-19, demonstrating a similar total impedance of bulk and grain boundaries of LLZO-SE around 53 and 43 ohm, while a large increase in interfacial resistance from 416 to 2480 ohm is apparent after cycling. This implies that LLZO-SE remains mostly intact while electrochemical byproducts tend to concentrate at interfaces. The separation process is shown in Figure S4-20, which highlights the efficient and successful separation of spent LFP, LLZO-SE and LTO.

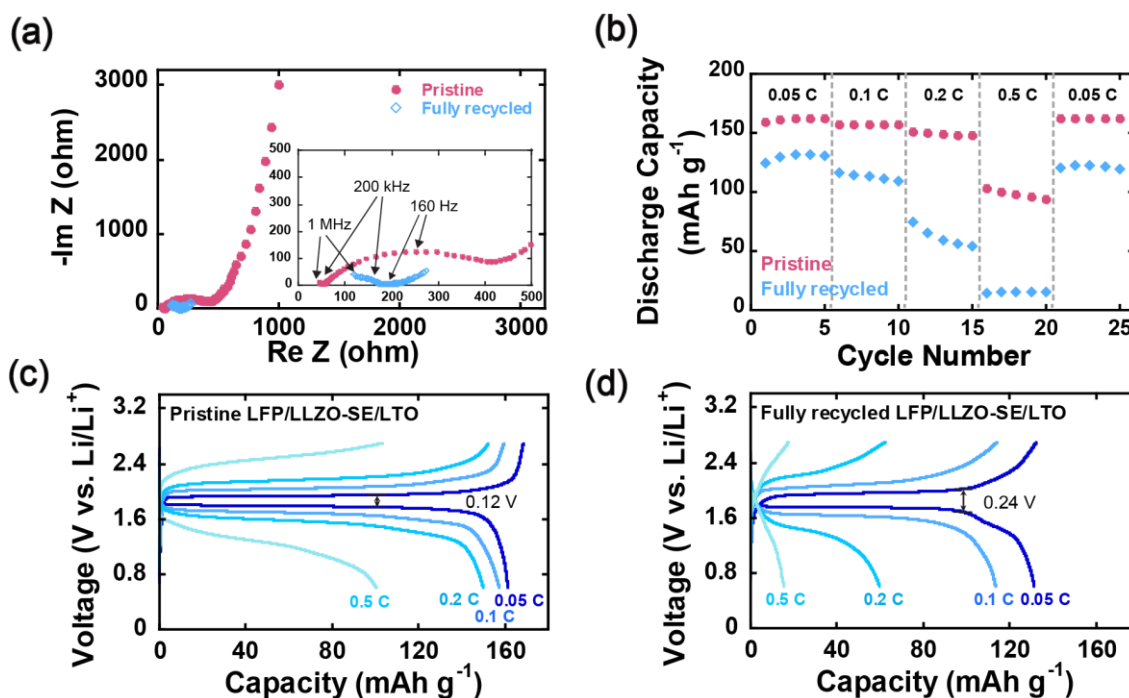


Figure 4-5: (a) Nyquist plots of pristine and fully recycled LFP/LLZO-SE/LTO. The inset depicts the high-frequency region of the plots. (b) Rate performance and (c-d) galvanostatic charge and discharge curves of pristine and fully recycled LFP/LLZO-SE/LTO at room temperature.

Fully recycled, LTO-based full cells were fabricated with the use of recovered battery components and compared with pristine full cells. Given that recovered electrodes did not undergo further processing to maintain compactness, cold sintering was used to co-sinter recovered electrodes with recovered LLZO powders to form compact tri-layer microstructures, denoted as LFP/LLZO-SE/LTO. Figure 4-5(a) presents the Nyquist plots of fully recycled LFP/LLZO-SE/LTO, which displays a total impedance of bulk and grain boundaries of LLZO-SE at 115 ohm and an interfacial impedance of 128 ohm. A noticeable reduction in the interfacial impedance between electrolyte and electrode is evident when compared to the cycled full cell (Figure S4-19). This indicates the successful elimination of undesired phases at interfaces during recycling. Nevertheless, the slight rise in total impedance of LLZO-SE suggests the presence of a small amount of contaminants.

The cycling performance of LTO-anode based full cells with interfacial layers at room temperature is shown in Figure 4-5(b-d). The rate performance of pristine and fully recycled LTO anode-based full cells (denoted as pristine LFP/i/LLZO-SE/i/LTO and fully recycled LFP/LLZO-SE/LTO, respectively) at various discharge rates is shown in Figure 4-5(b). Pristine LFP/i/LLZO-SE/i/LTO cells show a better rate performance compared to fully recycled cells, as the discharge capacities that pristine full cell can deliver are approximately 162, 157, and 149 mAh g⁻¹ at 0.05, 0.1, and 0.2 C, respectively. The fully recycled LFP/LLZO-SE/LTO cell can reach to 130, 113, and 62 mAh g⁻¹ at 0.05, 0.1, and 0.2 C, respectively. Approximately 80 % of the original discharge capacity can be recovered at 0.05 C.

The galvanostatic charge/discharge curves of pristine and fully recycled LTO anode-based full cells are shown in Figure 4-5(c-d). The cell voltage difference of the charge and discharge plateau of pristine and fully recycled full cells was approximately 120 mV and 240 mV, respectively. The slightly larger voltage interval of fully recycled LFP/LLZO-SE/LTO indicates higher polarization during the charge-discharge process, which can be attributed to the presence of non-lithium-ion conducting phases in both electrodes and electrolytes. The poorly conducting phases hinder lithium-ion and electron diffusion in fully recycled LFP/LLZO-SE/LTO.

The modest decrease in the electrochemical performance of fully recycled LFP/LLZO-SE/LTO might be a consequence of build-up of contaminants or electrochemical reaction byproducts and the incompact microstructures of recovered electrodes. Calendering is a crucial process to reduce porosity and to improve particles compaction.^[107, 116] As recovered LFP and recovered LTO did not experience any further treatment, the loose packing and inhomogeneity may consequently decrease electrochemical performance. In addition, during the recovery process, exposure to solvents may lead to the formation of poorly conductive oxides, hindering battery performance. Thus, we can attempt to dissolve oxide layers during the recovery process using ethylene carbonate (EC), which can partially dissolve lithium salts at solid electrolyte interfaces,

such as lithium fluoride (LiF), lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3), and lithium oxalate ($(\text{LiCO}_2)_2$).^[117] A full cell with an EC-treated recovered LTO anode shows a discharge capacity of 152, 138, and 88 mAh g^{-1} at 0.05, 0.1, and 0.2 C, respectively (Figure **S4-21**). Approximately 93.8 % of the original discharge capacity (162 mAh g^{-1} for a pristine full cell) can be recovered at 0.05 C. Our preliminary results suggest that with the proper post treatment to remove surface contaminants, recycled battery components can deliver improved electrochemical performance. Future work is needed to optimize recycling strategies.

Regardless of the modest loss in electrochemical performance, fully recycled Li metal and LTO-anode based-full cells deliver nearly the same rate performance as pristine cells, implying the preservation of electrochemical properties in recovered battery components after undergoing recovery and reprocessing. Polymer-salt layers promote contacts at interfaces and facilitate effective separation and recovery of spent battery components, and enable recycling of spent all-solid-state lithium batteries. The architectural design of recyclable all-solid-state batteries with engineered interfaces can be applied on other types of batteries with different chemistries. Overall, we provide an approach and insights on the design of recyclable all-solid-state lithium batteries to promote sustainable energy storage through the incorporation of polymer-salt interfacial layers that promote electrode-electrolyte contact and enable separation and recovery of components. Our work provides insights on the architectural design of recyclable all-solid-state batteries, and offers a scalable and sustainable pathway for managing spent batteries at end of life.

4.5 Conclusion

Here, we propose an approach to enable recycling of all-solid-state lithium batteries by introducing polymer interfacial layers at electrode interfaces. The introduction of interfacial layers provides better solid-solid contacts, improving the wettability of Li metal on LLZO-based electrolytes and lowering the interfacial resistance. The interfacial layers provide an avenue for separations of solid electrolytes and electrodes, which demonstrate the retention of crystalline structure of ceramics with modest degradation and contaminants. This strategy was applied on full cells with Li metal or LTO anodes to highlight the ability to accommodate various types of all-solid-state batteries. Full cells with the incorporation of recycled components were fabricated and cycled to demonstrate modest degradation in electrochemical properties of recycled components. This work provides insights on the architectural design of recyclable all-solid-state batteries, offering a scalable and sustainable pathway for managing spent batteries at end of life.

4.6 Supporting Information

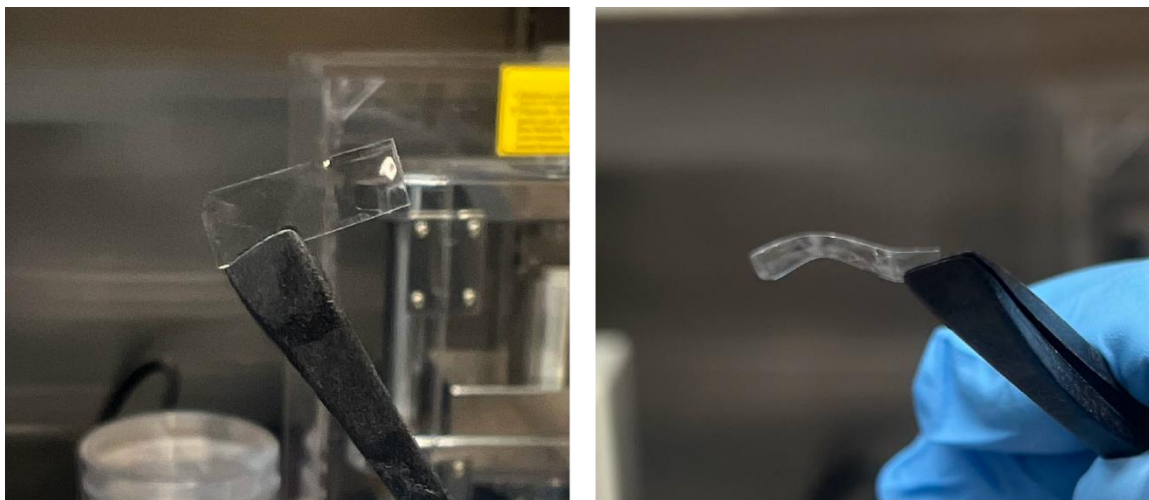


Figure S4-1: Images of the polymer interfacial layers, PPC-LiFSI, illustrating their transparency and flexibility.

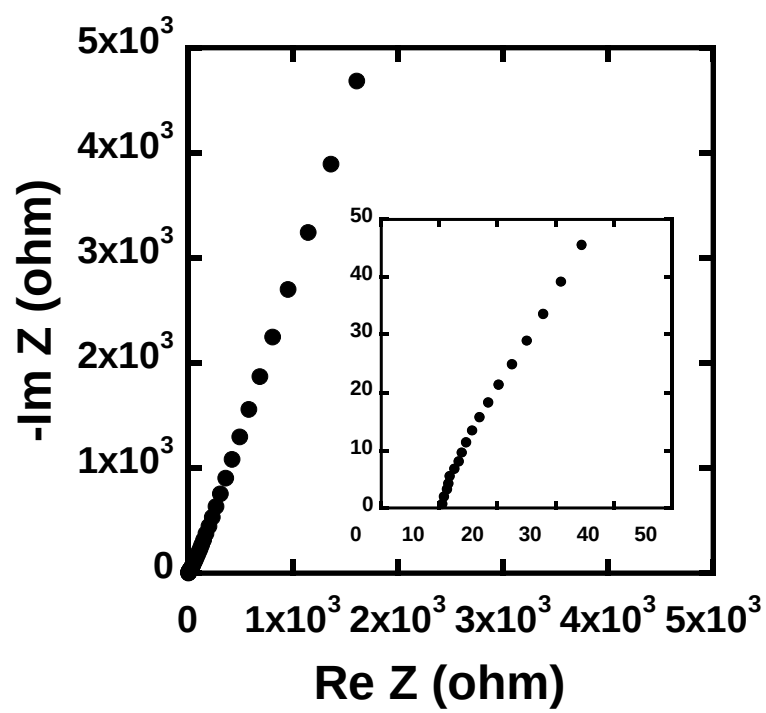
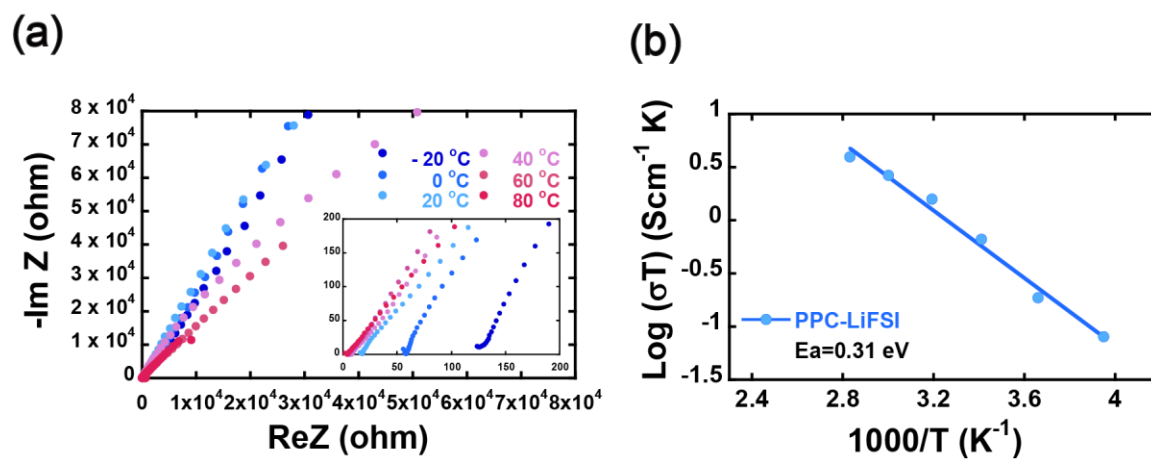


Figure S4-2: Nyquist plot of PPC-LiFSI at room temperature.



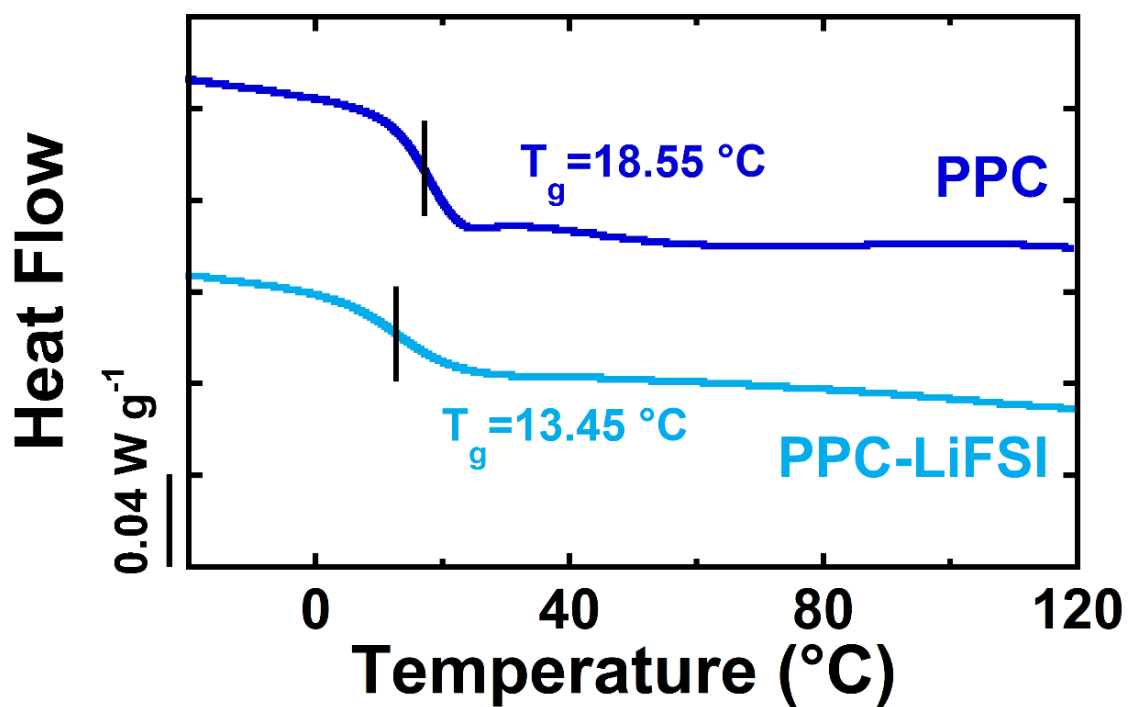


Figure S4-4: Thermograms from differential scanning calorimetry (DSC) of PPC-LiFSI interfacial layer in comparison to pure polypropylene carbonate on heating at 5 °C min⁻¹ from -30 to 120 °C.

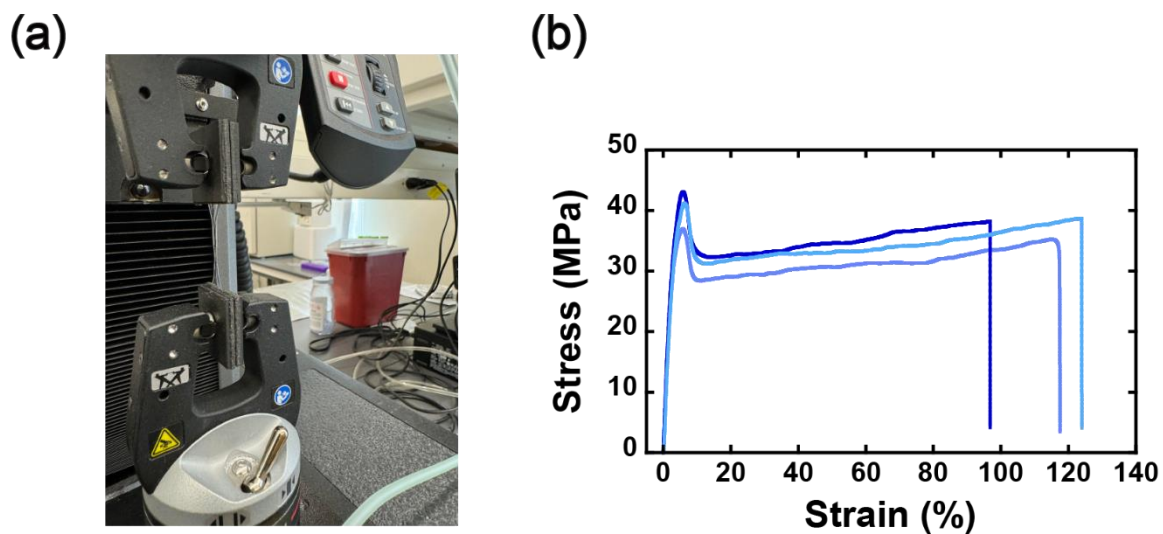


Figure S4-5: (a) Optical images of a dog-bone-shaped PPC-LiFSI on the load frame for mechanical property measurement. (b) Stress–strain curves of PPC-LiFSI (n=3).

Table S4-1: Mechanical properties of PPC-LiFSI.

Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
40.4 ± 2.6	112.7 ± 11.6	1495.1 ± 50.4

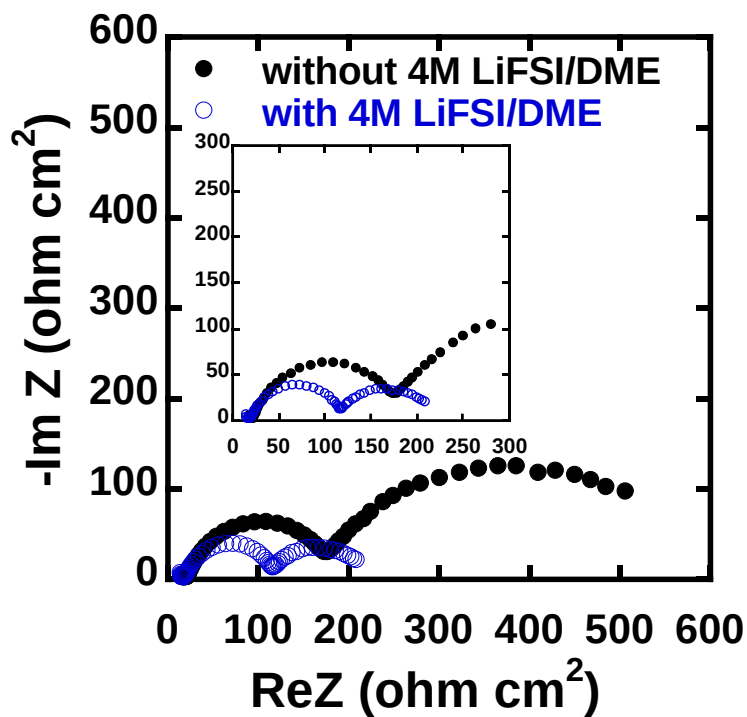


Figure S4-6: Nyquist plot of symmetric Li metal cells with PPC-LiFSI at interfaces, with and without 4M LiFSI/DME soaking of PPC-LiFSI.

To characterize the effect of 4M LiFSI/DME at interfaces on the cell resistance, symmetric cells with LLZO-SE sandwiched by PPC-LiFSI interfacial layers and Li metal electrodes, Li/i/LLZO-SE/i/Li, were fabricated. Figure S4-6 shows a Nyquist plot of the total impedance of a symmetric cell with and without the wetting of 4M LiFSI/DME at interfaces. Symmetric cells without 4M LiFSI/DME exhibit higher interfacial resistance of 149 ohm cm², compared to cells with incorporation of 4M LiFSI/DME at interfaces, with a value of 94 ohm cm².

While PPC-LiFSI demonstrates good adhesion to the electrode surface, an inability to effectively wet LLZO-SE ceramics can limit the number of ion transport pathways at the interface. This poor wetting may be attributed to microscale surface irregularities of LLZO-SE, which may hinder optimal interfacial contact in the absence of adequate wetting. To mitigate this issue, the incorporation of a small quantity of liquid, 4M LiFSI/DME solution, can significantly enhance the

wetting capability of the PPC-LiFSI layer at the interfaces between the Li metal and LLZO-SE. By improving wetting, the liquid facilitates better contact between the polymer layers and the ceramic particles, thereby facilitating ion transport and reducing interfacial resistance.

