

A free-standing and thermostable polymer/plastic crystal electrolyte for all-solid-state lithium batteries

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Abstract All-solid-state lithium batteries using flexible solid electrolytes instead of combustible organic liquid electrolytes are the ultimate solution to address the safety problem of commercialized lithium ion batteries. In this study, a free-standing and thermostable polymer/plastic crystal composite electrolyte (PPCE) based on polymerized trimethylolpropane trimethacrylate (TMPTMA)-1, 6-hexanediol diacrylate (HDDA) matrix, and plastic crystal electrolyte was prepared for all-solid-state lithium batteries. The polymerized TMPTMA-HDDA-based matrix of a porous network structure coupled with plastic crystal electrolyte (PCE) in the pores reveals good compatibility. The as-synthesized PPCE possesses excellent flexible performance, thermostability, and high conductivity, showing that PPCE can reach $8.53 \times 10^{-4} \text{ S cm}^{-1}$ with 7.5 wt% monomers (PPCE-7.5%) at 25 °C under a stability electrochemical window above 5.2 V. The assembled lithium batteries Li|PPCE|LiFePO₄ exhibit high capacity and highly cycling stability at room temperature, indicating great potential of all-solid-state lithium batteries.

Keywords All-solid-state lithium batteries · Composite electrolytes · Plastic crystal electrolyte · Electrical properties · Thermal properties

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Introduction

Recently, lithium ion batteries (LIBs) have attracted great attention as efficient power sources in smart phones, tablets, personal computers, digital cameras, and other portable devices due to the high energy density and long cycle life [1–3]. However, safety problems that initiate from the leakage and flammability of organic solvents are still the challenges and hinder the better development of LIBs [4, 5]. Thus, solid electrolytes have received increasing attention for its advantages in shape versatility and high safety [6]. Among various solid-state electrolytes, polymer electrolytes that consist of salt mixtures and solvating polymers have been extensively studied because of their excellent characteristics such as low toxicity, stability, and flexibility [7]. However, the ionic conductivity of polymer electrolytes is generally less than $10^{-6} \text{ S cm}^{-1}$ due to the limited chain mobility [8]. The plastic crystal electrolytes composed of lithium salts and plastic crystals with solvation capability are particularly attractive because of their unusual thermal stability and ionic transport behavior [9–12]. Succinonitrile ($\text{N} \equiv \text{C}-\text{CH}_2-\text{CH}_2-\text{C} \equiv \text{N}$, abbreviated as SN) is a non-ionic and highly polar plastic crystalline organic molecule, which has a plastic crystalline phase that approximately extends from -40 to 60 °C (melting point) [13, 14]. Owing to the presence of *trans-gauche* isomerism about C-C bonds in the SN, SN/lithium salt electrolytes provide a high ionic conductivity more than $10^{-3} \text{ S cm}^{-1}$ at room temperature since the *trans*-isomer decreases the activation energy for ionic conduction [14]. Although SN-based plastic crystal electrolytes are advantageous in delivering high ionic conductivity, the mechanical properties still to be enhanced. Combination of the SN-based plastic crystal electrolytes with a polymer matrix is considered to be an effective way to accomplish high mechanical properties. The mechanical properties of the plastic crystal electrolytes could be remarkably

enhanced via adding other polymers with high mechanical strength into SN-based electrolytes, such as polyethylene oxide (PEO) [15–18], polyacrylonitrile (PAN) [19, 20], poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) [15, 21], and other polymers [22–26]. Unfortunately, enhanced mechanical properties would largely suppress the ionic conductivity of the plastic crystal electrolytes. Therefore, it is an urgent problem to improve both the mechanical properties and ionic conductivity of the plastic crystal electrolytes.

