Safety-Reinforced Poly(Propylene Carbonate)-Based All-Solid-State Polymer Electrolyte for Ambient-Temperature Solid Polymer Lithium Batteries

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An integrated preparation of safety-reinforced poly(propylene carbonate)-based all-solid polymer electrolyte is shown to be applicable to ambient-temperature solid polymer lithium batteries. In contrast to pristine poly(ethylene oxide) solid polymer electrolyte, this solid polymer electrolyte exhibits higher ionic conductivity, wider electrochemical window, better mechanical strength, and superior rate performance at 20 °C. Moreover, lithium iron phosphate/lithium cell using such solid polymer electrolyte can charge and discharge even at 120 °C. It is also noted that the solid-state soft-package lithium cells assembled with this solid polymer electrolyte can still power a red light-emitting diode lamp without suffering from internal short-circuit failures even after cutting off one part of the battery. Considering the aspects mentioned above, the solid polymer electrolyte is eligible for practical lithium battery applications with improved reliability and safety. Just as important, a new perspective that the degree of amorphous state of polymer is also as critical as its low glass transition temperature for the exploration of room temperature solid polymer electrolyte is illustrated. In all, this study opens up a kind of new avenue that could be a milestone to the development of high-voltage and ambient-temperature all-solid-state polymer electrolytes.

1. Introduction

Rechargeable lithium-ion batteries become a vital technology in the contemporary society. They are expanding their application in electric vehicles and power grids.[1–18] However, there are huge potential safety hazards when commercialized lithium-ion battery employing organic carbonate solvent and polyolefin-based separators. These potential risks (combustion and explosion) would retard the commercialization of electric vehicles or hybrid electric vehicles. Thus, the safety issue of lithium-ion battery merits further study. Solid polymer electrolyte is attracting strong interest and is regarded as a perfect way to handle the potential safety issue of lithium batteries. Solid polymer electrolyte holds great promise for next-generation lithium batteries with significantly improved safety characteristics.[19] The advantages of poly(ethylene oxide) (PEO)-based solid polymer electrolytes are widely acknowledged.[20,21] However, their low ionic conductivity, poor mechanical strength and narrow electrochemical window limited their further applications.[22–25]

In an effort to address above-mentioned issues, there has been an ongoing search over the past few decades to boost the overall performance of solid polymer electrolyte, such as composite polymer electrolytes, interpenetrating network polymer electrolyte, nonwoven reinforced solid polymer electrolyte, and new materials for solid polymer electrolytes.[26–35] Despite these great efforts, solid polymer electrolyte with relatively low ionic conductivity, inferior mechanical strength, and narrow electrochemical window are still not satisfactory enough to meet practical needs. On the basis of this, it is essential to explore new solid polymer electrolyte with comprehensive performance in terms of high ionic conductivity, proper mechanical strength, superior heat resistance, wider electrochemical window, and excellent battery performance at room temperature.

Poly(propylene carbonate) (PPC), a copolymer of propylene oxide and carbon dioxide, is one of the new polycarbonates that have gained considerable interests due to the urgent need for the development of green materials.[36–39] It is generally known that cellulose is a renewable material and exhibits outstanding...
properties such as environmental friendliness, chemical stability, and thermal stability.\(^{40–42}\) Taichi, which has abundant Chinese traditional cultural contents, is thought by many people to be the half of Chinese boxing. “Rigid and soft” is the essence of Taijiquan. Inspired by Taichi, we herein put forward a scalable and smart strategy to exploit high-performance cellulose nonwoven as the backbone and use PPC as ionic transport material. Combining special properties of these two materials, we successfully develop a new class of rigid-flexible coupling cellulose supporting PPC all-solid-state polymer electrolyte for ambient-temperature solid polymer lithium batteries. To the best of our knowledge, ambient-temperature polymer lithium batteries using PPC all-solid-state polymer electrolyte have so far been barely explored. The present work is the first scientific report that addresses safety-reinforced and high-voltage PPC-based all-solid-state polymer electrolyte for ambient-temperature solid lithium batteries. It was demonstrated that such PPC-based solid polymer electrolyte exhibited superior mechanical strength, high electrochemical stability, and outstanding rate capability at broad temperature range. Thus, this research will open a new avenue for designing and exploiting new kind of solid polymer electrolyte for high-performance all-solid-state polymer lithium batteries. We clarified long-standing prejudice that room-temperature solid polymer electrolyte should possess a lower glass transition temperature \((T_g)\) than that of PEO. So, in previous researches, people placed undue emphasis on the function of \(T_g\).\(^{23–26,49–53}\) In our study, we illustrated a new point of view on high ionic conductivity of solid polymer electrolyte related to low degree of crystallinity of materials and appropriate glass transition temperature (rather than relatively low glass transition temperature). No doubt, our study opens up a new kind of perspective that is critical for exploring high-performance and ambient-temperature all-solid-state polymer electrolytes.

