



Co-blending based tribasic PEO-PS-PMMA gel polymer electrolyte for quasi-solid-state lithium metal batteries

Shusen Kang^{1,2} · Zelin Yang^{1,2} · Chengxiang Yang^{1,2} · Shan Zhao^{1,2} · Ningning Wu^{1,2} · Fuliang Liu^{1,2} · Xiaotao Chen^{1,2} · Bin Shi^{1,2}

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Abstract

A novel polymer film is developed by trapping tribasic gel polymer electrolyte (GPE), which blended the polyethylene glycol (PEO), polystyrene (PS), and poly(methyl methacrylate) (PMMA). The properties of the PEO-PS-PMMA polymer film and PEO-PS-PMMA GPE were investigated. The ionic conductivity of the PEO-PS-PMMA GPE is 0.12 mS/cm at 25 °C. Li⁺ transference number of PEO-PS-PMMA GPE is 0.2. Besides, PEO-PS-PMMA GPE shows high electrochemical stability and excellent interface stability to Li metal electrode. Li/PEO-PS-PMMA/LiFePO₄ cell achieved an initial specific discharge capacity of 97 mAh/g and good cycle performance at the current density of 0.1 C. This GPE is promising to be applied to rechargeable Li batteries with high safety and long cycle life.

Keywords Gel polymer electrolyte · Lithium metal batteries · Co-blending · PEO-PS-PMMA · Solid state

Introduction

In recent decades, carbon anode is the most widely used in secondary Li-ion batteries. However, the theoretical specific capacity of carbon is just 372 mAh/g [1]. At present, researchers are interested in lithium metal anode with a high theoretical specific capacity of 3860 mAh/g and a low potential of −3.04 V (vs. standard hydrogen electrode) [2] used in secondary batteries. The dendrite formation on the Li anode during charge/discharge cycling in the liquid electrolyte is great security risk [3], which hinders lithium metal anode practical application. Recently, the quasi-solid-state lithium metal batteries based on gel polymer electrolytes have been regarded as the most promising next-generation batteries because of their safety, flexibility, and high energy density [4].

Gel polymer electrolytes (GPEs) are made of polymers and liquid electrolyte plasticizers. Due to the adsorption of liquid electrolyte, their ion conductivity is higher than those of all solid polymer electrolyte [5]. What's more, GPEs are solid-state films, in which the solvent is very difficult to be evaporated and leaked, so the security question caused by the leakage of the liquid electrolyte can be solved. Now, various of GPEs have been investigated by researchers including poly(ethylene oxide) (PEO) [6], poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [7], poly(vinylidene fluoride) (PVDF) [8], polyacrylonitrile (PAN) [9], poly(methyl methacrylate) (PMMA) [10], and polystyrene (PS) [11]. Among them, PEO-based GPEs are the most widely and earliest studied in the quasi-solid-state lithium metal batteries field due to their high Li⁺ salt solubility, excellent stability with Li metal anode, and flexibility. However, their practical application is restricted by the low ionic conductivity at room temperature caused by crystallization at low temperature. The high electrochemical stability and absorbability make PVDF-HFP receive more and more attention. But the GPEs synthesized by PVDF-HFP own poor mechanical strength. Although the semi-crystalline PVDF owns good electrochemical stability and high dielectric constant, it is difficult to form suitable GPEs by using PVDF alone. The GPEs based on PAN have a widely electrochemical window, high ionic conductivity at room temperature, and severe passivation with Li metal anode. PMMA-based GPEs owning excellent

✉ Shusen Kang
kshusen@163.com

✉ Bin Shi
shibin3401@163.com

¹ Guizhou Meiling Power Source Company, Zunyi 563000, Guizhou Province, China

² State Key Laboratory of Advanced Chemical Power Sources, Zunyi 563000, Guizhou Province, China

compatibility with Li metal anode cannot be applied because of poor mechanical strength. As described above, GPEs containing one kind of polymers have their advantages and disadvantages and cannot be applied in quasi-solid-state batteries. Therefore, we should take account of mechanical strength, ionic conductivity, and the interface between GPEs and Li metal anode to improve the integrated property of GPEs. Combining the synergistic advantages of different polymer materials can be achieved by polymer blending, such as PEO-PVDF-HFP [12] and PAN-PEO [6]. PEO-PMMA-PVDF-HFP-based GPEs provide an ionic conductivity of 0.81 mS cm^{-1} at $25 \text{ }^\circ\text{C}$ and a high electrochemical window of 5.0 V (vs. Li/Li^+), which is promising to be applied to rechargeable Li batteries with high safety and long cycle life [5]. The PVDF-PAN polymer electrolyte membrane delivered excellent electrolyte uptake of 246.8%, the highest ionic conductivity of $3.32 \times 10^{-3} \text{ S/cm}$, and electrochemical stability up to 5.0 V (vs. Li/Li^+) [8].