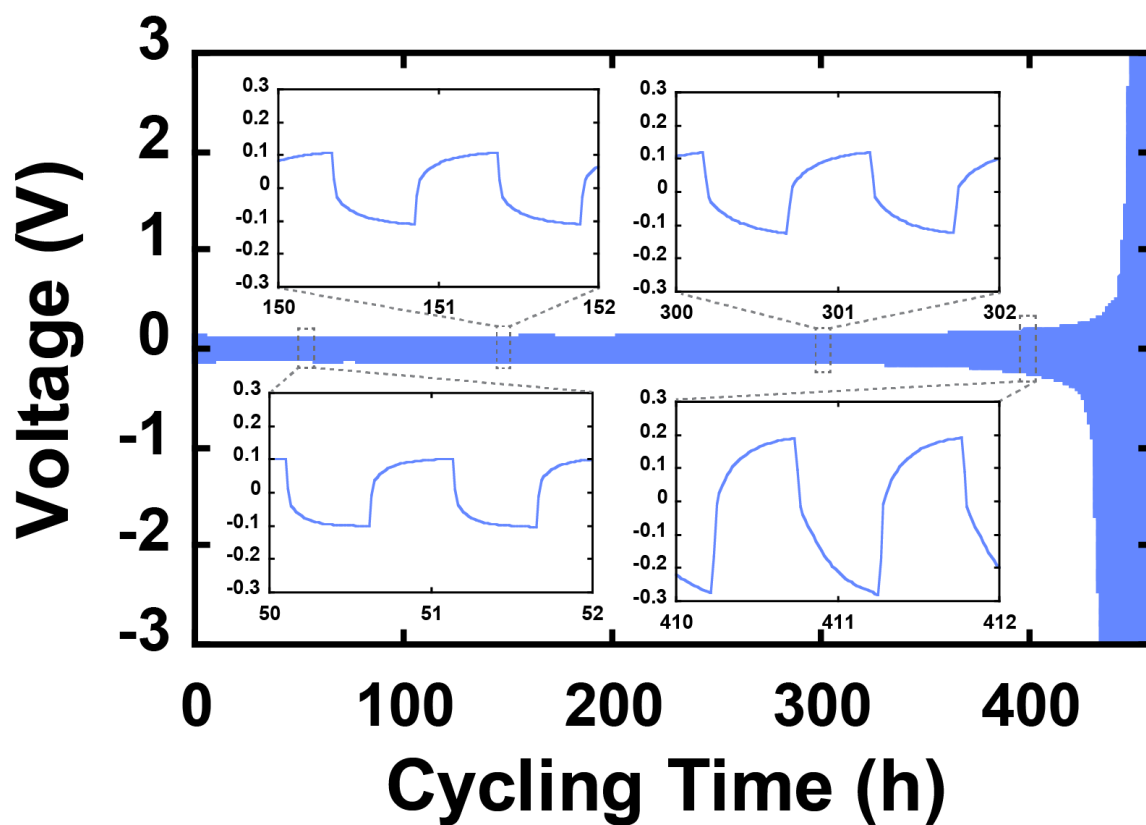


Figure S4-7: Time dependence of voltage profiles of symmetric cells with LLZO-SE sandwiched between Li metal electrodes incorporated with PPC-LiFSI interfacial layer, Li/i/LLZO-SE/i/Li, at a current density of 0.2 mA cm^{-2} over 410 h.

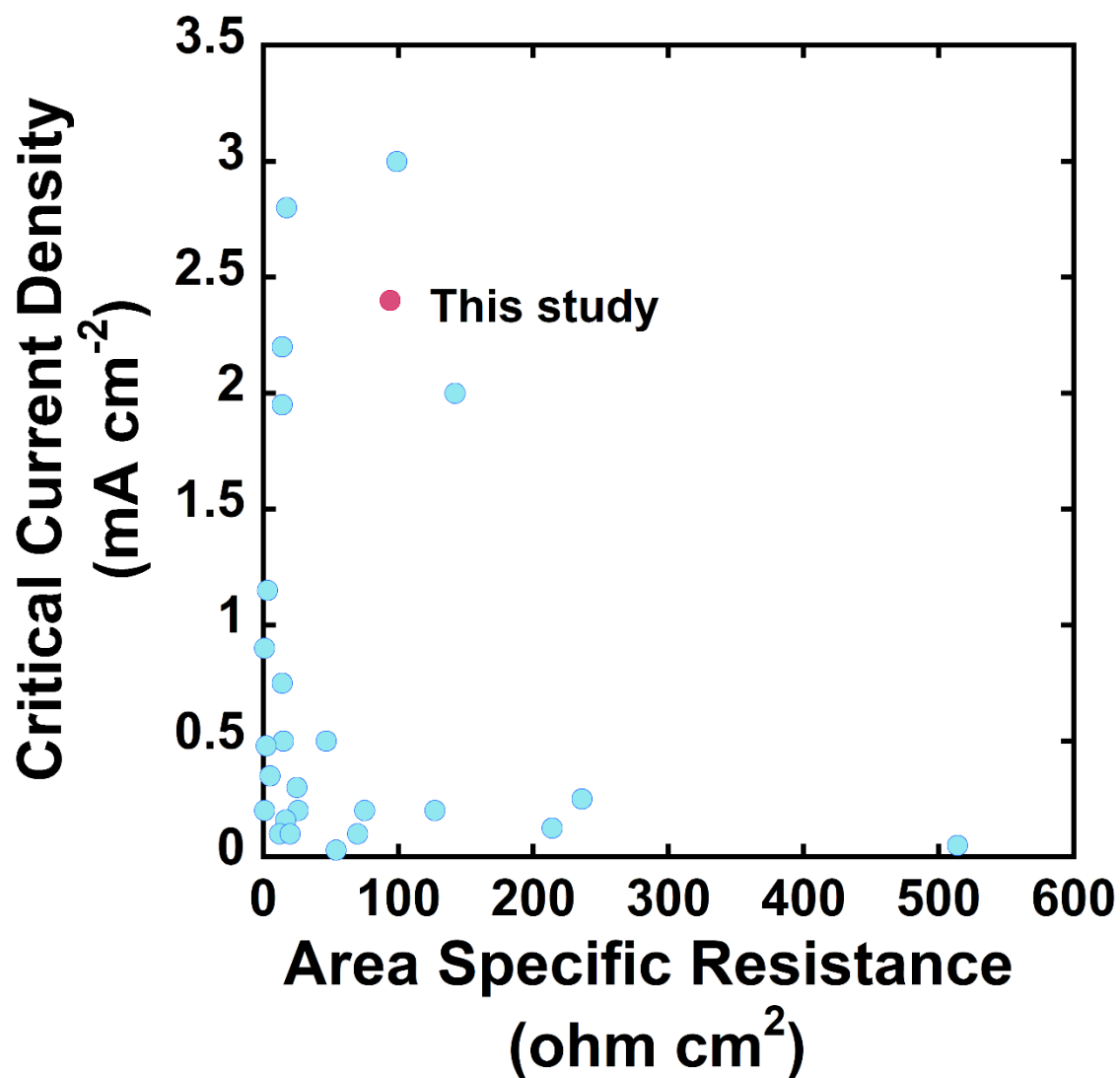


Figure S4-8: Critical current density (CCD) and area specific resistance (ASR) of symmetric cells (red, this study), Li/i/LLZO-SE/i/Li, and previous work (blue). References shown in **Table S4-2**.

Table **S4-2**: Comparison of critical current densities (CCD) and area specific resistance (ARS) of Li-metal symmetric cells with LLZO-based solid electrolytes from this study with previous work.

Material	Method	CCD (mA cm ²)	ASR (ohm cm ²)	Process temperature (°C)	Ref.
PPC–LiFSI	Drop casting	2.4	94	RT	This work
Au	Sputter coating	0.03	54	Curing at 180	[106a]
Al	Electron beam evaporation	0.2	75	Curing at 200	[106b]
Mg	Vapor deposition	0.1	70	Curing at 300	[106v]
Graphite	Pencil painting	0.3	25	Curing at 210	[106u]
Cu ₆ Sn ₅	Magnetron sputtering	0.25	236	Curing at 200	[106p]
Sn	Magnetron sputtering	0.5	46.6	Curing at 184	[106t]
Al ₂ O ₃	Atomic layer deposition	0.2	1	150	[106s]
Acid treatment (1M HCl)	Rapid washing	0.2	26	RT	[106r]
Carbon	Direct reacting	0.5	15	700	[106q]
Li ₃ BO ₃	Dry-pressing followed by sintering	0.35	5	1150	[106c]
MgO	Dry-pressing followed by sintering	1.95	14	1230	[106d]
Al ₂ O ₃	Pulsed laser deposition	0.48	2.2	RT	[106e]
MoS ₂	Dry-polishing	2.2	14	RT	[106f]
-	Polishing and spreading	2.8	17.5	RT	[106g]
-	Sanding and heat-pressing	0.05	514	175	[106h]
Al	Alloying	0.9	1	250	[54]
Au	Sputtering	1.15	3	250-300	[106i]
Sulfonated-covalent organic framework	Solution process	3	99	200	[106j]

Mg	Alloying	2	142	350	[106k]
LiAlO ₂	Coating	0.75	14	Sintering at 1100	[106l]
Si	Plasma-enhanced chemical vapor deposition	0.2	127	300	[106m]
Ga	Doping	0.16	16.7	Sintering at 1150	[106n]
PVDF–HFP	Casting	0.125	214	RT	[100]
Al	Doping	0.1	12.1	Sintering at 1175	[106n]
ZnO	Atomic layer deposition	0.1	20	150	[106o]

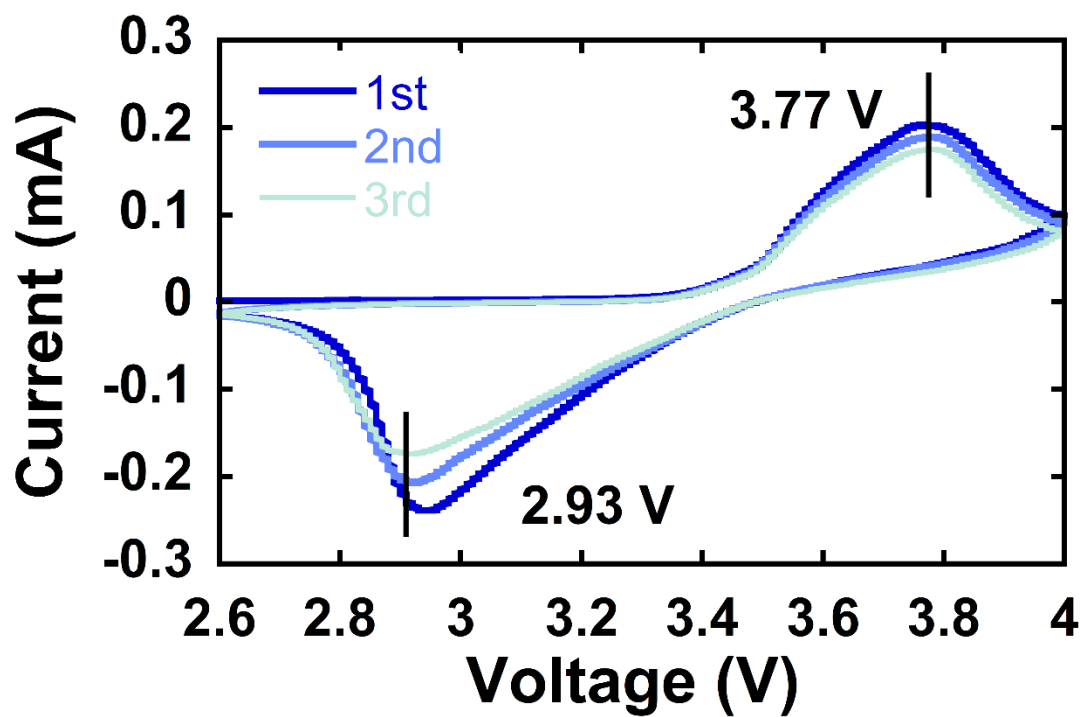


Figure S4-9: The cyclic voltammogram curves of LFP/i/LLZO-SE/i/Li with interfacial layers at a scan rate of 0.1 mV s^{-1} .

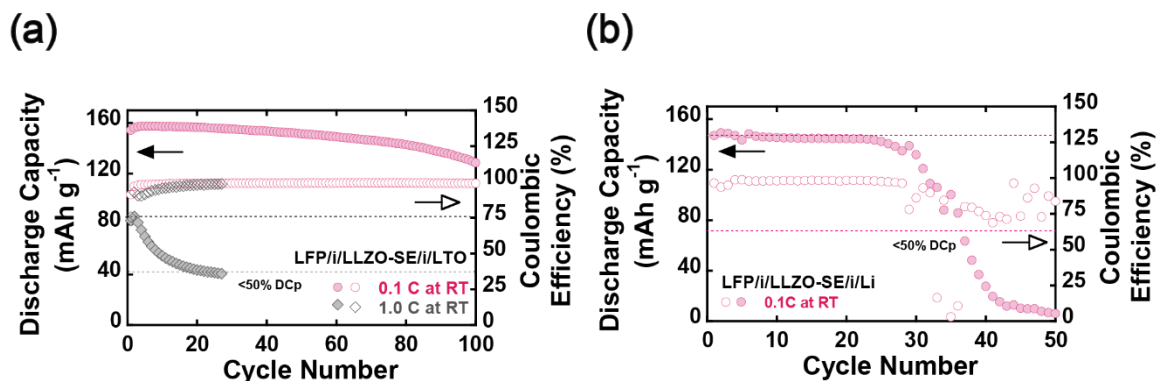


Figure S4-10: Long-term electrochemical performance of (a) LFP/i/LLZO-SE/i/LTO cycled at 0.1 and 1.0 C at room temperature; (b) LFP/i/LLZO-SE/i/Li cells cycled at 0.1 C at room temperature.

Figure S4-10 depicts the long-term electrochemical performance of LFP/i/LLZO-SE/i/LTO and LFP/i/LLZO-SE/i/Li at room temperature. LFP/i/LLZO-SE/i/LTO demonstrates an initial discharge capacity of 154 mAh g⁻¹. After cycling at 0.1 C for 100 cycles, the full cell shows a discharge capacity of 129 mAh g⁻¹ with a Coulombic efficiency of 99% and a capacity retention rate of 83.8%. The entire cycling measurement spanned approximately 76 days. To accelerate degradation, LFP/i/LLZO-SE/i/LTO cells were cycled at a higher rate of 1.0 C at room temperature. Under these conditions, the full cell demonstrates a reduced discharge capacity of 40.7 mAh g⁻¹ with a Coulombic efficiency of 98.6% and a capacity retention rate of 49.2%. At this stage, the cycled full cells, referred to as 50% DCp, are subjected to the recycling process. LFP/i/LLZO-SE/i/Li shows an initial capacity of 147 mAh g⁻¹. The discharge capacity of the full cell dropped to 63.5 mAh g⁻¹ with a Coulombic efficiency of 80% and a capacity retention rate of 43.2 %.

The full cell configuration employing a Li metal anode without the incorporation of PPC-LiFSI demonstrated a remarkably high total impedance, which severely impeded its ability to be cycled effectively. Moreover, the absence of PPC-LiFSI in the full cell also posed challenges to the separation process; consequently, in-depth studies of cycling behavior without PPC-LiFSI are outside of the scope of this work.



Figure S4-11: Optical images of the separation process where spent LLZO-SE and LFP were soaked in dimethylformamide followed by rinsed with dimethoxyethane to remove the polymer-salt layer along with a significant portion of lithium dendrites located near the surface of spent LLZO-SE.

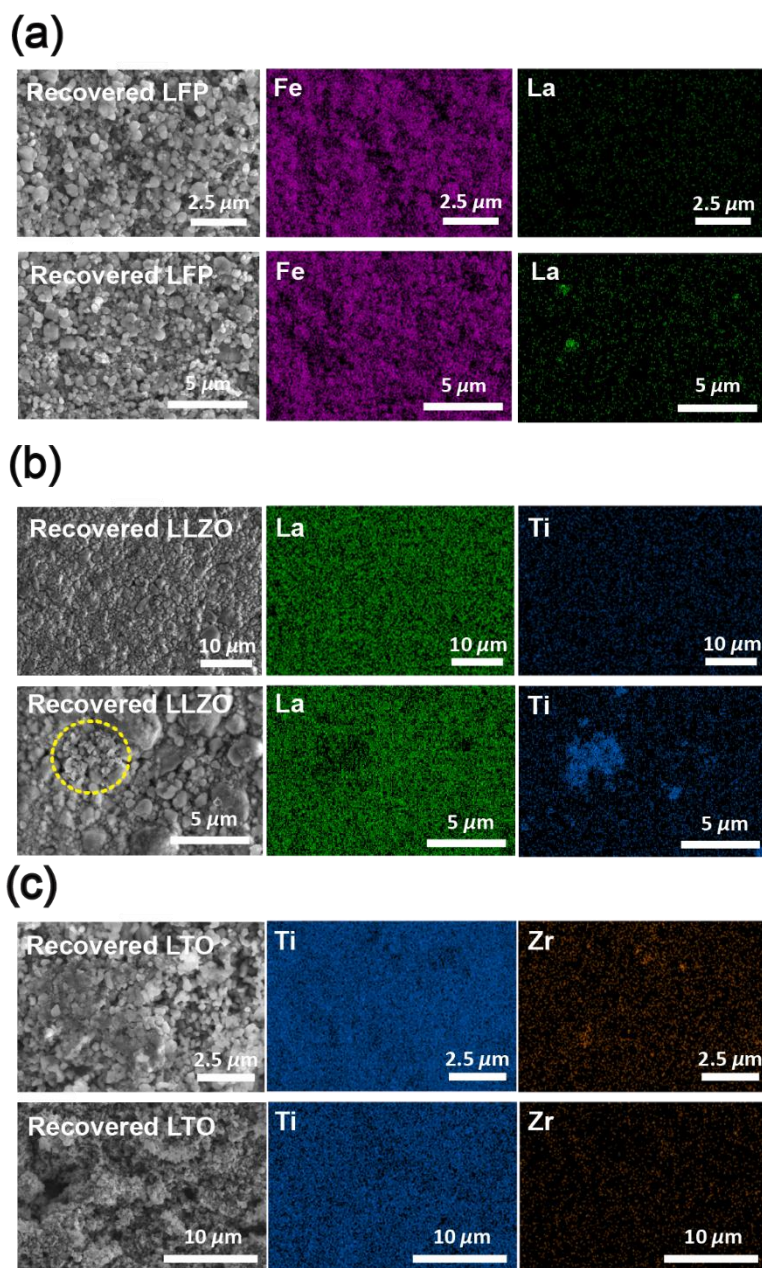


Figure S4-12: SEM images and EDS analysis of (a) recovered LFP cathodes from LFP/i/LLZO-SE/i/LTO full cells. (b) recovered LLZO from LFP/i/LLZO-SE/i/LTO full cells. Dotted circle highlights the presence of LTO on recovered LLZO. (c) recovered LTO anodes from LFP/i/LLZO-SE/i/LTO full cells.

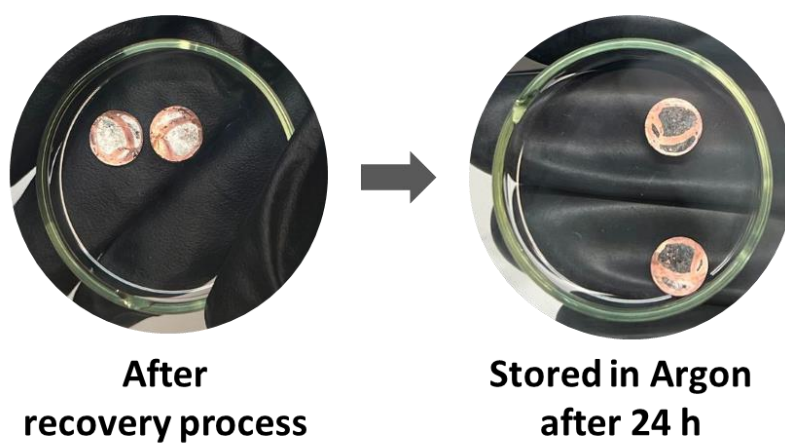


Figure S4-13: Optical images of recovered Li metal anodes from cycled symmetric cells.

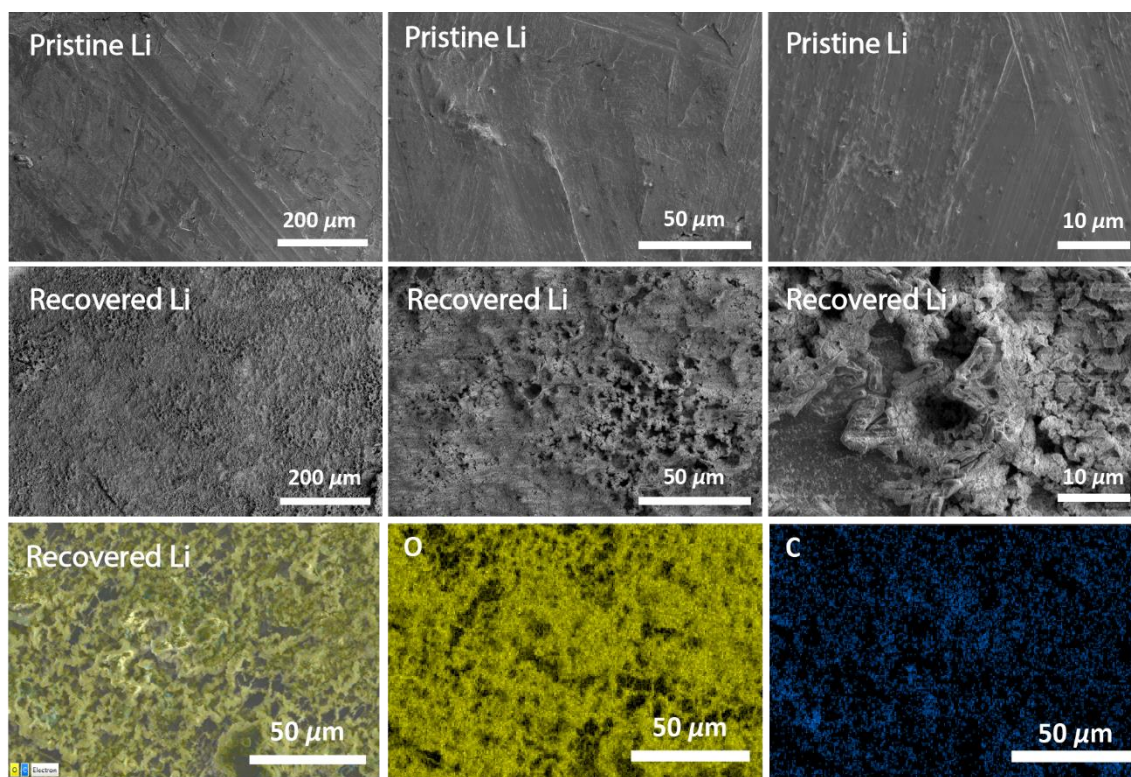


Figure **S4-14**: SEM and elemental mapping images of pristine and recovered Li metal from symmetrical cells.

Figure **S4-13** shows optical images of recovered Li metal anodes from symmetric cells cycled at 0.2 mA cm^{-2} for 459 hours. After the recovery process, the Li metal anodes exhibit a white surface layer. After storing the recovered Li metal electrode in an argon-filled glove box for 24 hours, the color of the layer changed to black. Figure **S4-14** shows SEM images of pristine and recovered Li metal anodes. The pristine Li metal sheet displays a smooth surface with only a small number of defects. In contrast, recovered Li metal is covered with a non-uniform surface layer. This non-flat surface can be attributed to the uneven deposition of lithium during the cycling process. EDS analysis revealed that the whitish components on the surface of the recovered Li metal primarily consist of oxygen and carbon.