2. Results and Discussion

2.1. Fabrication of PPC-Based Solid Polymer Electrolyte

PPC-based solid polymer electrolytes were fabricated by a facile solution-casting method. PPC (10 g) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (3 g) were added into anhydrous acetonitrile (100 mL) in sequence under intense stirring to form a homogeneous solution. Subsequently, flame-retardant cellulose nonwoven membrane was prepared according to the method of our previous literature.\(^{42}\) Followingly, homogeneous solution poured into cellulose nonwovens followed by the evaporation of the solvent in a vacuum oven at 100 °C for 24 h. The thickness of the resultant cellulose-supported PPC solid polymer electrolyte (CPPC-SPE) was 75 ± 5 µm. Pristine PPC solid polymer electrolyte (PPC-SPE) and pristine PEO solid polymer electrolyte (PEO-SPE) were fabricated via similar method without cellulose nonwoven supporting matrix.

2.2. Morphology and Physical Properties

The morphology of cellulose nonwoven and CPPC-SPE was vividly showed in Figure 1. As revealed by scanning electron microscopy, the cellulose nonwoven has a typical porous structure with uniform thickness. The CPPC-SPE film has a homogeneous distribution of PPC and LiTFSI, indicating a good compatibility between the two components. The FTIR spectra of cellulose nonwoven, PPC, LiTFSI, PPC-SPE, and CPPC-SPE are shown in Figure 1c. The characteristic peaks of cellulose are observed at 3400 cm\(^{-1}\) (O-H stretching), 2920 cm\(^{-1}\) (C-H stretching), and 1720 cm\(^{-1}\) (C=O stretching). The peaks at 1230 cm\(^{-1}\) (C-O stretching) and 1030 cm\(^{-1}\) (C-O-Li) are attributed to the salt formation. The stress-strain curves for PEO-SPE, PPC-SPE, and CPPC-SPE are shown in Figure 1d. The CPPC-SPE film exhibits a high tensile strength and excellent elongation at break, indicating a good mechanical performance.

Figure 1. Typical SEM images of a) cellulose nonwoven and b) CPPC-SPE. The inset is the cross-section image of CPPC-SPE. c) FTIR spectra of cellulose nonwoven, PPC, LiTFSI, PPC-SPE, and CPPC-SPE. d) Stress–strain curves for PEO-SPE, PPC-SPE, and CPPC-SPE.
microscopy (SEM) image of Figure 1a, cellulose nonwoven consisted of randomly arranged nanofibers with an average diameter size of 800 nm and it possessed large-sized pores (>2 μm). This was a favorable framework for supporting mechanically polymer electrolyte. Figure 1b was the surface and cross-section SEM image of CPPC-SPE. It was noticed that the surface of CPPC-SPE is smooth and homogenous. The cross-section SEM image of CPPC-SPE (the inset of Figure 1b) showed that the thickness of solid polymer electrolyte was about 75 ± 5 μm. It was also seen that the pores of the fibrous matrix of cellulose nonwoven were filled with PPG and LiTFSI, demonstrating the cellulose-supported solid polymer electrolyte with continuous structure had been successfully obtained. In addition, the cross-section of CPPC-SPE was consistent and homogeneous structure, which was of great importance to prevent possible microshort circuiting.[43–46]. In addition, it was observed vividly in Figure S1 (Supporting Information) that PPC-SPE and CPPC-SPE were really all-solid-state polymer electrolyte rather than viscous quasi solid state. Thus, such CPPC-SPE could fundamentally be favorable to solve safety risks of lithium batteries.