In this work, a free-standing and thermostable polymer/plastic crystal composite electrolyte (PPCE) membrane that consists of polymer matrix and plastic crystal electrolyte (PCE, lithium bis-trifluoromethanesulphonamide (LiTFSI) in SN) was prepared for all-solid-state lithium batteries. The polymer matrix is formed by the addition of trimethylolpropane trimethacrylate (TMPTMA) and 1,6-hexanediol diacrylate (HDDA). The results suggest an effective way to enhance the flexible performance of the PCE and meanwhile maintain the high ionic conductivity. According to the understanding of structural features, the membrane performance of PPCE (as a novel solid-state electrolyte) was investigated based on mechanical bendability, dimensional thermostability, ionic conductivity, and electrochemical stability. Finally, the electrochemical properties of the cell assembled with PPCE were examined, indicating that great potential for developing novel stable all-solid-state lithium batteries.

Experimental

The synthesis of PPCE membranes

PPCE membranes were synthesized by thermal polymerization. LiTFSI ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, Sigma-Aldrich) and succinonitrile (Sigma-Aldrich) were mixed with a molar ratio of 5:95 and melted at 70 °C to get a plastic crystal electrolyte (PCE). For the preparation of the PPCE, two monomers, TMPTMA ($\text{C}_{18}\text{H}_{26}\text{O}_6$) and HDDA ($\text{C}_{12}\text{H}_{18}\text{O}_4$), were mixed in a weight ratio of 1:2, and then, the mixtures were blended with PCE and thermal initiator 2,2'-Azobisisoheptonitrile (ABVN, $\text{C}_{14}\text{H}_{24}\text{N}_4$). The weight composition of (TMPTMA-HDDA)/PCE were 5/95, 7.5/92.5, and 10/90 (abbreviated as PPCE-5%, PPCE-7.5%, and PPCE-10%), respectively. The concentration of the ABVN was fixed at 1 wt% of the monomers. The mixture solution was cast onto a Teflon plate and then placed in an oven under 70 °C for 30 min. Finally, a free-standing, flexible polymer/plastic crystal electrolyte membrane ($180 \pm 10 \mu\text{m}$) incorporated with crosslinked polymer networks was obtained. All of the above procedures were carried out in an Ar-filled glove box.

Physical characterization

The surface morphology of the PPCE membranes was observed by a field-emission scanning electron microscopy (FE-SEM, JSM-6330). In order to observe the unique plastic crystal behavior, the PPCE was evaluated by differential scanning calorimetry (DSC, TA 2920 modulated instrument) measurements to obtain the thermal characteristics including T_{pc} (plastic crystal phase transition temperature) and T_m (melting temperature) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

Electrochemical measurement

The ionic conductivities of the PPCE membranes were measured by the electrochemical impedance spectroscopy (EIS) method with a CHI660C Electrochemical Workstation (Shanghai Chenhua). The EIS measured in the frequency range from 100 kHz to 0.1 Hz at temperatures between -20 and $80 \text{ }^\circ\text{C}$ with the potential amplitude of 5 mV. A piece of PPCE membrane was stuck in the middle of two stainless steel blocking electrodes to form Swagelok-type cells and then kept the cells at each test temperature for at least half an hour to reach the thermal equilibrium before EIS measurements. The electrochemical stability window of the PPCE was evaluated by linear sweep voltammetry in the potential range from 2.0 to 6.0 V (vs. Li^+/Li) at a scan rate of 1.0 mV s^{-1} with a stainless steel blocking electrode as the working electrode and lithium-metal as the counter and reference electrode [27]. The transference numbers of lithium ion (T_{Li^+}) were measured by chronoamperometry on the CHI660C Electrochemical Workstation at room temperature in Swagelok-type cells using lithium-metal as both electrodes with a step potential of 10 mV.

