Polypropylene Carbonate-Based Adaptive Buffer Layer for Stable Interfaces of Solid Polymer Lithium Metal Batteries

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ABSTRACT: Solid polymer electrolytes (SPEs) have the potential to enhance the safety and energy density of lithium batteries. However, poor interfacial contact between the lithium metal anode and SPE leads to high interfacial resistance and low specific capacity of the battery. In this work, we present a novel strategy to improve this solid–solid interface problem and maintain good interfacial contact during battery cycling by introducing an adaptive buffer layer (ABL) between the Li metal anode and SPE. The ABL consists of low molecular-weight polypropylene carbonate, poly(ethylene oxide) (PEO), and lithium salt. Rheological experiments indicate that ABL is viscoelastic and that it flows with a higher viscosity compared to PEO-only SPE. ABL also has higher ionic conductivity than PEO-only SPE. In the presence of ABL, the interface resistance of the Li/ABL/SPE/LiFePO4 battery only increased 20% after 150 cycles, whereas that of the battery without ABL increased by 117%. In addition, because ABL makes a good solid–solid interface contact between the Li metal anode and SPE, the battery with ABL delivered an initial discharge specific capacity of >110 mA·h/g, which is nearly twice that of the battery without ABL, which is 60 mA·h/g. Moreover, ABL is able to maintain electrode–electrolyte interfacial contact during battery cycling, which stabilizes the battery Coulombic efficiency.

KEYWORDS: adaptive interface, all-solid-state battery, solid polymer electrolyte, lithium metal anode, interfacial adhesion, viscoelastic

INTRODUCTION

Lithium-ion batteries (LIBs) are valuable in portable devices, electrical vehicles, and electric grids.1–6 However, with the maturation of LIBs, it is challenging to improve the safety and energy-density. Recently, lithium metals have attracted interest as an alternative anode material because it has a high theoretical capacity (3860 mA·h/g), which is more than ten times that of graphite (372 mA·h/g) and the lowest negative electrochemical potential (~3.04 V vs standard hydrogen electrode)7–11 among all possible anodes. The Li–LMO battery (M represents a transition metal, such as Co, Ni, and Mn) has a specific energy of ~440 W·h/kg, which is higher than that of the state-of-the-art LIBs (~250 W·h/kg).7 Pairing with new cathodes such as sulfur and oxygen can increase the theoretical energy density to 2600 W·h/kg (Li–S)12 and 3500 Wh/kg (Li–O2), respectively.13 Thus, development of the Li metal anode is an enabling technology for future batteries.

When used with a Li metal anode, traditional organic liquid electrolytes have severe safety concerns due to their low flash point, toxicity, and complex side reactions with Li.14–16 The potential safety issues of liquid organic electrolytes restrict some applications in large-scale systems.17 Because of its low or nonflammability, the solid-state electrolyte (SSE) is an exciting research direction to mitigate the safety concerns of organic electrolytes. SSEs generally have two categories: inorganic ceramic electrolytes and solid polymer electrolytes (SPEs).18,19 The list of inorganic ceramic electrolytes mainly includes oxide-based ceramic electrolytes such as NASICON-like ceramic electrolytes,20 garnet structure electrolytes,21 and sulfide-based ceramic electrolytes.22 As for SPEs, poly(ethylene oxide) (PEO) is one of the most popular polymer approaches due to its relatively high ionic conductivity, reasonable mechanical stability, good compatibility with electrodes, and excellent film-forming ability.23–25 The Li+ transport mechanism in PEO originates from the ether repeat linkages, which enable lithium salt dissociation and lithium ion mobility.
In a lithium battery system with SSE and Li metal, the Li–SSE interfaces are important to the electrochemical reaction because only the active materials that are in direct contact with the electrolyte can be effectively utilized. However, unlike liquid electrolytes that are able to easily deform to maintain interfacial contact with the surface of electrodes, it is hard to maintain a solid–solid interface between the Li anode and SSE, especially during battery cycling because the surface morphology of the Li metal continuously changes.\textsuperscript{19,20} Expansion and contraction of the cathode during cycling can also be a problem. Thus, the overall interfacial resistance of the battery with SSE increases during battery cycling, which leads to a decay in specific capacity. To improve the solid–solid interfacial contact, many surface modification methods have been developed. For inorganic ceramic SSEs, the methods of ball-milling,\textsuperscript{24,31} pulsed laser deposition,\textsuperscript{32,33} atomic layer deposition,\textsuperscript{34,35} and composite electrolytes\textsuperscript{36,37} have been widely used. As for SPEs, gel polymer electrolytes (GPEs), where the organic liquid electrolyte is incorporated into the matrix of the SPE, have attracted increasing attention. Combining the advantages of liquid electrolytes and SPEs, GPEs have good interfacial contact with Li metal and excellent interfacial stability.\textsuperscript{37} However, because of the existence of the organic liquid electrolyte, the safety performance of GPEs is not ideal. “Self-healing” additives have been used in battery electrodes (e.g., LiMn$_2$O$_4$ and LiTi$_2$(PO$_4$)$_3$ electrodes,\textsuperscript{38} silicon anode,\textsuperscript{39} and Li metal anode\textsuperscript{40,41}) to in situ repair damaged electrical networks during cycling in liquid electrolytes.