FTIR spectroscopy was identified as a powerful tool to characterize the structure of cellulose nonwoven, PPG, LiTFSI, PPC-SPE, and CPPC-SPE (Figure 1c). It can be seen that, in the case of cellulose nonwoven, it is characterized with dominant O–H stretching (3200–3500 cm⁻¹) and slight C–H stretching (2850–3000 cm⁻¹) corresponding to the aliphatic. The strong absorption peak at 1065 cm⁻¹ should be the stretching vibration of C–O bond.[43] The characteristic absorption bands for pristine PPG are due to stretching vibration of C=O at 1743 cm⁻¹; C–O at 1360, 1220, and 775 cm⁻¹; C–H at 2800–2900 cm⁻¹; and C–O–C band at 1100 cm⁻¹. The C=O region of PGC-based electrolytes is divided into two bands at around 1740 and 1720 cm⁻¹ when LiTFSI is added into the PPC matrix.[45] This indicates the formation of a transient cross-linking complex through the interaction of Li⁺ and some carbonyl oxygen of PGC.[47] Interacting C=O groups in PPC are considered to enable migration of Li⁺ faster than that coordinated with ether chains in PEO.[55] Similar phenomenon can be observed in other characteristic bands of PPC, such as C–O–C stretching vibrations at 1230 cm⁻¹. The addition of the Li salt leads to the band shifting from 1230 to 1237 cm⁻¹ due to the interaction between Li⁺ and ether oxygen. The appearance of all typical peaks of PPC and cellulose in the spectra of CPPC-SPE indicates that the composite electrolyte membrane is successfully prepared.

It is well known that the poor mechanical strength limits further application of polymer electrolyte, especially in large-scale energy storage systems. Digital camera images of the experimental setup and sample were shown in Figure S2 (Supporting Information). Figure 1d presented stress–strain curves for PEO-SPE, PPC-SPE, and CPPC-SPE. As shown in Figure 1d, the maximum stress of PEO-SPE is 2 MPa, which was consistent with previous study.[46] It was noted that the mechanical strength of pristine PPG solid polymer electrolyte (PPC-SPE) was only 3.8 MPa, which was not favorable to safety and reliability of solid polymer lithium battery. After the introduction of cellulose nonwoven, the maximum stress of CPPC-SPE reached 25 MPa. It was deduced that CPPC-SPE could reduce the possibility of the mechanical rupture of the membrane and improve the safety characteristics of the lithium-ion battery. As shown in Table S1 (Supporting Information), the mechanical strength of CPPC-SPE is much superior to previous references.[49–52] In terms of actual situation, CPPC-SPE could deliver more reliable mechanical property and subsequently alleviate the possibility of short circuit of the batteries, thus improving the safety and reliability of lithium batteries.

Thermal stability plays an influential role in practical application of solid polymer electrolyte in lithium batteries. Differential scanning calorimeter (DSC) thermograms from –40 to 120 °C for PEO-SPE, PPC-SPE, and CPPC-SPE were vividly displayed in Figure 2a. The data of T_g, T_m, and ΔH_m obtained from DSC thermograms were summarized in Table 1. From the DSC data shown in Figure 2a and Table 1, it was clear that a sharp endothermic peak appeared at 52.7 °C, demonstrating the melting of PEO crystallites.[53] These results suggested that lithium batteries using PEO-SPE operating above 53 °C could potentially suffer from seriously internal short circuit and explosion owing to poor mechanical integrity at elevated temperatures. Moreover, it is important to note that no melting transition for CPPC-SPE appears in the DSC thermogram up to 120 °C. This superior thermal stability of CPPC-SPE could significantly improve safety characteristic and eliminate potential risk of short circuits at abused condition or elevated temperature of lithium batteries.

