

Review

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Advancements in lithium solid polymer batteries: surface modification, *in-situ/operando* characterization, and simulation methodologies

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Abstract

The interest in lithium solid-state batteries (LSSBs) is rapidly escalating, driven by their impressive energy density and safety features. However, they face crucial challenges, including limited ionic conductivity, high interfacial resistance, and unwanted side reactions. Intensive research has been conducted on polymer solid-state electrolytes positioned between the anode and cathode, aiming to replace traditional liquid electrolytes. To alleviate interfacial resistance and mitigate adverse reactions between electrodes and polymer electrolytes, the interfacial modification strategy has been proven to enhance the energy density of LSSBs. This design process is grounded in precise and elaborate theories, with *in-situ/operando* techniques and simulation methods facilitating the interpretation and validation of structure-property relationships by simplifying them. This review first outlines the recent advancements in surface modification strategies specifically tailored for solid polymer electrolytes. Furthermore, it also provides an overview of innovative *in-situ/operando* characterizations and simulation methods featured in recent publications, which can gain a more accurate understanding of processes that occur within materials, devices, or chemical reactions as they are happening. Lastly, the review discusses the existing challenges and presents a forward-looking perspective on the future of the next-generation LSSBs.

Keywords: Solid-state battery, polymer electrolytes, interface, *in-situ/operando* characterization, simulation methods



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INTRODUCTION

The groundbreaking rechargeable lithium-ion battery (LIB), conceived by Goodenough *et al.* and Scrosati *et al.*, has evolved into a mature technology^[1,2]. Today, these enhanced LIBs have achieved widespread adoption across diverse sectors, including portable electronics, electric vehicles, and pivotal energy storage systems^[3,4]. Prevalent LIBs employ organic liquid electrolytes due to their outstanding ionic conductivity and exceptional electrode compatibility. Nevertheless, their inherent vulnerabilities, such as poor thermal stability and low ignition thresholds, pose a latent threat to human life and property^[5,6]. Solid-state batteries (SSBs) exhibit significant advantages in terms of safety, energy density, and cycle life, making them a key development direction for future battery technology^[7,8]. As the demands for battery endurance and fast-charging performance continue to increase, research institutions and enterprises have come to highly value lithium metal batteries. This is because lithium metal, when used as the anode, has a much higher theoretical capacity than graphite anodes in traditional LIBs. Additionally, lithium metal batteries can rapidly discharge a large amount of energy, making them ideal for applications requiring high power output. Since the interfacial compatibility between solid polymer electrolytes (SPEs) and lithium metal anodes is excellent, significantly minimizing interfacial side reactions^[9-12], SPEs emerge as an ideal candidate for use with lithium metal anodes. Their ability to maintain stability with lithium metal and reduce dendrite growth also makes them suitable for lithium metal batteries^[13-15].

Although SPEs show better interfacial contact than inorganic solid-state electrolytes, polymer-based electrolytes continue to grapple with challenges pertaining to effective penetration and wettability within cathodes, particularly when paired with high-mass-loading cathodes^[16,17]. Polymer electrolytes in lithium batteries suffer from suboptimal electrochemical performance due to issues such as interfacial side reactions, limited Li⁺ interfacial transport, and the formation of a detrimental space-charge layer at the electrode/electrolyte interface^[18-20]. Addressing these interfacial issues can increase battery energy density and extend its lifespan. This concise review summarizes advanced strategies aimed at modifying and optimizing electrode/electrolyte surfaces. However, while post-disassembly characterization offers valuable insights into interfacial morphology and microstructure, it lacks the capability to provide real-time feedback on the complex dynamics occurring at electrodes, electrolytes, and their interfaces during battery operation. Recently, Ning *et al.* have visualized crack propagation in Li₆PS₅Cl solid electrolyte (SE) using *in situ* X-ray computed tomography (XRCT) and spatially resolved X-ray diffraction techniques^[21]. Zhao *et al.* have devised a mesoscale electrochemical apparatus integrated within a focused ion beam-scanning electron microscopy (FIB-SEM), enabling real-time visualization of Li deposition and cracking in Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) SEs at nanoscale precision^[22]. However, these advanced *in-situ* characterization methods are primarily employed for monitoring lithium batteries based on inorganic SEs^[23,24]. As SPEs evolve, *in-situ* characterization techniques have been used to monitor internal battery changes. This review summarizes recent efforts in using these techniques to study lithium batteries with polymer electrolytes. These techniques help researchers understand battery material behavior during charging/discharging, guiding the design of higher-energy-density electrode materials and electrolytes.

The development of *in-situ* characterization techniques has significantly facilitated the resolution of crucial scientific issues in the field of lithium batteries, but monitoring the complex physical and chemical processes is expensive and time-consuming. Theoretical calculations and simulations can provide information without consuming any physical resources, saving both manpower and material resources. Some experiments are difficult or impossible to conduct under realistic conditions, such as those in extremely high temperatures, high pressures, or toxic environments, while theoretical analysis and simulation calculations are not constrained by these limitations. Advancements in theoretical concepts and methodologies across related disciplines such as solid-state physics, quantum chemistry, statistical

mechanics, and computational mathematics have provided a solid theoretical foundation for the design of materials' microstructures^[25-27]. The maturity of computational methods such as Molecular Orbital (MO) methods and Density Functional Theory (DFT) has significantly enhanced computational accuracy and efficiency, enabling more precise predictions of material properties.

In this comprehensive review, we will present and discuss the recent advancements in the development of lithium batteries based on polymer electrolytes. Given the plethora of review articles focusing on lithium SPEs^[28-30], in this review, we will organize our exploration of the topic in the following manner to ensure it is comprehensive and systematic: the surface modification strategies between polymer electrolytes and electrodes; *in-situ* characterization techniques; and the advanced modeling methods. Ultimately, this review will also elaborate on the bottlenecks hindering the development of polymer-based lithium batteries, propose corresponding solutions, and simultaneously provide insights into the future direction of development for this type of battery.

SURFACE MODIFICATION STRATEGY FOR LITHIUM SOLID-STATE BATTERY BASED ON POLYMER ELECTROLYTES

Compared with other inorganic SEs, SPEs possess numerous advantages, including flexibility, lightweightness, electrode compatibility, and ease of processing. These qualities make SPEs a powerful strategy for developing high-energy-density lithium batteries. However, despite their promising attributes, the lithium-ion conductivity of SPEs still urgently needs improvement. To address this issue, a significant amount of effort and technical innovations have been dedicated to enhancing their conductivity^[31,32]. Considering the overall performance of the battery, the lithium-ion conductivity of SPEs is an important parameter that determines the performance of SSBs. However, low charge transport kinetics and side reactions occurring between electrodes and SPEs also have a serious impact on the battery's output performance^[33-35]. Despite significant improvements in their surface contacts, there remains significant potential for further enhancement when compared to liquid electrolytes. Generally, the poor interfacial contacts initiate an increase in overpotential, which deteriorates the SSB performance and makes them not comparable to liquid batteries. Thus, many researchers have been committed to improving the insufficient surface contacts through various surface modification strategies [Figure 1], such as liquid lithium additives, a quasi-solid layer, multi-layered SE, and direct coating methods. We will provide a comprehensive review of the aforementioned four surface modification strategies based on previous research. These surface modification strategies enhance ion transport efficiency, stabilize the surface, prevent dendrite growth, and improve battery safety and durability.

Liquid lithium additives between SPE and electrodes

By adding liquid electrolytes between the electrode and the SPE, this type of SSB becomes a promising candidate to replace the current lithium battery, owing to its advantages of benign interfacial contact and the ability to create huge barriers against unwanted redox shuttles^[36-38]. Kim *et al.* developed a hybrid electrolyte that integrated a solid polyethylene terephthalate (PET) electrolyte with an organic liquid electrolyte [LiPF₆ in ethylene carbonate (EC), diethylcarbonate (DC) and dimethyl carbonate (DMC)], which was sandwiched between the anode and the PET electrolyte [Figure 2A]^[38]. The active cathode materials composed of In₂O₃-SnO₂ (ITO) were coated on another surface of PET by vacuum sputtering deposition. Because lithium-ions migrated much faster in the small amount of organic liquid electrolytes, the solid-state cell exhibited a Coulombic efficiency of over 100% [Figure 2B]. During subsequent cycles, the battery's capacity stabilizes, as evidenced by the long-term cycling results which indicate an average coulombic efficiency of approximately 110% over 1,278 cycles. The gravimetric capacity remained stable even at a higher charge rate (400 mA g⁻¹), four times the initial rate, suggesting good electrode interphase

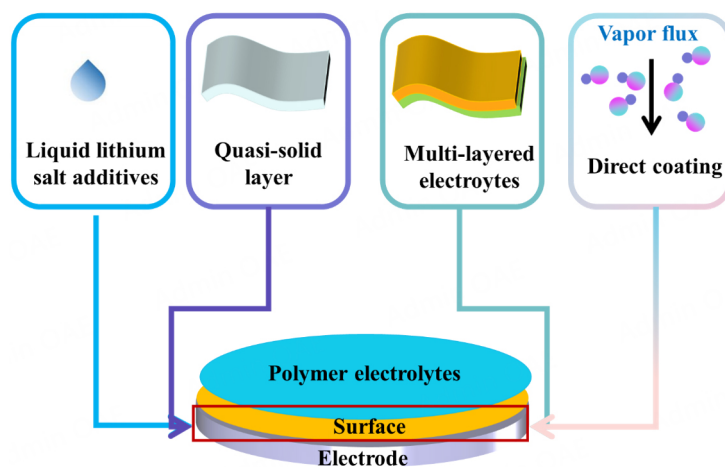


Figure 1. Schematic diagram of the surface modification strategies in solid lithium polymer battery.

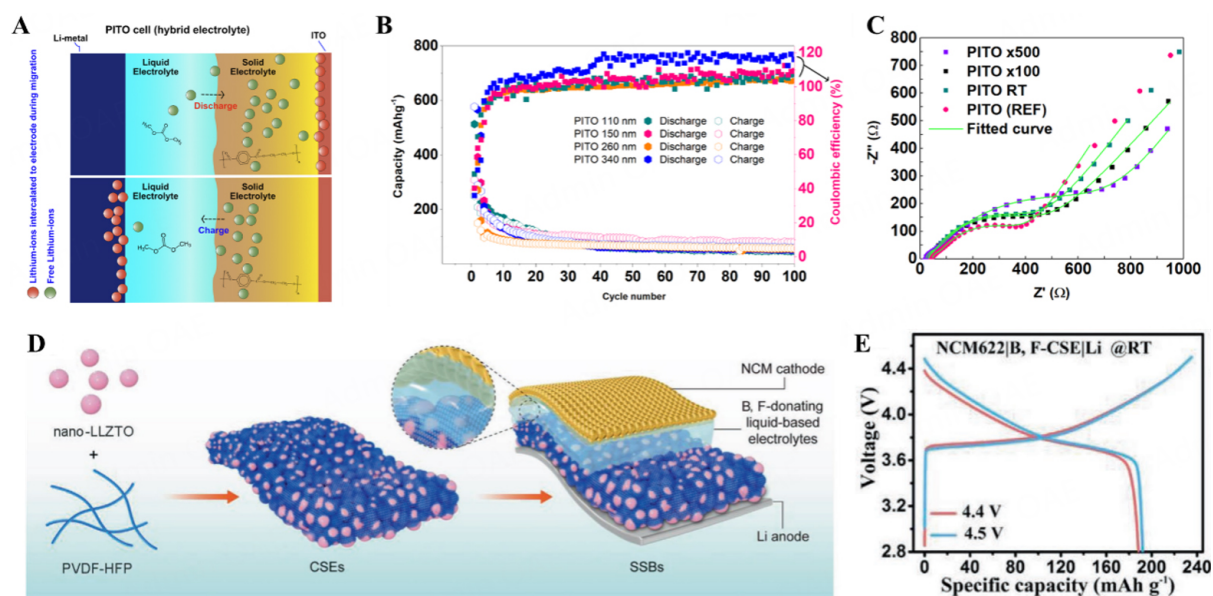


Figure 2. (A) An illustration depicting the standard lithium-ion battery electrode alongside the newly devised PITO. (B) Performance evaluation, including coulombic efficiency and cycling stability. (C) Nyquist plot for an uncycled reference cell (PITO REF), a cell subjected to rate capability testing (PITO RT), a cell cycled 100 times (PITO \times 100), and a cell cycled 500 times (PITO \times 500). Reproduced with permission from Ref. [38] Copyright 2021, IOPscience. (D) Schematic illustrations depicting the intricate synthesis process of CSEs and the assembly procedure for SSBs. (E) The initial voltage profiles of the NCM622|B, F-CSE|Li cell with voltage limits at 4.4 and 4.5 V, respectively. Reproduced with permission from Ref. [39] Copyright 2021, Wiley-VCH.