The electrochemical characterization was evaluated by galvanostatic charge/discharge method with a unit cell (CR2032 coin-type cell) which was assembled by sandwiching the electrolyte membrane between a PCE-soaked LiFePO_4 cathode and a lithium foil [7]. The sample of PPCE-7.5% was selected as the testing electrolyte membrane. The LiFePO_4 cathode was prepared by casting a mixture of active materials (80 wt% LiFePO_4), Super-P (15 wt%), and polyvinylidene fluoride (PVDF, 5 wt%) on an aluminum foil current collector followed by drying at 70 °C for 12 h. For comparison, conventional 2032 coin-type cells were assembled with polypropylene microporous film (Celgard 2400) as separators and 1 M LiPF_6 /ethylene carbonate (EC): dimethylcarbonate (DMC): ethylmethylcarbonate (EMC) (1:1:1, in volume ratio) as the electrolytes. Galvanostatic charged/discharged was tested under 0.2 C between 2.0 and 4.2 V using a cell test instrument (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.).

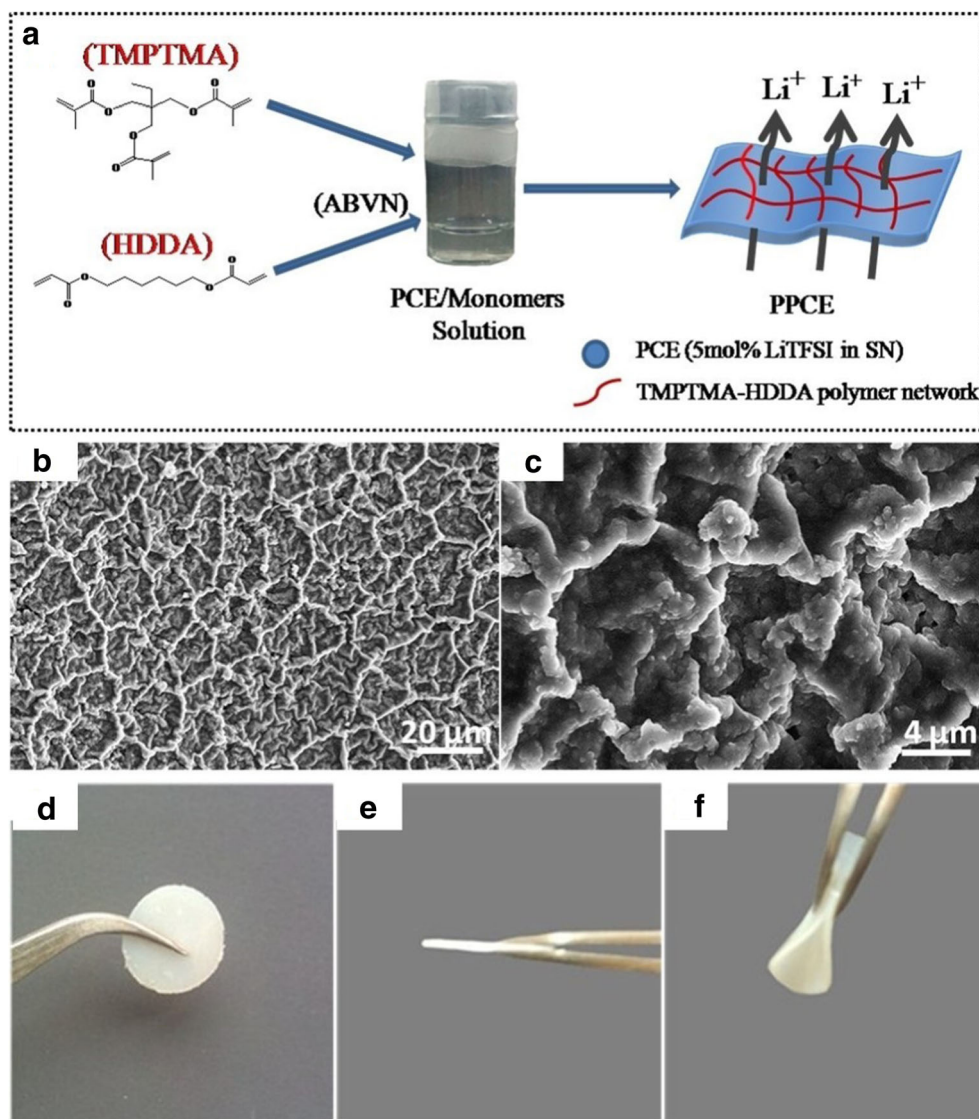
Results and discussion

The chemical structure and physical morphology of the major components are shown in Fig. 1. As depicted in Fig. 1a, TMPTMA is a polymer monomer with three functional groups while HDDDA has a long-chain molecular structure. Through free radical polymerization, the long linear hydrocarbon chains attached to the crosslinkable acrylate groups and, thereby, the polymerized TMPTMA-HDDDA would act as a compliant and flexible framework. As a result, the unique TMPTMA-HDDDA polymeric network is anticipated to present a beneficial feature on the bendability of the PPCE membrane. In Fig. 1b, d, e, f, electrolyte membranes are generated by thermal polymerization reaction with the precursor of 7.5 wt% monomer mixtures and 92.5 wt% plastic crystal electrolytes (PPCE-7.5%). It is observed that the three-dimension interconnected polymeric electrolyte matrix is formed in the PPCE (Fig. 1b, c). This unique structure would not only

provide good mechanical strength but also ensure the high conductivity for the PPCE [28]. Figure 1d, e shows that the PPCE membranes are free-standing even at a low concentration of polymers (PCE/TMPTMA-HDDA polymers = 92.5/7.5 w/w) by the incorporation of the TMPTMA-HDDA polymers. It is noted that the electrolyte membranes can be bent more than 180° without breaking (Fig. 1f), indicating an effective way to introduce the TMPTMA-HDDA polymers as a skeleton to improve the deformability of PPCE. The free-standing PPCE membrane with excellent flexibility can be directly assembled into cells without using commercial separators.