In addition, melting enthalpy, degree of crystallinity, and T_g of PEO-SPE are 69.7 J g⁻¹, 34.3%, and −25.0 °C, respectively. As is known, highly crystalline state of PEO would restrain lithium transportation and lower lithium-ion conductivity.[54] In contrast, PPC, PPC-SPE, and CPPC-SPE show no melting point, indicating that their crystallinity was very low. Glass transition temperatures of PPC, PPC-SPE, and CPPC-SPE were 24.4 °C, 4.7 °C, and 4.8 °C, respectively. For PPC-SPE in particular, the plasticizing effect of TFSI anions may influence the decrease in T_g of PPC.[55] In addition, the T_g of PPC-SPE and CPPC-SPE were almost the same, demonstrating that the addition of cellulose did not lead to more crystalline of solid polymer electrolyte. The result can also be well corroborated in the following X-ray diffraction (XRD) characterization.

The crystalline structures of PEO-SPE and PPC-SPE at varied temperature were analyzed by XRD as revealed in Figure 2b,c. At 20 and 40 °C, PEO-SPE represented two characteristic strong peaks at about 19° and 23° and several weak peaks in the XRD of the well-defined long-range ordered structure or crystallinity, which was in agreement with the previous literature.[54] With the increase of temperature (70 and 100 °C), the crystalline structure of PEO-SPE changed due to the melting of PEO crystallites.[53] As compared to PEO-SPE, PPC-SPE was homogeneous and amorphous and its phase composition remained invariant at 20, 40, 70, and 100 °C. Meanwhile, PGC-SPE exhibited broad peak at 20°, which indicated that PPC-SPE were amorphous.[56] This evidence is in very good agreement with the DSC results. Accordingly, it can be reasonably deduced that amorphous structure of PPC-SPE increases the mobility of the polymer chains as well as lowers the activation energy for ionic transport, further favorably improving ionic conductivity of PPC-SPE.[57,58]
2.3. Ionic Conductivity, Electrochemical Stability, and Interfacial Compatibility

Figure 3a and Figure S3 (Supporting Information) illustrated temperature dependency comparison of the ionic conductivity of PEO-SPE and CPPC-SPE at various temperatures ranging from 20 to 120 °C. It should be noted that there is a significant difference in ionic conductivity between PEO-SPE and CPPC-SPE. Obviously, ionic conductivity of CPPC-SPE was $3.0 \times 10^{-4}$ S cm$^{-1}$ at 20 °C, which was much higher than that of PEO-SPE ($2.1 \times 10^{-6}$ S cm$^{-1}$). In addition, ionic conductivity of CPPC-SPE is one or two orders of magnitude larger than that of PEO-SPE at the entire temperature range. As is known, highly crystalline structure of PEO greatly inhibits the migration of lithium ion, resulting in low ionic conductivity at ambient temperature.$^{[25]}$ The essential cause of high ionic conductivity of CPPC-SPE at room temperature was included for two reasons. On one hand, in the PPC-based polymer electrolyte system, there are complex interactions of Li$^+$ with carbonate unit. We think that the interacting single C=O groups may exist and this interaction makes Li$^+$ easy to migrate faster via the segmental motion of PPC chains. On the other hand, amorphous structure and facile internal rotation of PPC chain prominently enhance the mobility of the polymer chains and hence lower the activation energy for lithium-ionic transport.$^{[58]}$

Taking into account other factors, such as mechanical property and electrochemical stability, CPPC-SPE would be more beneficial to improve comprehensive performance of the cells.

Furthermore, the high temperature (120 °C) stability of CPPC-SPE is also investigated by the dimensionally thermal stability experiment and conductivity monitoring (Figures S4 and S5, Supporting Information). It is worthy to note that such solid polymer electrolyte can work without internal short circuit and retain high ionic conductivity of around $1.4 \times 10^{-3}$ S cm$^{-1}$.