In this work, PEO, PS, and PMMA are blended to prepare new films by the solvent casting technique, as shown in Fig. 1. A new kind of GPE could be prepared by immersing the PEO-PS-PMMA membrane into a liquid electrolyte. The new GPE exhibits reasonable ionic conductivity and a broad electrochemical window. The performance of PEO-PS-PMMA-based GPE for lithium metal battery was evaluated in cell LFP/PEO-PS-PMMA GPE/Li.

Experiments

Preparation of PEO-PS-PMMA GPE

Solvent casting is a common way to fabricate the GPEs. PEO (600,000), PS (MFCD00084450), PMMA (35,000), liquid electrolyte (1.0 mol/L $\text{LiPF}_6/\text{EC-DMC}$ 1:1 v/v), and dimethylacetamide (DMAc) were purchased from Aladdin and used directly without any treatment. The experiment was conducted in a dry room. We do lots of experiments to make sure the solvent and component ratio for the polymer membranes. The solvent and component ratios are very important to polymer membranes. After evaluating these

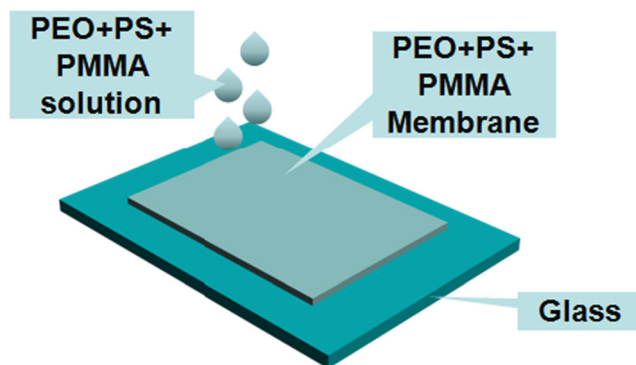


Fig. 1 Scheme to prepare PEO-PS-PMMA matrix membrane

polymer membranes systematically, the optimized ratio of the solvent components for our purpose was found by dissolving PEO, PS, and PMMA in a mass ratio of 3:1:1 in DMAc by stirring at $60 \text{ }^\circ\text{C}$ for 12 h. Drying the film at $70 \text{ }^\circ\text{C}$, the solution was cast on a glass plate at room temperature. The desired thickness of the films was controlled by a doctor blade. The best thickness of the GPE film was $80 \text{ }\mu\text{m}$.

PEO-PS-PMMA GPE was gotten by immersing the polymer membrane into liquid electrolyte for 4 h in a dry room. After the absorption of liquid electrolyte in the polymer membrane had been saturated, the mass of the GPE film did not increase anymore. The obtained GPE was thus ready for performance evaluation.

Characterization of GPE membrane

The morphology of PEO-PS-PMMA membrane was characterized by scanning electron microscopy (EVO-18). The differential scanning calorimetric analysis and thermogravimetric analysis were performed using a thermal analyzer (STA449F3) to analyze the thermal properties of PEO-PS-PMMA membrane from room temperature to $800 \text{ }^\circ\text{C}$. X-ray diffraction pattern of the polymer membrane was obtained with X-ray powder diffraction (Xpert3 Power) at a scanning rate of $4^\circ/\text{min}$ in the 2θ range of $5\text{--}90^\circ$. The porosity of the polymer membrane was measured by gravimetry. The electrochemical tests were carried out using CHI660E.