In this work, we have improved the interfacial contact between Li metal and SPE by designing a polymer-based adaptive buffer layer (ABL) with the ability to “self-heal”. As shown in Figure 1, the interfacial contact between Li metal and SPE in the battery without ABL deteriorates as the Li surface deforms during cycling. In contrast, ABL is able to maintain good interfacial contact by filling the undulations and voids on the lithium metal formed during battery cycling.\textsuperscript{40} Experimentally, we created this ABL by mixing lithium salt, high-molecular-weight PEO (600 000 Da), and low molecular-weight poly(propylene carbonate) (PPC) (2000 Da). PPC is a copolymer of propylene oxide and carbon dioxide and has a low degree of crystallinity.\textsuperscript{41,42} The addition of low molecular-weight PPC gives the ABL fluidity at elevated temperature (i.e., 50 °C). During battery cycling, the ABL is able to adapt to the shape change of Li metal anode, so it maintains good interfacial contact between the Li metal anode and SPE. Note that an ABL with too much fluidity will result in it being squeezed out during battery assembly, and should be avoided.

### Experimental Section

**Materials.** PEO (M$_w$ 600 000, Sigma-Aldrich), poly(propylene carbonate) (M$_w$ ≈ 2000, Novomer Inc.), bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Sigma-Aldrich), acetonitrile (AN) (Alfa Aesar), LiFePO$_4$ powder (LFP, MTI Corporation), Super P (MTI Corporation), and Li foil (thickness 0.75 mm, Alfa Aesar).

**Preparation of SPE and ABL.** PEO, PPC, and LiTFSI were carefully dried at 60 °C overnight before use. PEO and LiTFSI were dissolved in AN and stirred for 24 h. The molar ratio of EO:Li was set to 8:1. After stirring, the slurry containing PEO and LiTFSI was coated onto the stainless steel disk (0.001 in thickness, TBI Corporation) or LFP cathode and dried at 60 °C for 12 h to obtain samples for ionic conductivity or battery tests. The surface area of the stainless steel electrode for the conductivity test is 0.785 cm$^2$, and the thickness of SPE membrane is around 150 μm. To prepare the ABL, PEO, PPC, and LiTFSI were dissolved in AN and stirred for 24 h. The mass ratio of PEO, PPC, and lithium salt is 1:1:1.16. After stirring for 24 h, the ABL solution was cast onto stainless steel for conductivity tests or onto the top of the SPE membrane for battery tests. The above electrodes were transferred into an argon-filled glovebox and dried at 60 °C for 12 h. The areal sizes of the cathode, electrolyte, and anode in a working cell are 0.785, 0.785, and 0.503 cm$^2$, respectively. The thickness of ABL is around 10 μm in the full battery, which was measured by caliper (MITUTOYO Corp., CD-6 ASX) at room temperature, shown in Figure S1.