consistency. Since the increase in SE interphase (SEI) resistance (R_{SEI}) during severe cycling (PITO \times 100 and PITO \times 500) is minimal [Figure 2C], the aforementioned phenomenon is attributed to the gapless structure between ITO and the PET substrate, which lacks conductive additives and polymer binders, thereby hindering further growth of the SEI. Li *et al.* have introduced dual salts, consisting of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and lithium bis(oxalato)borate (LiBOB), into the surface between cathode and ultrathin composite SEs (CSEs), which are fabricated by complexing the poly(vinylidene fluoride-co-hexafluoropropylene) with LLZTO [Figure 2D]^[39]. The mentioned liquid electrolytes not only exhibited good chemical compatibility with CSE but also facilitated the rapid and

uniform transport of Li-ions, forming an electrochemically and chemically stable interface that is suitable for high-voltage cathodes. When the charge cutoff voltage was set at 4.4 V, the assembled NCM622|B, F-CSE|Li cell exhibited an initial discharge capacity of 191 mAh g⁻¹ at 0.1 C [Figure 2E], and after 100 cycles the discharge capacity slightly decreased to 187 mAh g⁻¹. The efforts should focus on searching for the outstanding liquid electrolyte additives into SSBs, and eventually transforming the solid-liquid electrolyte interphase (SLEI) from the so-called “real culprit” into the “savior”.

Quasi-solid layer between SPE and electrodes

Researchers typically modify the SPE surface by introducing functional polymers with low molecular weights, as the superior contact compatibility between these polymers enhances lithium-ion interfacial kinetics^[40,41]. Yang *et al.* prepared a polymeric buffer layer [adaptive buffer layer (ABL)] using polyacrylcarbonate, poly (ethylene oxide) (PEO) and LiTFSI, which was sandwiched between the SPE and the Li anode, thereby improving the surface contact among the cell [Figure 3A]^[42]. According to the reported results, after cell cycling, the R_t increased without the polymeric layer while there were no significant changes in the R_t with polymeric layer [Figure 3B]. The cross-sectional scanning electron microscopy (SEM) images [Figure 3C and D] revealed that, in the absence of a polymeric layer, the surface between the SPE and the Li anode was separated; in contrast, when a polymeric layer was present, the SPE and the Li anode were closely contacted with the polymeric layer. The Li/ABL/SPE/lithium iron phosphate (LFP) battery exhibited nearly double the initial specific discharge capacity (110 mAh/g) compared to the battery without ABL (60 mAh/g), due to improved interfacial contact between Li and SPE. Additionally, the battery with ABL demonstrated greater stability in Coulombic efficiency during cycling. Based on previous research works, quasi-solid layers can be tailored to specific battery chemistries and operating conditions. By adjusting the composition and structure of the layer, researchers can optimize battery performance for different applications.

Multi-layered solid electrolytes

All solid-state electrolytes, whether SPEs or inorganic SE, exhibit larger interfacial resistances between electrodes and electrolytes, primarily arising from poor surface adhesion^[43,44]. Liu *et al.* resolved the above issues by adopting a 3-dimension Li anode with high surface area connected to the bulk SE via a flowable polymer electrolyte interphase^[45]. A molten SPE was thermally infiltrated into 3D Li-reduced graphene oxide (Li-rGO) [Figure 3E]. This work adopted various SEs for the comparative research, including a composite polymer electrolyte combining PEO and silica, a cross-linked poly (ethylene glycol) diacrylate (PEGDA) electrolyte, and cubic garnet-type LLZTO ceramic. After flowable poly (ethylene glycol) (PEG) infiltration, it becomes evident that the polymer electrolyte has fully occupied the nanoscale pores within the Li-rGO anode. The SEM results [Figure 3F and G] reveal that the pristine Li-rGO anode displayed a uniform stacking of nanoscale Li particles and layered rGO, characterized by a high degree of porosity. Following thermal infiltration, a distinct change in color is visually evident [Figure 3H and I], with the Li-rGO electrode appearing notably darker, attributable to the filling of nanopores. The results demonstrated that the flowable polymer electrolyte interphase was vital to withstand the interfacial fluctuation and maintain excellent contact after experiencing cyclic charging and discharging. They demonstrated superior capacity delivery at varied rates of 0.2, 0.5, 1, 2, and 5 C compared to cells utilizing the Li foil anode [Figure 3J]. Notably, in both symmetric and full-cell configurations, the overpotential was significantly reduced, and the cycling stability was improved.

Direct coating on SPE or electrodes

The atomic layer deposition (ALD) technology can build up condensed layers at atomic level through multiple steps^[46-48]. Additionally, it addresses the “surface-wetting” issues by plasma exposure^[49]. To solve the “shuttle effects” of lithium polysulfide intermediates in the SPEs and the poor interfacial compatibility

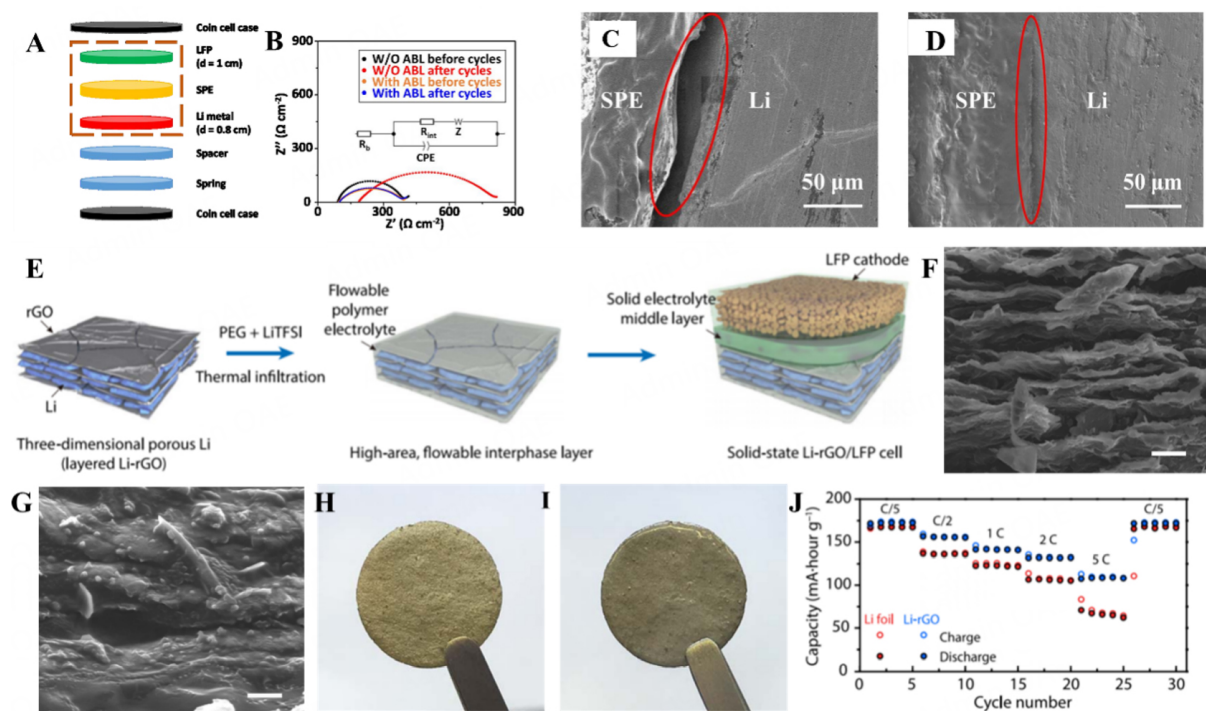


Figure 3. (A) Configuration of a full cell setup intended for cycling tests and EIS measurements. (B) Nyquist plots at a temperature of 50 °C (Insert: equivalent circuit model). Cross-sectional SEM images of symmetric cells (Li/SPE/Li) after being charged to a capacity of 20 mAh/cm² at a current density of 0.04 mA/cm² (C) with and (D) without ABL. Reproduced with permission from Ref.^[42] Copyright 2019, American Chemical Society. (E) Schematic diagrams outlining the step-by-step manufacturing process of a 3D lithium anode integrated with a flowable interphase. SEM images and digital photographs of the 3D Li-rGO anode (F and H) before and (G and I) after thermal infiltration of flowable PEG. (J) Rate capability performance. Reproduced with permission from Ref.^[45] Copyright 2017, Science.

between the anode and the SPE, Fan *et al.* successfully deposited a 5 nm Al₂O₃ layer on the two surfaces of poly(ethylene oxide)-LiTFSI SPE via ALD^[50]. The FIB-SEM images exhibited that lithium existed in the form of dense particle-like deposits in the all-solid-state cell, indicating the nano-thin layer efficiently suppressed the growth of lithium dendrite. The weakened lithium shuttle effect made the Coulombic efficiency of the cell high, over 95%, during the charge/discharge cycling. In addition, the cell using an Al₂O₃ coating on SPEs demonstrated excellent cycling stability over 200 cycles and significantly reduced the self-discharge rate. Garbayo *et al.* also used alumina nano-coatings with a thickness of about 10 nm in the cathode-SPE surface to inhibit the polysulfide shuttle effects^[51]. By enhancing interfacial stability and inhibiting the growth of lithium dendrites, nano-coating can alleviate fade and performance degradation during the battery cycling process.

ADVANCED *IN-SITU* /OPERANDO CHARACTERIZATION TECHNIQUES

As we all know, sophisticated electrochemical and chemical reactions usually occur at the interfaces between electrodes and electrolytes, and thus, it is difficult for conventional characterization systems to conduct a thorough investigation of the interfacial physical contact, interfacial ion transport, and interfacial reactions^[52-54]. Advanced characterization techniques, including spectroscopy techniques, microscopy techniques, X-ray, mass spectrometry, and neutron techniques, have been actively explored to understand the interface compatibility and ion transport mechanism at atomic, micro, meso, and macroscopic scales^[55-59]. Tracking the dynamic interface evolution in operating conditions can promote a deep and precise understanding of the electrochemical properties and stability of interfaces within batteries, providing theoretical guidance for the development of polymer-based batteries. This chapter will focus on

the research efforts that employ *in-situ/operando* spectroscopy, *in-situ/operando* X-ray techniques, and *in-situ/operando* neutron techniques for exploring microscopic information in solid-state polymer batteries [Figure 4]. These original characterization methods each exhibit unique strengths in studying the microstructural evolution, ion transport, and lithium dendrite growth processes within SSBs. They complement each other and collectively propel advancements in solid-state polymer battery technology.