The thermal stability of membranes was one of the most important factors for battery safety. To attain in-depth understanding of the influence of separators on internal short-circuit failure of batteries, the Celgard 2400 separator and PPCE-7.5% membrane were stored in an oven for 0.5 h in air at 130 °C. Figure 2a, b showed the photographs of membranes

Fig. 1 a The schematic description preparation of electrolytes. b, c SEM images of TMPTMA-HDDA polymer/plastic crystal electrolyte. d–f Photographs of TMPTMA-HDDA polymer/plastic crystal electrolyte membranes



before and after thermal shrinkage test at different temperatures. The area-based dimensional shrinkage (ΔA) of the PPCE-7.5% was found to be negligibly small, as compared to the Celgard 2400 separator ($\Delta A \sim 40\%$). This poor thermal stability of Celgard separators is considered as a major cause of the internal short-circuit failures. Therefore, from the viewpoint of the dimensional thermostability, it could be expected that the PPCE membrane would provide the excellent safety characteristic for high-power battery even at elevated temperature.

The plastic crystal behavior of SN, PCE, and PPCE- $x\%$ ($x = 5, 7.5, 10$) were investigated by measuring the characteristic transition temperatures T_{pc} (the transition temperature from crystal to plastic crystal phase) and T_m (the melting peak temperature) of SN in the heating. Figure 2c shows that the pristine SN has two endothermic peaks at -36 and 58 °C, which correspond to the T_{pc} and T_m , respectively. It shows an obvious reduction in T_m (58 °C \rightarrow 35 °C) with addition of LiTFSI in the SN, implying an isomer transition from *gauche* to *trans* [14]. All other composites (PPCE-5%, PPCE-7.5%, and PPCE-10%) exhibit the characteristic transition temperature of the PCE, indicating that the behavior of the plastic crystal is not impacted with the presence of a polymerized TMPTMA-HDDA network. It is also noticed that the addition of polymer slightly improved the T_m of the PCE. This result demonstrates that PPCE can improve the safety performance of the battery and could maintain a solid state in high temperature operation.