In addition, we compared ionic conductivity (120 °C) between CPPC-SPE and other solid polymer electrolytes from previous literatures (Table S2, Supporting Information).$^{[59,60]}$ Obviously, of all the samples, ionic conductivity is the best. The dimensional thermostability of CPPC-SPE solid polymer electrolyte (Figure S3, Supporting Information) was notably enhanced, which could significantly eliminate the risk of short circuit and improve safety characteristics at abused condition of solid polymer lithium batteries.

Apart from mechanical strength and ionic conductivity, electrochemical window of solid polymer electrolyte is also crucial for their practical application.$^{[60]}$ Figure 3b represents the

Table 1. Thermodynamic data for PEO-SPE, PPC, PPC-SPE, and CPPC-SPE. Melting temperature $T_m$ (onset), melting enthalpy $\Delta H_m$ of crystallinity, and glass transition temperature $T_g$. The reference melting enthalpy of 100% crystalline PEO is taken as 203 J g$^{-1}$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_m$ [°C]</th>
<th>$\Delta H_m$ [J g$^{-1}$]</th>
<th>Crystallinity [%]</th>
<th>$T_g$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO-SPE</td>
<td>52.7</td>
<td>69.7</td>
<td>34.3</td>
<td>-25.0</td>
</tr>
<tr>
<td>PPC</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>24.4</td>
</tr>
<tr>
<td>PPC-SPE</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>4.7</td>
</tr>
<tr>
<td>CPPC-SPE</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>4.8</td>
</tr>
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</table>
results of a linear sweep voltammetry (LSV) scan of the solid electrolyte sandwiched between stainless-steel working electrodes. There is no obvious decomposition of any components taking place till 4.6 V versus Li^+/Li, which demonstrates CPPC-SPE, can be used in high-voltage lithium batteries.

As is now common in the field, the interfacial compatibility of lithium metal with solid polymer electrolyte has a paramount importance in lithium batteries for practical applications. Figure S6 (Supporting Information) depicted the interfacial compatibility of CPPC-SPE with a lithium metal anode at 20 and 120 °C, which was characterized by the electrochemical impedance spectroscopy (EIS). As seen from Figure S3 (Supporting Information), the values of interfacial resistance of the freshly assembled symmetrical cell for CPPC-SPE at 20 and 120 °C are 142 and 67 Ω, respectively. After storage for 5 d, the values of interfacial resistance for CPPC-SPE gradually increase to a more or less extent. With further increase in the storage time, the values of interfacial resistance for CPPC-SPE remain relatively stable. These results suggest that CPPC-SPE has excellent compatibility with Li metal both at 20 and 120 °C.

2.4. Charge/Discharge Curves and Cycle Performance of LiFePO_4/Li Cells at 20 °C

In order to demonstrate the feasibility of the novel CPPC-SPE, all-solid-state polymer LiFePO_4/Li battery was assembled and typical charge–discharge curves at various rates and long-term cycling stability were also examined. Obviously, at 20 °C, the specific discharge capacity of the cell using CPPC-SPE (Figure 4a and Figure S7, Supporting Information) was 142 mAh g^{-1} at 0.1 C, 132 mAh g^{-1} at 0.2 C, 116 mAh g^{-1} at 0.5 C, 103 mAh g^{-1} at 1 C, 80 mAh g^{-1} at 2 C, and 52 mAh g^{-1} at 3 C, respectively. Whereas, PEO-SPE-based battery exhibited discharge capacity of 20 mAh g^{-1} at 0.1 C and could not charge and discharge at the rate exceeding 0.2 C at 20 °C. It is obvious that the rate capability and cycle performance of CPPC-SPE were much better than those of PEO-SPE at room temperature. This better rate performance is an indicator of a low resistance, which can be contributed to better ionic transport capability, demonstrating that CPPC-SPE has great potential in ambient-temperature all-solid-state lithium batteries.