***In-situ/operando* spectroscopy technique**

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) technique uses a broadband infrared beam to measure the amount of light absorbed by a sample. The technique reveals the diverse absorption frequencies by analyzing the attenuated beam, and processes the detected absorption patterns to generate an infrared spectrogram. So far, the *in-situ* FTIR technology has achieved remarkable results in real-time representation of the microdynamic behavior and structural evolution of materials under various working conditions^[60-62]. He *et al.* have developed near-field infrared nano-spectroscopy with nanoscale resolution, chemical selectivity, and surface sensitivity, to probe the graphene/Li/SPE interface information, where a single graphene sheet uniquely served as both an infrared transparent window and a current collector [Figure 5A]^[63]. To confirm that the nano-FTIR variations across the graphene/SPE interface are pronounced, we needed to conduct many control experiments. The nano-FTIR spectra of the graphene/SPE interface were captured at specific locations [Figure 5B] under room temperature conditions. To visualize these spectra, each dot corresponds to a unique nano-FTIR spectrum, with the dot's color serving as a visual representation of the corresponding spectrum. Nano-FTIR analysis revealed intensity variations in the absorption bands of TFSI and PEO. These variations are attributed to a complex interplay of factors, including changes in the PEO chain structure and its orientation, alterations in TFSI molecular conformations and orientations, and variations in LiTFSI concentrations [Figure 5C]. Ultimately, this study revealed that despite its initially atomically flat surface, the graphene was susceptible to transforming into a heterogeneous surface characterized by newly formed composition and structure. The observed phenomenon resulted in non-uniform Li-plating at the surface mentioned above, which is distributed at both the nano- and micro-scales. Wen *et al.* revealed the oxidation mechanism of a gel bisalt polyether electrolyte (BSPE) in lithium metal batteries, particularly at high voltage, where polymer electrolytes containing -OH, -O-, and -C=O groups are easily oxidized^[64]. They utilized *in-operando* FTIR, combined with X-ray photoelectron spectroscopy (XPS) technology, to achieve this insight. Calcium fluoride (CaF₂), which is transparent to FTIR light, was chosen as the optical prism, and a highly sensitive mercury cadmium telluride detector was selected and operated in a liquid nitrogen environment. As the battery charged, a growing vibration peak at 1,727 cm⁻¹ from the NCM/BSPE interface suggested the formation of O-C=O containing carbonaceous species [Figure 5D and E]. In addition, XPS was employed to validate the decomposition mechanism of the electrolyte in contact with the NCM811 surface, with *ex-operando* XPS results suggesting that ether molecules were prone to transforming into O-C=O based side products at the interface under a high voltage of 4.8 V.

Raman spectroscopy

Raman spectroscopy technology, utilizing the Raman scattering effect, is a powerful method for analyzing scattering spectra to extract valuable information on molecular vibration, rotation, and various other molecular properties^[65-67]. Raman spectroscopy is sensitive to Li⁺-solvent interactions and/or anion concentration, allowing it to track the Li-ion transport mechanism and dendrite growth^[68,69]. Given the limitations of conventional Raman spectroscopy, including weak signal and poor temporal resolution, Cheng *et al.* exploited stimulated Raman scattering (SRS) microscopy^[57]. This microscopy utilizes two spatially and temporally synchronized picosecond laser pulse trains^[70-72] to *in-operando* illustrate the Li-ion migration path in a SSB electrolyte [Figure 6A]. They prepared a cell model using a gel polymer electrolyte

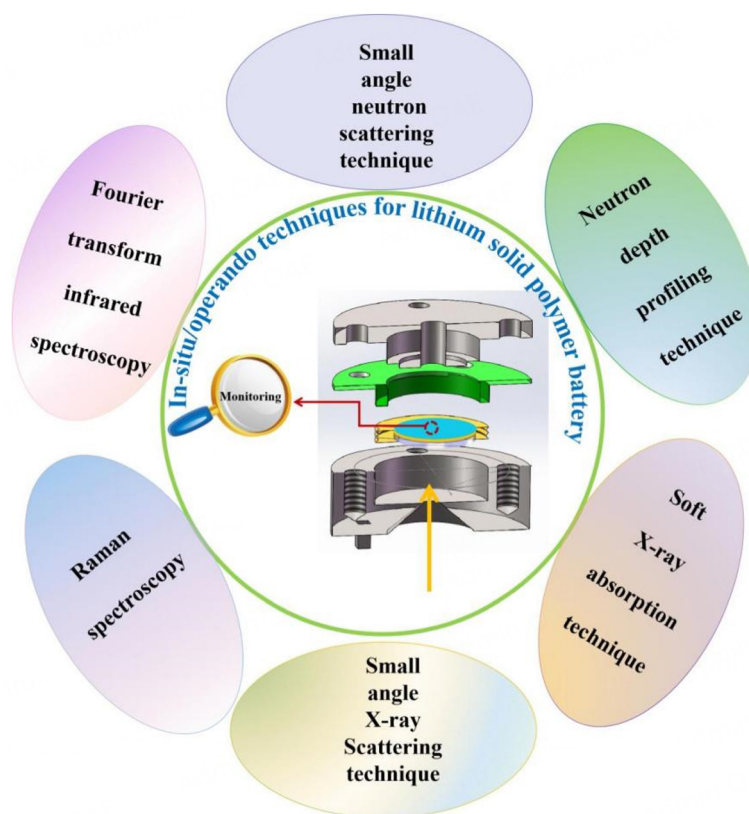


Figure 4. Schematic diagram of the *in-situ/operando* techniques in solid lithium polymer battery.

consisting of LiBOB, tetraethylene glycol dimethyl ether (TEGDME), and poly(vinylidene fluoride-cohexafluoropropylene) (PVDF-HFP), as shown in [Figure 6B](#). The SRS signal obtained directly correlates with the ion concentration, as depicted in [Figure 6C](#). Notably, this method exhibits minimal disruptive background noise. The detection threshold, based on a signal-to-noise ratio of 1, is remarkably low at 10 mm under the given scanning speed and power settings. These findings underscore the exceptional sensitivity of SRS microscopy, setting a robust basis for their subsequent imaging endeavors and quantitative assessments. Under an applied current density of 4.2 mA cm^{-2} , [Figure 6D](#) and [E](#) visualizes the gradual depletion of LiBOB in proximity to the lithium metal surface through 3D SRS imaging, which shows a clear temporal evolution of the process. In their laboratory, the detection window of the Raman setup could not satisfy direct Li-ion detection, so the researchers measured the anion BOB^- Raman intensity. This study showed Li deposition has three stages: slow mossy Li growth, mixed mossy Li and dendrite growth, and dendrite growth.

***In-situ/operando* X-ray technique**

Small angle X-ray scattering technique

Small-angle X-ray scattering (SAXS) can quantify nanoscale electron density differences in a sample, enabling detailed structural analysis through the scattering electron contrast between blocks of polymer electrolytes^[73-75]. SAXS typically provides structural information for sizes between 1 and 100 nm (up to 150 nm in partially ordered systems). The large-scale SAXS facility provides sufficient space to accommodate the construction of an in-operando SAXS-electrochemical workstation coupled device. Möhl *et al.* studied the nanoscale changes in polymer electrolytes in a capillary-based LIB using in-operando SAXS [[Figure 7A](#)]^[56]. The radial SAXS profiles presented in [Figure 7B](#) and [C](#) reveal that the unannealed

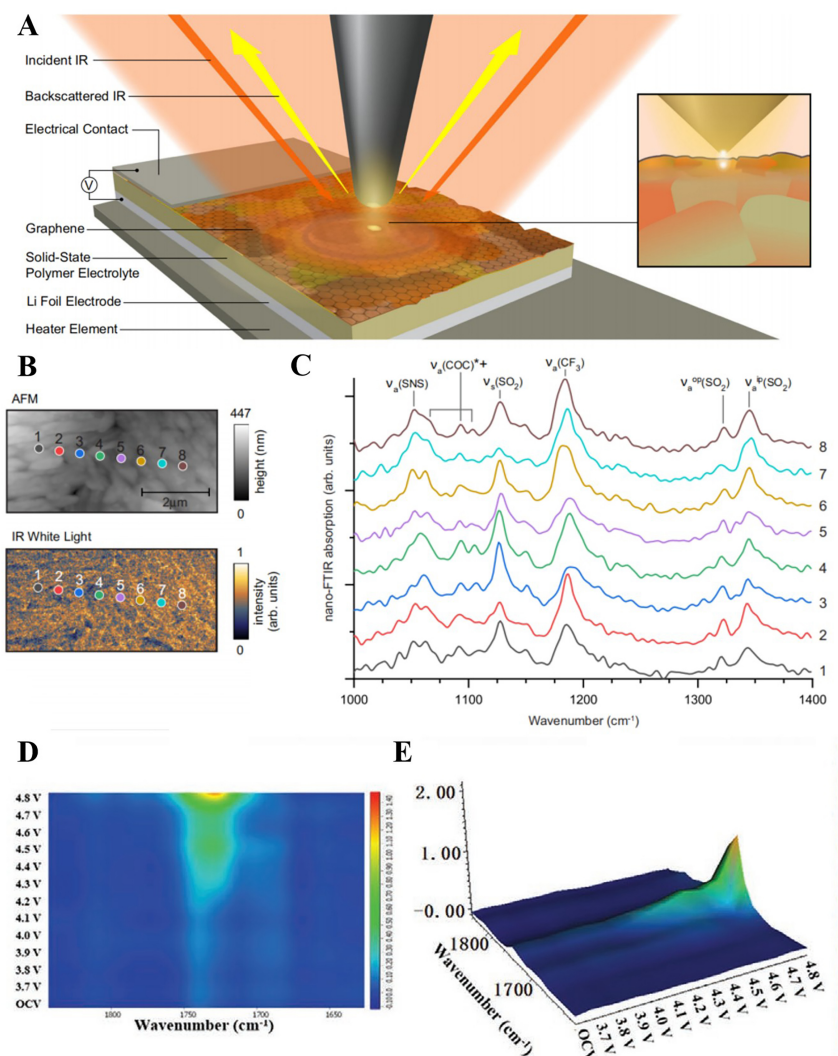
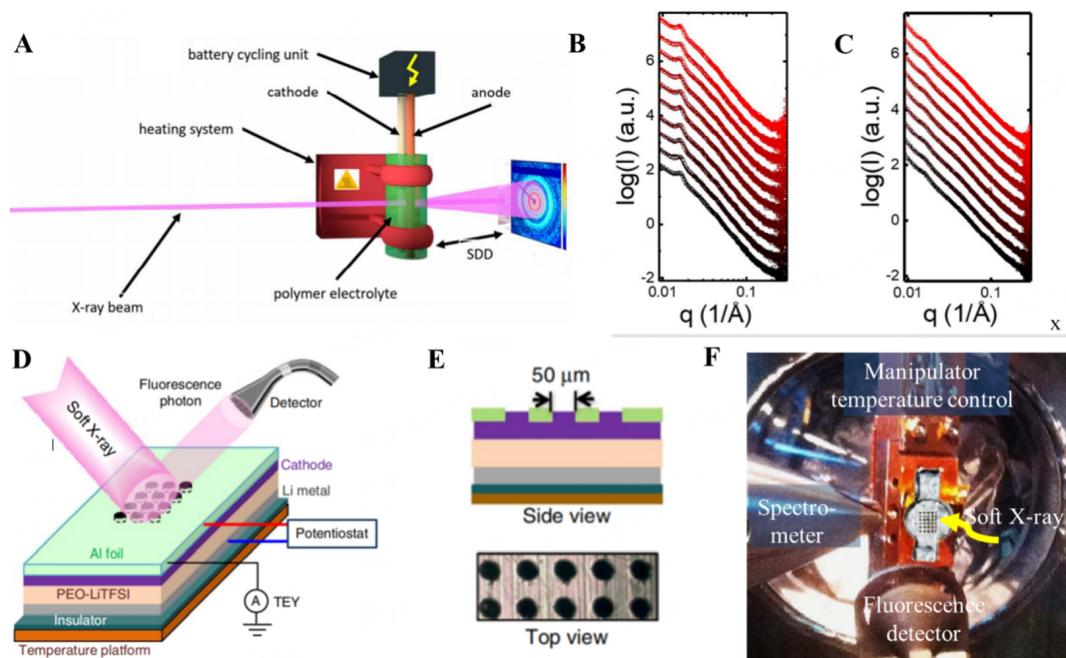
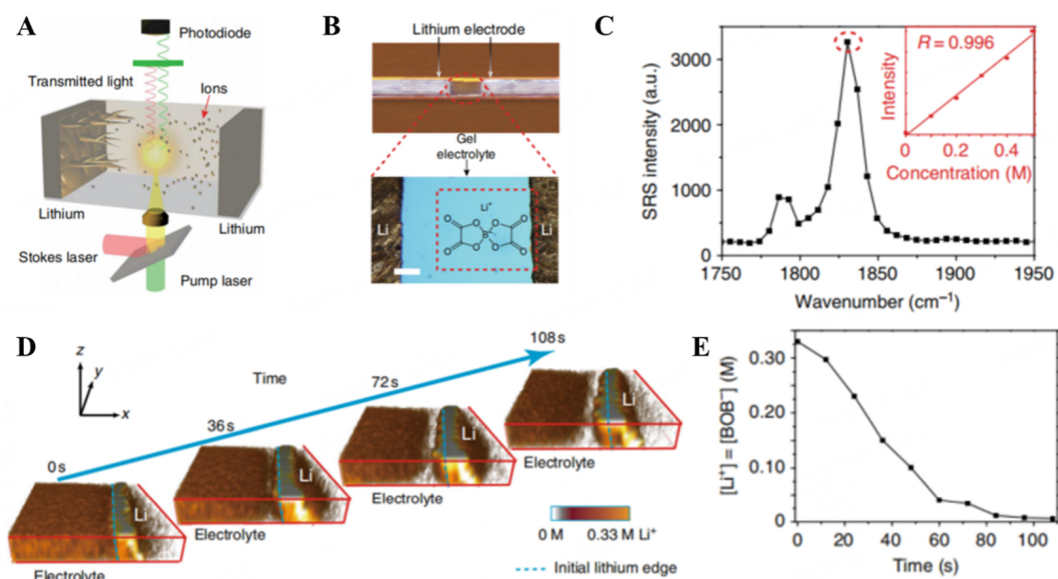