The temperature-dependent ionic conductivity of the PCE and PPCE- $x\%$ ($x = 5, 7.5, 10$) is examined as shown in Fig. 3a. PCE displays remarkably high conductivity of 2.63×10^{-3} S cm^{-1} at room temperature and 5.69×10^{-5} S cm^{-1} at -20 °C. A slight decrease in ionic conductivity was observed when adding TMPTMA-HDDA polymers, mainly because the polymerized TMPTMA-HDDA is not ionic conductive but a framework for hosting PCE. In addition, the conductivity decreases with the increase of the polymer content. In the experiment, the sample of PPCE-7.5% possesses excellent free-standing and bending performance, and the ionic conductivity of the electrolytes can reach a high level of 8.53×10^{-4} S cm^{-1} at 25 °C. Therefore, PPCE-7.5% was used to test the lithium ion transference number and charge/discharge properties in the following experiments.

The electrochemical stability window of the PCE and PPCE- $x\%$ ($x = 5, 7.5, 10$) was evaluated from linear sweep voltammograms. As shown in Fig. 3b, there is no meaningful component decomposition below 5.2 V vs. Li^+/Li . A considerable current appeared when the voltage exceeded 5.2 V, indicating the beginning of the decomposition in the PCE. In addition, the PPCE- $x\%$ ($x = 5, 7.5, 10$) shows a slight improvement in the anodic stability compared to PCE. The electrochemical working window of the PPCE-5% is higher than 5.5 V as no irreversible oxidation was observed below 5.5 V. The enhanced electrochemical stability is attributed to the improved interfacial characteristics of the PPCE, which indicates

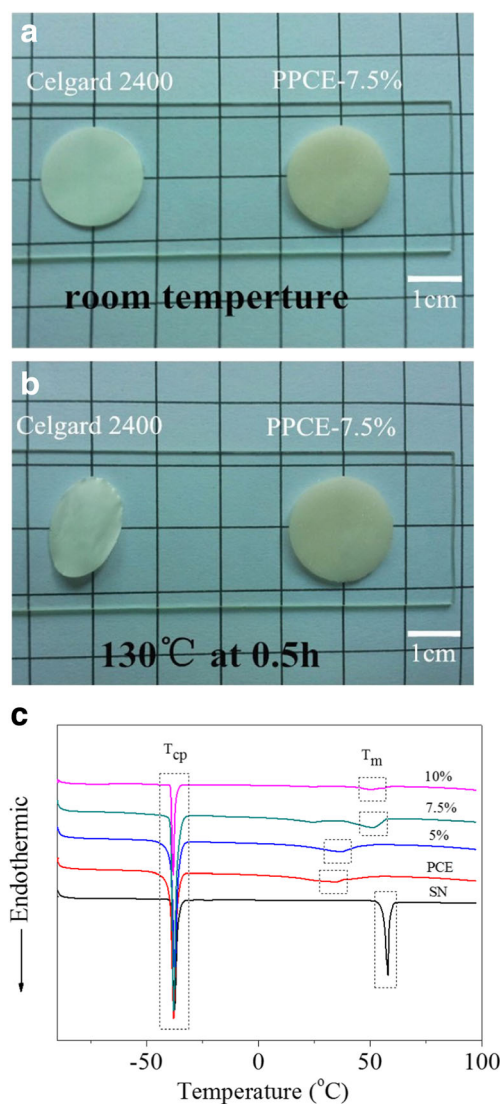


Fig. 2 Photographs of Celgard 2400 separator and PPCE-7.5% membrane at different temperatures. **a** Room temperature and **b** at 130 °C for 0.5 h. **c** DSC profiles demonstrating transition temperatures (T_{pc} and T_m) of SN in: pristine SN, PCE, PPCE-5%, PPCE-7.5%, and PPCE-10%