**Ionic Conductivity Measurements of SPEs.** The ionic conductivities of the SPEs were measured by electrochemical impedance spectroscopy (EIS) with an ac amplitude of 10 mV in the frequency range of 1 MHz to 0.1 Hz. The measurements were performed on a Bio-Logic SAS at various temperatures ranging from 30 to 70 °C. The PEO and ABL were separately sandwiched between two stainless steel round disks inside a 2032 type coin cell for testing. The batteries were kept at each test temperature for 30 min to reach thermal equilibrium. The ionic conductivity ($\sigma$) of SPEs could be calculated by the resistance ($R$), the electrode area ($S$), and the electrode thickness ($L$), according to the following equation

$$\sigma = \frac{L}{R S}$$

**Material Characterization and Electrochemical Test.** The rheology was measured by a cone-plate geometry in an Anton Paar MCR 501. The diameter of the cone, the cone angle, and the truncation height is 25 mm, 2°, and 0.051 mm, respectively. Frequency sweeps were performed at an applied strain amplitude of 0.1 at 50 °C. Differential scanning calorimetry (DSC, Q600) was carried out to measure the melting point of the polymer electrolyte from −30 to 80 °C at a heating rate of 5 °C/min under a nitrogen atmosphere.

A composition of 60:20:12:8 of LiFePO$_4$/PEO/Super P/LiTFSI was used in the cathode slurry. These components were dispersed in AN and stirred overnight. The slurry was cast onto carbon-coated aluminum (Guangzhou Nano New Material Technology Co., Ltd) round disks with 1 cm diameter. After drying at 70 °C for 12 h, the LFP cathode was obtained. The mass loading of LiFePO$_4$ on the cathode ranged from 2.2 to 2.5 mg/cm$^2$. To get the cathode with SPE, the PEO SPE solution was directly cast onto the LFP cathode. After drying the SPE layer in a vacuum dryer overnight, they were transferred into an argon-filled glovebox and heated at 70 °C for 12 h to remove the remaining traces of the solvent. For the cathodes with ABL, the ABL solution was cast onto PEO SPE in the glovebox and dried for another 12 h. The full battery consisting of the Li metal anode, SPE (with or without ABL), and LFP cathode were assembled into a 2031 coin cell inside the glovebox. Full cells and Li/Li symmetric cells were cycled using an 8-channel (Wuhan LANHE electronics Corporation) battery tester in a temperature chamber (Tenney Environment, Thermal Product Solutions). To visualize the
change of interfacial contact between the Li metal and SPE, the symmetric cells, Li/SPE/Li, with and without ABLs, were deeply discharged to 20 mA·h/cm² at 0.04 mA/cm². The morphology of the interfaces between the Li metal and SPE after deep discharge were characterized by scanning electron microscopy (SEM, Hitachi 8230). All tests of the batteries were conducted at 50 °C.

The total ionic conductivity measurements of full batteries were performed on a Bio-logic SAS. EIS measurements were performed at frequencies ranging from 1 MHz to 0.1 Hz before and after battery cycling at various temperatures (from 30 to 70 °C). The bulk resistance (Rb) and interface resistance (Rint) were simulated from the EIS curve. The total ionic conductivity (σt) of the full battery was calculated from the total resistance (Rt), the electrode area (S), and the electrode thickness (L), according to the following equation:

\[ Rt = R_b + R_{int} \]  
\[ \sigma_t = \frac{L}{(R_t \times S)} \]