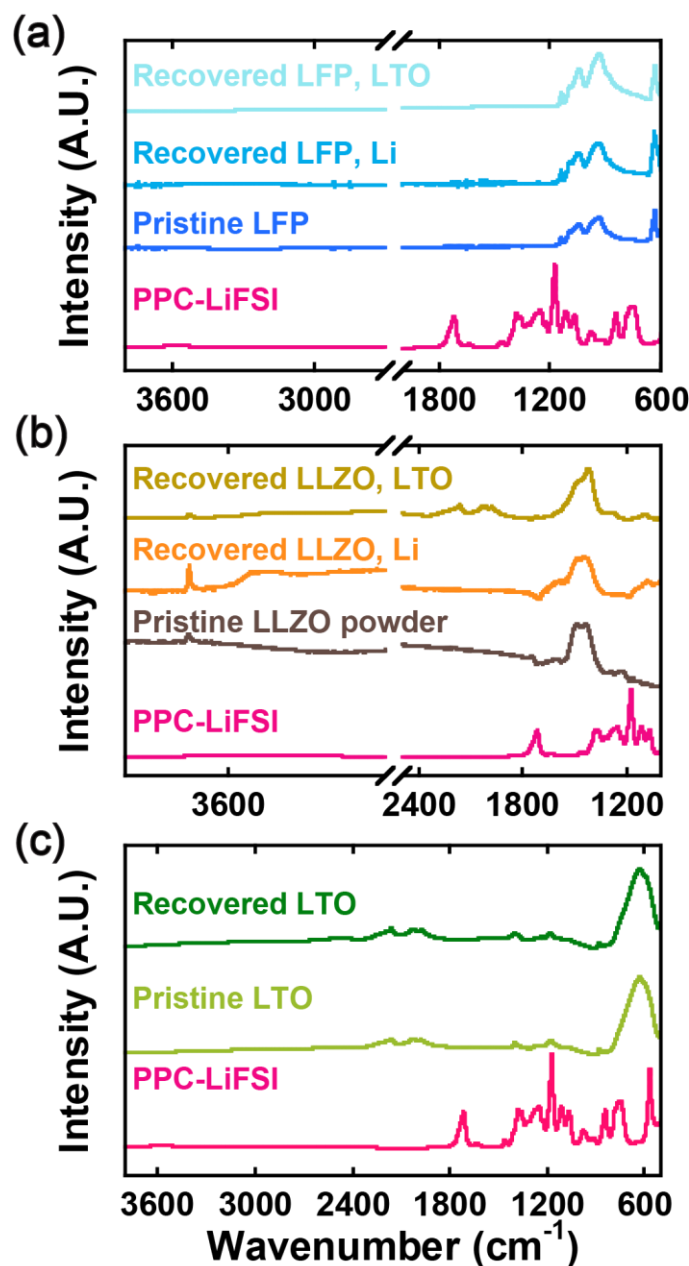


Figure S4-15: FTIR spectra of pristine and recovered components from Li metal anode and LTO anode-based full cells. (a) Spectra of recovered LFP that is extracted from LTO-based full cells (Recovered LFP, LTO) and Li metal full cells (Recovered LFP, Li metal) compared against spectra from pristine LFP and PPC-LiFSI. (b) Spectra of recovered LLZO that is extracted from LTO-based full cells (Recovered LLZO, LTO) and Li metal full cells (Recovered LLZO, Li metal) compared against spectra from pristine LLZO powder and PPC-LiFSI. (c) Spectra of recovered LTO that is extracted from LTO-based full cells (Recovered LTO) compared against spectra from pristine LTO and PPC-LiFSI.

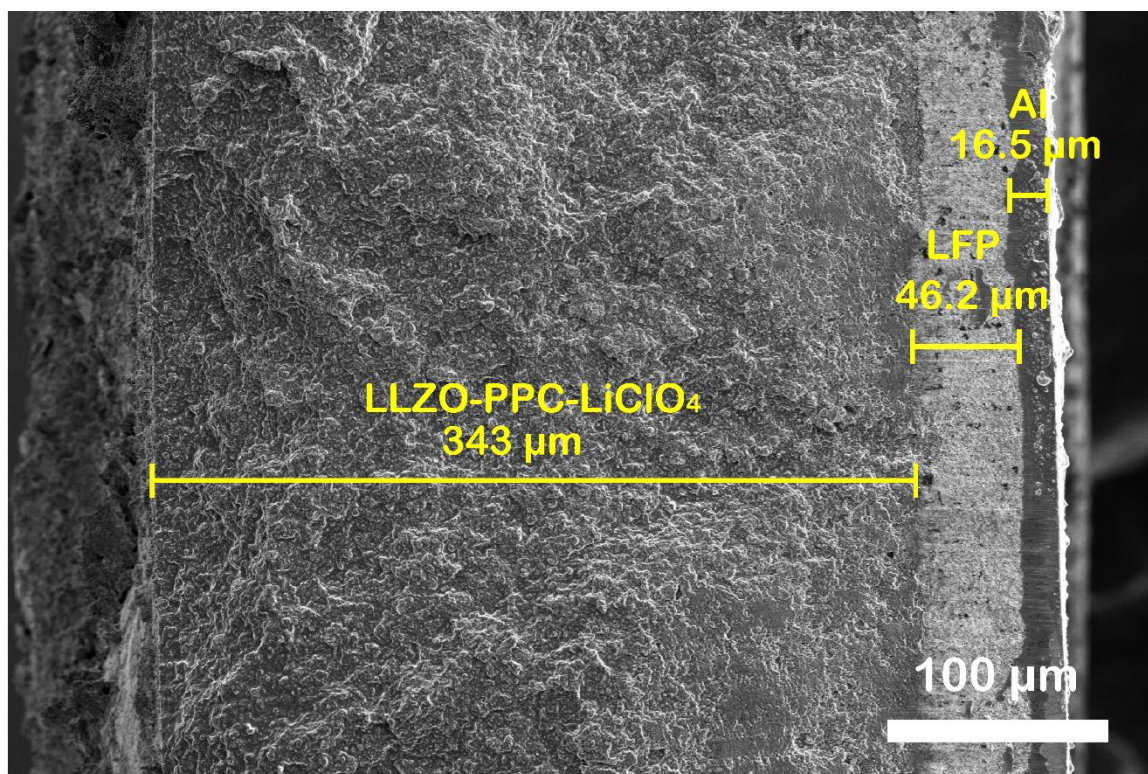


Figure S4-16: Post-mortem SEM image of spent LFP/LLZO-SE/i/Li with PPC-LiFSI at the anode interface suggests the thickness of PPC-LiFSI in LFP/LLZO-SE/i/Li is approximately 36.3 μm .

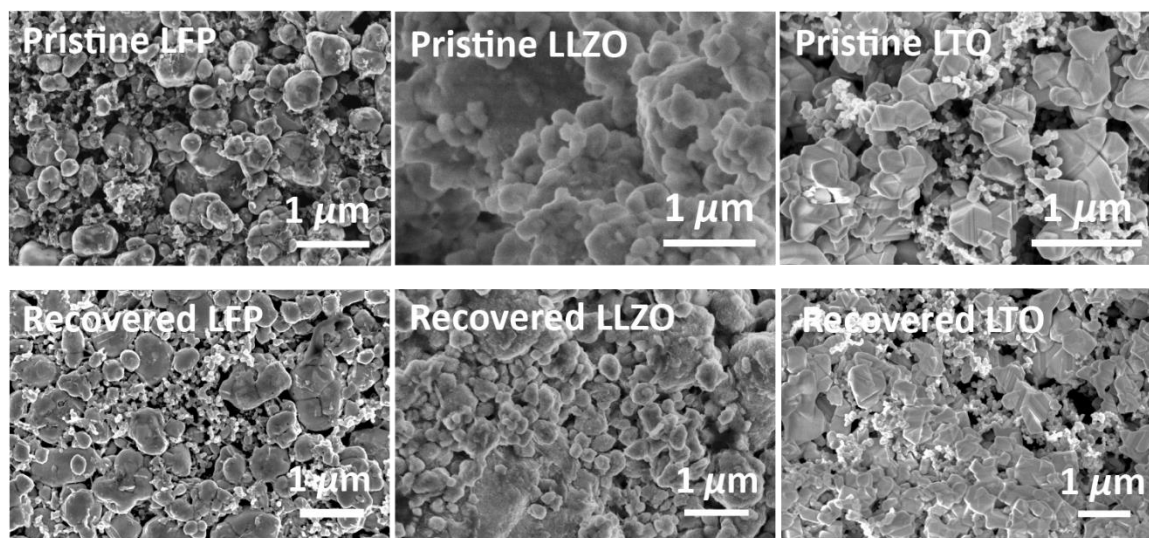


Figure S4-17: SEM images of pristine and recovered LFP, LLZO (from LTO anode-based full cell).

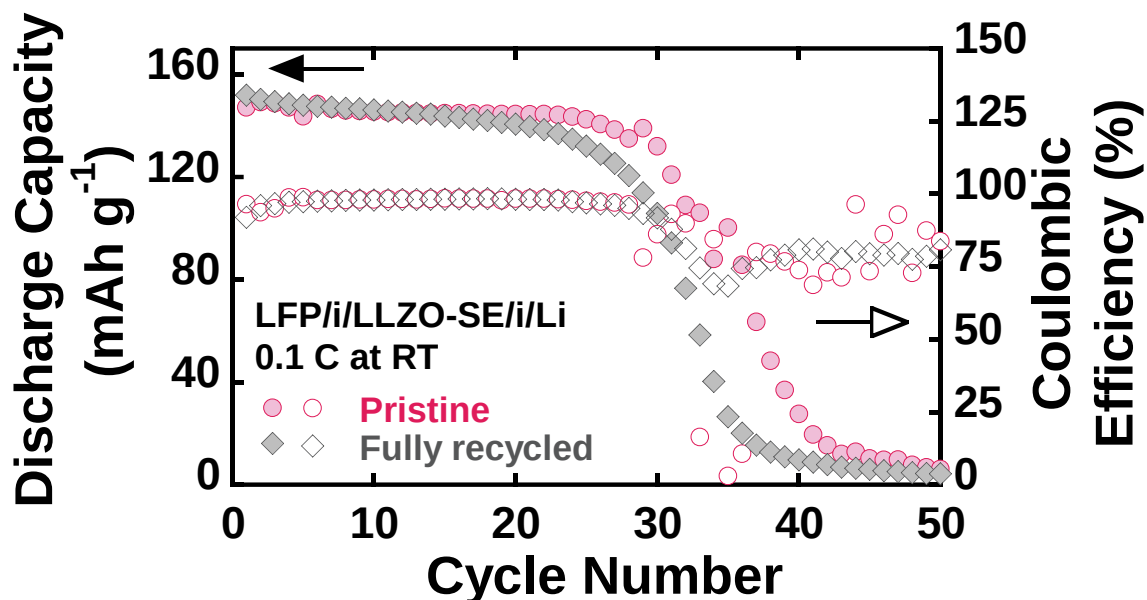


Figure S4-18: Cycling stability of pristine and fully recycled LFP/i/LLZO-SE/i/Li at 0.1 C at room temperature.

The cycling stability of pristine and fully recycled LFP/i/LLZO-SE/i/Li full cell at 0.1 C at room temperature is shown in Figure S18. The pristine full cell shows a stable cycling performance over 32 cycles with a discharge capacity of 109 mAh g^{-1} and a Coulombic efficiency of 90 % and a capacity retention rate of 74 %. The fully-recycled, full cell exhibits similar cycling performance, with perhaps a slightly earlier onset of decay in cycling stability compared to the pristine cell. Nonetheless, the full cell shows a stable retention performance over 30 cycles with a discharge capacity of 106 mAh g^{-1} with a Coulombic efficiency of 92 % and a capacity retention rate of 70 %. After the recycling process, the fully recycled, full cell incorporates recovered LLZO-SE and recovered LFP yet exhibits similar long-term cycling performance as the pristine cell. This suggests the of the incorporation of PPC-LiFSI allows effective component separation and direct recycling of battery components.

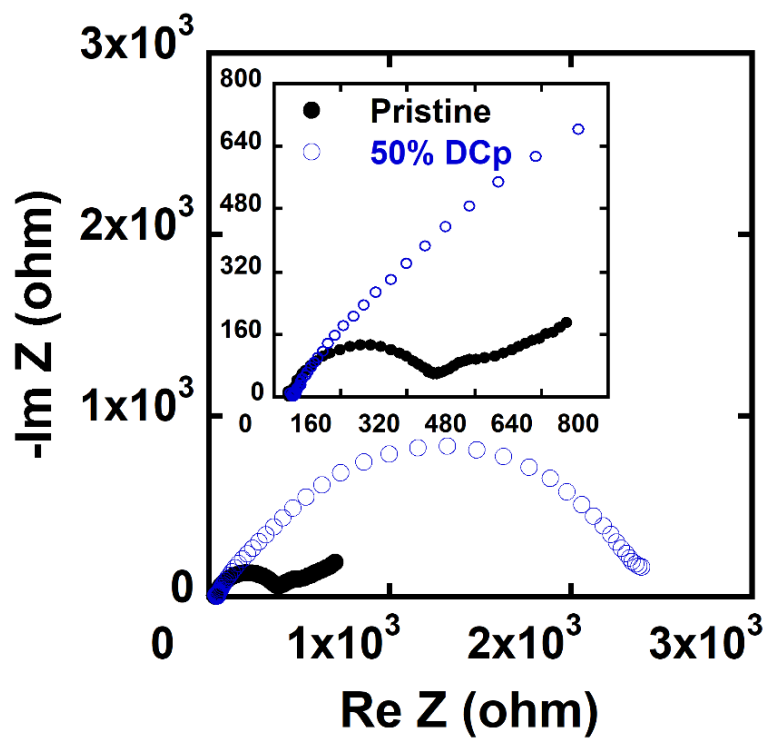


Figure S4-19: Nyquist plots of pristine and cycled LFP/i/LLZO-SE/i/LTO with discharge capacity lesser than 50% of its original value; Inset: data at high frequency.

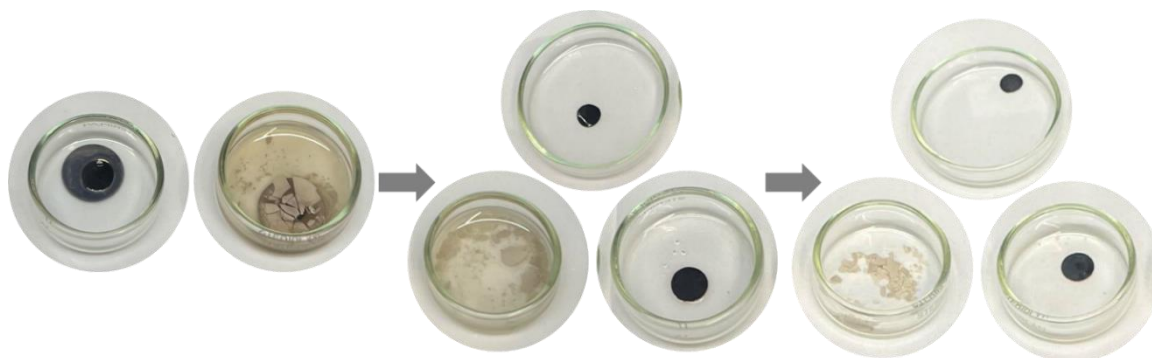


Figure S4-20: Optical images of the separation process for spent LFP/i/LLZO-SE/i/LTO, where spent LLZO-SE, LTO, and LFP were soaked in dimethylformamide followed by rinsed with dimethoxyethane to remove polymer-salt layers, allowing the recovery of battery components.

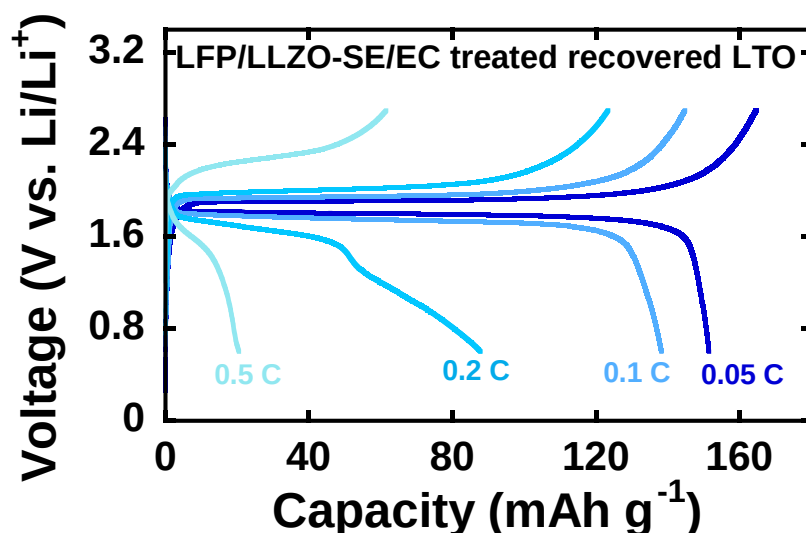


Figure S4-21: Galvanostatic charge and discharge curves of a full cell that contains recovered LTO treated with EC, denoted as LFP/LLZO-SE/EC treated recovered LTO, at various C-rates at room temperature.

Tasaki *et al.* studied the solubility of lithium salts formed at the lithium-ion battery negative electrode surface in organic solvents. They proposed that the primary components at solid electrolyte interfaces, such as lithium fluoride (LiF), lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3), lithium oxalate ($(\text{LiCO}_2)_2$), lithium methyl carbonate ($\text{LiOCO}_2\text{CH}_3$), and lithium ethyl carbonate ($\text{LiOCO}_2\text{C}_2\text{H}_5$), demonstrate a certain degree of dissolution in ethylene carbonate (EC), due to its high polarity.^[118] Therefore, we use DMF to first remove the PPC-LiFSI layer and effectively separate battery components. During the recovery process, EC was employed to treat the recovered LTO anode at 65°C for 30 minutes, followed by rinsing with DME. This post treatment process is expected to facilitate the dissolution of potential undesired phases on recovered LTO.

Full-cell that incorporates recovered LTO that is treated with EC, denoted as LFP/LLZO-SE/EC treated recovered LTO, is fabricated by cold-sintering the battery components to form the tri-layer structure. Figure S4-21 demonstrates the galvanostatic charge and discharge curves of LFP/LLZO-

SE/EC treated recovered LTO at various C-rates at room temperature. The full cell shows a discharge capacity of 152, 138, and 88 mAh g⁻¹ at 0.05, 0.1, and 0.2 C, respectively. Approximately 93.8 % of the original discharge capacity (162 mAh g⁻¹ for pristine full cell) can be recovered at 0.05 C. This suggests that with proper post treatment, batteries with recycled components can exhibit similar cycling performance as pristine cells. Nevertheless, more work is needed to optimize recycling efficiency.

Chapter 5

LiF-Rich Solid-Electrolyte-Interphase to Enhance the Cycling Performance and Recycling of All-Solid-State Lithium Batteries

5.1 Overview

While rechargeable lithium batteries have undergone notable advancements paving the way for commercialization, several challenges persist, particularly concerning the use of lithium metal anodes. Addressing the issue of interfacial stability is crucial for all-solid-state lithium batteries to unlock their full potential and gain broader market acceptance. Additionally, sustainable recycling technologies for these spent batteries remain largely unexplored. In this study, we introduce fluorine-containing lithium-salt solutions to mitigate undesired interfacial reactions at Li metal interfaces. The formation of a LiF-rich solid electrolyte interphase (SEI) resulting from this approach enhances cycling performance by passivating electrochemical side reactions and restricting the formation of poorly ion-conducting phases on the LLZO-based electrolytes. After the removal of undesired phases, full cells incorporating recycled LLZO solid electrolytes demonstrate improved overall battery performance, highlighting the potential of this approach in addressing the challenges associated with lithium metal anodes and promoting the recyclability of all-solid-state lithium batteries.

5.2 Introduction

All-solid-state lithium batteries, employing solid electrolytes, are considered as the next generation of energy storage technologies, which offer improved safety and higher energy density

compared to conventional batteries.^[1b, 2a] While rechargeable lithium batteries have undergone notable advancements, paving the way for their commercialization, several challenges remain to be addressed. A major obstacle is the interfacial stability between the solid electrolyte and lithium metal anode. Resolving this interfacial stability issue is critical for all-solid-state lithium batteries to realize their full potential and achieve widespread market adoption.^[1a, 2b]

Garnet type electrolytes $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) exhibit good chemical stability towards Li metal electrodes, while the lithiophobic nature of LLZO may result in inadequate physical contacts and elevated interfacial resistance.^[119] Strategies such as incorporating flexible polymers to bridge solid-state interfaces have been employed to enhance wettability and interface contacts.^[15a] Nonetheless, the limited mechanical strength of polymers impedes their capability to suppress lithium dendrite penetration. Moreover, when coupled with lithium metal anodes, their inadequate electrochemical stability leads to the formation of unstable interfaces, undermining the cycling performance and longevity of batteries.^[120]

Forming a stable solid electrolyte interphase (SEI) on the anode during cycling, which offers electronic insulation and ionic conductivity, acts as a robust protective film to prolong the cycling lifetime of lithium metal batteries.^[121] During the first charge and discharge process, fluorine-containing electrolytes can be reduced to LiF, which shows to be an ideal component in SEI due to its high mechanical strength, low solubility, wide band gap (effectively prevents electron tunneling), and a high voltage window (up to 6.4 V vs Li/Li^+).^[122] A uniform and dense fluorinated SEI can regulate the homogeneous deposition of lithium-ion flux, suppressing the growth of Li dendrite. Moreover, when synergizing with other components such as Li_2O , Li_2CO_3 , LiOH , they form a heterogeneous structure to enhance both ionic conductivity and electronic insulation at the anode side of the battery.^[123]

Despite significant advancements have been achieved in the development of all-solid-state batteries, technologies for sustainable recycling of these spent batteries remain largely

unexplored.^[4, 5b, 32] During the battery cycling process, the growth of an interphase layer leads to a buildup of pressure within the solid-state electrolytes, consequently causing mechanical fractures and eventually short-circuiting of the battery.^[69, 124] To promote the cycling performance and recycling efficiency, one strategy is to passivate the undesired interfacial reactions and to protect solid-state electrolytes from further degradation by forming stable fluorine-rich SEI layers. Herein, we introduce fluorine-containing lithium-salt solutions, lithium tetrafluoroborate (LiBF₄), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and lithium bis(pentafluoroethanesulfonyl)imide (LiPFSI) in dimethylformamide (DMF) or dimethoxyethane (DME), at the interfaces between the polymer-salt layer (polypropylene carbonate-lithium perchlorate, PPC-LiClO₄), and Li metal to investigate the effects of formation LiF-rich SEI on the battery performance and recycling efficiency. X-ray photoelectron spectra (XPS) confirm the presence of LiF on cycled Li-metal anodes, which attribute to the stable long-term cycling of Li metal half-cells and the improvement in discharge capacity of pristine and recycled all-solid-state batteries.

5.3 Experimental Methods

Preparation of Fluorine-Based Lithium Salt Solution

Lithium tetrafluoroborate (LiBF₄, ultra dry, powder), lithium bis(fluorosulfonyl)imide (LiFSI, anhydrous), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, anhydrous), and lithium bis(pentafluoroethanesulfonyl)imide (LiPFSI, anhydrous) are purchased from Sigma Aldrich with 99.99% trace metals basis. Fluorine-based lithium salt solutions with various concentration (1, 2, 4, and 6 M) are prepared by dissolving salts in dimethylformamide (DMF) or dimethoxyethane (DME) in argon environment.

Fabrication of Polymer-Salt Layers

Lithium salts, lithium perchlorate (LiClO_4) or lithium bis(fluorosulfonyl)imide (LiFSI), and polypropylene carbonate (Sigma Aldrich, average $M_n \sim 50000$ Da) were dissolved in acetonitrile (ACN, Sigma Aldrich, anhydrous) with a ratio of 1:2:12 *by mass* under argon atmosphere ($\text{O}_2 < 0.1$ ppm and $\text{H}_2\text{O} < 0.1$ ppm). The polymer-salt solution was deposited on Aclar sheets ($46.5 \mu\text{L}/\text{cm}^2$), dried and stored at the room temperature in argon environment. Polymer-salt thin films can be easily released from the substrates for further use.

Fabrication of LLZO-SE solid-state electrolyte composites

$\text{Li}_{7-2x+y}\text{Mg}_x\text{La}_{3-y}\text{Sr}_y\text{Zr}_2\text{O}_{12}$, (LLZO, $0.1 \leq x \leq 0.3$, $0 \leq y \leq 0.5$, NGK Spark Plug Co., Ltd, particle size $\sim 1 \mu\text{m}$) powders were mixed with polymer-salt solution and N, N-Dimethylformamide (DMF, Sigma Aldrich, anhydrous) (12:2.5:1 *by mass*) using a mortar and a pestle. The mixture was introduced into a hardened steel pressing die with a diameter of 13 mm and underwent the cold sintering process by being pressed and sintered under a uniaxial pressure of 100 bar at 100°C for 1 hour. To maintain a consistent sintering temperature, two heating platens and a band heater were used to encircle the die to mitigate any temperature fluctuations. Upon reaching a temperature below 50°C , the as-prepared composite electrolytes were extracted. All preparation procedures were conducted in an argon atmosphere.