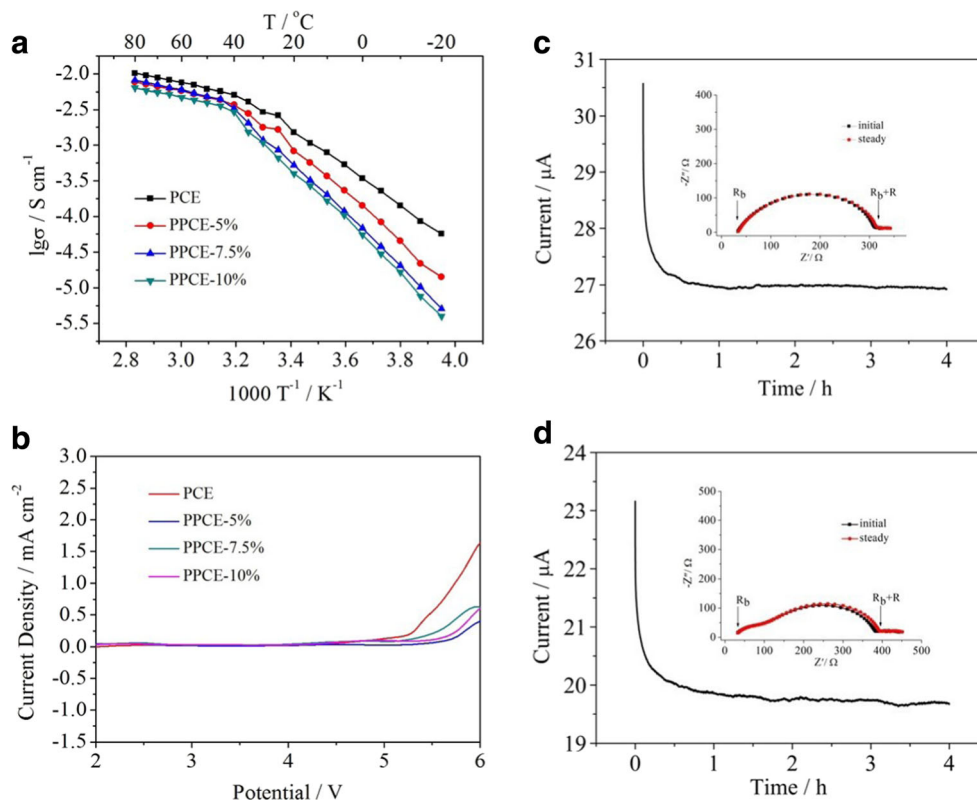
that the polymers of TMPTMA-HDDA play a positive role in the electrochemical stability and are well compatible with the electrode materials. In a word, PPCE could be applied to high-voltage LIBs due to their high anodic stability.

The transference numbers of lithium ions (T_{Li^+}) were measured for PCE and PPCE-7.5% membranes in the Swagelok-type cells (Fig. 3c, d). T_{Li^+} were estimated by chronoamperometry by comparing the initial and final resistance values and current values with the Eq. (1) [29],

$$T_{Li^+} = \frac{I^{SS}(\Delta V - I^O R^O)}{I^O(\Delta V - I^{SS} R^{SS})} \quad (1)$$

where I^O and I^{SS} are the currents at the initial state and steady state, respectively; R^O and R^{SS} represent the initial and

Fig. 3 **a** Temperature-dependent ionic conductivities of PCE, PPCE-5%, PPCE-7.5%, and PPCE-10%. **b** Linear sweep voltammograms of PCE, PPCE-5%, PPCE-7.5%, and PPCE-10% on a stainless-steel working electrode and lithium metal as a counter and reference electrode. Li ion transference number of PCE (**c**) and PPCE-7.5% (**d**) at room temperature in Swagelok-type cells using Li metal as both electrodes with step potential of 10 mV



steady-state values of Li/electrolyte interfacial resistances. The dc polarization was subsequently carried out in the measurement with a step potential (ΔV) of 10 mV. According to Eq. (1), the transference numbers of lithium ions are 0.55 and 0.57 for PCE and PPCE-7.5%, respectively. Compared with the T_{Li^+} of PCE, there is no significant change for PPCE-7.5%. It is suggested that the addition of the polymers has no negative effect on the transference numbers of lithium ions. It is also proved that the polymerized TMPTMA-HDDA forms a three-dimensional network channel that improves the lithium ion mobility.