RESULTS AND DISCUSSION

From a mechanical perspective, our ABL exhibits long-time flow behavior at 50 °C. To compare the PEO SPE, ABL, and PPC SPE solutions, we poured them into three vials, dried them for 24 h in the fume hood at 70 °C, for 12 h in the vacuum dryer, and for 12 h in an argon-filled glovebox at 70 °C to completely remove the solvent. The vials were then laid horizontally over a time span of 12 h at 50 °C. The PEO SPE showed nearly no fluidity and remained at the bottom of the vial (Figure 2a). The ABL exhibited flow behavior with relatively high viscosity, as qualitatively deduced from the slope-free surface developed by the system in the same time scale (Figure 2b). Without PEO, the PPC SPE showed fluid-like behavior with much lower viscosity compared to ABL, as reflected by the spreading of the material inside the vial (Figure 2c). Besides, the surface condition of the cathode with ABL was different from the one without ABL. In this work, LiFePO₄ (LFP) was used as the cathode material for the full battery. To reduce the interfacial resistance between the SPE and cathode, the SPE solution was directly cast onto the electrode. The surface of the cathode without ABL was dark and uneven, as shown in Figure 2d; in contrast, the one with ABL was smooth and reflective (Figure 2e). Ultimately, it is

the difference in mechanical properties that determines the differences between these two situations.

To more quantitatively characterize the mechanical properties of both ABL and PEO SPE, we performed oscillatory rheology in the linear regime at 50 °C. In these experiments, we apply a harmonic strain and measure the resultant stress, which is generally also harmonic but out-of-phase with respect to the applied strain. The material response thus includes both liquid-like and elastic-like responses. The loss modulus, \( G'' \), and the storage modulus, \( G' \), quantify the relative importance of viscous dissipation and elastic-energy storage, respectively. We measured these moduli as a function of frequency for low applied strain amplitudes. We find that for small frequencies, \( G'' > G' \), whereas at high frequencies, \( G'' > G' \). Hence, there is a crossover at certain frequency, \( \omega_c \). Although this is true for both PEO SPE and ABL, as shown in Figure 3a,b, we find that

the crossover is significantly different. Although for PEO SPE, \( \omega_c \approx 0.033 \text{ s}^{-1} \) and for ABL, \( \omega_c \approx 0.12 \text{ s}^{-1} \), indicating that the structural rearrangement in the latter happens at shorter time scales and that its liquid-like response is more pronounced. This is also reflected by the smaller values of the moduli at the crossover and of \( G' \) at the highest frequencies we can probe.

For SPEs, high ionic conductivity and interfacial retention during battery cycling are very important. At the same current density, batteries with higher ionic conductivities will have lower Ohmic voltage loss, more complete reactions, and higher specific capacities for the electrode materials. The mechanism
of Li⁺ transport in PPC is similar to that of PEO where ion conduction is assisted by chain-segment mobility.⁴¹,⁴⁴ PEO is a semi-crystalline polymer that includes both amorphous phases and crystalline phases. As the Li⁺ transport only occurs in the amorphous regions of the polymer, and the presence of the crystalline phase is detrimental to Li⁺ transport.⁴⁵ PEO SPE has low ionic conductivity, on the order of 10⁻³ to 10⁻⁶ at ambient temperature.⁴⁵ In contrast, the PPC SPE has higher Li⁺ conductivity due to greater presence of amorphous structures within PPC.⁴⁴ Amorphous polymers do not have a melting point (T_m) when analyzed by DSC. In previous DSC results, PPC SPE did not show a T_m which confirms its amorphous structure.⁴¹ The DSC curves of PEO SPE and ABL are shown in Figure 4a. The endothermic peak of PEO SPE appears at ca. 67 °C. The ABL used here showed no obvious T_m. The ionic conductivity was measured at various temperatures (ranging from 30 to 70 °C), using EIS in 2032 coin cells. The SPE and ABL/SPE were sandwiched between two stainless steel disks for measurement of conductivity. As shown in Figure 4b, ABL has higher ionic conductivity than PEO SPE at all measured temperatures due to the incorporation of low molecular weight PPC.