Figure 4b depicted cycle stability of LiFePO_4/Li cell using CPPC-SPE at 0.5 C. It was noted that the cell with CPPC-SPE displayed superior cycle durability after 1000 cycles at 20 °C, 95% of the initial capacity. This outstanding cycle performance would be attributed to better electrochemically interfacial stability. To further confirm cycling performance and safety, SEM imaging was carried out to observe the surface morphology of lithium anode after the battery was cycled 1000 times. As shown in Figure 4b, lithium metal after cycling showed a relatively smooth surface, indicating CPPC-SPE could effectively inhibit dendrite formation. To gain further understanding of the excellent cycling stability, the batteries were evaluated by EIS after cycling. As can be seen in Figure 4c, the intercept of the spectra with the real axis reflects the bulk resistance (R_{bulk}) of CPPC-SPE. In the middle frequency, there is an irregular semicircle attributed to the charge-transfer resistance. It can be seen from Figure 4c that the value of charge-transfer resistance after first cycle was 73 Ω. After 1000 cycles, the value became 83 Ω, indicative of a minor augment of charge-transfer resistance. Good interfacial properties are mainly due to the flexibility of the polymer electrolyte, which can lead to better capacity retention during cycling at 20 °C. Moreover, the discharge capacity of LiFePO_4/Li cells using CPPC-SPE at 5 °C was also listed in Figure S8 (Supporting Information). What is pleasantly surprising is that, at 5 °C, CPPC-SPE-based LiFePO_4/Li cells could deliver 138, 114, 89, 65, and 40 mAh g^{-1} at 0.05 C, 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively. Obviously, this achievement will greatly boost the development of room-temperature solid polymer electrolyte.

Finally, in order to explore practical utility of CPPC-SPE, illustration of solid-state soft-package lithium battery comprising LiFePO_4 and lithium metal was shown in Figure 4d. As one can see, the cell was successfully able to light up a red light-emitting diode (LED) lamp labelled with “SPE” at 20 °C. Besides, to further characterize the power and energy density of the soft-package solid polymer batteries quantitatively, we elevated the rate capability (Figure 4e) and Ragone plot (Figure 4f) of soft-package solid polymer LiFePO_4/Li cells at 20 °C. It was noted that the solid-state soft-package lithium cells assembled with this solid polymer electrolyte can still deliver excellent rate capability and relatively high energy density at 20 °C, further proving the practicability and reliability of this solid polymer electrolyte battery.
2.5. Rate Capability and Cycling Stability of LiFePO₄/Li Cell at 120 °C

For more practical applications of such solid polymer electrolyte, dimensionally thermal stability is highly desirable. For this purpose, we monitored rate capability and cycle performance of LiFePO₄/Li cell at an elevated temperature of 120 °C. As displayed in Figure 5a, LiFePO₄/Li cell using CPPC-SPE exhibited excellent rate performance. They could deliver capacities of 138.7, 128.7, 113.9, 97.6, and 73.6 mAh g⁻¹ at varied rates of 1 C, 2 C, 3 C, 4 C, and 5 C, respectively, which were much better than those with cellulose-supported PEO polymer electrolyte. We would suggest this could be related to high ionic conductivity and favorable interfacial properties between the electrodes and the electrolyte in the cell at the temperature of 120 °C. Figure 5b presented cycle performance of the LiFePO₄/Li cell using CPPC-SPE at 120 °C. It can be found that 95% of the discharge capacity is retained after 500 cycles, indicating that CPPC-SPE can afford better cycling performance at the elevated temperature. In addition, photographs showing the bulge phenomenon of soft-packing polymer lithium battery (a) before and (b) after 500 cycles at 120 °C were vividly displayed in Figure S9 (Supporting Information). There was no bulge phenomenon of soft-packing solid polymer lithium battery when operated at 120 °C, verifying the excellent thermal stability of CPPC-SPE. This is a solid evidence to prove that CPPC-SPE showed unprecedented improvements in safety characteristics at elevated temperatures. In view of the exciting performance, we can speculate that such PPC-SPE can also be promising to lithium batteries running at the elevated temperature.
2.6. Safety Evaluation of Soft-Package Solid Polymer LiFePO₄/Li Cells