Figure 5. (A) A detailed description of the experimental arrangement used for *in situ* near-field infrared imaging and nanospectroscopy. (B) AFM images and IR white light images, and (C) local nano-FTIR spectra obtained at room temperature. Reproduced with permission from Ref. [63] Copyright 2022, Nature. (D and E) A series of time-resolved, stacked FTIR plots focused on a $1,727\text{ cm}^{-1}$ peak at the interface. Reproduced with permission from Ref. [64] Copyright 2021, Wiley-VCH.

block copolymer electrolytes lack the well-defined structural order observed in the annealed samples, a finding that indicates a less organized microstructure. They claimed that the performance of this SSB was mainly affected by the electrolyte morphology, especially after the battery was annealed, which led to a serious mismatch between polymer electrolytes and electrodes, thereby deteriorating the battery performance.

Soft X-ray absorption technique

Soft X-ray spectroscopy is an element-specific technique that exhibits high sensitivity to the local chemical environment and structural order of materials. It can provide detailed information about the electronic structure and chemical bonds of materials, which is crucial for understanding the complex electrochemical reactions and interfacial phenomena in polymer-based batteries. Employing the intricate elemental, chemical, and surface probing capabilities of soft X-rays, Liu *et al.* unveiled unique lithium-ion and electron behavior patterns within the $\text{Li}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ and LiFePO_4 cathodes embedded in polymer electrolyte



matrices^[76]. The fabricated battery cell was affixed to a plate equipped with electrical contacts, facilitating electrochemical cycling and temperature regulation [Figure 7D-F]. To mitigate potential radiation-induced damage to the polymer electrolyte, rigorous testing and precise control of both the X-ray flux and beam dimensions were executed utilizing a specialized refocusing mirror system. While the primary motivation behind utilizing polymer electrolytes was to streamline technical design, their findings reveal intriguing charge transport characteristics associated with these electrolytes, suggesting that this cell configuration holds promise for exploring solid-state electrolyte research avenues as well.

***In-situ/operando* neutron technique**

Neutron depth profiling technique

In neutron depth profiling (NDP), a cold or thermal neutron beam interacts with the isotopes through a sample, which emit a proton and a recoil nucleus. As a near-surface analysis technique, NDP is often used to track the concentration profiles of light elements as a function of depth, since it is directly related to the residue energy of recoil nuclei after they penetrate the sample^[77-79]. Upon interaction with a cold neutron beam (within the energy spectrum of 0.1-10 meV), specific nuclides within the material emit charged particles, including ³He, ⁶Li, ¹⁰B, ¹⁴N, ¹⁷O, ³³S, ³⁵Cl, and ⁴⁰K. Leveraging its exceptional sensitivity towards ⁶Li detection, NDP is ideally suited for non-invasive quantification of the lithium concentration gradient throughout the electrode's depth^[80-82]. Liu *et al.* leveraged the unique features of NDP-selectivity, sensitivity, and non-destructive testing to monitor the lithium plating and stripping processes in LiNO₃-gel polymer electrolytes within a SSB [Figure 8A]^[83]. Firstly, they established the in-operando NDP setup. Subsequently, the detection data were collected as the assembled pouch cell underwent ten plating and stripping cycles at a current density of 1 mA cm⁻² [Figure 8B]. When compared with the control pouch cells assembled with either a single unit of LiNO₃ or gel polymer electrolyte, the pouch cell combining both LiNO₃ and gel polymer electrolyte showed a limited generation of inactive Li-species. Additionally, a thin and homogeneous SEI was formed, and Li₃N was observed within the SEI, which promoted conductivity.

Small angle neutron scattering technique

The small angle neutron scattering (SANS) technique is highly sensitive to light elements, enabling the acquisition of real-space structural information on various microstructural elements within materials^[84-86]. In the field of SSBs, *in-situ* SANS technology has the capability to monitor interfacial reactions between SE and electrode materials in real-time, thereby unveiling the microscopic mechanisms underlying ion transport and charge transfer within SSBs^[87-89]. Aqueous LIBs are popular for their safety, low cost, and environmental friendliness. Inevitably, lithium batteries based on aqueous electrolytes face many tough challenges, especially including low practical voltage and limited electrode materials. Extensive efforts have been made to construct a SEI to improve the electrochemical stability window. To form a more stable SEI, Hou *et al.* developed an aqueous polymeric electrolyte consisting of polyacrylamide (PAM) and LiTFSI, whose design was inspired by the "water-in-salt" concept^[90]. They investigated the formation and evolution mechanism of PAM-assisted SEI with the operando SANS technique [Figure 8C]. The morphological dimensions of SEI were obtained by collecting the scattering data [Figure 8D] fitting with Porod' law [Figure 8E]. According to the results, as the voltage is scanned towards lower values, the evolution behaviors of two electrolytes with PAM or without PAM diverge. Due to the addition of PAM into the electrolytes, SANS revealed that the SEI morphological changes were confined to a narrow voltage range of 2.0 to 1.5 V vs. Li|Li⁺, above which the SEI stabilized and parasitic reactions were minimized.

SIMULATION METHODS FOR INTERFACE BETWEEN SPES AND ELECTRODE

Advancements in simulation methodologies for SSBs span a wide range of technical approaches, offering vital support for the design, optimization, and commercialization of these batteries. Molecular dynamics

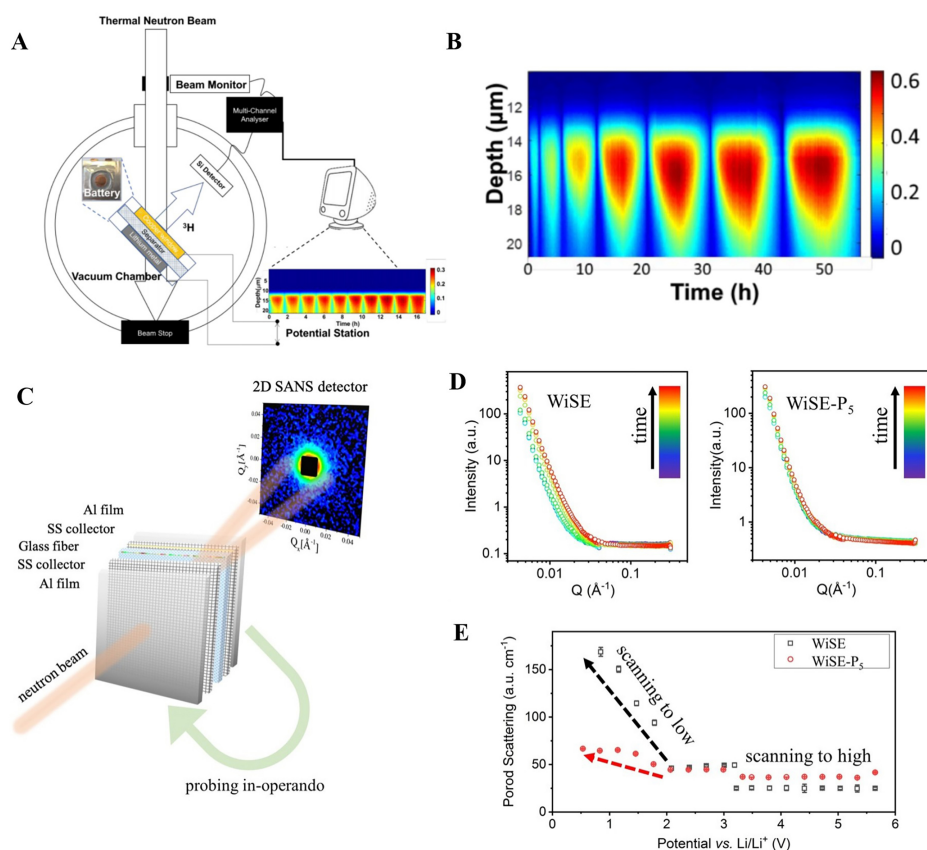


Figure 8. (A) Diagram of operando NDP for Li-metal plating and stripping. (B) Li distribution and mass in Cu/GPE-LNO/Li battery. Depth starts at $-11 \mu\text{m}$ (copper current collector thickness). Color scale shows Li density relative to Li-metal. Reproduced with permission from Ref.^[83] Copyright 2019, American Chemical Society. (C) Diagram of operando SANS experiments. (D) Scatter plots along with LSV measurements of cells with WiSE and with WiSE- P_5 during low-potential scanning. (E) Porod scattering amplitudes of cells with WiSE and WiSE- P_5 at various potentials. Reproduced with permission from Ref.^[90] Copyright 2021, Wiley-VCH.