To explore the PPCE as a solid electrolyte for LIBs, the charge/discharge performance and cyclic ability of the assembled Li|PPCE-7.5%|LiFePO₄ cells was evaluated at 0.2 C in a voltage range of 2.0–4.2 V. The LFP cathode was soaked in the PCE containing succinonitrile. The battery of LiFePO₄|1M LiPF₆/(EC + EMC + DMC, 1:1:1 in volume)|Li was also assembled for comparison. As shown in Fig. 4a, the initial discharge capacity of PPCE-7.5% is 145.5 mAh g⁻¹, slightly lower than that of the liquid electrolyte (160.2 mAh g⁻¹). It is mainly because of the slightly suppressed ion transport in the solid electrolyte. Besides, there are no substantial decrease in the capacity for both of the commercial liquid electrolyte (163.3 mAh g⁻¹) and PPCE-7.5% (143.4 mAh g⁻¹) after

25 cycles [16, 20]. Consistent with the previously reported LiFePO₄ cathodes, typical voltage profiles are observed around 3.3–3.5 V in the case of the liquid electrolyte (Fig. 4b). The platform voltage difference of PPCE-7.5% is slightly larger than the liquid electrolyte, indicating the lower degree of polarization in the electrodes during the electrochemical reaction. The voltage platform is also flat in the PPCE-7.5%, similar to the liquid electrolyte of 1M LiPF₆/(EC + EMC + DMC, 1:1:1 in volume). This suggests that the redox reaction is stable in the charge/discharge process which attributes to the excellent electrochemical stability of the PPCE. Finally, Fig. 4b inset demonstrates that the charged battery containing the LiFePO₄ cathode, the PPCE-7.5% membrane, and the lithium anode could light up the 3.3 V small bulb, suggesting the decent operation of the battery system and the applicability of the PPCE in various battery systems.

Conclusion

In summary, a free-standing, thermostable, flexible polymer/plastic crystal electrolyte (PPCE) was fabricated as a promising solid electrolyte for LIBs. PPCE possesses a crosslinked network and the plastic crystal

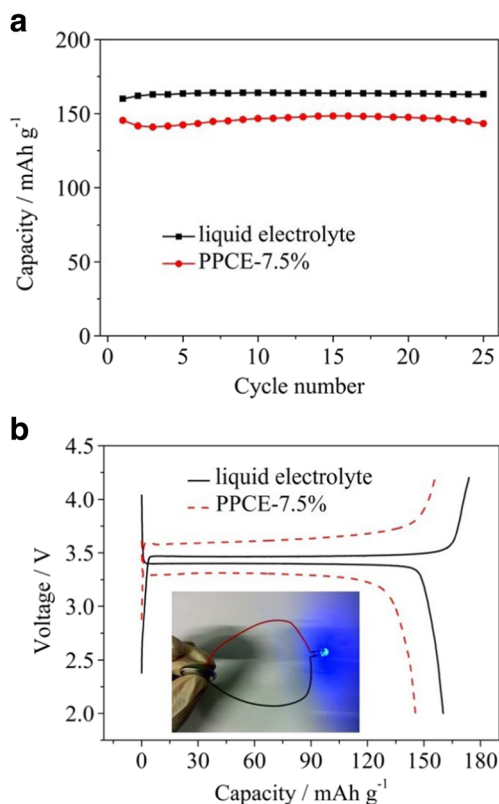


Fig. 4 Cycle performance (a) and the initial charge/discharge curves (b) at a constant charge/discharge current density (0.2 C/0.2 C) for LiFePO₄ | PPCE-7.5% | Li and LiFePO₄ | 1M LiPF₆/(EC + EMC + DMC, 1:1:1 in volume) | Li cells at 25 °C, inset is the LED bulb lighted by all-solid-state Lithium ion batteries

behavior is not impacted during the polymerization process. The electrolyte possesses high ionic conductivity, stable electrochemical window, and excellent component compatibility. In the cell assembled with the LiFePO₄ cathode, the battery shows high capacity and high cycling stability at room temperature. These results suggest that this polymer/plastic crystal electrolyte could be a potential candidate for solid-state LIBs.

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