Fabrication of All-Solid-State Batteries and Electrochemical Tests

Anode discs were punched from single side laminated lithium copper foils (MSE Supplies, thickness of lithium and copper ~ 40 and $11 \mu\text{m}$, respectively) and single-sided $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) copper sheets (NEI corporation, tape thickness $\sim 60 \mu\text{m} \pm 12 \mu\text{m}$). Cathode discs were cut from

single side coated LiFePO_4 (LFP) sheets (MTI Corporation, coating thickness $\sim 68 \mu\text{m} \pm 10 \mu\text{m}$). Before full cell assembly, surface oxides were scratched off from lithium discs by razor blades to show metallic surface. LTO and LFP electrodes are heated at 100°C for over 1 hour under argon environment. For the fabrication of Li symmetric cells, composite electrolytes were placed between two Li metal discs with and without the introduction of polymer-salt films at the interfaces. To fabricate LFP/LLZO-SE/Li and LFP/LLZO-SE/LTO full cells, polymer-salt thin films were placed on electrodes along with the addition of lithium salt solutions (7.07 and 8.95 , $7.95 \mu\text{L}/\text{cm}^2$ on the LFP, LTO, and Li surfaces, respectively) to wet the interfaces. LLZO-SE composite electrolytes were sandwiched between LFP cathodes and Li or LTO anodes with polymer-salt layers at interfaces. The as-assembled full cells were sealed in CR2032 coin cells for further characterization. Galvanostatic cycling tests were carried out in the voltage range from 2.7 to 4.0 V vs. Li^+/Li for LFP/LLZO-SE/Li and 0.6 to 2.8 V vs. Li^+/Li for LFP/LLZO-SE/LTO cells using a Neware CT-4008 battery testing system. The charging and discharging current densities were determined from the theoretical capacity of LFP cathodes, 170 mAh g^{-1} . Electrochemical impedance spectroscopy (EIS, ModuLab XM MTS) measurements were performed in a frequency range of 0.1 to 10^6 Hz with a 10-mV amplitude. Zview was used to analyze obtained spectra and produce equivalent circuit models. The activation energies of electrolytes were calculated using the Arrhenius equation, $\sigma = A \times e^{-\frac{E_a}{k_B T}}$, based on the ionic conductivities measured over a temperature range of -20 to 120°C . In the equation, A represents the pre-exponential factor, k_B is the Boltzmann constant, and E_a denotes the activation energy.

Material Characterization

The crystal structure and secondary phases of battery components were analyzed by X-ray diffractometry (Malvern Panalytical Empyrean, $\text{Cu K}\alpha$ radiation, 40 kV , 40 mA). Collected spectra

were analyzed using MDI JADE. Field emission scanning electron microscope and energy dispersive spectrometer (FE-SEM and EDS, Verios G4, Thermo Scientific) were performed to characterize the surface morphology, cross-sectional structures, and elemental mapping of battery components. Fourier-transform infrared spectroscopy (FTIR) was carried out using a Bruker Vertex 80 spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were conducted using a Physical Electronics VersaProbe III instrument equipped with a monochromatic Al K α X-ray source (photon energy = 1486.6 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu (Cu 2p_{3/2} = 932.62 eV, Cu 3p_{3/2} = 75.1 eV) and Au foils (Au 4f_{7/2} = 83.96 eV). Peaks were charge referenced to CH_x band in the carbon 1s spectra at 284.8 eV. Measurements were performed at a takeoff angle of 45° with respect to the sample surface plane, resulting in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons. On homogeneous samples major elements (>5 atom%) tend to have standard deviations of <3% while minor elements can be significantly higher. The analysis size was ~200 μ m in diameter.

5.4 Results and Discussion

We introduce a soft polymer-salt layer, polypropylene carbonate-lithium perchlorate (PPC-LiClO₄), to bridge solid-solid interfaces and enable lithium-ion transport between electrode and electrolyte. The polymer-salt layer, PPC-LiClO₄, is transparent and flexible (Figure 5-1(a)). The conductivity of the polymer-salt layer was measured in half cells with the PPC-LiClO₄ between two aluminum blocking electrodes. The polymer-salt film was 115 μm thick on average with a conductivity around $7.78 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature (Figure 5-1(b)). As ion transport in polymer-salt films depends strongly on polymer properties, we characterized the thermal properties of the polymer-salt layers (Figure 5-1(c)). The introduction of lithium salt into polypropylene carbonate ([O]:[Li⁺]=6:1), PPC-LiClO₄ reduces the glass transition temperature (T_g) to around 13 °C from 19 °C for pure PPC. The low T_g suggests high segmental mobility of PPC, which can facilitate lithium-ion transport across the interfacial layer.

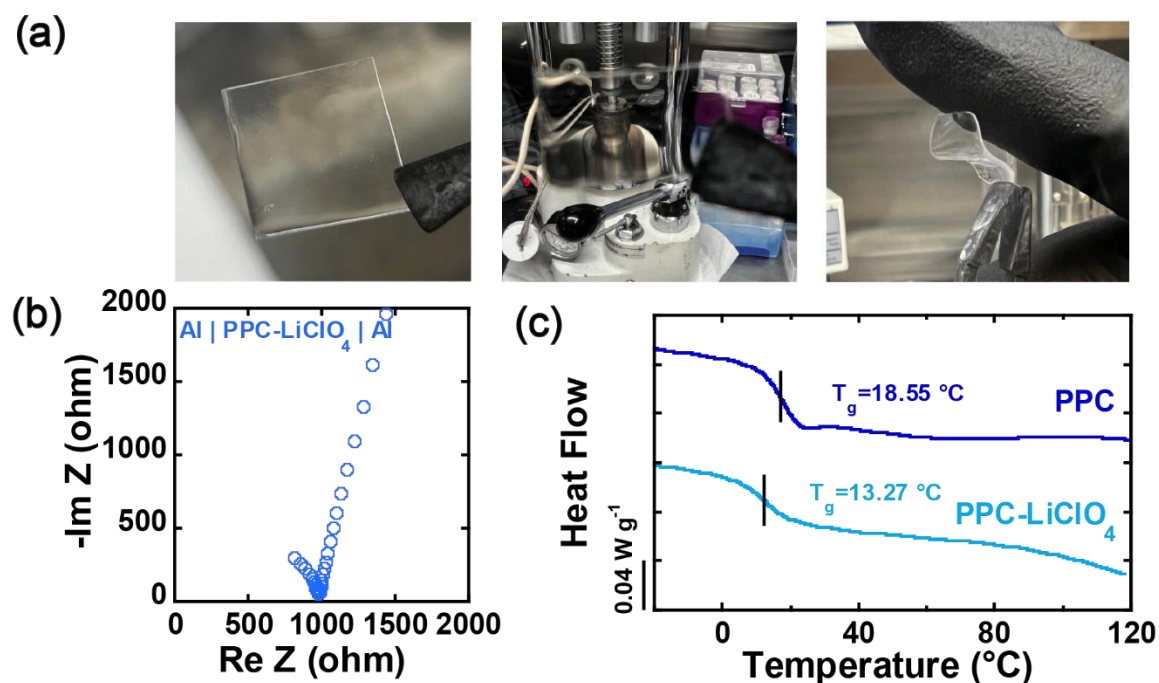


Figure 5-1: (a) Images of the polymer-salt interfacial layer, PPC-LiClO₄, illustrating its transparency and flexibility. (b) Nyquist plot of PPC-LiClO₄ interfacial layer in a frequency range

of 0.1 to 10^6 Hz with a 10-mV amplitude exhibiting an ionic conductivity of $7.78 \times 10^{-5} \text{ S cm}^{-1}$. (c) Thermograms from differential scanning calorimetry (DSC) of PPC-LiClO₄ interfacial layer in comparison to pure polypropylene carbonate on heating at $5 \text{ }^\circ\text{C min}^{-1}$ from -30 to 120 $^\circ\text{C}$.

To study interfacial resistance, half cells with Li-metal as non-blocking electrodes were fabricated with LLZO composite electrolytes both with and without PPC-LiClO₄ layers introduced at the interfaces. Figure 5-2(a) shows the total area specific resistance of half cells with and without PPC-LiClO₄ layers. Half cells that include polymer thin films show a substantial improvement in the total resistance, which is estimated to be around 176 ohm cm²; whereas half-cells without interfacial modifications have a total resistance around 2.9×10^4 ohm cm². The impedance spectrum of the half cells with interfacial layers was fit using an equivalent circuit model, shown in Figure 5-2(b). The first poorly-resolved semicircle at high frequency is attributed to the bulk (R_b) and grain boundary ($RCPE_{gb}$) resistances (~ 43 and $152.6 \text{ } \Omega$, respectively) of the solid electrolyte. The second semicircle has an associated capacitance of $5.65 \times 10^{-6} \text{ F}$, which can be ascribed to the electrolyte-electrode interfaces ($RCPE_{in}$) with an area specific resistance of 76.7 ohm cm². The third semicircle in the low frequency region with a capacitance of $1.3 \times 10^{-3} \text{ F}$ can be attributed to the electrochemical reaction ($RCPE_{ecr}$) at Li metal anode interfaces.

The stability of electrode–electrolyte interfaces was assessed using the critical current density (CCD). The rate performances of Li metal symmetric cells were examined at current densities ranging from 0.1 to 1.5 mA cm⁻², as shown in Figure 5-2(c-d). The critical current density was determined as the maximum current density that a cell can sustain without exceeding the safety voltage limit (5 V) of the battery testing system. Symmetric cells without PPC-LiClO₄ layers failed to safely cycle at a current density of 0.1 mA cm⁻². The failure mechanism is due to the pore formation during stripping and poor contact between Li metal and solid electrolytes. With PPC-LiClO₄, the symmetric cell shows a critical current density of 1.25 mA cm⁻², suggesting a stable lithium-ion transport path across electrode interfaces under much higher cycling current densities.

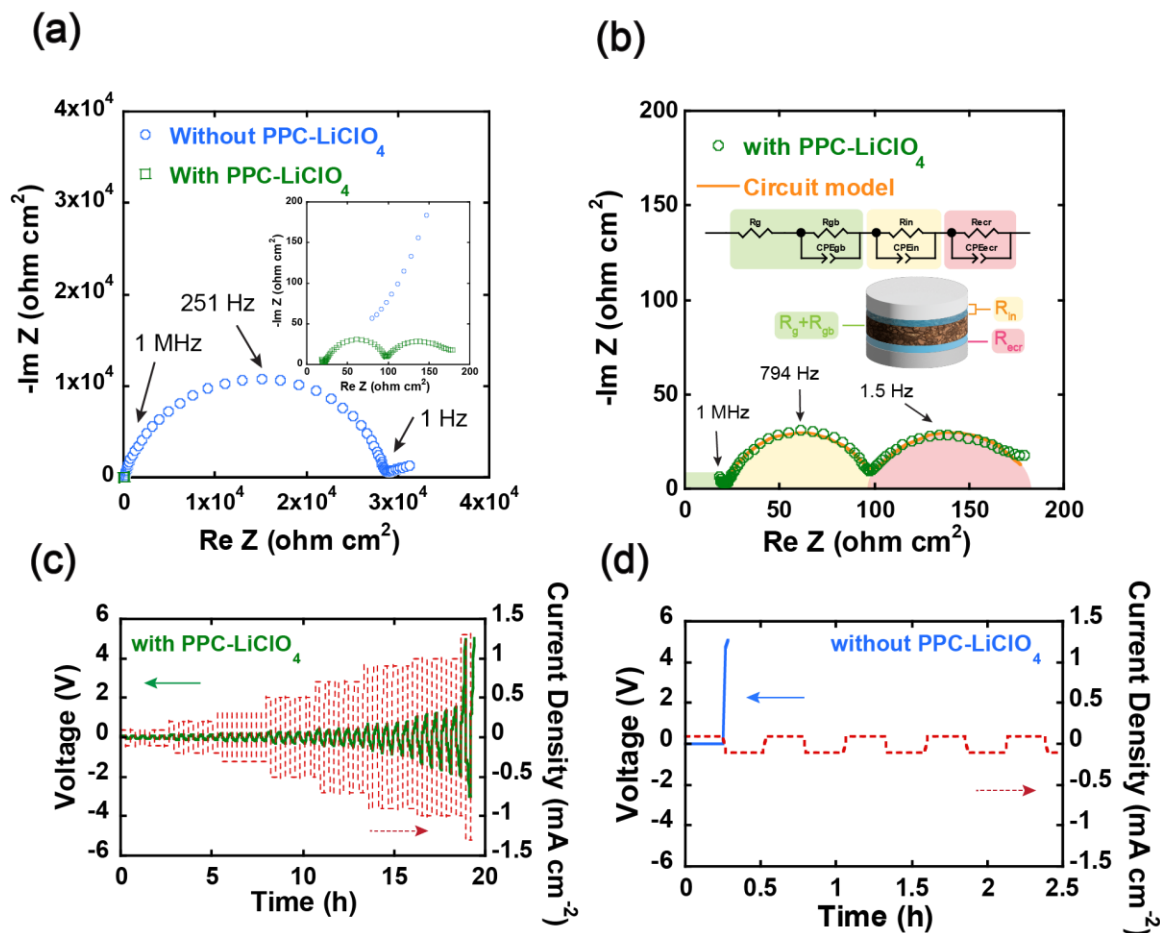


Figure 5-2: Nyquist plots (a) and equivalent circuit model (b) of Li metal symmetric cells with and without PPC-LiClO₄ layers. Critical current density of Li metal symmetric cells and wettability of molten Li metal on the surface of LLZO (c) with and (d) without PPC-LiClO₄ layers.

To ensure good cycling performance of full cells with interfacial layers, fluorine-based lithium salt solution was introduced at the interfaces to form a LiF-rich solid-electrolyte-interface. The stable solid-electrolyte interface can prevent the further interactions between polymers and Li metal and facilitate the homogeneous deposition of lithium metal, as illustrated in Figure 5-3.

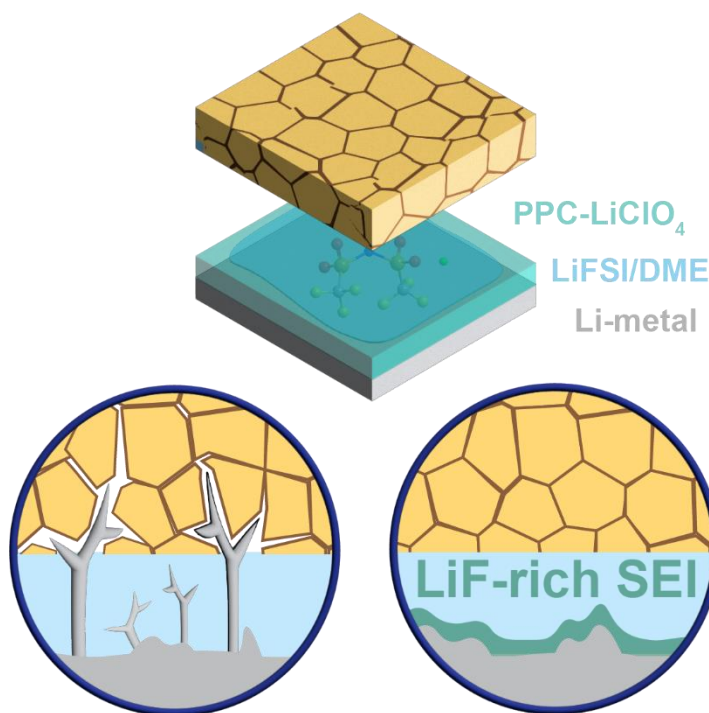


Figure 5-3: Schematic illustration of the formation of LiF-rich protective layer by introducing fluorine-based Li-salts at the interfaces.

Lithium salts of different molecular sizes and configurations (varying in fluorine content and bonding arrangements) were selected to investigate the compatibility against Li metal. Lithium salt solutions with a concentration of 4 M were prepared by dissolving lithium salts, lithium tetrafluoroborate (LiBF₄), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethylsulfonimide) (LiTFSI), and lithium bis(pentafluoroethanesulfonyl)imide (LiPFSEI), in dimethoxyethane (DME). Optical images of bare Li metal with lithium salt solutions deposited on the surfaces after 22 hours and 4 days in argon environment were shown in Figure 5-4. After four days, lithium metal treated with LiFSI/DME solutions displays a silver metallic appearance, whereas others exhibit a gray surface with the formation of undesired phases. This suggests that LiFSI/DME serves as a shield to prevent interactions between lithium metal and the atmosphere.

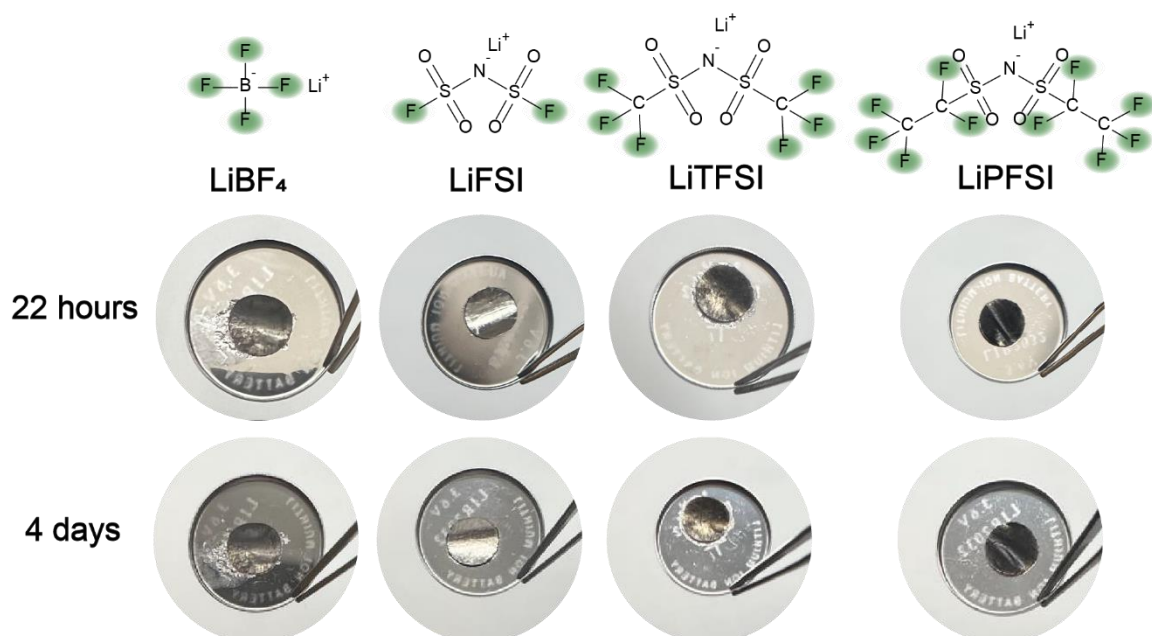


Figure 5-4: Optical images of Li metal with lithium salts deposited on the surface after 22 hours and 4 days.

To study the effect of introduction of fluorine-based lithium salts on the battery performances and recycling efficiency, symmetric cells with Li metal as non-blocking electrodes and full cells with the use of LiFePO_4 (LFP) as cathodes and Li metal or lithium titanate (LTO) as anodes (denoted as LFP/LLZO-SE/Li or LFP/LLZO-SE/LTO) were fabricated. Symmetric cells with interfacial layer wetted with DMF and LiFSI/DME were cycled at a current density of 0.2 mA cm^{-2} over long cycles, where 0.05 mAh cm^{-2} capacity of lithium metal was plated/stripped during each cycle (Figure 5-5(a)). The cycling curves of symmetric cell with the introduction of LiFSI/DME show a stable voltage-time profile with minimizing polarization up to 300 hours, whereas the one with DMF shows an increasing polarization phenomenon since the early stage. This suggests a stable lithium plating/stripping process with the introduce of fluorine-based salts.

To demonstrate that LiFePO_4 cathodes are compatible with interfacial layers, LFP-PPC- LiClO_4 was fabricated by drop-casting polymer-salt solutions on cathode discs. LFP cathodes retain evidence for high crystallinity with a PPC- LiClO_4 layer on the surface, although a secondary phase

that can be ascribed to Li_2C_2 is apparent from X-ray diffraction data (Figure S5-1(a-b)). The presence of carbon additives that serve as electron conducting pathways is also observed. FTIR spectra of LFP-PPC- LiClO_4 confirms that there is no formation of side products from chemical reactions when LFP contacts with interfacial layers (Figure S5-1(c)).

Figure 5-5(b) displays the cycling performance of LFP/LLZO-SE/Li wetted with 4M of LiFSI-based solutions at various C rates ($1\text{ C} = 170\text{ mA h/g}_{\text{LFP}}$). LFP/LLZO-SE/Li incorporated with 4 M LiFSI/DME at Li metal interfaces demonstrates an optimal discharge capacity of 157 and 103 mAh g^{-1} at 0.05 and 0.1 C; while LFP/LLZO-SE/Li incorporated with DMF shows an average discharge capacity of 108 and 26 mAh g^{-1} . This suggests the incorporation of fluorine-based lithium salt in DME facilitates enhanced battery cycling performance. The concentration effects of LiFSI/DME solutions on cycling performance of all-solid-state batteries are shown in Figure 5-5(c), which suggests that increasing the salt concentrations doesn't necessarily improve the cycling performance. Figure 5-5(d) illustrates the discharge capacities of LFP/LLZO-SE/Li incorporated with PPC or PPC- LiClO_4 at LLZO-Li metal interfaces and wetted with 4M LiFSI-DME at anode interfaces. Without the doping of lithium salt in the polymer layer, LFP/LLZO-SE/Li shows a decreasing discharge capacity with an average value of 83 C at 0.05 C. This implies the doping of lithium salts is crucial for supplying lithium-ion source within the polymer layer, which is essential for maintaining good cycling performance.