(MD) simulations are employed to investigate the dynamic behaviors of ions and molecules within SSBs, encompassing diffusion, migration, and reaction processes. By simulating the system's response under varying temperatures and pressures, insights into the performance variations of SSBs under operational conditions can be unveiled. Quantum mechanical electronic structure methods, particularly DFT, serve as crucial tools for predicting material properties^[91,92]. By solving the Schrödinger equation for electronic systems, DFT provides information on materials' electronic structure, predicting their physical and chemical properties. In this chapter, we will provide an overview of the research advancements in the field of solid-state polymer batteries utilizing first-principles calculations, MD simulation, and Laplace-Fourier transform solution modeling methods [Figure 9]. First-principles calculations, MD simulations, and Laplace-Fourier transform solution modeling methods have made significant contributions to the research and development of solid-state polymer batteries. By providing insights into the fundamental properties of materials, the dynamic behavior of materials, and the transport processes within the battery, these methods have facilitated the design of new materials and battery systems with improved performance and reliability.

First-principles calculations

Density functional theory

As we know, polymer electrolytes are complex in terms of their chemical structure; fortunately, computational methods have been developed to elucidate the Li^+ binding property and its migration

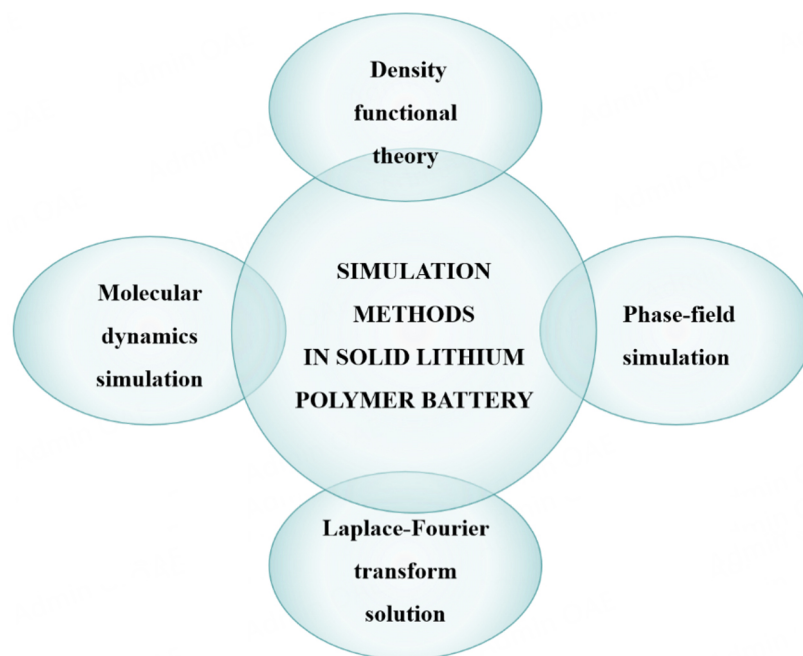


Figure 9. Schematic diagram of the simulation and modeling methods in solid lithium polymer battery.

pathway, and to partially study the complex degradation pathways and reactions at electrode surfaces^[93,94]. DFT is primarily utilized to investigate the electronic structure and chemical properties of SSB materials at the microscopic scale. By calculating parameters such as the energy band structure and the density of states, one can gain a profound understanding of the electrochemical performance and ion transport mechanisms of the materials. Wu *et al.* developed a computational method that combines DFT and Ab initio MD (AIMD) calculations, which was used to investigate the Li-nucleation process at the interface between electrolytes and metal electrodes, where Li atoms were introduced on the electrode surface^[25]. **Figure 10A** depicts the flowchart illustrating the simulation process for the PEO-lithium anode system. The comprehensive computational analysis was conducted in a sequential manner, encompassing four distinct stages. **Figure 10B** and **C** illustrates the distribution of atomic charges among oxygen and carbon atoms within the PEO system and the PEO-Li anode system, respectively, at various stages of Li-nucleation. This study found that highly reactive Li atoms induced PEO decomposition during the simulated nucleation process, and the resulting SEI films contained lithium alkoxide, ethylene, and lithium ethylene complexes.

Phase-field simulation

Multi-physics simulations comprehensively consider the interactions among various physical fields, such as electrochemistry, thermodynamics, and mechanics, within SSBs. By establishing coupled multi-physics models, these simulations facilitate a comprehensive understanding of the complex behaviors exhibited by SSBs during operation. A phase-field model, as a mathematical tool, is utilized to address interfacial problems, making it suitable for exploring interfacial issues in lithium batteries^[95-97]. Currently, phase-field simulations of lithium dendrites are predominantly based on a single physical field, which limits the ability to comprehensively study the interactions between various influencing factors. Geng *et al.* developed a mechanical stress-thermodynamic phase-field theory to investigate the growth mechanisms of lithium dendrites in solid-state polymer lithium batteries [**Figure 10D-F**]^[98]; in other words, their lithium dendrite growth model incorporates both mechanical stress and the thermal field. The research showed that high temperature, high electrolyte modulus, and external stress slow lithium dendrite growth and reduce long

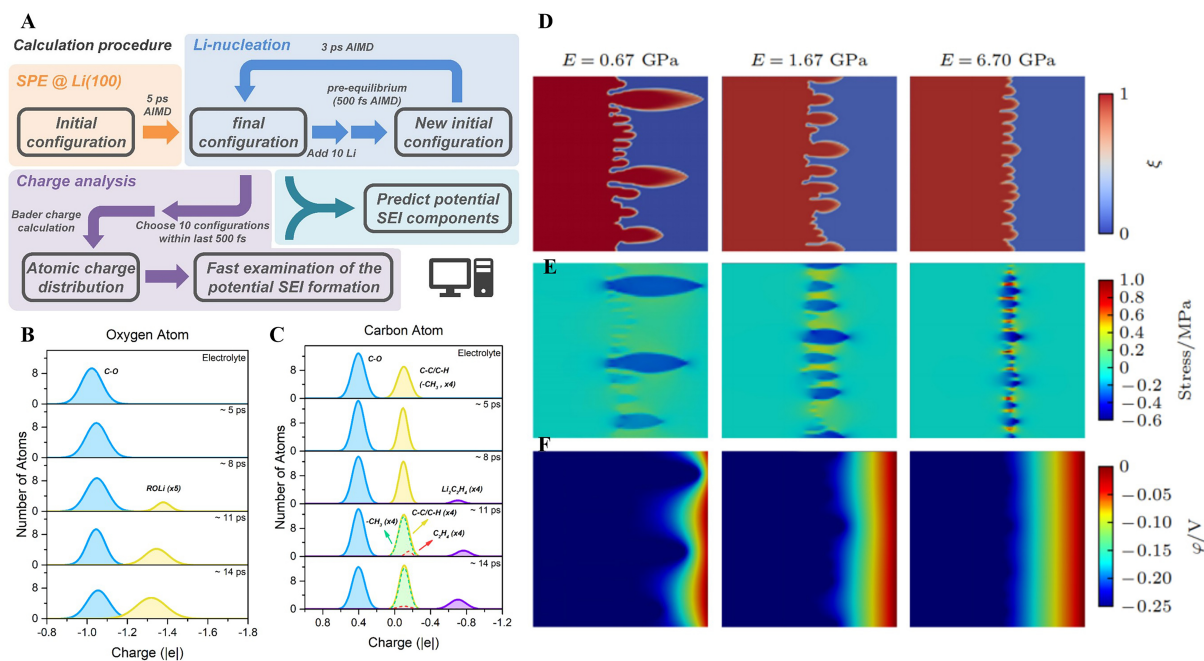


Figure 10. (A) The overall process to predict potential SEI components. The atomic charge distribution of (B) oxygen and (C) carbon in pure PEO and on the surface of a Li (100) anode at various stages of Li nucleation. Reproduced with permission from Ref.^[25] Copyright 2023, Nature. Lithium dendrite growth model in SPEs with different Young's modulus: (D) Morphology of lithium dendrite growth. (E) Stress distribution along the X-axis of the dendrite. (F) Electric field and voltage distribution within the dendrite. Reproduced with permission from Ref.^[98] Copyright 2023, Chinese Physical SOC.

dendrites. Furthermore, they discovered that altering the Young's modulus of SPE is 19% more effective in inhibiting lithium dendrite growth than changing the ambient temperature.

Molecular dynamics simulation

MD simulation addresses complex systems at the atomic and molecular levels, and visualizes the dynamic evolution of these systems over time through the corresponding equations^[99-101]. As for LIBs, the cyclic high-rate charging and discharging processes often generate massive heat, leading to performance degradation and even thermal runaway, which poses challenges for thermal management. There is an urgent need to explore the internal heat transfer mechanism of lithium batteries, particularly at the interfaces. Zhao *et al.* used MD simulations to study thermal transport between a polyethylene oxide electrolyte and lithium anode, inserting 2D materials such as silicene, graphene, and germanene at the interface [Figure 11A]^[102]. Compared to the pristine lithium/SPE interface, the interfacial thermal resistances of lithium/graphene/SPE, lithium/silicene/SPE, and lithium/germanene/SPE were reduced by 76.05%, 83.89%, and 55.99%, respectively. The results showed that adding 2D materials with high thermal conductivity reduced temperature distribution discontinuity [Figure 11B-D]. Since these 2D materials exhibited excellent in-plane heat transfer capabilities, heat could be uniformly distributed across the plane within a relatively short period of time, thereby increasing the effective in-plane heat transfer area. In conclusion, they have partially understood and addressed the heat distribution mechanisms and thermal management problems at the micro-scale. However, it is necessary to further explore studies aimed at reducing interfacial thermal resistance at the meso-scale and macro-scale.

