The Role of Mechanical Compliance in Polymer Solid Electrolytes for Solid-State Batteries

Zerui Hua*

Department of Chemistry, Virginia Tech, USA

Abstract. Solid-state batteries are widely regarded as a promising technology for next-generation energy storage, particularly for electric vehicles requiring improved safety and higher energy density. However, their practical performance is often limited by interfacial instability and restricted ionic transport within solid-state systems. Recent studies suggest that these limitations are closely related to mechanical effects occurring at electrode–electrolyte interfaces. This paper analyses how mechanical compliance will influence the electrochemical performance of polymer solid electrolytes. It firstly discusses the interfacial and transport challenges in solid-state batteries and then evaluates the mechanical-electrochemical coupling mechanism. It mainly focuses on the stress generated at the solid interface, stress-induced electrolyte failure, and the influence of mechanical deformation on ionic transport. Meanwhile, this article discusses the potential of polymer and quasi-solid-state electrolyte systems as a solution to improve the interface's contact. These findings ultimately demonstrate that refining the mechanical compliance of electrolytes is the key requirement to push the practical application of solid-state batteries.

1 Introduction

With the rapid growth of the electric vehicle (EV) market, the demand for higher quality of rechargeable batteries has increased over time, especially in areas like energy density, safety, and life cycle. Although traditional liquid lithium-ion batteries can already operate at a large scale in commercial applications, their flammability has always been a risk. In addition, their energy density is approaching its theoretical limit. These limitations make it hard to meet the increasing demands for high security and high energy density. Thus, SSBs have been recognized as the most promising solution for next-generation energy storage [1].

By replacing liquid-state electrolytes with solid-state ones, it can theoretically improve the security of batteries. It also could make high-capacity anodes like lithium metal or silicon available for battery application. Among all kinds of electrolyte systems, polymer solid electrolytes (PSEs) provide excellent film-forming properties, process-ability, and relatively low interfacial impedance between electrode materials. However, despite PSEs have these advantages, many SSB systems still have problems like rapid performance degradation and unstable interfaces during cycling [2]. One of the reasons that causing these issues is mechanical compliance. During the battery operation, electrode materials undergo volume

* Corresponding author: jerryh24@vt.edu

changes, forming stresses on the interface between electrode and electrolyte. Different from liquid electrolytes that maintain contact through fluid flow, solid electrolytes must accommodate these stresses by mechanical deformation. Thus, low mechanical compliance will lead to impedance and rapid degradation of battery performance.

In recent years, researchers have begun to focus on the role that mechanical compliance plays in SSBs by introducing polymer electrolytes with elastic or elastic-viscous characteristics, which can improve the system's ability to adapt to volume changes and interfacial stresses. PSEs with high mechanical compliance can stabilize the electrode-electrolyte contact without requiring additional external pressure. This improves ions transport and increases overall battery performance. This approach provides a new research perspective by examining the mechanical principles of PSEs, and trying to introduce a new path to achieve a well performing and long-life SSBs.

2 Interfacial and transport limitations in solid-state systems

SSBs have been widely identified as a potential method to replace traditional liquid lithium-ion batteries. However, under the actual operating conditions, their performance is often restricted by the interface instability and the limited ion transport pathway. It has been shown that high interface impedance, side reactions between electrodes and electrolytes, and interface structure degradation during the circulation are the main changes faced by multiple solid electrolyte systems at present [3].

While liquid electrolytes can fully wet the electrode surface and reestablish contact through flow after the interface disconnects, the solid-solid interface is formed by solid electrolytes and the electrode. The contact quality of the interface is highly dependent on the surface morphology of the material, processing conditions, and the degree of mechanical matching between different components. In the cycling process of rapid charging and discharging, the electrode will eventually undergo volume changes. When the system lacks sufficient size adaptability, the interface could easily have stress concentration, which in turn induces micropore formation, crack expansion, and effective contact area decline [4]. Once the continuity of the interface is broken, the ion transport passway will be partially or completely blocked, leading to increased polarization and rapid attenuation of capacity.

Apart from the interface contact problem, the SSBs also have many challenges at the structural level in the actual high energy density. For the structural material of the composite electrode and the thick electrode, lithium ions have to move through a complex route involving various phases. Therefore, the conductivity of the lithium ions at the system level is generally low compared to the material conductivity. Past research on the subject indicated that the polymer electrolyte system is related to the mobility of the polymer chain. Therefore, it is difficult to solve the ionic conductivity without reference to the mechanical and structural properties of the material [5]. This implies that it is difficult to solve the basic problem of the system-level transmission bottleneck by improving the conductivity of the material.