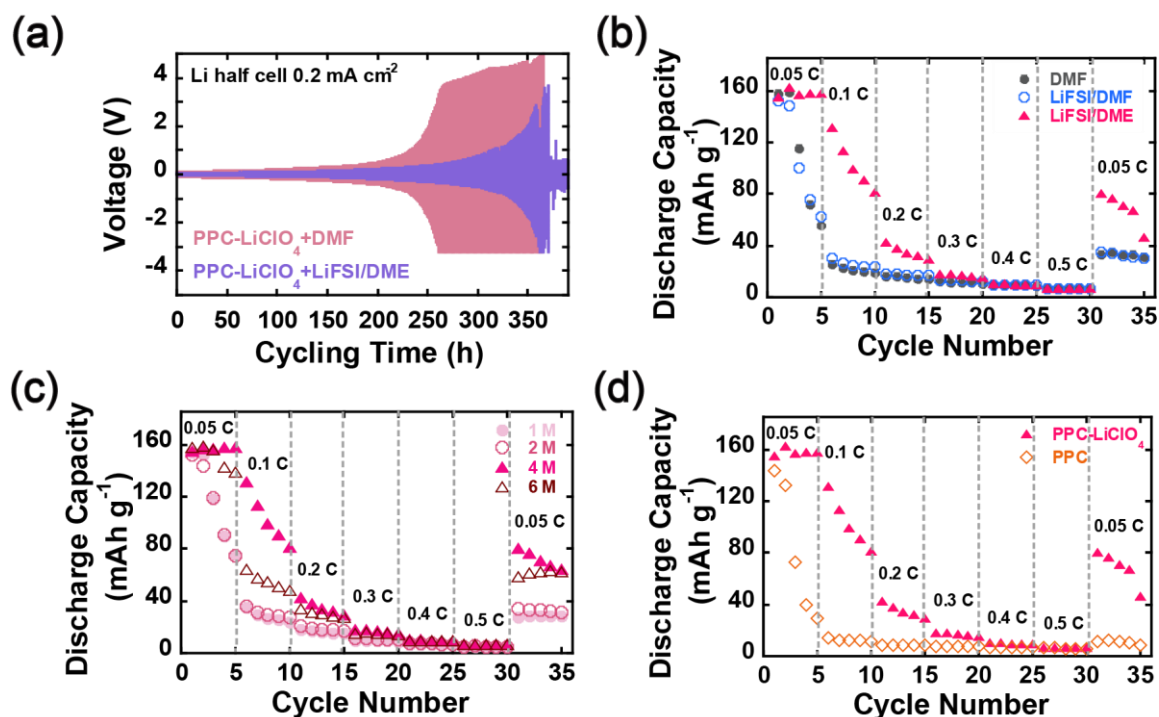


Figure 5-5: (a) Time dependence of voltage profiles of symmetric cells with PPC-LiClO₄ layer, at a current density of 0.2 mA cm⁻². Electrochemical rate performance of LFP/LLZO-SE/Li with (b) PPC-LiClO₄ layers wetted with DMF, 4 M LiFSI/DMF, and 4 M LiFSI/DME. (c) PPC-LiClO₄ layers wetted with LiFSI/DME solutions with various concentrations. (d) PPC or PPC-LiClO₄ layers wetted with 4M of LiFSI/DME.

Figure 5-6 show the electrochemical performance of Li metal or LTO anode-based all-solid-state batteries (denoted as LFP/LLZO-SE/Li and LFP/LLZO-SE/Li) with with PPC-LiClO₄ and wetted with 4M LiFSI/DME at Li metal interfaces. Figure 5-6(a) display the Nyquist plots of LFP/LLZO-SE/LTO and LFP/LLZO-SE/Li featured with a high-frequency region semicircle and a low-frequency spike, which shows a total resistance of 33 ohm cm² and 108 ohm cm², respectively. LFP/LLZO-SE/LTO delivers an average discharge capacity of 152, 140, 98, and 33 mA h g⁻¹ at 0.05, 0.1, 0.2, and 0.3 C, respectively; whereas LFP/LLZO-SE/Li shows a discharge capacity of 157, 103, 35, and 17 mA h g⁻¹ at 0.1, 0.2, 0.5, and 1.0 C, respectively, as shown in Figure 5-6(b).

Charge and discharge curves of LFP/LLZO-SE/Li and LFP/LLZO-SE/Li full cell at various C rates are shown in Figure 5-6(c-d). Both of them shows a flat discharge plateau at a low

C rate of 0.05 and 0.1 C with a charge/discharge potential gap of 0.24 V and 0.22 V for LFP/LLZO-SE/LTO and LFP/LLZO-SE/Li, respectively. The increase in voltage difference observed at higher C rates (faster charge/discharge rates) can be attributed to the occurrence of undesirable side reactions. The formation of secondary phases may obstruct ion transport pathways, leading to an increase in Ohmic resistance and exacerbating the polarization effect within the full cell.

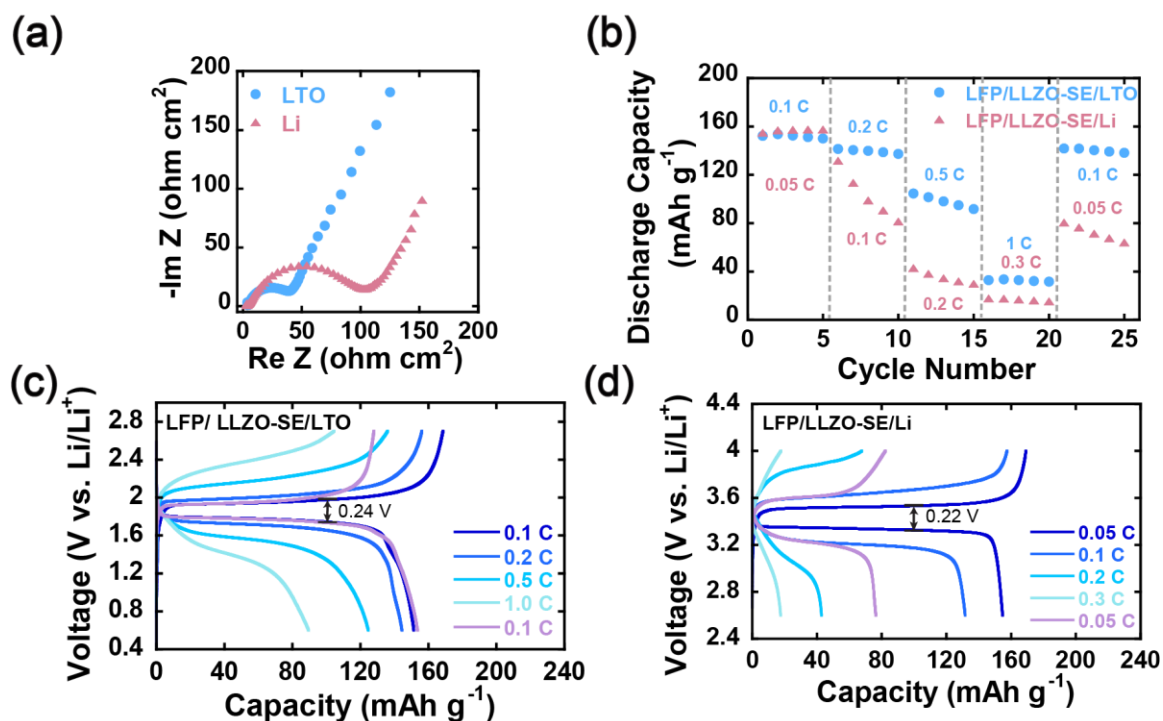


Figure 5-6: (a) Nyquist plot of LFP/LLZO-SE/LTO and LFP/LLZO-SE/Li full cells. (b) Discharge capacities of LFP/LLZO-SE/LTO and LFP/LLZO-SE/Li at different C rates at room temperature. Galvanostatic charge and discharge curves of (c) LFP/LLZO-SE/LTO and (d) LFP/LLZO-SE/Li at room temperature.

To confirm that the formation of LiF-rich SEI enables improved full cell performance, XPS analysis was conducted on the cycled Li metal anodes to investigate the compositions of SEI and the effect of the addition of fluorine-based lithium salts (Figure 5-7). The low-resolution survey spectrum (Figure 5-7(a)) shows that elemental signatures of cycled Li metal anodes primarily consist of C 1s, F 1s, O 1s, N 1s, and La 3d, which can be ascribed to the presence of SEI, PPC,

LiFSI, and a trace amount of LLZO. The concentration of elements of the neat top surface and sputtered surface is shown in Figure 5-7(b). Top surface of cycled Li metal is enriched with C, O, Li, which can be attributed to the formation of Li_2CO_3 and the presence of PPC according to the C 1s spectra (Figure S5-2). Lithium carbonate results from the oxidation of Li metal to form LiOH, which further reacts with CO_2 to form Li_2CO_3 . F 1s spectra confirms that the fluorine from the top surface of Li metal mainly comprised of LiF and a trace amount of fluorocarbons (Figure 5-7(c)). Subsequent to the sputtering process, the sample surface exhibited an increase in the concentrations of Li and F, which can be attributed to LiF, indicating a relatively high ratio of LiF on the inner side of spent Li metal anodes (Figure 5-7(d)). The observed increasing concentration gradient of LiF supports the idea that the formation of LiF could result from the decomposition of LiFSI when in contact with Li metal to generate LiF.^[125] Overall, the XPS analysis indicates that incorporating fluorine-containing lithium salts facilitates the formation of stable LiF-rich SEI layer, which in turn contributes to the homogenized lithium-ion transport and protects the Li anode to enhance battery cycling performance.

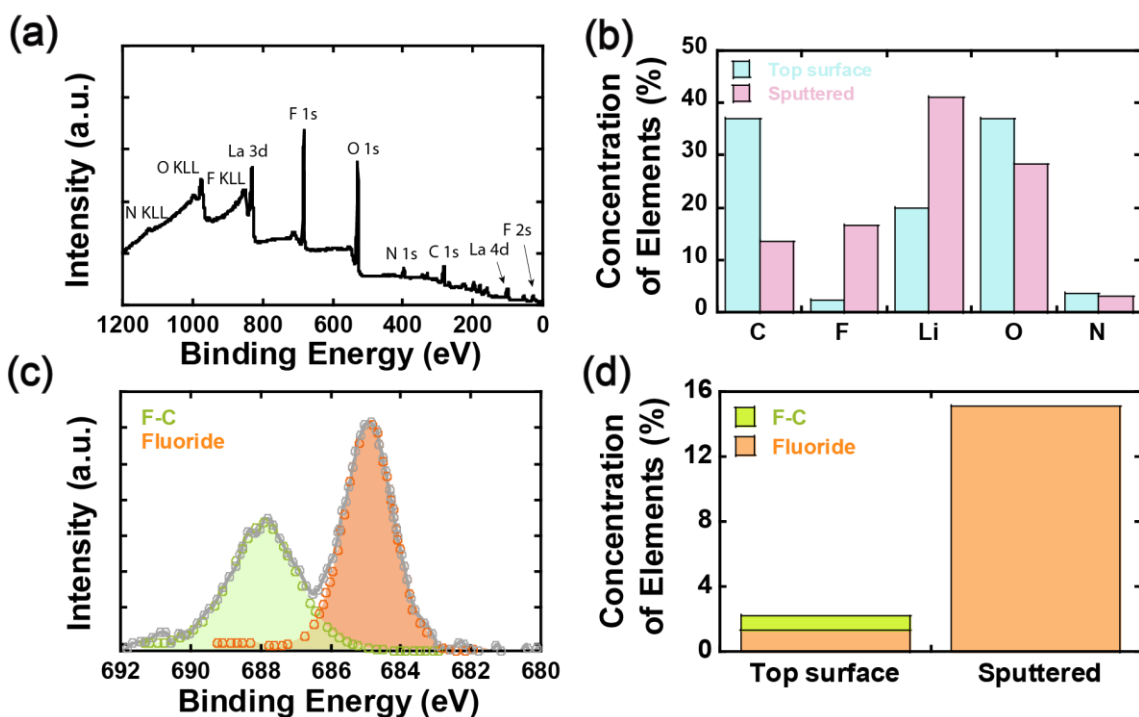


Figure 5-7: Post-mortem XPS analysis on recovered Li metal anodes. (a) XPS survey scan of sputtered surface, (b) concentration of elements of the neat top surface and sputtered surface, (c) F 1s spectra, and (d) concentration of elements of the F 1s spectra before and after sputtering.

To evaluate the electrochemical performance of recycled batteries, full cells were fabricated by integrating recovered component(s) (LFP and/or LLZO-SE) with other components in their pristine states. Charge and discharge curves of the pristine full cell with the use of Li metal at various C rates ($1\text{ C} = 170\text{ mA h/g}_{\text{LFP}}$) are shown in Figure 5-8, and these performance metrics are compared to full cells that include recovered components (recovered LFP/LLZO-SE/Li, LFP/recovered LLZO-SE/Li, and recovered LFP/recovered LLZO-SE/Li) as shown in Figure 5-8(b-d). Pristine full, LFP/LLZO-SE/Li, cells show a discharge capacity of 146 and 135 mAh g^{-1} at 0.1 and 0.2 C (Figure 5-8(a)), while recovered LFP/LLZO-SE/Li cell show a comparable discharge capacity of 168 and 140 mAh g^{-1} (Figure 5-8(b)). As the discharge capacity is calculated based on the presence of active materials in the cathodes, the weight loss in recovered LFP may not be significant enough to be detectable, resulting in the overestimated discharge capacity.

Charging and discharging curves of recycled full cells with recovered LLZO, LFP/recovered LLZO-SE/Li are shown in Figure 5-8(c). The decreasing discharge capacity along with the increasing cycling C-rate may result from a surface contaminant, lithium hydroxide. Although lithium hydroxide was found to be present on surfaces, recycling mixes surface and bulk layers and embeds LiOH into the bulk phase during cold sintering. Thus, the presence of lithium hydroxide with low ionic conductivity may explain the decreasing discharge capacity in LFP/recovered LLZO-SE/Li.

The decrease in cycling performance of recovered LFP/recovered LLZO-SE/Li (139 mA h g⁻¹ at 0.1 C) implies the retention of electrochemical properties in recovered components regardless of the buildup of contaminants, as shown in Figure 5-8(d). The fluctuations in the voltage profile that fails to reach the cutoff voltage during charging was apparent as the battery was reversely cycled back to low C rate. This short circuit phenomenon may originate from the presence of lithium hydroxide. As the non-lithium-ion conductive phase may hinder ion transport pathway leading to the inhomogeneous distribution of applied current density that facilitates the growth of lithium dendrites.^[115] The penetration of lithium dendrites in solid electrolytes shorten the pathway for transport, thus changing the voltage profile by reducing the Ohmic resistance between two electrodes.^[53, 126]

To demonstrate that the recyclability of all-solid-state lithium batteries is not limited to Li metal anodes, full cells with LTO anodes (LFP/LLZO-SE/LTO) were recycled and evaluated, as shown in Figure 5-8(e-h). Recycled full cells with recovered electrolyte or electrodes (recovered LFP/LLZO-SE/LTO, LFP/recovered LLZO-SE/LTO, and LFP/LLZO-SE/ recovered LTO) display good discharge capacities (>125 mA h g⁻¹ at 0.1 C). The capacity drops in recovered LFP/LLZO-SE/LTO and LFP/LLZO-SE/recovered LTO is perhaps due to the incompact microstructures of recovered electrodes. Calendering is a crucial process to reduce porosity and to improve particles

compaction.^[107, 116] As recovered LFP and recovered LTO did not experience any further treatment, the loose packing and inhomogeneity may consequently decrease electrochemical performance.

Recycled full cells, that are fabricated from recovered electrolytes and recovered electrodes, demonstrates a discharge capacity around 124 mA h g^{-1} at 0.1 C , as shown in Figure 5-8(i). The loss in electrochemical performance can result from the build-up of contaminants and electrochemical reaction byproducts. In addition, during the recovery process, exposure to solvents may lead to lithium loss, hindering battery performance. Further work is warranted to identify the routes for degradation chemistry. Through this simple approach for recycling, recovered components show the preservation of electrochemical properties after undergoing recovery and reprocessing. The architectural design of recyclable all-solid-state batteries with engineered interfaces can be applied on other types of batteries with different chemistries.

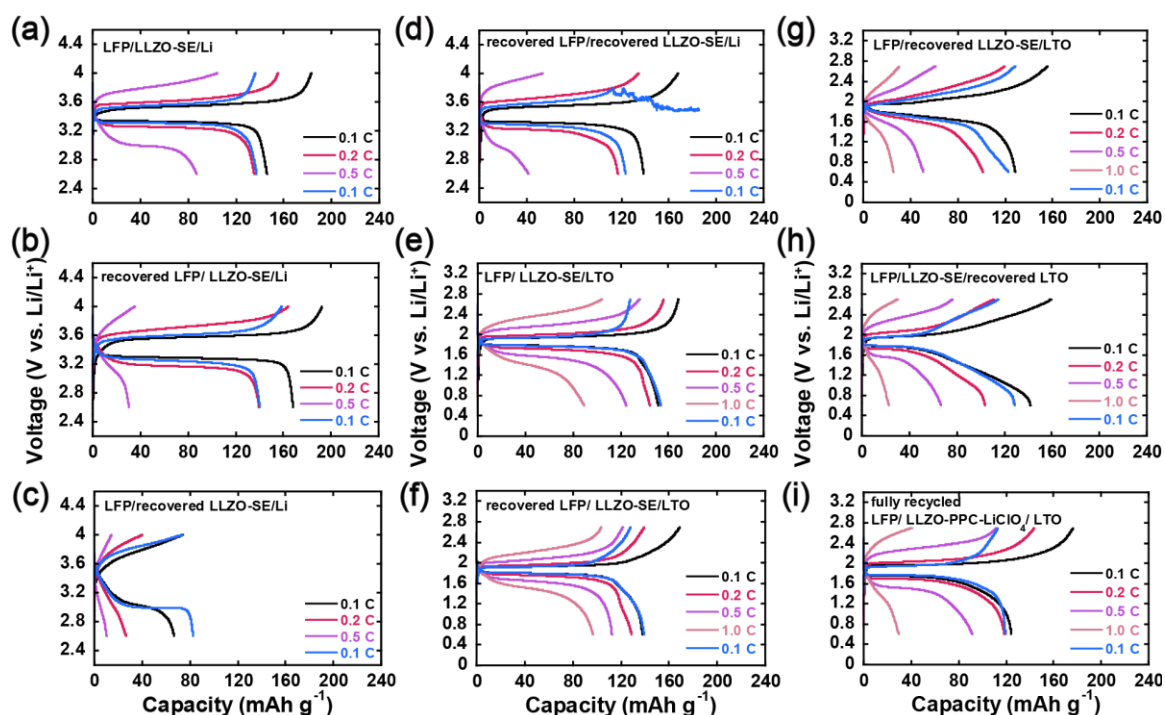


Figure 5-8: Cycling performance of Li metal cells, LFP/LLZO-SE/Li, incorporated with (a) pristine materials, and (b) recovered LFP, (c) recovered LLZO-SE, (d) recovered LFP and recovered LLZO. LTO cells, LFP/LLZO-SE/LTO, incorporated with (e) pristine materials, (f) recovered LFP, (g)

recovered LLZO, (h) recovered LTO, (i) fully recycled all-solid-state battery (recovered LFP, recovered LLZO-SE, and recovered LTO).

By introduction fluorine-based salt in the polymer layers, we are able to generate the LiF-rich SEI. In a typical lithium-ion battery utilizing liquid electrolytes containing 1 M LiPF₆ in a 1:1 wt% ratio of ethylene carbonate (EC) to dimethyl carbonate (DMC), the SEI shows some degree of dissolution when exposed to the liquid electrolytes. The primary components in the SEI, such as lithium fluoride (LiF), lithium hydroxide (LiOH), lithium carbonate (Li₂CO₃), lithium oxalate ((LiCO₂)₂), lithium methyl carbonate (LiOCO₂CH₃), and lithium ethyl carbonate (LiOCO₂C₂H₅) demonstrate higher dissolution rate in EC than in DMC, due to the higher polarity of EC.^[117] Therefore, we utilize EC during the recovery process by immersing the spent electrolytes in EC at 65°C for 30 minutes. This is expected to facilitate the dissolution of potential undesired phases such as LiOH on recovered LLZO.

DMF and EC were used during the recovery process to investigate their impact on the efficiency of removing cycling byproducts. Figure 5-9(a) shows the discharge capacity of the control group, full cells (LFP/recycled LLZO-SE/Li) with recovered LLZO cleaned with DMF. Spent LLZO is recovered from half cells, with Li metal as non-blocking electrodes, and wetted with DMF or LiFSI/DME. These cells are then fabricated and cycled at a specific current density for 20 cycles. We didn't observe a significant change in the cycling performance regardless of the presence of the LiF-rich SEI. This suggests that DMF may not be an effective solvent for removing undesired phases. The discharge capacity of full cells (LFP/recycled LLZO-SE/Li) with recovered LLZO cleaned with EC is shown in Figure 5-9(b). Full cell integrated with recovered LLZO with LiF-rich SEI demonstrate a higher average discharge capacity of 131, 111, and 14 mAh g⁻¹ at 0.1 C, 0.2, and 0.5 C, respectively. The charge and discharge voltage profiles are shown Figure 5-9(c). Whereas, full cells integrated with recycled LLZO without LiF-rich SEI deliver an average discharge capacity of 91, 65, and 10 mAh g⁻¹ at 0.1 C, 0.2 C, and 0.5C, respectively.

Regardless of the formation of stable SEI layer, DMF fail to wash away to unwanted phases, resulting the poor cycling performance of full cell with recovered LLZO. The incorporation of fluorine-based lithium salts could result in the formation of electrochemically stable LiF-rich SEI, which protects Li metal from undergoing reaction with polymers and limits the extend of degradation of solid-state electrolytes. By utilizing EC during the recovery process, certain lithium salts, such as LiOH, Li_2CO_3 , and LiF, dissolve in the EC, leaving a clean surface of recovered LLZO. This contributes to the enhancement in the cyclin performance of full cell integrated with recycled electrolytes, which exhibit less undesired non-lithium conducting phases.

We measured ionic conductivities as a function of temperature, ranging from 20°C to 120°C, to determine the activation energy associated with lithium-ion conduction in pristine and recovered LLZO-SE, as shown in Figure 5-9(d). The recovered LLZO-SE is cleaned with EC during the recovery process. Pristine LLZO-SE exhibits an activation energy of 0.14 eV. The Arrhenius temperature dependence indicates the activation energy of recycled electrolyte from half cells with the LiF-rich SEI is 0.18 eV, while without it is lower, at 0.20 eV. This suggests that a stable protective layer, LiF-rich SEI, on Li metal enables the passivation of electrochemical reactions and limits the generation of poorly ion-conducting phases on LLZO electrolytes. As the contaminants were successfully removed by EC, the recycled LLZO-SE demonstrate fast lithium-ion transport.

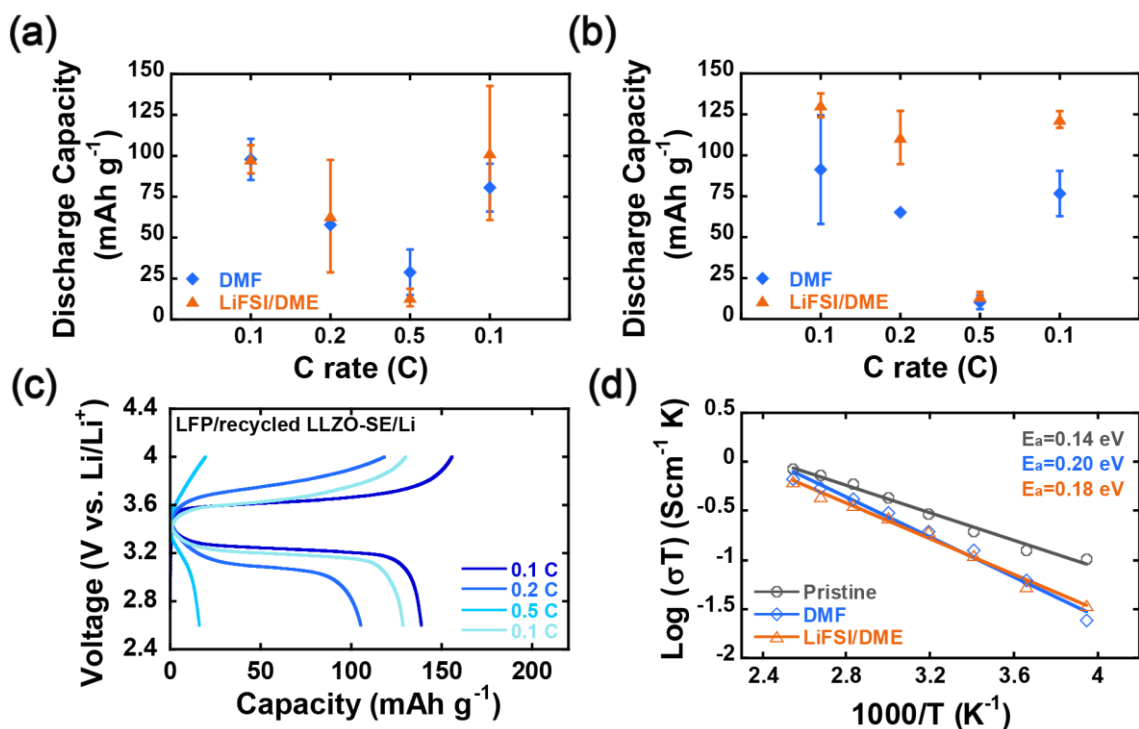


Figure 5-9: Discharge capacity of full cells (LFP/recycled LLZO-SE/Li) with recycled LLZO cleaned with (a) DMF or (b) EC from Li metal half cells wetted with DMF or LiFSI/DME cycled at 0.1, 0.2, and 0.5 C rates. (c) Charge and discharge curves of full cell incorporated with recycled LLZO cleaned with EC cycled at 0.1, 0.2, and 0.5 C rates. (d) Temperature dependence of ionic conductivity of pristine LLZO-SE, recycled LLZO-SE cleaned with EC from Li metal half cells wetted with DMF or LiFSI/DME. The solid lines represent Arrhenius fits, with the corresponding activation energies provided in the inset.