Preparation of the electrode

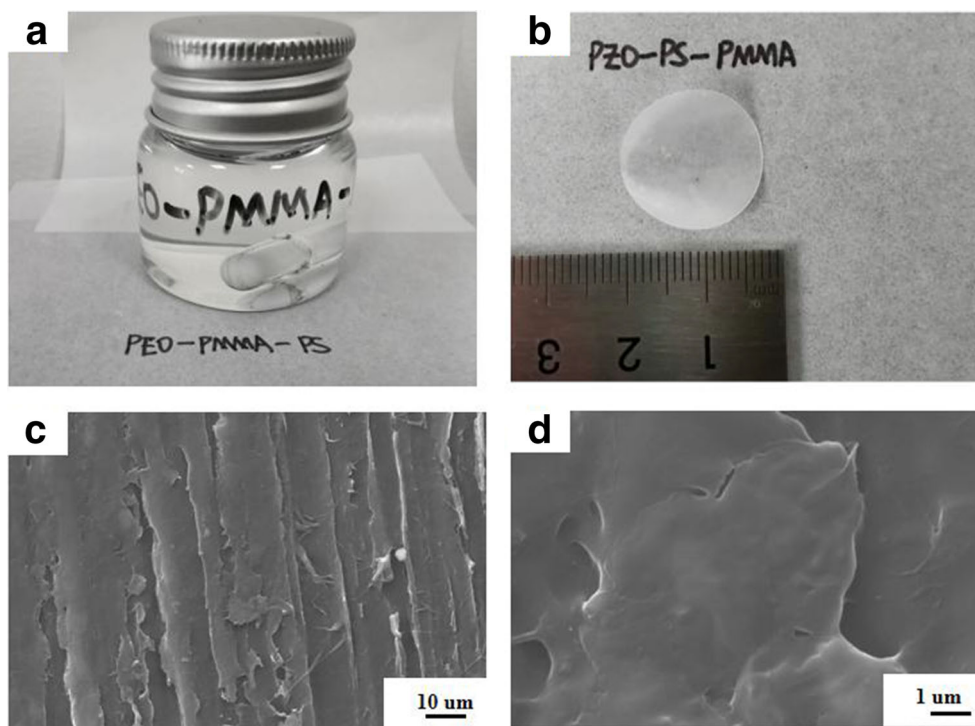
The LiFePO_4 electrode used for Li/PEO-PS-PMMA GPE/ LiFePO_4 cell assembly was prepared by mixing LiFePO_4 , PVDF, and Super P in the ratio 94:3:3 in NMP. Then, the homogeneous viscous slurry was coated on the aluminum (Al) foil using the doctor blade technique with a thickness of $25 \text{ }\mu\text{m}$. The resulting electrode was dried in the oven at $80 \text{ }^\circ\text{C}$ for 2 h, then in a vacuum oven at $100 \text{ }^\circ\text{C}$ for 24 h to remove the solvent. Li/PEO-PS-PMMA GPE/ LiFePO_4 cells were assembled in Ar-filled glovebox.

Result and discussion

Properties of the PEO-PS-PMMA film

PEO, PS, and PMMA polymers in DMAc could form a clear, transparent, and homogeneous solvent as shown in Fig. 2a. The viscous solvent was coated on the glass using a doctor blade with a thickness of $80 \text{ }\mu\text{m}$ to form the white PEO-PS-PMMA film (Fig. 2b). The surface morphology of the PEO-PS-PMMA film was investigated by SEM. Usually, the solvent in the polymer matrix evaporates to form the porous structure. As Fig. 2c and d show, there are no obvious pores

Fig. 2 **a** Optical image of PEO, PS, and PMMA solvent. **b** Optical image of PEO-PS-PMMA membrane. **c, d** SEM images of PEO-PS-PMMA membrane



on the surface of PEO-PS-PMMA film, which is different from other films prepared by solvent casting. The blending of the polymer materials had a strong influence on the pore size and distribution; the adding of PS and PMMA into PEO inhibits the pores forming and growing. Eventually, the PEO-PS-PMMA film has rare pores. Therefore, the specific surface area of PEO-PS-PMMA film was not measured by the nitrogen adsorption method.