Because of the absence of adaptive wetting behavior in liquid electrolytes, the integrity of interfaces in solid-state systems is heavily dependent on material contact states and matching structural compatibility [3]. Nevertheless, in practical EV systems, high pressures over long periods are likely to increase system complexity and cost, and possibly raise additional problems related to safety and structural reliability. As such, solely relying on external pressures to ensure interface stability is unlikely to be a compelling argument from an engineering perspective.

The performance bottleneck in SSBs systems is not only related to insufficient intrinsic ionic conductivity. Additionally, it could be related to contact behavior associated with the solid-solid interface, mechanical mismatching during cycles, and transmission restrictions under high-energy-density structure circumstances. These factors indicate that understanding

the relationship between mechanical flexibility and ion conduction continuity is crucial to ensuring system stability in SSBs systems. Moreover, it is caused by the contact characteristic of the solid-solid interface, the mechanical mismatch in the cycle, and the transmission restrictions under the high-energy-density structure circumstance. These factors indicate that understanding the relationship between mechanical adaptability and ion conduction continuity is crucial to ensuring system stability in SSBs systems.

3 Mechanical–electrochemical coupling in SSBs

3.1 Stress generation and mechanical mismatch

In SSBs, electrochemical reactions and mechanical responses are highly coupled. Different with traditional liquid-state batteries, SSBs do not have a flowing electrolyte. Which makes it unable to buffer the volume change of electrode during batteries' charging and discharging. This kind of volume mismatch will create significant amount of mechanical stress at rigid solid-solid interfaces. Making it one of the key reasons for interface failure [6].

This kind of stress originates from the electrode material's compositional strains. On the cathode side, the insertion and extraction of lithium ions lead to changes in lattice parameters. In a particular example, Layered oxide cathode materials like $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{22}$ (NMC111) and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) have a volume change of around 3.3% and 7.8% [6]. Both show obvious expansion and shrinkage in their volume. Since solid electrolytes have characteristics as high elastic modules and lack fluidity, these percentage volume changes will transform into stresses.

On the anode side, the plating process of lithium metal will also trigger serious issues in the mechanical area [6]. When lithium's growth is restricted in pores on the surface of the electrolyte or at the grain boundaries, it will create extremely hydrostatic stress. If these local stresses cannot be unleashed, it will not only change the mechanical process of lithium plating, but rather leads to electrolyte's internal stress concentration. This will become the main reason for subsequent structural damage.

3.2 Stress-induced structural failure of solid electrolytes

As these stresses keep accumulating at the interface, it will lead to irreversible structural failure once it goes beyond the bearing limit of the solid electrolyte. Based on the real-time observation by in situ TEM, when high current density causes Li eruption, the instantaneous pressure could reach 10 GPa. For ceramic electrolytes that only have 0.95 MPa $\cdot m^{1/2}$ fracture toughness (K_{IC}), this kind of stress concentration is enough to form cracks within single-crystal grains [7].

The specific structure failure usually shows in two modes: the first one is particle splitting, where local stress drives the crack vertically through the entire electrolyte particle, providing a low resistance passway for penetration of lithium metal. The second one is surface peeling, indicating the crack is spread horizontally under the electrolyte surface. This condition will peel off the surface material and leave pit. Even though these peelings will not directly lead to a short circuit, these pits on the surface will become a risk. They will act as vulnerable sites where strain energy and penetration of lithium metal in subsequent cycles are focused on [7]. As lithium metal permeates deeper into the electrolyte, battery failure will be the result. These experimental data have shown that the accumulation of interfacial stress is the main reason for lowering the mechanical reliability of SSBs.

3.3 Mechanical influence on ionic transport in polymer electrolytes

The ion transport of polymer electrolytes is highly reliant on the dynamic motion of the polymer chains. On the other hand, the microscopic structural arrangement of the matrix is also very important to the efficiency of ion migration. Mechanical change will directly change the microstructure of the polymer, which will open or close the migration route for ions.

Mechanical stretching has significant impact on the modification of the microstructure. During deformation, the crystalline region will reorganize, and the polymer chains are more favorable to align along the stretching direction. This structural change will cause anisotropy in ion transport, which will greatly improve the in-plane ionic conductivity. Research shows that this kind of influence is regulated by the temperature: Under the melting point of poly(ethylene oxide) (PEO), stretching will induce the generation of a necking region. Within this region, structure that was in disarray will transform into a fibrous structure. This significantly reduces the effective path length of ion transport [8].