5.5 Conclusion

We provide insights on the formation of stable LiF-rich SEI layer on Li metal anodes by introducing fluorine-based lithium salt to promote the cycling performance of both pristine and recycled all-solid-state lithium batteries. All-solid-state batteries (LFP/LLZO-SE/Li and LFP/LLZO-SE/LTO), wetted with 4M LiFSI/DME at polymer-anode interfaces, demonstrate optimal discharge capacities of 152 mAh g^{-1} at 0.05 C and 157 mAh g^{-1} at 0.1 C, respectively. XPS measurement confirms that spent Li metal exhibits a relatively high ratio of LiF after sputtering. Ethylene carbonate (EC) demonstrates efficient removal of cycling byproducts such as LiOH, Li_2CO_3 , and LiF that present in the SEI. Full cells integrated with recycled LLZO electrolytes cleaned with EC and obtained from half cells with a LiF-rich SEI exhibited higher discharge capacities of 131 mAh g^{-1} at 0.1 C and 111 mAh g^{-1} at 0.2 C, compared to those integrated with recycled LLZO electrolytes from half cells without a stable SEI layer. Overall, this stable SEI layer serves two key functions: it passivates electrochemical side reactions at Li metal interfaces and restricts the formation of poorly ion-conducting phases within the LLZO electrolyte. Following the effective removal of unwanted phases, full cells incorporating recycled LLZO-SE exhibit enhanced overall battery performance.

5.6 Supporting Information

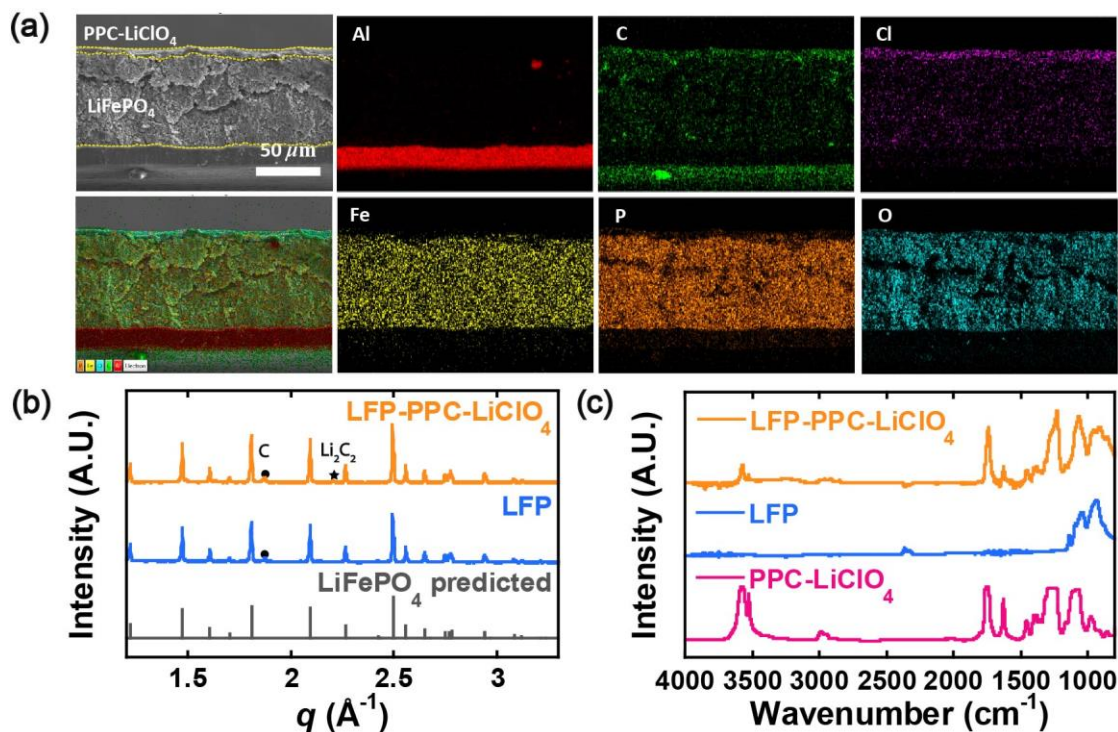


Figure S5-1: LiFePO₄ cathodes demonstrate excellent compatibility with PPC-LiClO₄ layers. (a) Elemental mapping of LiFePO₄ cathodes with the incorporation of interfacial layers present on the surfaces. (b) XRD data of a PPC-LiClO₄ coated LFP cathode compared with data from LFP and predicted LFP XRD profiles. Filled circle denotes peaks from carbon additives, star denotes a peak from lithium carbide. (c) FTIR spectra of a PPC-LiClO₄ coated LFP cathode compared with spectra from LFP and PPC-LiClO₄.

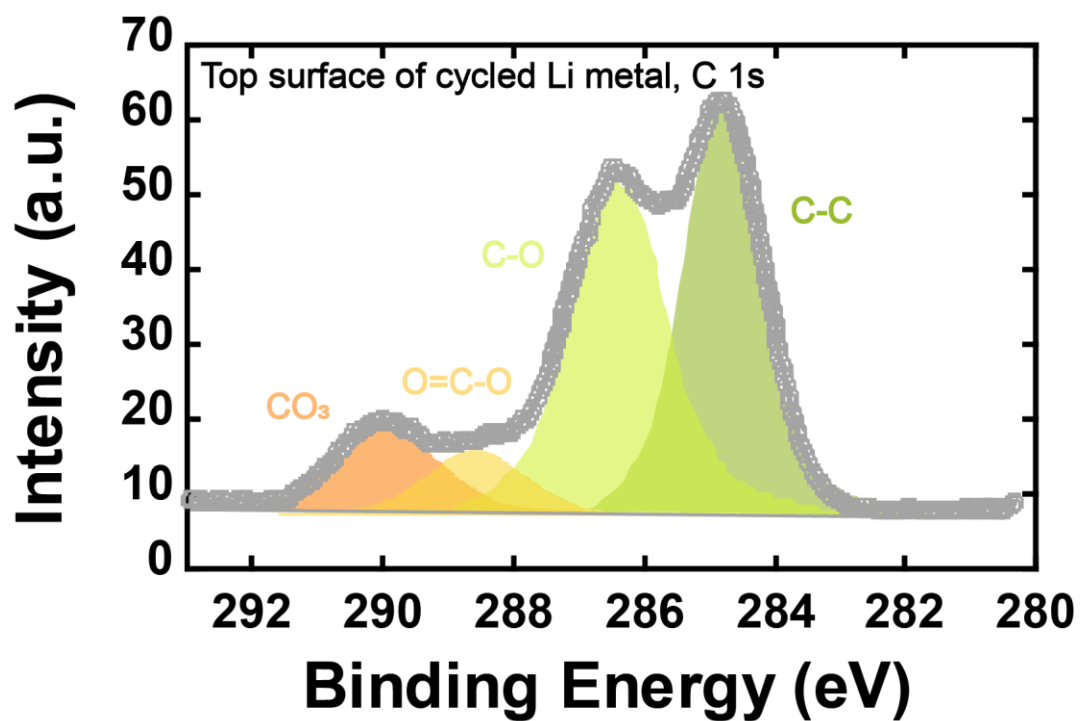


Figure S5-2: Post-mortem C 1s XPS Spectra of top surface of cycled Li metal anode.

Chapter 6

Reprocessing NASICON-Type Solid-State Electrolytes Using Cold Sintering Process

6.1 Overview

All-solid-state lithium batteries offer enhanced safety, higher energy density, and longer cycle life compared to traditional lithium-ion batteries. However, their commercialization is still in its early stages, and the lack of established recycling processes poses a major challenge for environmental sustainability. We utilize the cold-sintering process to repair fragmented LATP–LiTFSI and LAGP–LiTFSI composite electrolytes that simulate the cycled solid-state electrolyte undergoing severe mechanical degradation. By optimizing the amount of deionized water as a transient solvent, we enhance water domains while maintaining the water-in-salt structures and tailoring intergranular properties. Furthermore, we substitute water vapor for liquid water to reduce incongruent dissolution during the cold-sintering process of LAGP–LiTFSI without compromising densification effects. Overall, this work demonstrates the remarkable potential of the cold sintering process in altering and enhancing the intergranular properties within recycled solid-state composite electrolytes.

6.2 Introduction

All-solid-state lithium batteries (ASSBs) have shown promise as a next-generation energy storage technology, potentially offering improved safety, higher energy density, and longer cycle life compared to traditional lithium-ion batteries that use liquid electrolytes.^[1b, 2a, 3a, 3c] Although

significant progress has been made in ASSB research and development, commercialization is still in its early stages. One important aspect that has been overlooked is the recycling of these batteries. ASSBs contain a complex mixture of materials, such as ceramics, polymers, and metals, which may render conventional battery recycling methods ineffective or inefficient.^[4-5] The lack of established recycling processes for ASSBs poses a major challenge in terms of environmental sustainability and resource conservation. As a result, it is essential to develop efficient and cost-effective recycling techniques for ASSBs to ensure the sustainable adoption of this technology and reduce the environmental impact of battery waste.

LATP ($\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$) and LAGP ($\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$) are two promising solid-state electrolyte materials that have attracted significant attention in the development of all-solid-state lithium batteries. Both electrolytes feature a three-dimensional network of PO_4 tetrahedra and TiO_6 (or GeO_6) octahedra that allows for fast lithium-ion conduction, with room temperature conductivities reaching up to $10^{-3} \text{ S cm}^{-1}$.^[22] Unlike other oxide-based solid-state electrolytes, this NaSICON-type structure is relatively stable in an aqueous environment.^[21] This characteristic opens up the possibility of using environmentally friendly solvents, such as water, during the fabrication process, making them promising candidates for the development of greener and more sustainable all-solid-state lithium batteries.

The cold sintering process (CSP) has been effectively utilized in fabricating LATP and LAGP-based composite electrolytes.^[71b, 127] This technique enables the co-sintering of ceramic materials with salts or polymers at low temperatures, facilitating the development of composite electrolytes with rapid lithium-ion transport properties.^[35-38] Recently, the cold sintering process was employed to reprocess fragmented LLZO-based composite electrolytes.^[108] The low sintering temperature allows for the re-densification of ceramics with salts and polymers, resulting in a compact bulk phase to restore the lithium-ion transport pathway. However, incongruent dissolution

occurring during the cold sintering process leads to the formation of amorphous grain boundaries, which may adversely affect the electrochemical performance of the composite electrolytes.

Herein, we employ cold-sintering process to repair the fragmented structures of LATP–LiTFSI and LAGP–LiTFSI composite electrolytes. By optimizing the amount of deionized water as a transient solvent, we successfully increase the water domain while maintaining the water-in-salt structures and tailoring the intergranular properties in LATP–LiTFSI. Additionally, we employ water vapor to substitute liquid water, reducing the incongruent dissolution effect without compromising the densification effects during the cold-sintering process of LAGP–LiTFSI. Overall, our findings highlight the potential of the cold sintering process for effectively recycling and reprocessing solid-state composite electrolytes. Leveraging this innovative technique represents a significant advancement towards achieving material sustainability in the field of all-solid-state batteries.

6.3 Experimental Methods

Materials

LATP powders ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2$, LICGCTM powder) with an average particle size around 1 μm are purchased from Ohara Inc.. LAGP powders with a volume mean diameter of 26 μm are purchased from Toshima and Manufacturing Co.. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) are from Sigma Aldrich. All of materials were used without further treatment or purification.

Preparation of Ceramic-Salt Composite Electrolytes

To fabricate LATP–LiTFSI, LATP powders were thoroughly mixed with 20 wt% of 1.74 M LiTFSI/deionized water (DIW) solutions using a mortar and pestle. As for LAGP–LiTFSI, composite mixtures were obtained by homogeneously mixed with 10 wt% of 2.3 M LiTFSI/DIW solutions. The moistened powder was cold-sintered in a hardened steel die under a uniaxial pressure of 380 MPa at 130 °C for 1 h using a Carver press. To ensure a uniform heating temperature, the die was wrapped with a band heater and the platen temperature is controlled. As-prepared electrolytes are in a pellet form with a thickness of around 1.0 mm and a diameter of about 12.7 mm.

Material Characterization

Relative densities of pristine and reprocessed LATP–LiTFSI and LAGP–LiTFSI are determined from the ratios of the measured densities to the theoretical densities of the composite. The theoretical density of a composite can be calculated based on the volume fractions and theoretical densities of each constituent (LATP=2.72 g cm⁻³, LAGP=3.43 g cm⁻³, LiTFSI=1.33 g cm⁻³). Crystal structures and phase purities were determined by X-ray diffraction (XRD, Malvern Panalytical Empyrean) with Cu K α radiation. The acquired spectral data were analyzed using the MDI JADE software. The surface morphology and elemental compositions of pristine and reprocessed composite electrolytes were characterized using a Field Emission Scanning Electron Microscope (FE-SEM, Verios G4) and Energy Dispersive Spectrometer (EDS, Thermo Scientific). The dissolution rates of metal elements in LATP and LAGP were analyzed by inductively coupled plasma emission spectrometry (ICP-AES, Thermo iCAP 7400) Fourier-transform infrared

spectroscopy (FT-IR) were conducted using a Bruker Vertex 80 spectrometer. Raman spectra were performed using a Horiba LabRam HR.

Electrochemical Characterization

Electrochemical impedance spectroscopy (EIS, ModuLab XM MTS) measurements of symmetric cells using Al as blocking electrodes were carried out in a frequency range of 0.1 to 10^6 Hz with a 10-mV amplitude. The ionic conductivities were calculated using the formula, $\sigma = \frac{h}{Z_{re} \times A}$, where Z is the impedance on the real axis from the Nyquist plot, h is the thickness of the cold-sintered composite electrolyte, and A is the contacting area of blocking electrodes. The activation energies for lithium-ion conduction were determined by analyzing the temperature dependence of the ionic conductivities over a range of -20°C to 120°C , using the Arrhenius equation, $\sigma = A \times e^{-\frac{E_a}{k_B T}}$, where A is the pre-exponential factor, k_B is the Boltzmann constant, and E_a is the activation energy.

6.4 Results and Discussion

In spent solid-state composite electrolytes, defects such as voids and cracks may obstruct lithium-ion transport pathways, leading to battery short circuits. To simulate an extreme case of mechanical degradation, which is one of the primary degradation mechanisms in all-solid-state electrolyte batteries, the electrolytes are deliberately broken into pieces through grinding. In order to recycle these mechanically degraded electrolytes, a cold sintering process is employed to re-densify the microstructures with a low sintering temperature, which enables the integration of ceramics and lithium salts without compromising their active properties.

The recycling process for solid-state composite electrolytes comprises four main steps: coin cell disassembly, component separation, cold sintering, and reuse of the reprocessed electrolytes. After separating from the aluminum blocking electrodes, surface contaminants were removed by sanding with 2500 grit sandpapers. Using a mortar and pestle, composite electrolytes were crushed into a powder form and thoroughly mixed with DIW, which functions as a transient solvent to facilitate mass transport and regulate the dissolution-precipitation processes during cold sintering process.

To investigate the effects of the recycling process on the performance of the reprocessed electrolytes, multiple cycles of reprocessing were carried out on the as-synthesized electrolytes. During reprocessing cycles, the density and ionic conductivity of the reprocessed electrolytes were tracked, as shown in Figure **6-1(a-b)**. LATP–LiTFSI demonstrates the fast lithium-ion transport with a conductivity in excess of $10^{-4} \text{ S cm}^{-1}$ and a relative density of 87%, after experiencing four-time recycling cycles. Three-time reprocessed LAGP–LiTFSI shows a conductivity around $2.7 \times 10^{-5} \text{ S cm}^{-1}$ and a relative density of 83%. While the relative densities of the reprocessed composite electrolytes remain comparable to those of the pristine electrolytes, their ionic conductivity exhibits an obvious decrease of approximately one order of magnitude lower than the pristine state. The dense microstructures of the reprocessed electrolytes imply that the cold-sintering process is capable of repairing fractured structures. However, the decrease in ionic conductivity suggests hindered lithium-ion transport, despite the compact microstructures obtained after reprocessing.

As the ionic transport in ceramics is highly related to their crystalline structures, we examined the consequences of reprocessing through cold sintering using X-ray diffraction (XRD). Both reprocessed LATP and LAGP-based composite shows the retention of pristine crystal structure, which explains the retention of ionic conductivity after reprocessing. Aluminum phosphate (AlPO_4) appears with a new peak at $1.86 \text{ \AA}^{-1}$ in reprocessed LATP–LiTFSI (Figure **6-1(c)**). After reprocessing, the formation of non-conductive secondary phases, acting as a barrier

layer, may impede the lithium-ion transport at grain boundaries. In reprocessed LAGP–LiTFSI, the increased intensity of the peak at $1.86 \text{ \AA}^{-1}$ in the diffraction pattern indicates the formation of germanium oxide (GeO_2) as secondary phases (Figure **6-1(d)**). The XRD spectra of reprocessed LAGP–LiTFSI exhibited a shift towards higher angles, indicating a better correspondence with the reference pattern for $\text{LiGe}_2(\text{PO}_4)_3$ (LGP) (Figure **S6-1**). LGP shows a poor conductivity of $10^{-6} \text{ S cm}^{-1}$ at room temperature, whereas this can be improved with partial replacement of Ge^{4+} by Al^{3+} ions.^[128] With the observation of right-shift spectrum, we attributed the decrease in ionic conductivities to the presence of non-conducting and LGP-like phases within the reprocessed LAGP–LiTFSI. SEM and EDS mapping images reveal densely packed microstructures for pristine and reprocessed composites, suggesting the fragmented structures was re-integrated by cold sintering process, as shown in Figure **6-1(e)** and Figure **S6-2**. Overall, the presence of undesired phases explains the loss in ionic conductivities of reprocessed composite electrolytes, despite the compact structures. Therefore, developing strategies to enhance lithium-ion conduction in the reprocessed electrolytes is necessary in order to reuse spent electrolytes.

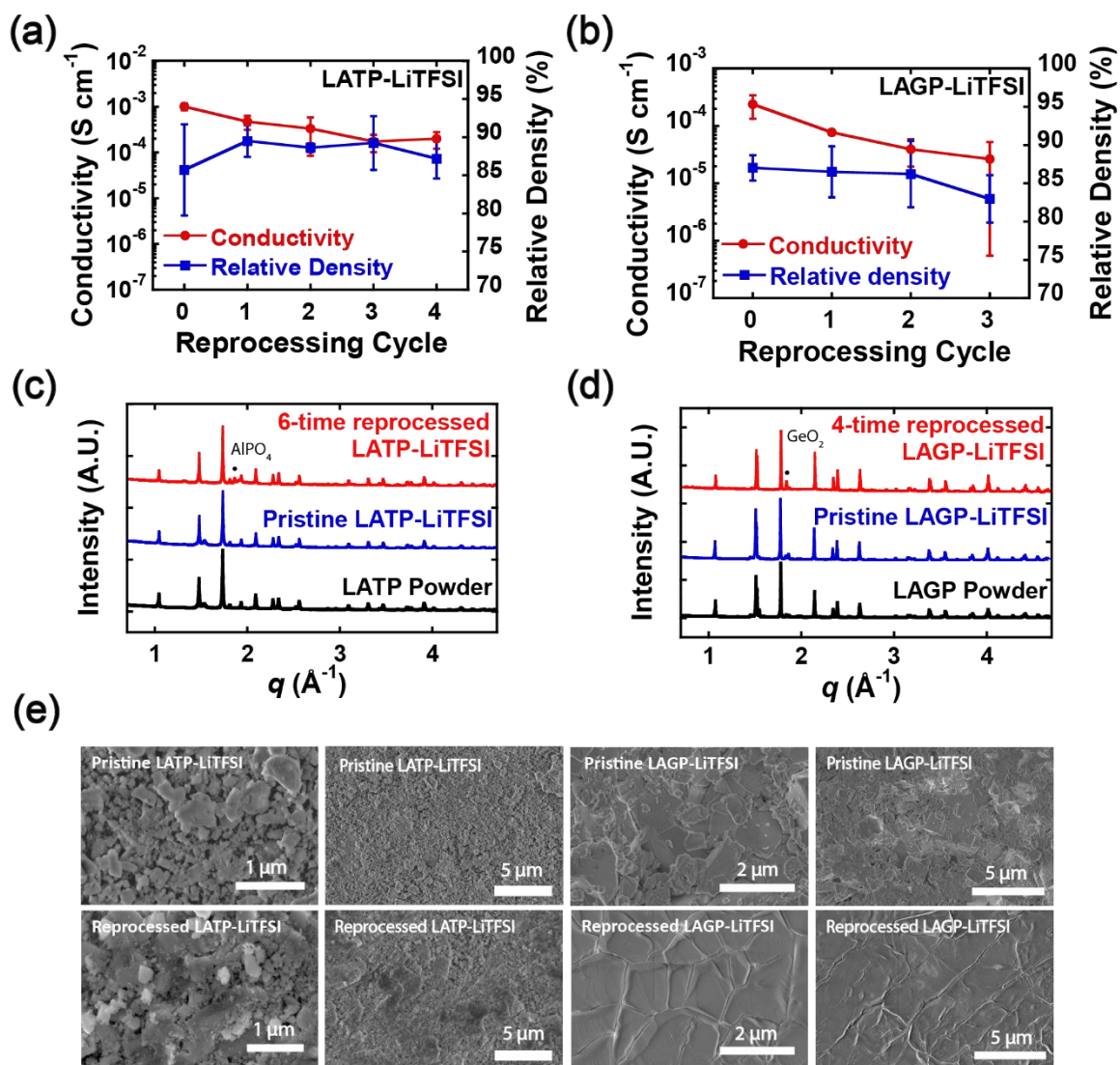


Figure 6-1: Ionic conductivities and relative densities of (a) LATP-LiTFSI and (b) LAGP-LiTFSI after undergoing various reprocessing cycles. X-ray diffraction (XRD) spectra of (c) LATP-LiTFSI and (d) LAGP-LiTFSI at the pristine and reprocessed states. (e) SEM images of pristine and reprocessed LATP-LiTFSI and LAGP-LiTFSI.

Incongruent dissolution is especially pronounced in multicomponent materials, where the individual constituents exhibit varying dissolution rates when exposed to solvents. This phenomenon results in the formation of secondary phases, which may hinder the densification process and cause irreversible phase transformations. Therefore, we hypothesize that the occurrence of incongruent dissolution causes the stoichiometry variations in reprocessed

electrolytes resulting in poor ionic conductivities. Dissolution concentrations of elements present in LATP and LAGP under corresponding cold sintering conditions were studied. NACISON powers are heat-treated in DIW at 100 for 1 h, which replicate the time and temperature conditions used in the cold sintering process. The clear solution obtained after removing the particles by centrifugation and filtration was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES) to determine the dissolved elemental concentrations.