Polymer matrix retaining large amounts of liquid electrolyte is significant for the GPE. The dry PEO-PS-PMMA film was weighted before being immersed in liquid electrolyte for 4 h in the glovebox. PEO-PS-PMMA GPE was weighted after the absorption of liquid electrolyte in the polymer membrane had been saturated. The GPE was wiped with filter paper after taking out the liquid electrolyte. The absorbability for liquid electrolyte could be calculated according to the following Eq. (1):

$$\eta = (m_1 - m_0) / m_0 \tag{1}$$

where m_0 is the weight of dry PEO-PS-PMMA film before being immersed in the liquid electrolyte, and m_1 is the weight of PEO-PS-PMMA GPE. The liquid electrolyte used in this work is 1.0 mol/L $\text{LiPF}_6/\text{EC-DMC}$ (1:1 v/v). The absorbability of PEO-PS-PMMA film was 63%, because of the swelling effect of liquid electrolyte for PEO-PS-PMMA film.

The crystalline content of polymer electrolyte has a significant effect on the ionic conductivity. The lower crystalline content of polymer electrolyte is, the higher the ionic

conductivity is. The crystalline content of PEO-PS-PMMA film was characterized by XRD, and the result is shown in Fig. 3. There is a broad diffraction peak in the 2θ range of $16\text{--}25^\circ$ and two sharp peaks at 19° and 23.5° . The two sharp peaks at 19° and 23.5° are attributed to the crystal of PEO. And there are no peaks of PS and PMMA crystals, as shown in Fig. S2. But the broad diffraction peak in the 2θ range of $16\text{--}25^\circ$ indicates that the crystalline content of the polymer film is very low, because the PMMA is amorphous. The blending of PEO-PS-PMMA can reduce the crystalline content.

TG-DSC trace of PEO-PS-PMMA film is depicted in Fig. 4. There is a weight loss of about 6% from 40 to 70°C , which can be seen from Fig. 4, due to the evaporation of residual solvent and moisture. The DCS curve of the sample around 70°C shows an exothermic peak, which agrees with the weight loss from 40 to 70°C . The endothermic peaks at 73° and 367° are due to the

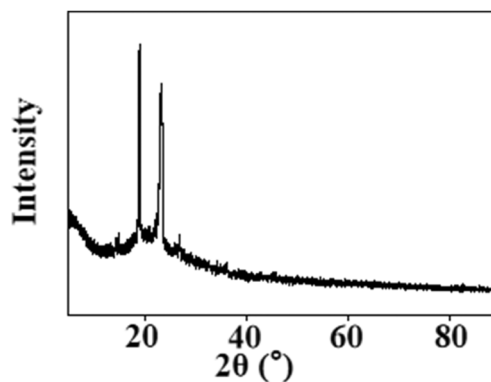


Fig. 3 XRD curve of PEO-PS-PMMA membrane

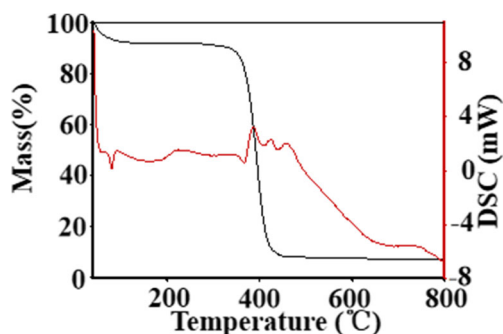


Fig. 4 TG and DSC curves of PEO-PS-PMMA membrane

glass transition temperature and a melting point of PEO-PS-PMMA film. The beginning decomposition of PEO-PS-PMMA film is about 300 °C, which meets the thermal safety requirement of the Li metal battery. PEO-PS-PMMA film completely decomposes between 370 and 420 °C, which is in good agreement with the exothermic peaks at 365 °C in the DSC curve. The crystallinity of the polymer determines the melting enthalpy. The melting enthalpy of the PEO-PS-PMMA film is very low, which can be seen from the DCS curve. This means the crystallization degree of PEO-PS-PMMA film is very low.

Properties of GPE

Ionic conductivity is a significant parameter for GPE material. The ionic conductivity of GPE was measured by A.C. impedance spectrum analysis from room temperature to 90 °C. The frequency range is 1 Hz to 1 MHz. The two stainless steel electrodes were used to form a symmetrical cell, and the GPE was in the middle. The ionic conductivity is calculated by Eq. (2):

$$\sigma = d / (S \times R_b) \quad (2)$$

where σ represents the ionic conductivity, d is the thickness of the GPE, and S is the area of polymer electrolyte.