Laplace-Fourier transform solution

Many researchers have fully utilized electrochemical and contact mechanics theories to uncover the

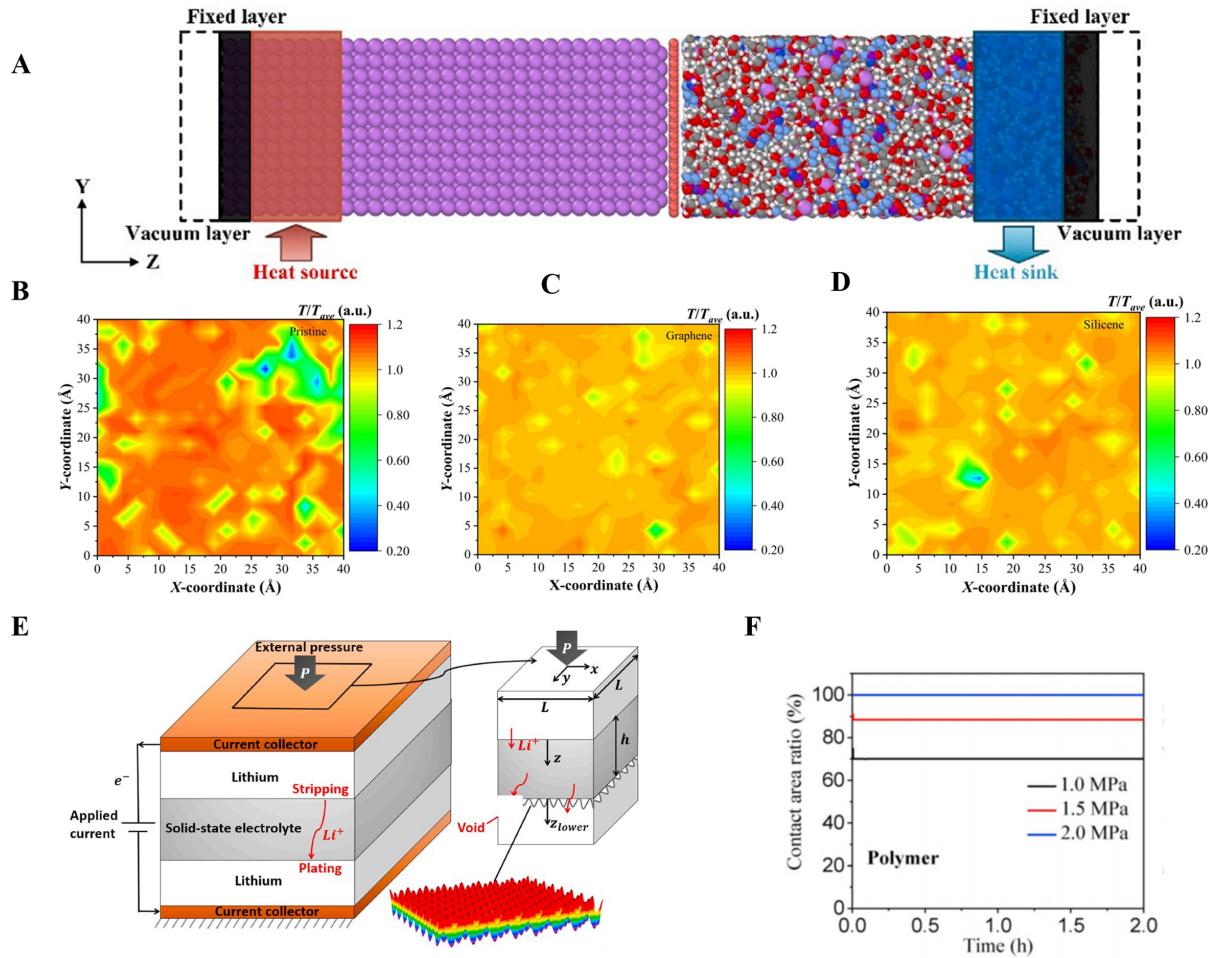


Figure 11. (A) A structural model for NEMD simulations of the lithium/Xene (Xene = C, Si, Ge)/SPE interface. Temperature profiles of SPE at the interface, pristine sample (B) and with (C) graphene and (D) silicene. Reproduced with permission from Ref. ^[102] Copyright 2023, Elsevier. (E) Model of a symmetric solid-state lithium battery with two Li-metal electrodes, SSE, and current collectors. (F) Contact area ratio of electrodes with polymer electrolyte under varying pressures. Reproduced with permission from Ref. ^[103] Copyright 2022, Elsevier.

complex interface behaviors in solid-state lithium batteries. The Laplace-Fourier transform solution has been successfully applied in the simulation of solid-state lithium batteries ^[103,104]. Through this algorithm, researchers can develop more precise and reliable models that capture the complex interactions between the internal components of the battery. Additionally, this domain solution can be utilized to predict the battery's performance under various conditions. Zhao *et al.* proposed a 3D cell model **Figure 11E** based on the Nernst-Planck equation and electroneutrality, using Talbot's Laplace and Fourier transforms ^[103]. It links interface conformity, pressure, modulus, and ionic conductivity to solid-state lithium cell performance. Imperfections in contacts often emerge at the interface between solid-state electrolytes and electrodes during the charging and discharging cycles, arising from interactions between the Li-metal anode surface and solid-state electrolytes. Two types of electrolytes - a ceramic electrolyte system and a polymer electrolyte system - were selected to demonstrate the field distributions. **Figure 11F** shows how different volume fractions of external pressure affect the SSE-Li interface contact area ratio during 2-h plating at 0.3 mA cm^{-2} . After analyzing numerous cases, the study suggested that increasing external pressure could exponentially decrease the plating potential drop, and that a lower external pressure was required for uniform Li deposition in a polymer electrolyte system.

CONCLUSION AND OUTLOOK

Significant advancements have been made in surface modification, *in-situ* characterization, and theoretical simulation methods for enhancing the performance and safety of polymer-based lithium batteries. Rational surface modification designs can significantly improve the stability and adhesion of the SEI, thereby reducing the growth of lithium dendrites. *In-situ* characterization techniques provide robust support for real-time monitoring of battery performance, facilitating a deeper understanding of battery operating and performance degradation mechanisms. Theoretical simulation methods offer new tools for battery design and optimization, aiding in the prediction of battery performance and optimization of material selection. However, there are still challenges pertaining to the aforementioned three advanced approaches, and the following is a specific analysis of these challenges:

In terms of polymer-based lithium battery surface treatment, advanced nanotechnology, surface coating technology, chemical modification techniques, and other means need to be employed to optimize interface performance. The application of these technologies not only increases production costs but also raises the difficulty of production. Furthermore, while current surface modification methods can suppress the growth of lithium dendrites to a certain extent, their effectiveness is limited, and it is difficult to maintain stability over long-term cycling.

In-situ characterization techniques need to simultaneously meet the requirements of real-time performance and high accuracy, which poses significant technical challenges. Moreover, *in-situ* characterization equipment is often complex and costly, limiting its widespread application. Importantly, the volume of data generated by *in-situ* characterization techniques is immense and complex, encompassing various types of information such as images, spectra, signals, and more. Effectively integrating this information and extracting the critical factors that impact battery performance poses a significant challenge.

The interface issues in polymer-based solid-state lithium batteries, such as surface contact and interface reactions between the polymer electrolyte and electrodes, are critical factors affecting battery performance. However, the complexity of these interface problems poses significant challenges for theoretical modeling and computation. The physicochemical properties at the interface are difficult to accurately describe, and the kinetic processes of interface reactions are challenging to precisely simulate, leading to notable discrepancies between theoretical simulation results and experimental observations. Currently, the computational models employed for theoretical simulations and calculations of polymer-based solid-state lithium batteries are mostly based on simplified assumptions and approximations, making it difficult to fully capture the intricate physical and chemical processes within the battery. For instance, some models may overlook crucial factors such as the ion transport mechanisms within the polymer chains and charge transfer processes at the interfaces, resulting in less accurate simulation outcomes.

In summary, polymer-based lithium batteries demonstrate immense potential in the field of energy storage, yet their development still faces numerous challenges. Further research should be conducted to delve into the chemical composition and structure of interface modification, aiming to enhance the adhesion and stability of the SEI. More advanced *in-situ* characterization technologies should be developed to improve the accuracy and real-time performance of data acquisition. Additionally, the integration of theoretical simulations with experimental verifications should be strengthened to enhance the accuracy and reliability of simulation results. Through continuous technological innovations, material improvements, and optimization of production processes, it is anticipated that those challenges can be overcome, propelling polymer-based lithium batteries towards higher energy densities, longer lifespans, enhanced safety and reliability, as well as more environmentally friendly and sustainable development.

DECLARATIONS

Authors' contributions

Conceived the review and wrote the manuscript: Gu, Y.; Guo, S.; Zhang, Z.; Zhao, C.

Reviewed the manuscript and acquired funding: Li, X.; Gu, Y.; Xu, X.; Wang, H.

Contributed to the discussion of the manuscript: Guo, S.; Li, X.

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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REFERENCES

1. Goodenough, J. B.; Park, K. S. The Li-ion rechargeable battery: a perspective. *J. Am. Chem. Soc.* **2013**, *135*, 1167-76. DOI PubMed
2. Scrosati, B.; Garche, J. Lithium batteries: Status, prospects and future. *J. Power. Sources.* **2010**, *195*, 2419-30. DOI
3. Pereira, N.; Amatucci, G. G.; Whittingham, M. S.; Hamlen, R. Lithium-titanium disulfide rechargeable cell performance after 35 years of storage. *J. Power. Sources.* **2015**, *280*, 18-22. DOI
4. Yu, X.; Chen, R.; Gan, L.; Li, H.; Chen, L. Battery safety: from lithium-ion to solid-state batteries. *Engineering* **2023**, *21*, 9-14. DOI
5. Zhao, Q.; Stalin, S.; Zhao, C. Z.; Archer, L. A. Designing solid-state electrolytes for safe, energy-dense batteries. *Nat. Rev. Mater.* **2020**, *5*, 229-52. DOI
6. Tang, X.; Lv, S.; Jiang, K.; Zhou, G.; Liu, X. Recent development of ionic liquid-based electrolytes in lithium-ion batteries. *J. Power. Sources.* **2022**, *542*, 231792. DOI
7. Tang, L.; Xu, Q.; Zhang, Y.; Chen, W.; Wu, M. MOF/PCP-based electrocatalysts for the oxygen reduction reaction. *Electrochem. Energy. Rev.* **2022**, *5*, 32-81. DOI
8. Reddy, R. C. K.; Lin, X.; Zeb, A.; Su, C. Metal-organic frameworks and their derivatives as cathodes for lithium-ion battery applications: a review. *Electrochem. Energy. Rev.* **2022**, *5*, 312-47. DOI
9. Han, L.; Wang, L.; Chen, Z.; et al. Incombustible polymer electrolyte boosting safety of solid-state lithium batteries: a review. *Adv. Funct. Mater.* **2023**, *33*, 2300892. DOI
10. Zhai, Y.; Hou, W.; Tao, M.; et al. Enabling high-voltage "superconcentrated ionogel-in-ceramic" hybrid electrolyte with ultrahigh ionic conductivity and single Li⁺-ion transference number. *Adv. Mater.* **2022**, *34*, e2205560. DOI
11. Zhang, W.; Koverga, V.; Liu, S.; et al. Single-phase local-high-concentration solid polymer electrolytes for lithium-metal batteries. *Nat. Energy.* **2024**, *9*, 386-400. DOI
12. Zhou, S.; Zhong, S.; Dong, Y.; et al. Composition and structure design of poly(vinylidene fluoride)-based solid polymer electrolytes for lithium batteries. *Adv. Funct. Mater.* **2023**, *33*, 2214432. DOI
13. Zhang, H.; Chen, Y.; Li, C.; Armand, M. Electrolyte and anode-electrolyte interphase in solid-state lithium metal polymer batteries: a perspective. *SusMat* **2021**, *1*, 24-37. DOI
14. Shen, Z.; Huang, J.; Xie, Y.; Wei, D.; Chen, J.; Shi, Z. Solid electrolyte interphase on lithium metal anodes. *ChemSusChem* **2024**, *17*, e202301777. DOI