Figure 6-2(a-b) reveal that lithium exhibits preferential dissolution in deionized water (DIW) for both LATP and LAGP, likely due to its high volatility. Despite the phenomenon of incongruent dissolution occurs in LATP, the solubilities of elements are low, limiting the unfavorable effects that incongruent dissolution induce. Yet, the preferential dissolution of phosphorus and aluminum may explain the formation of AlPO_4 observed in the XRD spectra. The presence of amorphous secondary phases may hinder the lithium-ion transport between grains, hindering ion transport pathways. Elements in LAGP exhibit noticeable incongruent dissolution effects with higher dissolution rates, which may amplify unfavorable effects of incongruent dissolution. Leaching of aluminum suggests a lower aluminum content in reprocessed LAGP–LiTFSI, which may explain the right shift of XRD pattern. The change in aluminum contents is observed by *Safanama et al.* as LAGP undergoes lithium-ion exchange process in aqueous solutions.^[129] In addition, the preferential dissolution of germanium results in the formation of amorphous grain boundaries and non-conductive germanium oxide. Overall, preferential dissolution occurs during cold sintering process, resulting in the appearance of impurities or poor lithium-ion conducting phases. This attributes to the decrease of ionic conductivities in reprocessed composite electrolytes.

Lee et al. studied the local environment of LiTFSI with the presence of water in cold-sintered composites and suggested a “water-in-salt” electrolyte system present along the grain boundaries.^[71b] As water channel acts as conducting wires for the transport of hydrated lithium-ion,

low salt concentrations with more bulk-like water domains favor high ion conductivity under the concentrated environment.^[130] As such, by increasing the amount of water introduced into the recovered composite powders during cold sintering, we can enhance the conductivity of reprocessed samples by generating additional water domains. Various amounts of DIW (100, 125, and 150 μL) was introduced during the cold-sintering process to improve lithium-ion transport in LATP–LiTFSI. In the control experiment, the transient solvent was introduced at 18% of the mass weight of the ceramics. As shown in Figure 6-2(c), with the introduction of 100 μL of water, samples demonstrate improved conductivity as reprocessing times increase compared to control samples. However, the expected improvement in conductivities was not observed upon adding 125 and 150 μL of water into the reprocessed powders. The additional water presence enhances the mobility of the recovered powders, resulting in a slurry-like mixture that complicates sample handling. Consequently, the mixture is continuously stirred until most of the water evaporates, leaving behind a wet sand-like mixture. The amount of water remaining in the structure shows no significant difference after cold sintering. Reprocessed LATP–LiTFSI cold-sintered with 100 μL of DIW shows a similar activation energy of 0.35 eV for lithium-ion transport in the composites, compared to the pristine one. Introducing of increasing amount of DIW during cold sintering does not necessarily contribute to enhancing ion transport in reprocessed LATP–LiTFSI. (Figure 6-2(e)). This implies that introducing a higher amount of water into the "water-in-salt" concentrated environment enable the increase in the formation of hydrated lithium $\text{Li}^+(\text{H}_2\text{O})_4$ domains, thereby enhancing lithium-ion transport within the recycled LATP-based composites.

Given that LAGP has more noticeable effect of incongruent dissolution, reprocessed LAGP powders were treated with water vapor from heated DIW at 60 °C before cold sintering for various time (Figure 6-2(d)). After undergoing three times reprocessing cycles, reprocessed LAGP–LiTFSI shows an obvious improvement in lithium-ion conduction with an ionic conductivity of $4.2 \times 10^{-4} \text{ S cm}^{-1}$ when reprocessed powders being treated with water vapor for 10 mins before cold sintering

process. Increase the amount of vapor by raising the heating temperature of DIW to 80 °C shows negative effects on the ionic conductivity of reprocessed electrolytes (Figure S6-3). Reprocessed LAGP–LiTFSI prepared by cold-sintering water vapor wetted reprocessed powders, exhibits an activation energy of 0.42 eV, suggesting faster lithium-ion transport compared to the sample cold-sintered with DIW shows a higher activation energy of 0.54 eV (Figure 6-2(f)). This suggests that regulating the amount of transient solvents introduced during the cold sintering process for materials exhibiting high dissolution rates can significantly mitigate the effects of preferential dissolution, without compromising the densification effects.

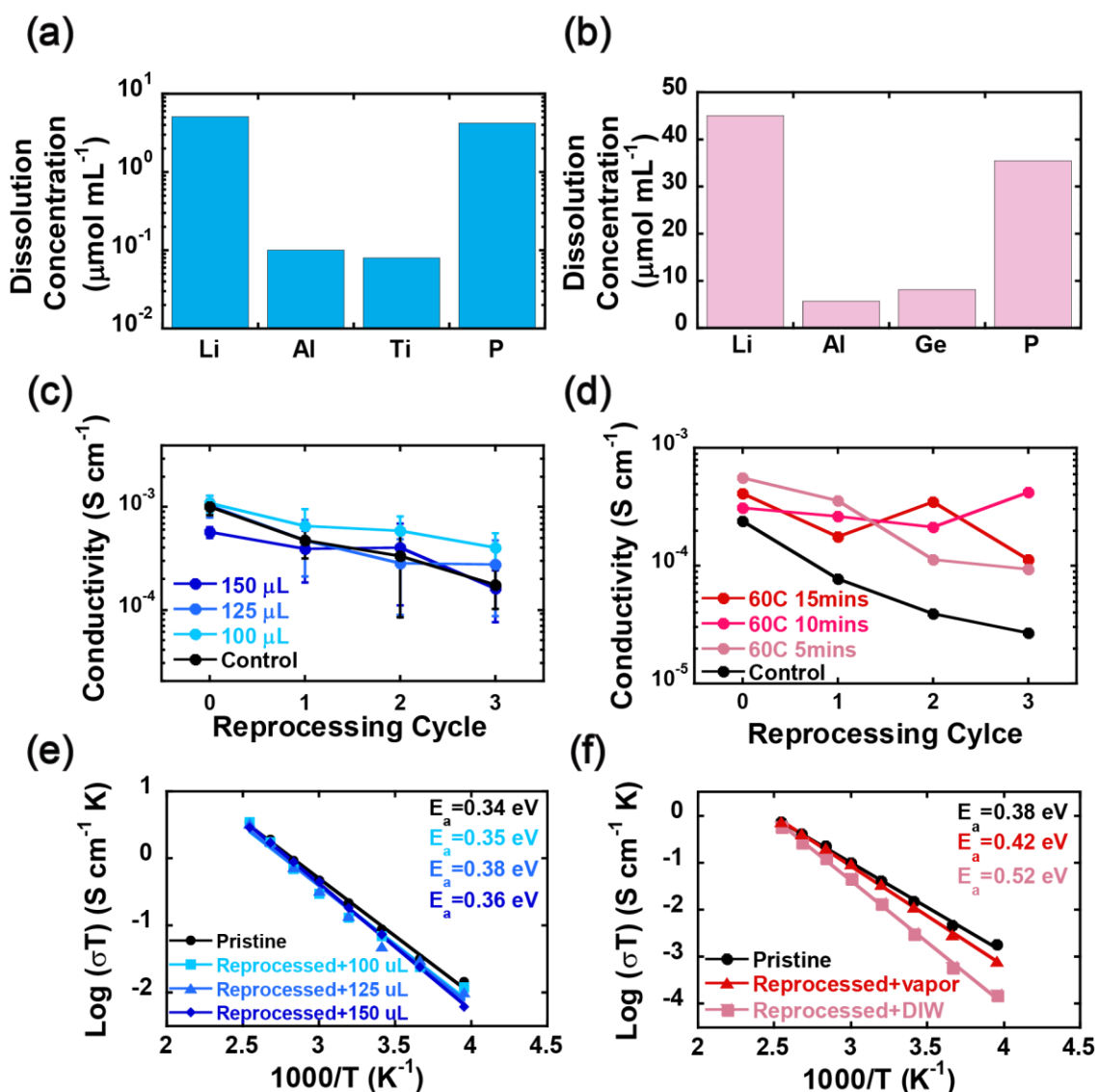


Figure 6-2: Dissolution concentration of elements in (a) LATP and (b) LAGP when being heated in DIW at 100 °C for 1 hour. Ionic conductivities of reprocessed (c) LATP–LiTFSI and (d) LAGP–LiTFSI reprocessed with various amounts of DIW and water vapor, respectively. Temperature dependence of ionic conductivity for pristine and reprocessed (e) c reprocessed with various amount of DIW; pristine and reprocessed (f) LAGP–LiTFSI treated with DIW or water vapor. The solid lines represent the Arrhenius fits with the corresponding calculated activation energies in the inset.

To further understand the “water-in-salt” environment in composite electrolytes, FT-IR and Raman were conducted on the reprocessed LATP–LiTFSI. FTIR spectra of pristine and reprocessed composites demonstrate characteristic peaks of SNS symmetric ($\nu_{(s)}\text{SNS}$, $\sim 750\text{ cm}^{-1}$) and asymmetric stretch ($\nu_{(as)}\text{SNS}$, $\sim 800\text{ cm}^{-1}$) from LiTFSI (Figure 6-3(a)). When LiTFSI presents in a high concentration environment, SNS symmetric peaks shifted to higher wavenumbers. LiTFSI in reprocessed LATP–LiTFSI shows a local environment closer to the LiTFSI water solution with a concentration of 20 M ($\nu_{(s)}\text{SNS} = 745.8\text{ cm}^{-1}$). With the incorporation of less amount of DIW in reprocessed LATP–LiTFSI, SNS symmetric peak at a higher wavenumber is observed with $\nu_{(s)}\text{SNS}$ around 746.4 cm^{-1} (Figure 6-3(b)). Raman spectra show the S–N–S bending vibration of TFSI anion in the range of $740\text{--}760\text{ cm}^{-1}$ (Figure 6-3(c)). Pristine and reprocessed LATP–LiTFSI demonstrate a sharp Raman shift at 744.1 cm^{-1} , which can be ascribed to the presence of LiTFSI. Raman spectra also confirm that TFSI anions in reprocessed composites share a similar the local coordination environment to the highly concentrated “water-in-salt” electrolytes.

To investigate the water-in-salt structures along the grain boundaries, XRD profiles of reprocessed LATP–LiTFSI cold sintered with various amount of water are shown in Figure 6-3(d). We observed two peaks in the low q range. The faint broad peak in a range of $0.4\text{--}0.8\text{ \AA}^{-1}$ can be ascribed to the distance between solvated TFSI^- in the water domain. The sharp peak at around $1.0\text{ \AA}^{-1}$ is attributed to the distance between TFSI^- in TFSI network (TFSI^- bridged by water molecules, $\text{TFSI}^- \cdots \text{HOH} \cdots \text{TFSI}^-$).^[131] As the peak at $1.0\text{ \AA}^{-1}$ is overlapped with the LATP spectrum, we fail to distinguish coordination environment of LiTFSI in high concentration regime in the composites.

As the concentration of LiTFSI increases, the broad peaks shift towards higher scattering vector values with decreasing intensity. This suggests that the average spacing between TFSI⁻ anions in the water domain become smaller, and the number of solvated TFSI⁻ anions decrease in the concentrated environment. The d spacing of solvated TFSI⁻ anions can be calculated using $d = \frac{2\pi}{q}$ and plotted as a function of induced amount of water during cold sintering process, as shown in Figure 6-3(e). With the introduction of a higher amount of water, a larger distance between solvated TFSI⁻ anions was observed, indicating an expansion of the water-rich domains. The distances between solvated TFSI⁻ anions in reprocessed composites are in a range of 8.6–10.9 Å, which is smaller than the one in 15 m LiTFSI aqueous solution with a value of 12 Å.^[131a] We attribute the closer TFSI⁻ anions to the presence of LATP grains, which may confine the "water-in-salt" structures within the grain boundary regions. While the calculated distance is higher than the intermolecular distance of TFSI⁻ anions in pure molten LiTFSI (TFSI⁻···Li⁺···TFSI⁻) and the distance of TFSI⁻ anions in high concentration regime (TFSI⁻···HOH···TFSI⁻), which is around 5.3 Å and 6.4 Å, respectively.^[131a, 132]

The XRD analysis on the reprocessed LATP–LiTFSI indicates that varying the amount of introduced water during cold sintering allow the modification of the solvation behavior of LiTFSI in water presenting along the grain boundaries. It is noteworthy that by introducing 100 μL of water during each reprocessing cycle, we are able to increase the water-rich domains while preserving the "water-in-salt" structured regions along the grain boundaries. In this supersaturated system, where LiTFSI molecules outnumber the water molecules, interionic attractions become more pronounced compared to solvent-ion interactions, resulting in the association of Li⁺ cations and TFSI⁻ anions. This leads to the formation of a nano-heterogeneous liquid structure, where ion-ion networks (Li⁺(TFSI⁻)_x) are intertwined with nanometric water hydrogen-bonding networks (Li⁺(H₂O)₄). The decoupled lithium-ions exhibit faster transport through the bulk-like water

channel in a vehicular mechanism by coordinating with H_2O molecules instead of the solvent exchange mechanism.^[133] This explains the high mobility of lithium-ion in the reprocessed LATP–LiTFSI cold sintered with 100 μL of water, where more decoupled Li^+ transport through the bulk-like water channel in the water-in-salt structures.

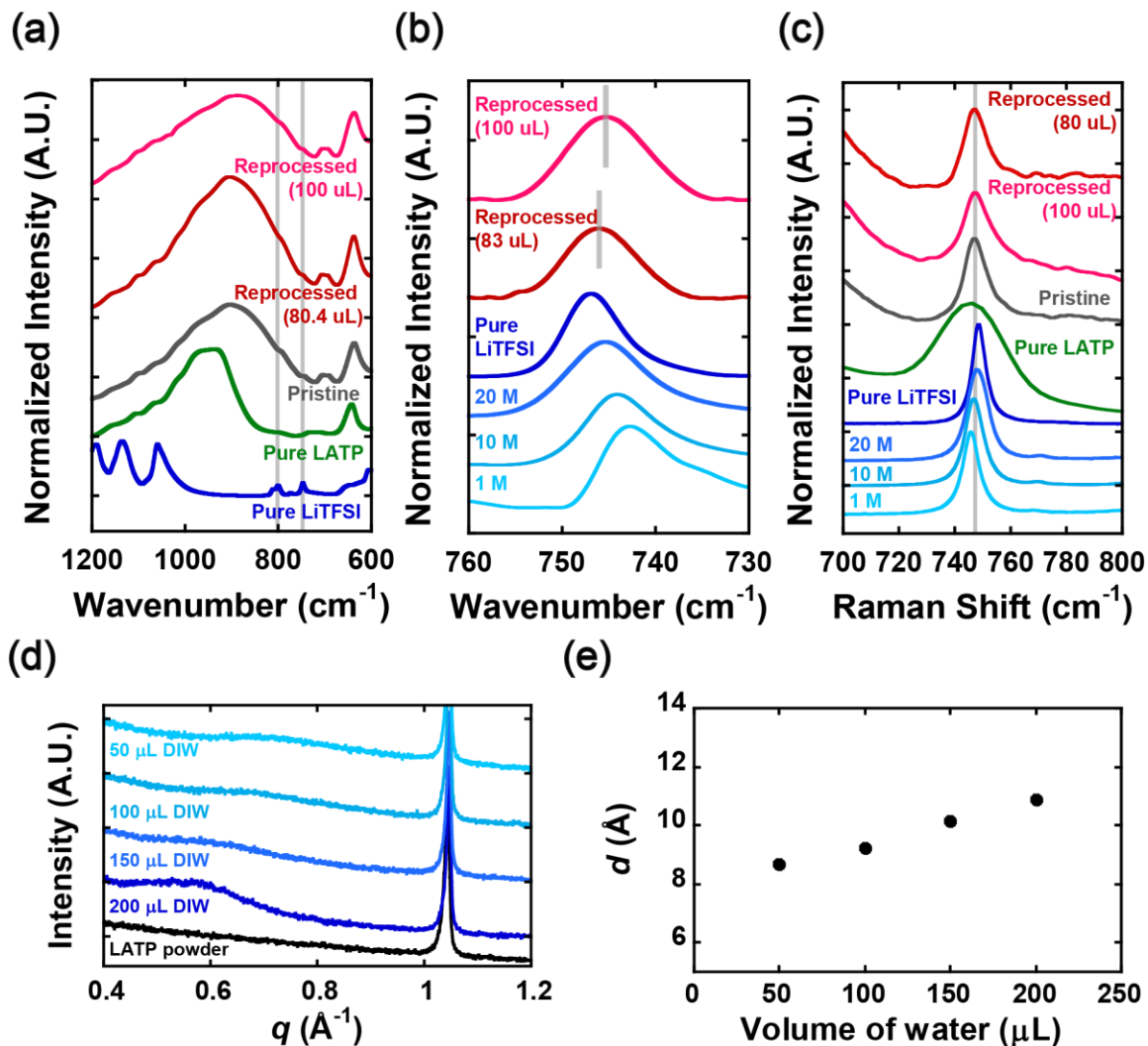


Figure 6-3: FT-IR spectra of (a) pristine and reprocessed LATP–LiTFSI cold sintered with 100 and 84 μL of DIW, pure LiTFSI, and pure LATP. (b) SNS symmetric stretch (ν_{S}) SNS) from LiTFSI in reprocessed LATP–LiTFSI and LiTFSI solution in DI water with different concentrations. (c) Raman spectra in the range of 700–800 cm^{-1} (S–N stretching, C–S stretching, and CF_3 bending mode of TFSI ions). (d) XRD patterns of reprocessed LATP–LiTFSI cold-sintered with various amount of DIW. (e) The average distance (d) between solvated TFSI ions in reprocessed LATP–LiTFSI as a function of concentrations.

6.5 Conclusion

We directly reprocessed LATP–LiTFSI and LAGP–LiTFSI composite electrolytes using the cold sintering process. Reprocessed LATP–LiTFSI demonstrates ionic conductivities that exceed $10^{-4} \text{ S cm}^{-1}$ at room temperature and a relative density of 87%, after experiencing four recycling cycles; While tree-time reprocessed LAGP–LiTFSI shows a conductivity around $2.7 \times 10^{-5} \text{ S cm}^{-1}$ and a relative density of 83%. The occurrence of incongruent dissolution during cold sintering results in the appearance of impurities or poor lithium-ion conducting phases. By introducing more amount of water during cold sintering, we are able to increase the water-rich domains while preserving the "water-in-salt" structured regions along the grain boundaries. With more decoupled Li^+ transport through the bulk-like water channel in the water-in-salt structures, reprocessed LATP–LiTFSI demonstrates high mobility of lithium-ion along with low activation energy. Overall, we highlight the capability of the cold sintering process to modify and optimize the properties of the grain boundaries in reprocessed solid-state composite electrolytes. This achievement also represents a significant advancement towards enhancing material sustainability for all-solid-state battery technologies.

6.6 Supporting Information

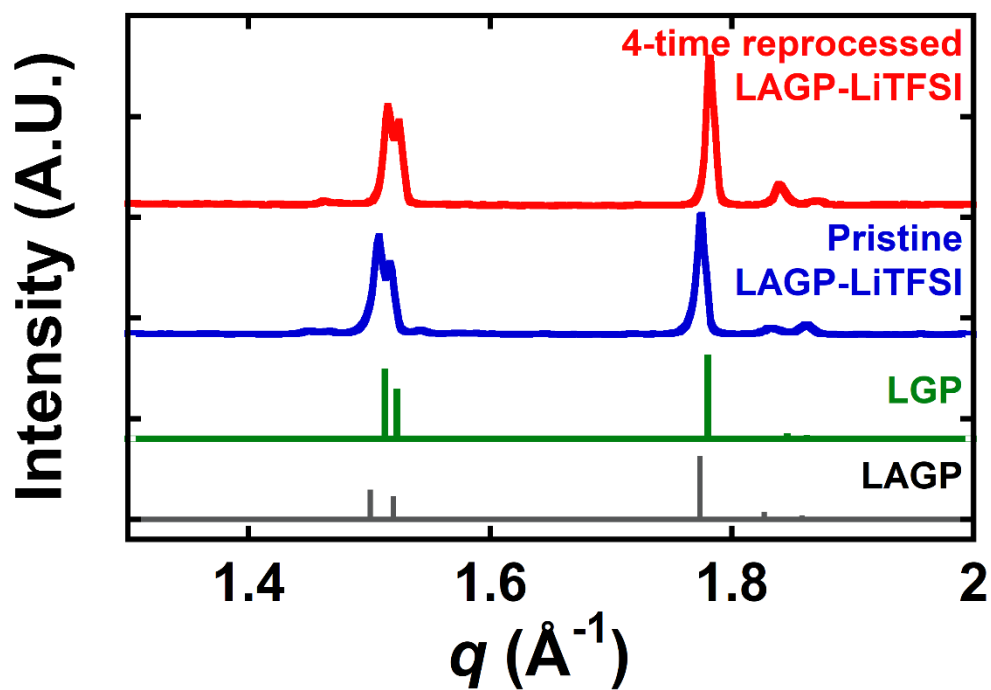


Figure S6-1: X-ray diffraction analysis of pristine and reprocessed LAGP–LiTFSI indicates that the spectra of the reprocessed composite are right-shifted, showing closer correspondence with the reference pattern for $\text{LiGe}_2(\text{PO}_4)_3$ (LGP).

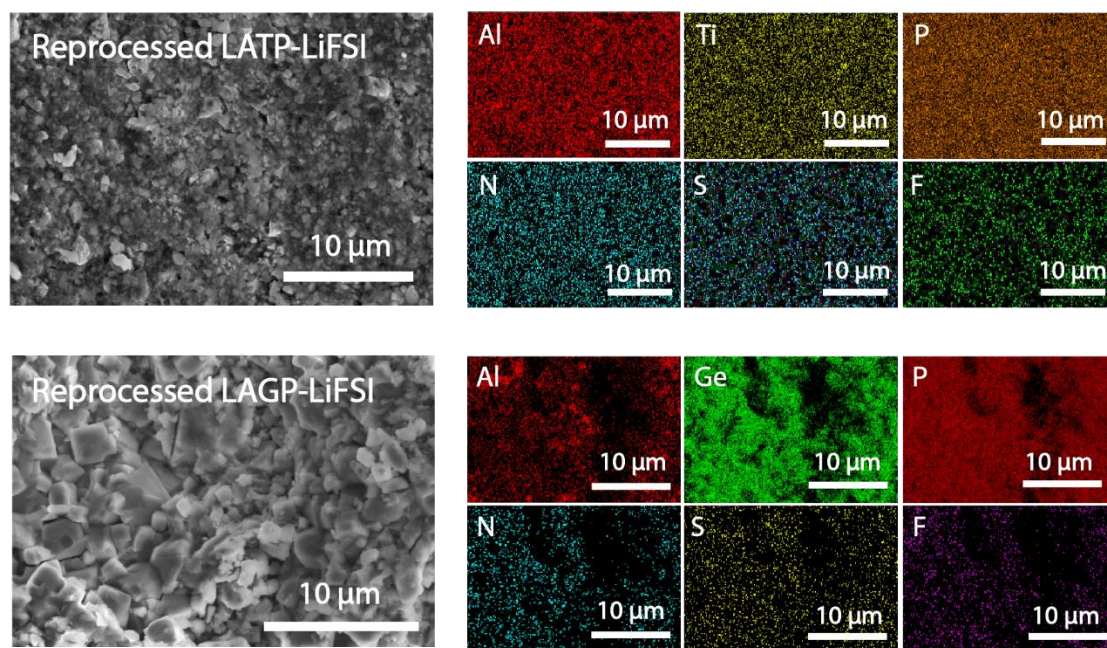


Figure S6-2: SEM images and the corresponding EDS mapping of microstructures of reprocessed LATP-LiTFSI and reprocessed LAGP-LiTFSI.