Figure 5 a shows the EIS spectrums of PEO-PS-PMMA GPE at different temperatures. During the EIS test, the Li^+ cannot deposit on the GPE/stainless steel electrode, because the electrode potential at GPE/stainless steel electrode is much higher than that of the Li/electrolyte system. Therefore, there are only inclined straight lines that are related to the ion

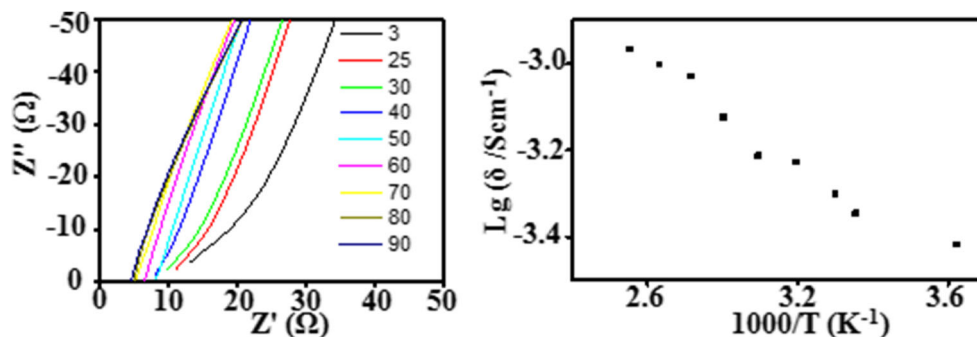
diffusion impedance in the PEO-PS-PMMA GPE's EIS spectrums. The half-circle lines which are related to the charge transfer on the electrode/GPE interface do not occur in the EIS spectrums. The R_b of the PEO-PS-PMMA GPE was 3.18 Ω at room temperature, which can be seen from Fig. 5a. The ionic conductivity of PEO-PS-PMMA GPE is 0.12 mS/cm. The high ionic conductivity of PEO-PS-PMMA GPE is attributed to the low crystalline content.

The Arrhenius curve of PEO-PS-PMMA GPE from 25 to 90 °C is shown in Fig. 5b. In a temperature range of 25–50 °C, the ionic conductivity increases with the temperature, and the Arrhenius curve is inclined straight line because the dissociation of lithium salt and polymer segmental motion was enhanced. When the temperature is around 60 °C, the crystalline phase of PEO transforms into amorphous. Therefore, the PEO-PS-PMMA GPE has no crystalline phase at all; the ionic conductivity can be enhanced. The conductive mechanism of GPE is complex. There are several models proposed, such as Arrhenius theory and Vogel-Tammann-Fulcher (VTF) equation [13], which are suitable to different temperature ranges. The battery is used from 10 to 50 °C. And from 25 to 50 °C, the Arrhenius model is used to treat the relation of ion conductivity with temperature. The activation energy of ionic conduction is the slope of $\lg(\sigma)$ vs. $1/T$. The activation energy is the lowest energy for ion transport in an electric field. And the activation energy of PEO-PS-PMMA GPE is 15.9 kJ/mol, which is very low for ion transport. Therefore, the PEO-PS-PMMA GPE is a good ionic conductor.

Li^+ transference number is another parameter used to describe the Li^+ transporting ability. The ionic conductivity contains two parts, one is Li^+ conductivity, and another is the electron conductivity. Li^+ transference number is the ratio of Li^+ conductivity with ionic conductivity. The Li^+ transference number was characterized by AC impedance and chronoamperometry. The PEO-PS-PMMA GPE sandwiched between two lithium electrodes to form a Li/PEO-PS-PMMA GPE/Li symmetrical cell. The Li^+ transference number was calculated by the following Eq. (3):

$$t_{\text{Li}^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \quad (3)$$

Fig. 5 a EIS curves of PEO-PS-PMMA GPE at different temperatures. b Arrhenius curve of PEO-PS-PMMA GPE



I_0 represents the initial polarization currents; I_s represents the steady-state polarization currents; R_0 represents the initial interfacial resistance; R_s represents the steady-state interfacial resistance; and voltage amplitude is set at 0.1 V.

Li^+ transference number of PEO-PS-PMMA GPE is 0.2. The low crystalline content and high absorbability of PEO-PS-PMMA GPE are beneficial to enhance the Li^+ movement (Fig. 6).