15. Wu, L.; Wang, Y.; Guo, X.; Ding, P.; Lin, Z.; Yu, H. Interface science in polymer-based composite solid electrolytes in lithium metal batteries. *SusMat* **2022**, *2*, 264-92. DOI
16. Wu, F.; Zhang, K.; Liu, Y.; et al. Polymer electrolytes and interfaces toward solid-state batteries: recent advances and prospects. *Energy Storage Mater.* **2020**, *33*, 26-54. DOI
17. Su, G.; Zhang, X.; Xiao, M.; et al. Polymeric electrolytes for solid-state lithium ion batteries: structure design, electrochemical properties and cell performances. *ChemSusChem* **2024**, *17*, e202300293. DOI
18. Lu, X.; Wang, Y.; Xu, X.; Yan, B.; Wu, T.; Lu, L. Polymer-based solid-state electrolytes for high-energy-density lithium-ion batteries - review. *Adv. Energy Mater.* **2023**, *13*, 2301746. DOI
19. Hu, L.; Gao, X.; Wang, H.; et al. Progress of polymer electrolytes worked in solid-state lithium batteries for wide-temperature application. *Small* **2024**, *20*, e2312251. DOI
20. Lin, Z.; Sheng, O.; Cai, X.; et al. Solid polymer electrolytes in all-solid-state lithium metal batteries: from microstructures to properties. *J. Energy Chem.* **2023**, *81*, 358-78. DOI
21. Ning, Z.; Jolly, D. S.; Li, G.; et al. Visualizing plating-induced cracking in lithium-anode solid-electrolyte cells. *Nat. Mater.* **2021**, *20*, 1121-9. DOI
22. Zhao, J.; Tang, Y.; Dai, Q.; et al. In situ observation of Li deposition-induced cracking in garnet solid electrolytes. *Energy Environ. Mater.* **2022**, *5*, 524-32. DOI
23. Liu, M.; Ganapathy, S.; Wagemaker, M. A direct view on Li-ion transport and Li-metal plating in inorganic and hybrid solid-state electrolytes. *ACC. Chem. Res.* **2022**, *55*, 333-44. DOI PubMed PMC
24. Lucero, M.; Qiu, S.; Feng, Z. In situ characterizations of solid-solid interfaces in solid-state batteries using synchrotron X-ray techniques. *Carbon Energy* **2021**, *3*, 762-83. DOI
25. Wu, L. T.; Andersson, E. K. W.; Hahlin, M.; Mindemark, J.; Brandell, D.; Jiang, J. C. A method for modelling polymer electrolyte decomposition during the Li-nucleation process in Li-metal batteries. *Sci. Rep.* **2023**, *13*, 9060. DOI PubMed PMC
26. Qiu, W.; Wang, Y.; Liu, J. Multiscale computations and artificial intelligent models of electrochemical performance in Li-ion battery materials. *WIREs. Comput. Mol. Sci.* **2022**, *12*, e1592. DOI
27. Li, C.; Bao, L.; Ji, Y.; et al. Combining machine learning and metal-organic frameworks research: novel modeling, performance prediction, and materials discovery. *Coordin. Chem. Rev.* **2024**, *514*, 215888. DOI
28. Gu, Q.; Liu, X.; Zhou, X.; Li, J.; Lin, X.; Ma, Y. Recent progress on polymer solid electrolytes for lithium metal batteries. *Acta Chim. Sin.* **2024**, *82*, 449. DOI
29. An, Y.; Han, X.; Liu, Y.; et al. Progress in solid polymer electrolytes for lithium-ion batteries and beyond. *Small* **2022**, *18*, e2103617. DOI
30. Zhu, J.; Zhang, Z.; Zhao, S.; Westover, A. S.; Belharouak, I.; Cao, P. Single-ion conducting polymer electrolytes for solid-state lithium-metal batteries: design, performance, and challenges. *Adv. Energy Mater.* **2021**, *11*, 2003836. DOI
31. Wu, Y.; Li, Y.; Wang, Y.; Liu, Q.; Chen, Q.; Chen, M. Advances and prospects of PVDF based polymer electrolytes. *J. Energy Chem.* **2022**, *64*, 62-84. DOI
32. Zhao, Y.; Wang, L.; Zhou, Y.; et al. Solid polymer electrolytes with high conductivity and transference number of Li ions for Li-based rechargeable batteries. *Adv. Sci.* **2021**, *8*, 2003675. DOI PubMed PMC
33. Liu, W.; Yi, C.; Li, L.; et al. Designing polymer-in-salt electrolyte and fully infiltrated 3D electrode for integrated solid-state lithium batteries. *Angew. Chem. Int. Ed.* **2021**, *133*, 13041-50. DOI
34. Deng, T.; Cao, L.; He, X.; et al. In situ formation of polymer-inorganic solid-electrolyte interphase for stable polymeric solid-state lithium-metal batteries. *Chem* **2021**, *7*, 3052-68. DOI
35. Ma, Q.; Fu, S.; Wu, A.; et al. Designing bidirectionally functional polymer electrolytes for stable solid lithium metal batteries. *Adv. Energy Mater.* **2023**, *13*, 2203892. DOI
36. Sen, S.; Richter, F. H. Typology of battery cells - from liquid to solid electrolytes. *Adv. Sci.* **2023**, *10*, e2303985. DOI PubMed PMC
37. Weiss, M.; Simon, F. J.; Busche, M. R.; et al. From liquid- to solid-state batteries: ion transfer kinetics of heteroionic interfaces. *Electrochim. Energy Rev.* **2020**, *3*, 221-38. DOI
38. Kim, T.; Son, D. Y.; Ono, L. K.; Jiang, Y.; Qi, Y. B. A solid-liquid hybrid electrolyte for lithium ion batteries enabled by a single-body polymer/indium tin oxide architecture. *J. Phys. D: Appl. Phys.* **2021**, *54*, 15. DOI
39. Li, X.; Cong, L.; Ma, S.; et al. Low resistance and high stable solid-liquid electrolyte interphases enable high-voltage solid-state lithium metal batteries. *Adv. Funct. Mater.* **2021**, *31*, 2010611. DOI
40. Ferreira, M.; Schmidt, R.; Xu, F.; Ketabi, S.; Cai, M.; Zhu, Y. Polydopamine-based polymer layer for enhanced interfacial properties of hybrid ceramic-polymer solid electrolytes. *ACS Appl. Energy Mater.* **2023**, *6*, 12095-104. DOI
41. Liu, Q.; Dan, Y.; Kong, M.; Niu, Y.; Li, G. Sandwich-structured quasi-solid polymer electrolyte enables high-capacity, long-cycling, and dendrite-free lithium metal battery at room temperature. *Small* **2023**, *19*, e2300118. DOI PubMed
42. Yang, H.; Zhang, Y.; Tennenbaum, M. J.; et al. Polypropylene carbonate-based adaptive buffer layer for stable interfaces of solid polymer lithium metal batteries. *ACS Appl. Mater. Interfaces.* **2019**, *11*, 27906-12. DOI
43. Guan, D.; Huang, Y.; He, M.; et al. Multilayer PEO/LLZTO composite electrolyte enables high-performance solid-state Li-ion batteries. *Ionics* **2021**, *27*, 4127-34. DOI
44. Nassir, W. B.; Mengesha, T. H.; Chang, J.; Jose, R.; Yang, C. Multilayer hybrid solid-state electrolyte membrane for the high rate and

- long-life cycle performance of lithium-metal batteries. *Colloid. Surface. A.* **2024**, *691*, 133839. DOI
45. Liu, Y.; Lin, D.; Jin, Y.; et al. Transforming from planar to three-dimensional lithium with flowable interphase for solid lithium metal batteries. *Sci. Adv.* **2017**, *3*, eaao0713. DOI PubMed PMC
 46. Kobayashi, N. P.; Donley, C. L.; Wang, S. Y.; Williams, R. S. Atomic layer deposition of aluminum oxide on hydrophobic and hydrophilic surfaces. *J. Cryst. Growth.* **2007**, *299*, 218-22. DOI
 47. Johnson, R. W.; Hultqvist, A.; Bent, S. F. A brief review of atomic layer deposition: from fundamentals to applications. *Mater. Today.* **2014**, *17*, 236-46. DOI
 48. Oviroh, P. O.; Akbarzadeh, R.; Pan, D.; Coetzee, R. A. M.; Jen, T. C. New development of atomic layer deposition: processes, methods and applications. *Sci. Technol. Adv. Mater.* **2019**, *20*, 465-96. DOI PubMed PMC
 49. Zhao, B.; Li, J.; Guillaume, M.; Dendooven, J.; Detavernier, C. In vacuo XPS investigation of surface engineering for lithium metal anodes with plasma treatment. *J. Energy. Chem.* **2022**, *66*, 295-305. DOI
 50. Fan, Z.; Ding, B.; Zhang, T.; et al. Solid/solid interfacial architecturing of solid polymer electrolyte-based all-solid-state lithium-sulfur batteries by atomic layer deposition. *Small* **2019**, *15*, e1903952. DOI
 51. Garbayo, I.; Santiago, A.; Judez, X.; de Buruaga, A. S.; Castillo, J.; Muñoz-márquez, M. A. Alumina nanofilms as active barriers for polysulfides in high-performance all-solid-state lithium-sulfur batteries. *ACS. Appl. Energy. Mater.* **2021**, *4*, 2463-70. DOI
 52. Ding, P.; Lin, Z.; Guo, X.; et al. Polymer electrolytes and interfaces in solid-state lithium metal batteries. *Mater. Today.* **2021**, *51*, 449-74. DOI
 53. Su, S.; Ma, J.; Zhao, L.; et al. Progress and perspective of the cathode/electrolyte interface construction in all-solid-state lithium batteries. *Carbon. Energy.* **2021**, *3*, 866-94. DOI
 54. Yu, X.; Jiang, Z.; Yuan, R.; Song, H. A review of the relationship between gel polymer electrolytes and solid electrolyte interfaces in lithium metal batteries. *Nanomaterials* **2023**, *13*, 1789. DOI PubMed PMC
 55. He, Y.; Wang, C.; Zhang, R.; et al. A self-healing plastic ceramic electrolyte by an aprotic dynamic polymer network for lithium metal batteries. *Nat. Commun.* **2024**, *15*, 10015. DOI PubMed PMC
 56. Möhl, G. E.; Metwalli, E.; Müller-buschbaum, P. In operando small-angle X-ray scattering investigation of nanostructured polymer electrolyte for lithium-ion batteries. *ACS. Energy. Lett.* **2018**, *3*, 1525-30. DOI
 57. Cheng, Q.; Wei, L.; Liu, Z.; et al. Operando and three-dimensional visualization of anion depletion and lithium growth by stimulated Raman scattering microscopy. *Nat. Commun.* **2018**, *9*, 2942. DOI PubMed PMC
 58. Liu, J.; Song, Z.; Yu, F.; et al. In situ optical observation of lithium dendrite pattern in solid polymer electrolytes. *Small. Methods.* **2024**, e2401233. DOI
 59. Otto, S. K.; Riegger, L. M.; Fuchs, T.; et al. In situ investigation of lithium metal-solid electrolyte anode interfaces with ToF-SIMS. *Adv. Mater. Inter.* **2022**, *9*, 2102387. DOI
 60. Pereira, R.; Sarode, K. K.; Rafie, A.; Fafarman, A.; Kalra, V. In-operando FTIR study on the redox behavior of sulfurized polyacrylonitrile as cathode material for Li-S batteries. *J. Phys. Chem. C.* **2023**, *127*, 19356-65. DOI
 61. Lee, T. H.; Jung, J. G.; Kim, Y. J.; et al. Defect engineering in metal-organic frameworks towards advanced mixed matrix membranes for efficient propylene/propane separation. *Angew. Chem. Int. Ed.* **2021**, *60*, 13081-8. DOI
 62. Du, Y.; Sun, G.; Li, Y.; et al. Pre-oxidation of lignin precursors for hard carbon anode with boosted lithium-ion storage capacity. *Carbon* **2021**, *178*, 243-55. DOI
 63. He, X.; Larson, J. M.; Bechtel, H. A.; Kostecki, R. In situ infrared nanospectroscopy of the local processes at the Li/polymer electrolyte interface. *Nat. Commun.* **2022**, *13*, 1398. DOI PubMed PMC
 64. Wen, Z.; Zhao, Z.; Li, L.; et al. Study on the interfacial mechanism of bisalt polyether electrolyte for lithium metal batteries. *Adv. Funct. Mater.* **2022**, *32*, 2109184. DOI
 65. Lipinski, G.; Jeong, K.; Moritz, K.; et al. Application of Raman spectroscopy for sorption analysis of functionalized porous materials. *Adv. Sci.* **2022**, *9*, e2105477. DOI PubMed PMC
 66. Tharraul, M.; Desgué, E.; Carisetti, D.; et al. Raman spectroscopy of monolayer to bulk PtSe₂ exfoliated crystals. *2D. Mater.* **2024**, *11*, 6. DOI
 67. Cao, G.; An, F. Effectiveness of the elastic moduli characterization of graphene or other 2D materials via Raman spectroscopy. *Diam. Relat. Mater.* **2024**, *146*, 111201. DOI
 68. Matsuda, Y.; Kuwata, N.; Okawa, T.; Dorai, A.; Kamishima, O.; Kawamura, J. In situ Raman spectroscopy of Li_xCoO₂ cathode in Li/Li₃PO₄/LiCoO₂ all-solid-state thin-film lithium battery. *Solid. State. Ion.* **2019**, *335*, 7-14. DOI
 69. Cheng, X. Q.; Li, H. J.; Zhao, Z. X.; Wang, Y. Z.; Wang, X. M. The use of in-situ Raman spectroscopy in investigating carbon materials as anodes of alkali metal-ion batteries. *New. Carbon. Mater.* **2021**, *36*, 93-105. DOI
 70. Freudiger, C. W.; Min, W.; Saar, B. G.; et al. Label-free biomedical imaging with high sensitivity by stimulated Raman scattering microscopy. *Science* **2008**, *322*, 1857-61. DOI PubMed PMC
 71. Prince, R. C.; Frontiera, R. R.; Potma, E. O. Stimulated raman scattering: from bulk to nano. *Chem. Rev.* **2017**, *117*, 5070-94. DOI PubMed PMC
 72. Min, W.; Freudiger, C. W.; Lu, S.; Xie, X. S. Coherent nonlinear optical imaging: beyond fluorescence microscopy. *Annu. Rev. Phys. Chem.* **2011**, *62*, 507-30. DOI PubMed PMC
 73. Aliyah, K.; Appel, C.; Lazaridis, T.; et al. Operando scanning small-/wide-angle X-ray scattering for polymer electrolyte fuel cells: investigation of catalyst layer saturation and membrane hydration- capabilities and challenges. *ACS. Appl. Mater. Interfaces.* **2024**,