Lithium batteries can offer great energy with comparable power densities but the safety is an issue of concern compared to other aqueous batteries.[65,66] To elucidate the effect of CPPC-SPE on safety issue of a cell, soft-package lithium cells were fabricated. As shown in Figure S10 (Supporting Information), a steel rod of 2 mm in diameter was daggered into a fully charged cell. The cell employing commercial liquid electrolyte was promptly short-circuited by nail insertion and ignited easily as thermal runaway occurred. The maximum temperature of the cell outside was about 231.5 °C. However, there was no explosion or ignition for the cell using CPPC-SPE; moreover, the temperature of cell surface remains minor changes owing to no presence of thermal runaway. Therefore, safety characteristics of CPPC-SPE-based all-solid-state polymer lithium batteries were significantly improved compared to the commercial lithium batteries using liquid electrolyte.

Potential safety hazards of commercial lithium batteries using liquid electrolyte, to a certain degree, will undermine the confidence of consumers and obstruct the further development of electric vehicles or hybrid electric vehicles. Thus, the safety issue of all-solid-state polymer lithium batteries merits further study by self-designed cutting-corner experiment. Figure 6a shows that one all-solid-state cell using CPPC-SPE can successfully light up a red LED lamp under a normal condition. To further underline the excellent safety issue, the cell was cut into two pieces, which was shown in Figure 6b. It was observed that the cell can still power a red LED lamp. We also provided cycle performance and charge/discharge profiles of soft-package solid polymer LiFePO₄/Li cells under the condition of being cut away a corner (Figure S11, Supporting Information). It is worth mentioning that solid polymer lithium battery can still charge and discharge for finite number of times. Meanwhile, the cell exhibited almost no loss in the voltage during this process (Figure 6c). More interestingly, the obtained cut corner of the cell was proved to light up a red LED lamp (Figure 6d). Here, it is worthwhile to note that the reliability of cells incorporating CPPC-SPE was remarkably improved. This is a powerful evidence to prove that CPPC-SPE-based solid-state polymer lithium batteries display unprecedented improvements in safety issues with an excellent internal short-circuit prevention of cells.

High-voltage lithium batteries have been a focus in the current energy storage research due to their potential application in high energy density batteries for electric vehicles. Pristine PEO based solid polymer electrolyte decompose readily on the high voltage cathode surface when the cell is charged over 4 V. Accordingly, fabrication of high voltage electrolyte membrane plays an important role in developing high-energy lithium...
batteries. Thus, the feasibility of its high anodic stability was evaluated using LiFe$_{0.2}$Mn$_{0.8}$PO$_4$/Li cell at room temperature. As shown in Figure 7b, the charge and discharge voltages exhibited obvious and flat profiles for typical LiFe$_{0.2}$Mn$_{0.8}$PO$_4$. In addition, the obtained capacity retention of LiFe$_{0.2}$Mn$_{0.8}$PO$_4$/Li cell was 96% after 100 cycles (Figure 7a). The stable voltage profiles would be attributed to good electrochemical stability and superior mechanical integrity of CCPL solid polymer electrolyte. Besides, we did not see obvious aluminum corrosion phenomena of solid polymer lithium battery using CPPC-SPE after 100 cycle test (Figure S12, Supporting Information).\[^{[67]}\]

Relying on obtained results, it can be assumed that CPPC-SPE could be a suitable electrolyte candidate that could afford a good cycling performance at a relatively high voltage (4.3 V vs Li$^+$/Li$^-$).

On the basis of this, research will pave the way for designing and exploiting safety-reinforced, wider electrochemical window and ambient-temperature PPC-based solid polymer electrolyte for high-performance all-solid-state polymer lithium batteries.