Electrochemical stability of GPE at the range of operating voltage in lithium is significant for application. The useful GPEs do not suffer any redox reactions when the batteries charge and discharge. The electrochemical stability window can be determined by the linear sweep voltammetry experiment (LSV). The GPE is sandwiched between stainless steel and Li electrodes to form a SS/GPE/Li asymmetrical cell. And the sweeping rate is 1 mV/s. The electrochemical stability of the PEO-PS-PMMA GPE was evaluated between 0 and 5 V. Figure 7 presents the LSV curve of PEO-PS-PMMA GPE. It clearly shows that the electrochemical stability of PEO-PS-PMMA GPE is higher than 4.3 V. The current increases above 4.3 V indicate the onset of the electrolyte membrane decomposition. Li deposition makes the current increases sharply in the negative scan. Therefore, we consider that the PEO-PS-PMMA GPE can be a good candidate for an electrolyte of lithium-ion batteries operated at high voltage.

A good Li metal battery requires good compatibility of GPE with Li metal electrodes to guarantee acceptable performance. Evaluating the EIS impedance of symmetrical Li/GPE/Li at a different time is a good way to analyze the compatibility of the GPE with Li metal. We tested the EIS impedance variation of Li/PEO-PS-PMMA GPE/Li cell in storage for 15 days, and the results are shown in Fig. 8. There are four parts made up of the resistance of a Li/GPE/Li cell, the two main parts are bulk resistance (R_b) and the interface resistance (R_f) [14]. R_b is the intercept of the impedance curve with the real axis at the high-frequency region, which can be seen from Fig. 8 directly. The electrode/electrolyte interfacial resistance

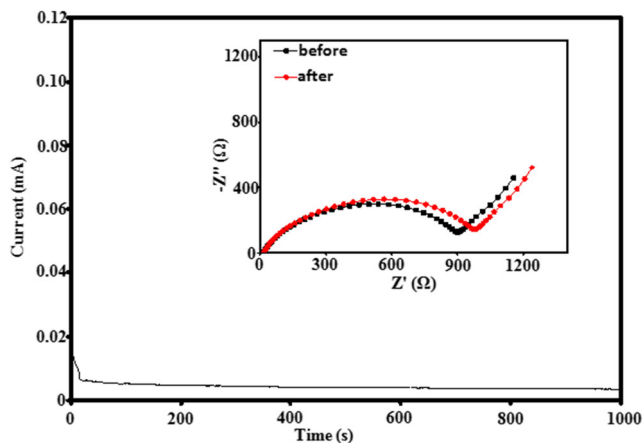


Fig. 6 Chronoamperometry profile of Li/PEO-PS-PMMA GPE/Li cell

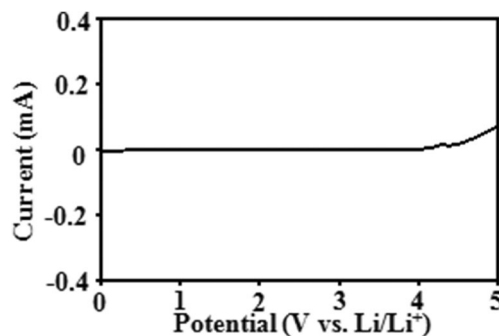


Fig. 7 LSV curve of PEO-PS-PMMA GPE

of Li/GPE/Li cell can be seen from the semicircle. The R_b and R_f at different storage time are in Fig. 8b and c. The intrinsic property of PEO-PS-PMMA GPE is related to the R_b , which is stable with the storage time. And a low R_b indicates the high conductivity of PEO-PS-PMMA GPE. The R_f between the PEO-PS-PMMA GPE and the Li electrode increases gradually in the storage time, which can be seen from Fig. 8c. This means the interface is changing. A small section before the semicircle in Fig. 8c may be due to the formation of an incomplete SEI film. The R_f between the PEO-PS-PMMA GPE and the Li electrode change from 250 to 850 ω , is very low. This means the interface between the PEO-PS-PMMA GPE and the Li electrode is stable.