- 16, 25938-52. DOI PubMed PMC
74. Liang, Y.; Zheng, T.; Sun, K.; et al. Operando study insights into lithiation/delithiation processes in a poly(ethylene oxide) electrolyte of all-solid-state lithium batteries by grazing-incidence X-ray scattering. *ACS Appl. Mater. Interfaces.* **2024**, *16*, 33307-15. DOI
 75. Xu, M.; Liang, S.; Shi, H.; et al. High-strength MOF-based polymer electrolytes with uniform ionic flow for lithium dendrite suppression. *Small* **2024**, *20*, e2406007. DOI
 76. Liu, X.; Wang, D.; Liu, G.; et al. Distinct charge dynamics in battery electrodes revealed by *in situ* and *operando* soft X-ray spectroscopy. *Nat. Commun.* **2013**, *4*, 2568. DOI PubMed PMC
 77. Zhao, L.; Xiao, C.; Yao, Y.; Jin, X. Measurement of nanoscale film thickness using neutron depth profiling technique. *ACS Appl. Mater. Interfaces.* **2023**, *15*, 35639-47. DOI PubMed
 78. Lv, S.; Gao, J.; Liu, Y.; Zhao, Y.; Cheng, J.; Li, Z. Neutron depth profiling study on ⁶lithium and ¹⁰boron contents of nuclear graphite. *J. Nucl. Sci. and Technol.* **2021**, *58*, 1018-24. DOI
 79. Möller, S.; Schwab, C.; Seidlmayer, S.; et al. The Li battery digital twin - combining 4D modelling, electro-chemistry, neutron, and ion-beam techniques. *J. Power. Sources.* **2024**, *610*, 234681. DOI
 80. Liu, D. X.; Wang, J.; Pan, K.; et al. In situ quantification and visualization of lithium transport with neutrons. *Angew. Chem. Int. Ed.* **2014**, *53*, 9498-502. DOI
 81. Persson, K.; Sethuraman, V. A.; Hardwick, L. J.; et al. Lithium diffusion in graphitic carbon. *J. Phys. Chem. Lett.* **2010**, *1*, 1176-80. DOI
 82. Lyons, D. J.; Weaver, J. L.; Co, A. C. Considerations in applying neutron depth profiling (NDP) to Li-ion battery research. *J. Mater. Chem. A.* **2022**, *10*, 2336-51. DOI
 83. Liu, M.; Cheng, Z.; Qian, K.; Verhallen, T.; Wang, C.; Wagemaker, M. Efficient Li-metal plating/stripping in carbonate electrolytes using a LiNO₃-gel polymer electrolyte, monitored by operando neutron depth profiling. *Chem. Mater.* **2019**, *31*, 4564-74. DOI
 84. Mortensen, K.; Borger, A. L.; Kirkensgaard, J. J. K.; Huang, Q.; Hassager, O.; Almdal, K. Small-angle neutron scattering study of the structural relaxation of elongationally oriented, moderately stretched three-arm star polymers. *Phys. Rev. Lett.* **2021**, *127*, 177801. DOI PubMed
 85. Sun, R.; Melton, M.; Safaie, N.; et al. Molecular view on mechanical reinforcement in polymer nanocomposites. *Phys. Rev. Lett.* **2021**, *126*, 117801. DOI
 86. Terban, M. W.; Billinge, S. J. L. Structural analysis of molecular materials using the pair distribution function. *Chem. Rev.* **2022**, *122*, 1208-72. DOI PubMed PMC
 87. Chen, X. C.; Soulen, C.; Burdette-trofimov, M. K.; et al. Origin of rate limitations in solid-state polymer batteries from constrained segmental dynamics within the cathode. *Cell. Rep. Phys. Sci.* **2023**, *4*, 101538. DOI
 88. Yang, J.; Mo, F.; Hu, J.; et al. Revealing the dynamic evolution of Li filaments within solid electrolytes by operando small-angle neutron scattering. *Appl. Phys. Lett.* **2022**, *121*, 163901. DOI
 89. Teusner, M.; Mata, J.; Sharma, N. *In situ* synthesis of Cu(II) dicarboxylate metal organic frameworks (MOFs) and their application as battery materials. *Phys. Chem. Chem. Phys.* **2023**, *25*, 12684-93. DOI PubMed
 90. Hou, X.; Wang, R.; He, X.; et al. Stabilizing the solid-electrolyte interphase with polyacrylamide for high-voltage aqueous lithium-ion batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 22812-7. DOI PubMed PMC
 91. Bao, W.; Fan, W.; Luo, J.; et al. Imidazolium-type poly(ionic liquid) endows the composite polymer electrolyte membrane with excellent interface compatibility for all- solid-state lithium metal batteries. *ACS Appl. Mater. Interfaces.* **2022**, *14*, 55664-73. DOI
 92. Lin, W.; Zheng, X.; Ma, S.; Ji, K.; Wang, C.; Chen, M. Quasi-solid polymer electrolyte with multiple lithium-ion transport pathways by *in situ* thermal-initiating polymerization. *ACS Appl. Mater. Interfaces.* **2023**, *15*, 8128-37. DOI
 93. Ebadi, M.; Costa, L. T.; Araujo, C. M.; Brandell, D. Modelling the polymer electrolyte/Li-metal interface by molecular dynamics simulations. *Electrochim. Acta.* **2017**, *234*, 43-51. DOI
 94. Wu, L. T.; Nachimuthu, S.; Brandell, D.; Jiang, J. C. Prediction of SEI formation in all-solid-state batteries: computational insights from PCL-based polymer electrolyte decomposition on lithium-metal. *Batteries. Supercaps.* **2022**, *5*, e202200088. DOI
 95. Cao, X.; Lu, Y.; Chen, Z.; Zhao, X.; Wang, F. Phase-field investigation of dendrite suppression strategies for all-solid-state lithium metal batteries. *J. Energy. Storage.* **2024**, *99*, 113309. DOI
 96. Jiang, W.; Wang, Z.; Hu, L.; Wang, Y.; Ma, Z. Simulations of dendrite and crack and their interactions in solid electrolyte by phase field method. *J. Energy. Storage.* **2024**, *86*, 111126. DOI
 97. Wang, W.; Wang, J.; Lin, C.; Ruan, H. Modeling of void-mediated cracking and lithium penetration in all-solid-state batteries. *Adv. Funct. Mater.* **2023**, *33*, 2303484. DOI
 98. Geng, X. B.; Li, D. G.; Xu, B. Mechanical stress-thermodynamic phase-field simulation of lithium dendrite growth in solid electrolyte battery. *Acta. Phys. Sin.* **2023**, *72*, 220201. DOI
 99. Daru, J.; Forbert, H.; Behler, J.; Marx, D. Coupled cluster molecular dynamics of condensed phase systems enabled by machine learning potentials: liquid water benchmark. *Phys. Rev. Lett.* **2022**, *129*, 226001. DOI PubMed
 100. Perumanath, S.; Chubynsky, M. V.; Pillai, R.; Borg, M. K.; Sprittles, J. E. Rolling and sliding modes of nanodroplet spreading: molecular simulations and a continuum approach. *Phys. Rev. Lett.* **2023**, *131*, 164001. DOI
 101. Zhu, Y.; Lao, Z.; Zhang, M.; et al. A locally solvent-tethered polymer electrolyte for long-life lithium metal batteries. *Nat. Commun.* **2024**, *15*, 3914. DOI PubMed PMC
 102. Zhao, W.; Wang, S.; Zhou, L.; Du, X. Reducing interfacial thermal resistance between polyethylene oxide-based solid-state polymer

- electrolyte and lithium anode by using IVA group two-dimensional materials: a molecular dynamics study. *Int. J. Heat. Mass. Transf.* **2024**, *219*, 124864. DOI
103. Zhao, L.; Wang, Q. J.; Zhang, X.; et al. Laplace-Fourier transform solution to the electrochemical kinetics of a symmetric lithium cell affected by interface conformity. *J. Power. Sources.* **2022**, *531*, 231305. DOI
104. Zhang, X.; Luo, C.; Menga, N.; Zhang, H.; Li, Y.; Zhu, S. Contact mechanics modeling for pressure and polymer selections in solid-state batteries. 2022. Available from: https://papers.ssrn.com/sol3/papers.cfm?abstract_id=4277267 [Last accessed on 16 Jan 2025].