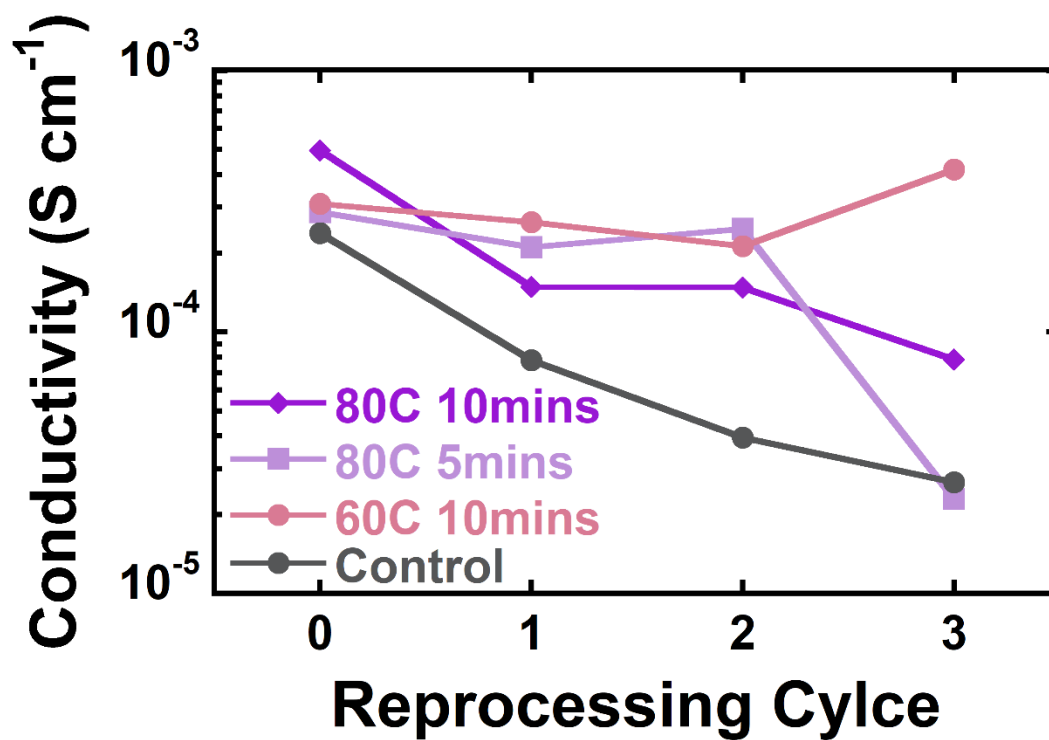


Figure S6-3: Ionic conductivities of reprocessed LAGP–LITFSI with composite powders treated with water vapor from 80°C DIW for various time before cold sintering process.

Chapter 7

Conclusions and Future Directions

7.1 Conclusions

All-solid-state batteries (ASSBs) mark a significant leap forward in energy storage technology, offering distinct advantages over conventional lithium-ion batteries. As technological advancements bring ASSBs nearer to commercialization, the pressing necessity to address their recycling and end-of-life management becomes more apparent. However, despite the growing recognition of this issue, the recycling of ASSBs remains in its early stages, with inadequate research and infrastructure to effectively address this challenge. The thesis focuses on addressing the critical challenge of recycling ASSBs through several innovative approaches.

In Chapter 3, we directly reprocessed LLZO–PPC–LiClO₄ composite electrolytes via the cold sintering process. The reprocessed LLZO–PPC–LiClO₄ exhibits room temperature ionic conductivities exceeding 10^{-4} S cm⁻¹ after undergoing five reprocessing cycles. During cold sintering, incongruent dissolution leads to a partial shift from a highly conductive cubic phase to a less conductive tetragonal phase. Cubic phases can be stabilized through thermal annealing at 170 °C, which recovers ionic conductivity after reprocessing. All-solid-state lithium batteries employing thermally annealed reprocessed electrolytes demonstrate a high discharge capacity of 168 mAh g⁻¹ at 0.1 C and excellent performance retention at 0.2 C for over one hundred cycles. Life cycle assessment (LCA) indicates that using reprocessed electrolytes significantly reduces both energy consumption and greenhouse gas emissions by eliminating the need for raw materials and complex synthetic reprocessing. In summary, cold sintering enables direct reprocessing of composite electrolytes, offering a sustainable approach for energy storage device sustainability.

Chapter 4 introduces a novel design for recyclable all-solid-state lithium batteries, featuring polymer interfacial layers strategically positioned between electrodes and electrolytes. These interfacial layers enhance the solid-solid contact, improving the wettability of lithium metal on LLZO-based solid electrolytes and reducing interfacial resistance. Crucially, these polymeric interfacial layers facilitate the separation of solid electrolytes from electrodes during the recycling process, enabling further direct recycling. The recovered battery components maintain their crystalline structures with minimal degradation and contamination. This recycling strategy is demonstrated for full cells utilizing either lithium metal or lithium titanate anodes, highlighting its versatility across different battery chemistries. Full cells reassembled with recycled components exhibit modest degradation in electrochemical performance compared to pristine cells. Overall, this architectural design provides insights for developing recyclable all-solid-state batteries, offering a scalable and sustainable end-of-life management solution for spent batteries.

Chapter 5 provide insights on the formation of stable LiF-rich SEI layer on Li metal anodes by introducing fluorine-based lithium salt to promote the cycling performance of both pristine and recycled all-solid-state lithium batteries. All-solid-state batteries (LFP/LLZO-SE/Li and LFP/LLZO-SE/LTO), wetted with 4M LiFSI/DME at polymer-anode interfaces, demonstrate optimal discharge capacities of 152 mAh g⁻¹ at 0.05 C and 157 mAh g⁻¹ at 0.1 C, respectively. Ethylene carbonate (EC) demonstrates efficient removal of cycling byproducts such as LiOH, Li₂CO₃, and LiF that present in the SEI during recovery process. Full cells integrated with recycled LLZO electrolytes cleaned with EC and obtained from half cells with a LiF-rich SEI exhibited higher discharge capacities of 131 mAh g⁻¹ at 0.1 C and 111 mAh g⁻¹ at 0.2 C, compared to those integrated with recycled LLZO electrolytes from half cells without a stable SEI layer. Overall, we demonstrate that the formation of LiF-rich SEI can promote the cycling performance of both pristine and recycled all-solid-state batteries. This stable SEI layer serves a dual purpose: it passivates electrochemical side reactions at the Li metal interfaces, and it limits the generation of

poorly ion-conducting phases within the LLZO electrolyte. After efficient removal of undesired phases, full cells integrated with recycling LLZO-SE demonstrate improved overall battery performance.

Chapter 6 highlights the direct reprocessing of LATP–LiTFSI and LAGP–LiTFSI composite electrolytes via the cold sintering process. The reprocessed LATP–LiTFSI exhibited room temperature ionic conductivities exceeding $10^{-4} \text{ S cm}^{-1}$ and a relative density of 87% after four recycling cycles, whereas the thrice-reprocessed LAGP–LiTFSI demonstrated a conductivity of approximately $2.7 \times 10^{-5} \text{ S cm}^{-1}$ and a relative density of 83%. Incongruent dissolution during cold sintering led to the emergence of impurities or poorly lithium-ion conducting phases. Through the introduction of a higher water content during cold sintering, we could augment water-rich domains while preserving the "water-in-salt" structured regions along the grain boundaries in LATP–LiTFSI. This facilitated more decoupled Li^+ transport through the bulk-like water channels within the water-in-salt structures, resulting in reprocessed LATP–LiTFSI exhibiting high lithium-ion mobility along with low activation energy. In summary, we highlight the ability of the cold sintering process to tailor the intergranular properties of reprocessed solid-state composite electrolytes, marking a significant advancement in material sustainability for all-solid-state batteries.

Altogether, this thesis proposes innovative solutions to the crucial issue of recycling ASSBs. Through a multifaceted approach involving materials processing techniques, battery architecture design, and microstructural engineering methods, the thesis presents comprehensive strategies to overcome the recycling challenges associated with ASSBs. The overarching objective is to advance the sustainability of energy storage devices by shifting towards a manufacturing design approach centered on recovery rather than solely focusing on performance optimization. Through these efforts, the thesis aims to foster a transition towards a more environmentally conscious and resource-efficient battery recycling ecosystem.

7.2 Future Directions

Optimizing Polymer Interfacial Layers

In chapter 4, we introduce a novel battery configuration design to enable the direct recycling of all-solid-state lithium batteries through the incorporation of polymer-salt interfacial layers between electrodes and electrolytes. However, these polymer layers typically require a low glass transition temperature (T_g) to achieve high ionic conductivity, which consequently compromises the mechanical strength. This lack of mechanical robustness fails to effectively suppress lithium dendrite penetration, leading to poor cycling performance and limited battery life.

To enhance the effective separation during recycling without compromising cycling performance, an alternative approach involves incorporating inorganic fillers into polymers to create composite electrolytes.^[134] Chen *et al.* conducted a study on PEO/garnet composite electrolytes to investigate the impact of transitioning from a "polymer-in-ceramic" to a "ceramic-in-polymer" configuration on the cycling performance of all-solid-state lithium metal batteries.^[135] When ceramic particles are added at concentrations below their percolation threshold, they enhance lithium-ion conductivity within the polymer matrix, primarily through facilitating the formation of amorphous polymers with improved polymer chain movement. Upon reaching the percolation threshold, the composite electrolytes exhibit dual conduction pathways, leveraging both polymer and ceramic ionic conductivity. Figure 7-1 illustrates the transfer process of composite electrolytes, transitioning from "ceramic-in-polymer" to "intermediate", and finally to "polymer-in-ceramic". The incorporation of LLZO ceramic particles into the polymer layer creates a robust and stable interface between the electrolyte and anode.^[136] This stable interface enables effective suppression of lithium dendrite growth, thereby contributing to superior cycling performance and longevity of the battery.

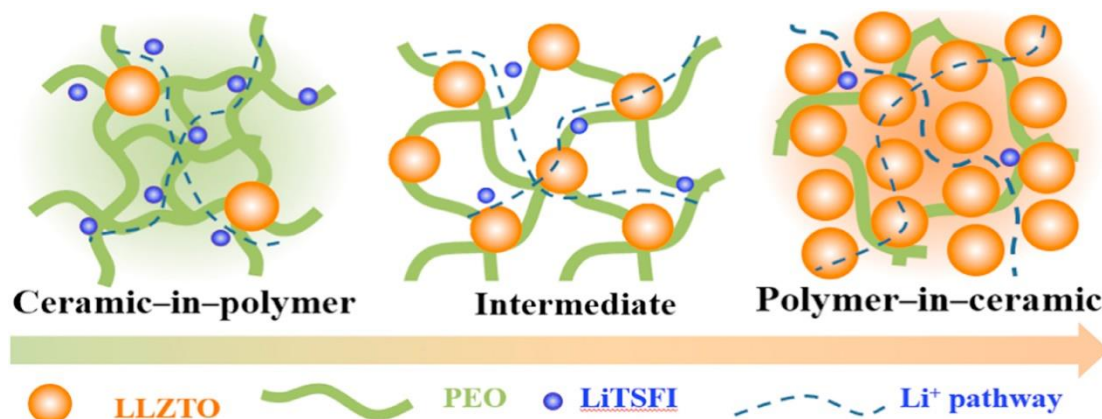


Figure 7-1: Schematic illustration of composite electrolytes demonstrating ceramic-in-polymer, intermediate, and polymer-in-salt structural configurations.^[135]

Employing Green Solvents in the Recovery Process

In chapter 4, the component separation process is enabled by soaking the whole full cell in DMF to remove the polymer interfacial layers and followed by DME to rinse away residuals and contaminants. To ensure efficient separation, these solvents need to satisfy the ability of good compatibility of both electrode and electrolyte materials and good dissolution ability of the polymers. To achieve reactions and processes that are safer for human health and the environment, alternative solvents that are less toxic to human health and the environment referred to as green solvents. With the growing environmental consciousness and the ongoing promotion of green chemistry principles, the search for alternative green solvents that can replace conventional organic solvents without causing secondary pollution has become essential in the recycling of battery materials.^[137]

Water, a solvent widely used in everyday life, is known for being environmentally friendly, green, and non-toxic. Due to the high reactivity of lithium with water, using water in the separation process could potentially aid in removing small dendrites that are embedded within solid-state

electrolytes. Additionally, it is possible to fulfill efficient separation when employing water to dissolve water-soluble polymer interfacial layers, such as polyethylene oxide (PEO), polyvinyl alcohol (PVA), and poly(acrylic acid) (PAA).^[138] However, assessing the compatibility of electrodes and electrolytes with water is essential as materials that are sensitive to water may degrade or undergo side reactions, leading to safety concerns and affecting performance.

Lithium iron phosphate (LiFePO_4 or LFP) is a promising cathode material for batteries due to several advantages, including its affordability, stable capacity, structural integrity, and low toxicity.^[139] However, LFP undergoes the irreversible aging process when being exposed to moisture in the air atmosphere, as shown in Figure 7-2. Lithium extraction occurs and leads to the formation of two distinct phases: a disordered ferric phosphate phase with the chemical formula FePO_4 , and clusters of lithium hydroxide.^[140] The presence of a disordered surface layer, $\text{Li}_x\text{FePO}_4(\text{OH})_x$, enable the intercalation of lithium ions, but with poor reversibility at around 2.6 V.^[141] The formation of this disordered surface layer results in an increased resistance within the electrode, ultimately leading to a deterioration in the overall electrochemical performance of the batteries.

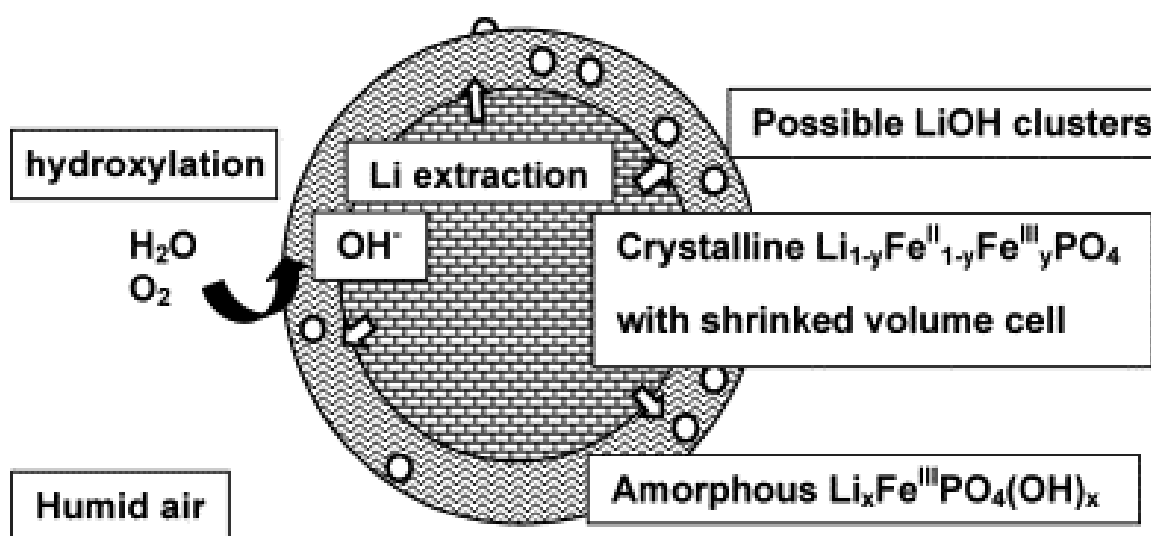


Figure 7-2: The aging process of olivine LiFePO_4 when being exposed to atmosphere at $120\text{ }^\circ\text{C}$.^[141]

Visualizing the Water Channel in LATP-LIFSI Composite Electrolytes

In chapter 6, we increase the water-rich domains of the "water-in-salt" structured regions in reprocessed LATP–LiTFSI to enhance the amount of decoupled Li^+ transport through the bulk-like water channel. However, to validate this concept and gain a deeper understanding of the intergranular properties of the water-in-salt structure in reprocessed LATP–LiTFSI, we need solid evidence that can probe the coordination environment at the nanometer scale. The spatial resolution of Fourier-transform infrared spectroscopy (FTIR), which is limited to the range of 2.5–75 μm , is insufficient to detect subtle variations in the coordination environment at such small length scales.^[142]

Atomic force microscopy-based infrared spectroscopy (AFM-IR) is a hybrid technique that merges the spatial resolution of atomic force microscopy (AFM) with the chemical analysis capacity of infrared (IR) spectroscopy.^[142] This development offers the chemical analysis capabilities of infrared spectroscopy alongside the spatial resolution of AFM, which can reach less than 20 nm. This remarkable resolution is attained by utilizing the tip of an atomic force microscope to sense the thermal expansion of a sample caused by the local absorption of IR radiation.^[143]

AFM-IR analysis was performed by Yen-Ting Lin and Jongcheol Lee using a NanoIR3 system (Bruker) with a gold-coated silicon nitride probe (0.07–0.4 N m⁻¹ spring constant, 13 ± 4 kHz resonant frequency, Bruker) in a contact scan mode. Figure 7-3 presents the results from the AFM-IR analysis conducted on LATP–LiTFSI, which was cold sintered with 50 μL of DIW. The analysis reveals distinct IR spectra at different locations within the sample, providing insights into the local structure and coordination environment of water molecules. At locations 1–4, we observed a broad peak in the IR spectra that corresponds to the bulk water spectrum. This suggests that these locations represent water-rich domains, where a significant fraction of water molecules behaves similarly to bulk water, donating two hydrogen bonds (H-bonds) to neighboring water

molecules.^[144] In contrast, at locations 5-7, we observed a pair of peaks centered at 3450 and 3550 cm^{-1} in the IR spectra. These frequencies are associated with water molecules that have one H-bond coordinating to another water molecule, while the other OH group coordinates to a non- or weakly-H-bonded species.^[144] Based on this observation, we can attribute locations 5-7 to regions enriched with LiTFSI, forming an ion channel with interfacial water molecules between the salt ions. In these LiTFSI-enriched regions, the water molecules donate one H-bond to another water molecule and the other H-bond to a TFSI⁻ anion. This coordination environment differs from that of bulk water, as the water molecules in these regions interact with both other water molecules and the salt anions.

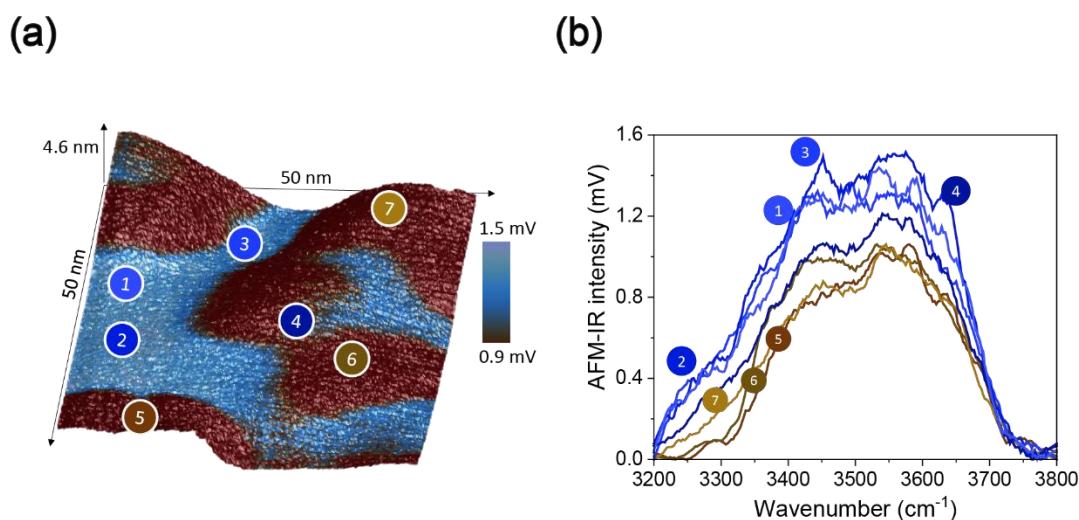


Figure 7-3: (a) Topography and AFM-IR intensity map at 3600 cm^{-1} of LATP–LiTFSI. (b) AFM-IR spectra collected at various locations marked in the AFM-IR intensity map on the surface of LATP–LiTFSI.

To the best of our knowledge, this is the first time in the literature that such a technique has been employed to visualize the structure of water-in-salt in the composite materials. Figure 7-4 shows the transmission electron microscopy (TEM) image of LATP–LiTFSI with crystalline LATP and the amorphous grain boundaries. The width of these grain boundaries, ranging from 8 to 16 nm, is consistent with the scale observed in our AFM-IR measurements. However, it is

important to note that the reported diameter of the water channels within these structures is approximately 1.2 nm. While AFM-IR appears to be a useful tool for detecting the coordination environment at the grain boundaries, it may have limitations in providing detailed information about the size of the water-rich domains within the water-in-salt structures found at these boundaries. Furthermore, we have encountered some challenges during the AFM-IR measurements. The detecting signals from AFM-IR can sometimes be unstable, which may affect the reliability of the data. Additionally, the high mechanical strength of LATP has been found to cause damage to the tips of the AFM probes, which can further complicate the measurement process. Further improvements in the stability and resolution of AFM-IR may enhance its applicability in future studies of these complex systems. In addition to experimental advancements, incorporating simulation methods could provide valuable insights to support and validate the concepts.

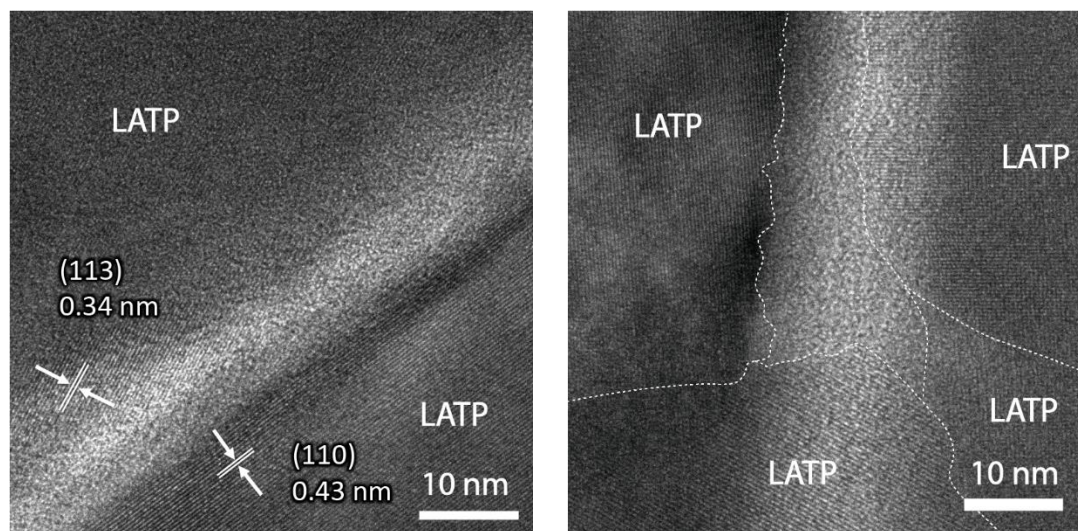


Figure 7-4: TEM image of LATP–LiTFSI showing the crystalline LATP grains and the amorphous grain boundary.

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Graduate Research Assistant , National Taiwan University The water holding capacity of bacterial cellulose membranes for wound healing applications	2015-2017

PUBLICATIONS

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