Full-cell battery cycling tests were performed using a lithium metal anode, lithium iron phosphate cathode, and SPE electrolyte, as shown in Figure 5. The electrolyte Ohmic loss is related to the mobility of Li⁺ and the number of carriers in the solid electrolyte. However, if there is loss of interfacial contact between the SPE and either electrode, the resistance increases because that section of the electrolyte is effectively useless. The purpose of the ABL is to maintain good interfacial contact between the Li metal anode (or cathode) and SPE keeping the resistance of the battery constant during cycling. To study the change in interfacial contact before and after battery cycling, batteries were assembled and tested at 50 °C and 1 C rate using Li/SPE/LiFePO₄ and Li/ABL/SPE/LiFePO₄ full batteries, Figure 5a. The details of assembling the batteries with ABL are shown in Figure S2. The impedance of full-cell batteries before and after 150 cycles was measured using EIS. Figure 5b showed the fitted EIS results and the inset shows the equivalent circuit model used to simulate the EIS curves. R_L and R_int represent the bulk resistance and interface resistance, respectively. The low frequency resistance, R_int, increased from 202 to 439 Ω (117%) for the battery without ABL, showing a loss in interfacial surface area between the SPE and electrodes because the fundamental exchange current is assumed to remain about the same. With the ABL, there was only a 20% increase in resistance from 156 to 187 Ω. Furthermore, the EIS tests of full batteries before and after 150 cycles were carried out from 30 to 70 °C to measure the total resistance (R_t) or low-frequency intercept, which is the sum of bulk resistance (R_b) and interface resistance (R_int). Total conductivity based on R_b is shown in Figure 5c,d. The battery without ABL had an increase in R_b (ranging from 43 to 63%) after cycling as indicated by the blue arrow in Figure 5c. In contrast, there is essentially little change in R_b (increase of 6–14%) of the battery with ABL, showing that the ABL is effective in keeping the overall ionic conductivity from decreasing during cycling.

The increase in interfacial resistance was mitigated by incorporation of low molecular weight PPC in the ABL, which resulted in higher specific capacity after cycling. The rate capabilities of the Li/SPE/LiFePO₄ battery are presented in Figure 6a. The battery with ABL had higher specific capacity at all tested rates. Figure 6b,c show the voltage profiles, which are additional evidence that the battery with ABL is capable of delivering higher specific capacity. At 0.5, 1, 1.5, 2, and 3 C discharge rates, the capacities of the battery with ABL are 30, 40, 57, 89, and 240% higher than the one without ABL, respectively.

The capacity retention and Coulombic efficiency of batteries at 1 C and 50 °C are shown in Figure 6d,e. Because the ABL made a good solid-solid interface contact between Li and SPE, the battery with ABL delivered a higher initial specific capacity (110 mA·h/g) than the one without ABL (60 mA·h/g). Moreover, as the surface morphology of Li metal changes during battery cycling, the Coulombic efficiency fluctuates due to the continuously changing interfacial contact between Li metal and SPE. In contrast, the semi-liquid ABL is able to deform and maintain good interfacial contact, therefore delivering a more stable Coulombic efficiency over 150 cycles. To evaluate the cycling stability with ABL, symmetric cells Li/SPE/Li and Li/ABL/SPE/LiFePO₄ were assembled and tested at 0.25 mA·cm⁻², 50 °C. As shown in Figure S3, the cell without ABL exhibits severer voltage polarization during the 360 h cycling. This can be ascribed to the unstable interface
In addition, the SPE with ABL is better matched to higher temperature operation because there are no volatile solvents and the conductivity of the SPE and ABL improve with temperature. The ABL working temperature can also be adjusted by modifying the structure of PPC to encourage greater segmental mobility at lower temperatures. This should be the subject of future studies. Our work offers a new way to maintain stable interfaces between dimensionally changing electrodes and electrolyte, particularly for all-solid-state batteries.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b08285.

Measurement of the thickness of ABL with caliper at room temperature, preparation of the battery with ABL, and voltage–time curves of symmetric Li/Li cells (current density: 0.25 mA·cm$^{-2}$; capacity: 0.25 mA·h·cm$^{-2}$) (PDF)

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**Notes**

The authors declare no competing financial interest.

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