Specific lab data have proven this theory: For PEO homopolymer electrolytes, the conductivity in the necking region can be higher to the 1.7 times the initial value; For some block copolymer electrolytes, the number could even go up to 18 times [8]. These findings all show that the mechanical state of polymer electrolytes is not just physical support, but also the critical factor to determine the efficiency of their ion transport.

4 Polymer electrolytes as a practical pathway toward scalable SSBs

After clarifying that mechanical conformability is the core factor affecting the interface stability and long-term performance of SSBs, a key question arises: which kind of electrolyte system can ensure safety while maintaining interface adaptability and engineering feasibility? Rather than inorganic solid electrolytes like oxides and sulfides, polymer-based electrolytes show unique advantages in areas of mechanical properties and manufacturing compatibility.

From a mechanical perspective, polymer materials themselves are flexible and have certain viscoelasticity, enabling them to adapt to the volume change of the electrode by self-deformation. This conformability helps to alleviate the problem of stress concentration at the solid-solid interface, reducing the risk of interface deformation and micro-crack formation, in order to maintain a stable ion transport pathway. In contrast, it is difficult for rigid ceramic electrolytes to maintain good interface fit during cycling; it often relies on external stacking pressure to maintain contact stability, which has obvious engineering limitations in actual EV applications [9, 10].

From an industrialization perspective, polymer electrolytes are more advantageous in terms of processing methods. It can achieve large-scale production through solution casting, extrusion, and roll-to-roll process, which is highly compatible with the existing lithium-ion battery manufacturing system. This continuity process significantly reduces the cost of equipment transformation and the complexity of production. In contrast, oxide electrolytes usually require high-temperature sintering, while sulfide systems are extremely sensitive to water and oxygen and need to be operated in strict moisture-free environments. These factors increase the difficulty of industrialization. Some studies have compared different solid electrolyte systems from multiple perspectives. These perspectives include ionic conductivity, interface adaptability, processing compatibility, and large-scale manufacturing potential. They have concluded that polymer electrolyte systems provide a more balanced development pathway. Especially in terms of the use of solution casting or roll-to-roll process, no need for high-temperature sintering and large-scale equipment transformation, polymer systems have a more realistic feasibility in promoting industrialization [3].

Besides theoretical advantages, the quasi-solid-state (QSS) electrolyte system further provides a compromise way to fill in the gap between liquid and solid architectures. By immobilizing ionic liquids or coordinated complexes within nanoparticle frameworks or polymer matrices, QSS electrolytes combine liquid-like ionic transport with enhanced structural stability. This combination provides higher security and suppresses leakage, while preserving interfacial conformability. There has been multiple experimental evidences to support the practical feasibility of such a system. Some studies have developed QSS electrolytes based on Li-Lyme complexes. Using this electrolyte, researchers constructed a double-layer and three-layer bipolar stacked all-solid-state lithium battery structure. Both of them have achieved stable plateau voltages of approximately 6.7V and 10V without internal short circuits. Beyond that, they maintained 99% of the capacity retention rate after 200 cycles at 0.5C [8]. These results confirm that mechanically adaptable QSS electrolytes can operate reliably in high-voltage stacked architectures.

Thus, from the comprehensive analysis of multiple levels, such as interface mechanical adaptability, manufacturing compatibility, and experimental feasibility, polymer and QSS electrolyte systems provide a more realistic development path for breaking through the structural limitations of traditional inorganic solid electrolytes. In the process of engineering and large-scale application of SSBs technology in the future, optimizing the mechanical-electrochemical coupling characteristics of polymer systems will be the key direction to promote its further development.

5 Conclusion

SSBs have shown great potential as next-generation energy storage system, especially fit for applications that require high energy density and safety, like EVs. However, there remain some non-neglectable problems faced by SSBs, like interface stability and ion transport limitations. These challenges show that there is no direct connection between theoretical advantages and real-world performance. In particular, intrinsic ionic conductivity cannot determine battery performance alone. Mechanical factors also play an important role in the structural stability of SSB systems. During the battery operation, it will generate mechanical stresses and disrupt ion transport pathways, and accelerate interfacial degradation.

All these challenges will be addressed if PSEs are considered. This is because the flexibility and viscoelasticity of PSEs will enable them to maintain the interface between the electrode and the electrolyte due to their ability to adapt to the change in the volume of the electrolyte. On the other hand, the scalability of the polymer-based systems will be advantageous. Therefore, it will be very useful to consider the production of the battery using the scalability of the polymer-based systems. The QSS electrolyte systems have also been considered. This shows that the structural stability of the electrolytes will be advantageous in improving the performance of the battery. Therefore, it is essential that the research be directed towards the development of the electrolytes that will be able to balance the conductivity and the flexibility of the battery.

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