The Li plating and stripping cycling stability of Li/GPE/Li is another method to characterize the compatibility of the GPE with Li metal electrode. Figure S1 shows the Li plating and stripping cycling stability result of Li/PEO-PS-PMMA GPE/Li with a current density of 0.5 mA/cm². The charging time and discharging time both are 0.5 h. The change in the polarization characteristics of the lithium electrode and also the ohmic resistance of the electrolyte could be characterized by this test. The cell voltage was unstable at the first 25 h, and then, the voltage is stable at 0.4 V, because of the unstable interface between PEO-PS-PMMA GPE and Li metal electrode and serious polarization. The SEI occurs during the cycles and becomes stable. Therefore, battery voltage becomes stable. This state could keep after 100 h, demonstrating the good compatibility of the PEO-PS-PMMA GPE with Li metal electrode.

Properties of PEO-PS-PMMA GPE in Li/PEO-PS-PMMA GPE/LiFePO₄ battery

The PEO-PS-PMMA GPE-based battery was evaluated by the full Li/PEO-PS-PMMA GPE/LiFePO₄ cell. Figure 9 shows the result of the Li/PEO-PS-PMMA GPE/LiFePO₄. The discharge capacity of the first cycle is 97 mAh/g, which is obtained at a constant current of 0.1 C, as shown in Fig. 9a. The discharge capacity of the PEO-PS-PMMA GPE-based battery is 97, 78, 55, and 38 mAh/g at a constant current of 0.1 C, 0.2 C, 0.5 C, and 1 C. When the current recovered to 0.1

Fig. 8 **a** EIS curve of PEO-PS-PMMA GPE at different times. **b** Bulk resistance of PEO-PS-PMMA GPE at different times. **c** Interfacial resistance of PEO-PS-PMMA GPE at different time

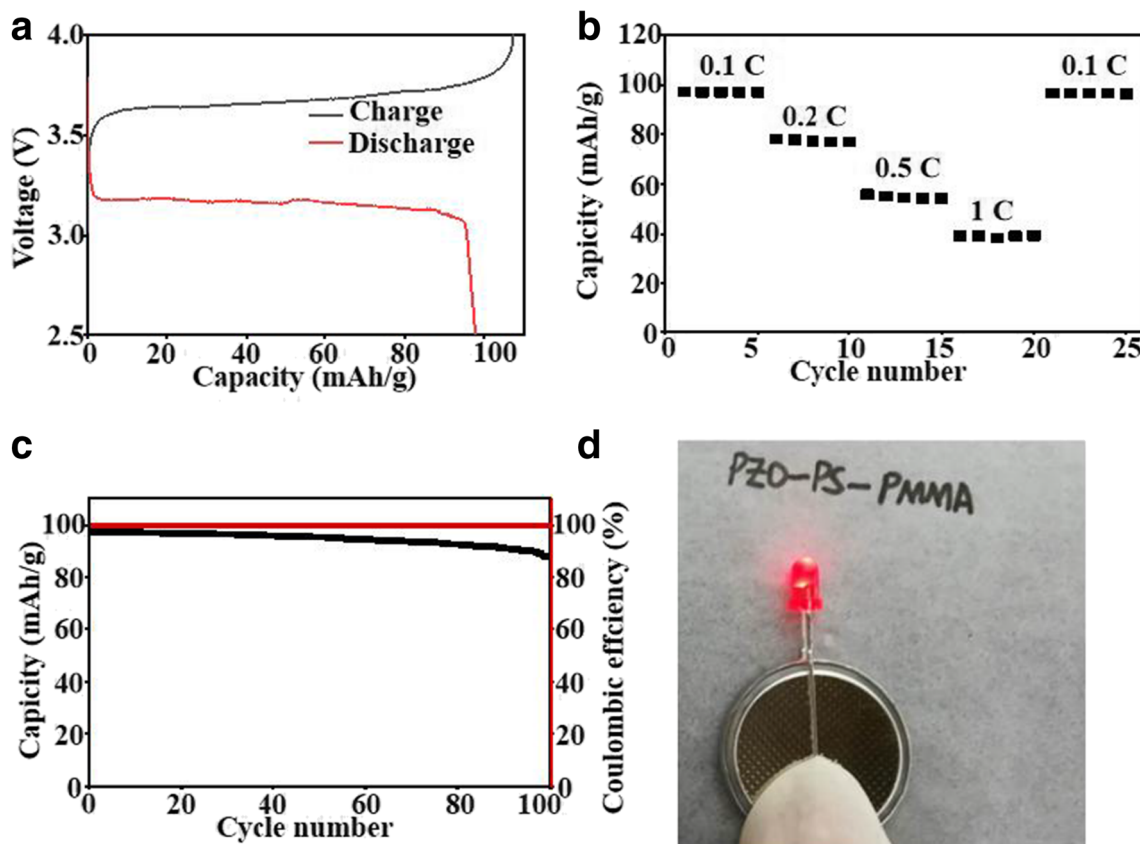
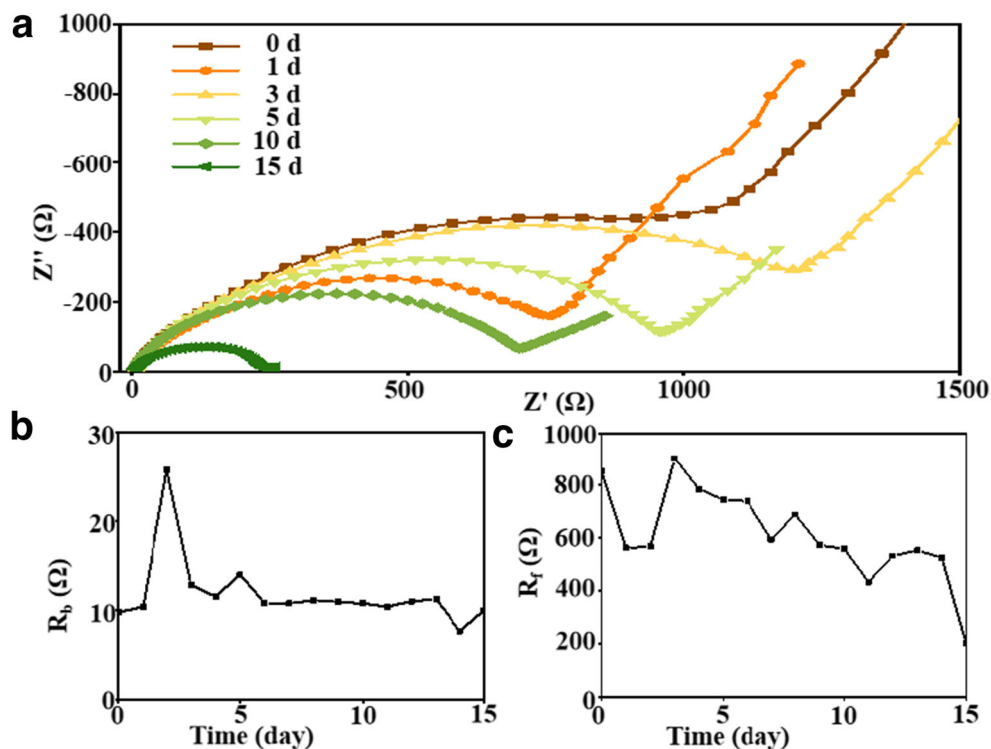