3. Conclusion

In summary, we proposed a new class of safety-reinforced, wide voltage window and ambient-temperature PPC-based solid polymer electrolyte for next-generation all-solid-state polymer lithium batteries. It was demonstrated that such CPPC-SPE could not only possess high ionic conductivity at room temperature but also wider electrochemical window exceeding 4.6 V. In addition, solid state polymer LiFePO$_4$/Li cells using this solid polymer electrolyte exhibited both superior rate capability and excellent electrochemical performance at room temperature. More importantly, solid-state soft-package lithium batteries using CPPC-SPE can present excellent safety characteristic even in extremely harsh condition. A corollary of this is that, this class of CPPC-SPE is very promising to develop next-generation all-solid-state lithium batteries that require high energy density, superior safety, and excellent reliability. Most significantly, the main innovation of our work will highlight a reference for subsequent scientific research of room-temperature solid polymer electrolyte and also boost the development of high performance all-solid-state polymer lithium batteries.

4. Experimental Section

Sample Collection: PPC (MW = 50 000) used in this work was purchased from Sigma-Aldrich; PEO (MW = 100 0000) was supplied by Alfa Aesar Company. Battery-grade LiTFSI was supplied by Suzhou Fosai New Materials Co. Ltd. Acetonitrile was commercially available.

Sample Characterization: The FTIR spectra of the membranes are obtained using the attenuated total reflection attachment on a Frontier FTIR spectrometer (Perkin-Elmer) in the transmission mode from 800 to 4000 cm$^{-1}$, which is collected with 32 scans and a resolution of 4 cm$^{-1}$. The morphology of the samples was characterized by a field emission scanning electron microscope (Hitachi S-4800, operating at 3 kV). All the samples for SEM are coated with a very thin gold layer using a sputter coating. The mechanical property was investigated by an Inston-3300 universal testing machine (USA) at a stretching speed of 1.66 mm sec$^{-1}$ with the sample strips of about 1 cm wide and 8 cm long. The gauge length is 6 cm. The thickness of solid polymer electrolyte was tested through screw micrometer. DSC (Perkin Elmer) was carried out to measure the thermal properties of the polymer electrolyte from −40 to 180 °C at a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere. XRD were recorded in the range of 9°–80°. Data were collected with a step-width of 0.01° at 20, 40, 70, and 100 °C, respectively.

Electrochemical Evaluation: Ionic conductivity of the solid polymer electrolytes was tested by EIS using an Autolab PGSTAT 302N system at varied temperatures ranging from 20 to 120 °C. The solid polymer electrolyte membranes were sandwiched between two stainless-steel plate electrodes and the spectra were recorded in the frequency range from 1 Hz to 1 MHz with an AC amplitude of 10 mV. The bulk resistance ($R_b$) of membranes was determined from the impedance spectrum. The ionic conductivity was calculated from Equation (1)

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

where $R_b$ is the bulk resistance and $L$ and $S$ are the thickness and area of the solid polymer electrolyte, respectively. The electrochemical stability of the samples was measured using LSV experiment performed on a working electrode of stainless steel as a counter and reference electrode of lithium metal. An electrochemical analyzer (Solartron 1255B) was operated at a sweep rate of 1 mV s$^{-1}$ between 0 and 6.0 V. The LiFePO$_4$ cathode was composed of 80 wt% LiFePO$_4$, 10 wt% LiTFSI, and 10 wt% carbon black. Areal density of obtained LiFePO$_4$ cathode was 5 mg cm$^{-2}$. The solid-state soft-package LiFePO$_4$/Li battery was charged and discharged between 2.5 and 4.0 V at varied currents. The C rates in all of the electrochemical measurements are defined based on 1 C = 150 mA g$^{-1}$. The LiFe$_{0.2}$Mn$_{0.8}$PO$_4$ cathode was composed of 80 wt% LiFe$_{0.2}$Mn$_{0.8}$O$_4$, 10 wt% PPC-LiTFSI, and 10 wt% carbon black. Areal density of obtained LiFe$_{0.2}$Mn$_{0.8}$O$_4$ cathode was 5 mg cm$^{-2}$. The LiFe$_{0.2}$Mn$_{0.8}$PO$_4$/Li battery was charged and discharged between 2.5 and
4.35 V at 0.5 C (1 C = 170 mA g⁻¹). The cell assembly was carried out in an argon-filled glove box, with oxygen content less than 2 ppm and H₂O content less than 1 ppm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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