Fig. 9 **a** Charging and discharging curve of quasi-solid-state lithium metal batteries with PEO-PS-PMMA GPE. **b** Discharge capacity of quasi-solid-state lithium metal batteries with PEO-PS-PMMA GPE at different

rates. **c** Cycle performance of quasi-solid-state lithium metal batteries. **d** Image of quasi-solid-state lithium metal batteries with PEO-PS-PMMA GPE

C, the discharge capacity was still 97 mAh/g. The battery showed good cycling performance; the capacity was still kept at 88 mAh/g after 100 cycles. The coulombic efficiency was 98% at 100 cycles, and the capacity retention of the cell was 88%. The result demonstrates that Li/PEO-PS-PMMA GPE/LiFePO₄ battery provides a high initial discharge capacity and good cycle stability. And as seen from Fig. 9d, the LED light can be lighted by the Li/PEO-PS-PMMA GPE/LiFePO₄ battery.

Conclusion

In this study, the PEO-PS-PMMA GPE was prepared and tested for the Li metal battery successfully. The blending of PEO, PMMA, and PS in a suitable ratio can form a uniform transport polymer matrix. The PEO-PS-PMMA film has high absorption. The high ionic conductivity of PEO-PS-PMMA GPE is 0.12 mS/cm at 25 °C. PEO-PS-PMMA GPE shows high electrochemical stability and excellent interface stability to Li metal electrodes. The full cell based on PEO-PS-PMMA has a discharge capacity of 97 mAh/g and good cycle performance.

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Author contribution The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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