



Advanced semi-interpenetrating polymer network gel electrolyte for rechargeable lithium batteries



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ABSTRACT

A new type of semi-interpenetrating polymer network (Semi-IPN) gel polymer electrolyte (GPE) membrane based on the cross-linked poly(ethylene glycol) diacrylate-co-poly(vinylene carbonate) P(EGDA-co-VC) and PVDF-HFP linear polymer is successfully synthesized by UV-cured technology. The cross-linked P(EGDA-co-VC) can accommodate a large amount of liquid electrolyte inside the non-porous membrane via its strong interaction with Li⁺ and solvents, which avoids the liquid electrolyte leakage. The ionic conductivity of the Semi-IPN GPE reaches $1.49 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and the electrochemical stability window up to 4.2 V (versus Li/Li⁺). It demonstrates excellent interface stability to lithium metal electrode, superior thermal stability and good mechanical properties. A symmetric Li/Li cell with the above electrolyte displays a lower voltage polarization and longer valid cycle life than that based on conventional liquid electrolyte. Moreover, the Li/LiFePO₄ cells using the Semi-IPN GPE show superior cycling stability and rate performance comparable to the cell based on conventional liquid electrolyte. This Semi-IPN GPE is promising for rechargeable lithium batteries with high safety and energy density.

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1. Introduction

Rechargeable lithium (or Li-ion) batteries have been regarded as important next-generation power sources for electric vehicles and energy storage systems [1,2]. Moreover, safety issue becomes crucial for the application of high power rechargeable lithium batteries. Traditional lithium ion batteries adopt porous membrane separators, which impregnate liquid electrolytes. Such a battery system is unsafe because the used organic solvents are often highly volatile, flammable, and easily leaky. In order to improve the battery safety, poly(ethylene oxide) (PEO)-based all-solid-state polymer electrolytes, also functioned as a separator, have been extensively studied. They exhibit the ionic conductivities ranging from 10^{-7} to $10^{-5} \text{ S cm}^{-1}$ at room temperature, which are not sufficient for practical application [3]. Gel polymer electrolytes (GPEs) have the acceptable conductivity and can suppress the solvent volatilization and avoid the leakage. Thus, they are just good alternatives to all-solid-state polymer electrolytes and conventional liquid electrolytes. Various polymers including PEO [4], poly(propyleneoxide)

(PPO) [5], poly(methylmethacrylate) (PMMA) [6,7], poly(acrylonitrile) (PAN) [8] and poly(vinylidene fluoride) (PVdF) [9,10] have been investigated as GPE matrix to absorb electrolyte solutions. However, these GPE membranes mostly present poor mechanical property because they have been softened after uptake of liquid electrolytes. This drawback might cause the problems of winding tension and internal short-circuits during the cell assembly and operation, and it is the main obstacle for the practical application.

Chemical cross-linking can significantly enhance thermal and dimensional stability of GPEs. The cross-linked polyether system is regarded as one of the most potential gel bases for GPEs because of the ideal interaction between electrolyte components (lithium ion and solvent) and ethylene oxide (EO) unit. Nevertheless, the chemically cross-linked GPEs are mostly brittle, being short of the necessary flexibility for battery assembling and application. On the other hand, although thermal curing is a feasible method for preparation of a cross-linked GPE and has been used for the practical lithium ion battery with gel polymer electrolyte [11], the processing at the elevated temperature (around 60–100 °C) might produce impurities during chemical crosslink and the unwanted side reactions including gas evolution owing to the use of the thermal initiators, and thereby might degrade the battery performance [12].

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In order to improve the mechanical properties of chemically cross-linked GPE, here we report the synthesis and characterization of a new semi-interpenetrating polymer network (Semi-IPN) gel polymer electrolyte membrane by irradiation with UV-light. The advantage of UV-curing is its high energy efficiency, short polymerization time and easy processing control. A notable feature of the semi-IPN is the finely tuned architecture integration of a cross-linked polymer network and a flexible linear polymer, which leads to synergistic effects, particularly regarding the dimensional stability and mechanical properties [13]. D. He et al. [14] has prepared a semi-IPN solid polymer electrolyte which shows good ionic conductivity more than $5.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. However, its mechanical strength is not sufficiently high for practical application due to the high concentration of solid-state plasticizer. The semi-IPN matrix proposed in this study is based on incorporation of highly cross-linked PEGDA-co-PVC network with a linear PVDF-HFP polymer. The former tends to endow GPE with a strong rigidity and thermal stability, while PVDF-HFP with flexible backbone chains may bring about mechanical softness. The mechanical and electrochemical properties of this semi-IPN gel polymer electrolyte system are systematically investigated.

2. Experimental

2.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA) with the number-averaged molecular weight of 575 Da, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) were purchased from Aladdin. Vinylene carbonate (VC) was purchased from Fujian Chuangxin Technology Co., Ltd. Other materials, such as methanol and acetone were used as received. 1.0M liquid electrolyte was made by dissolving a certain quality of LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume, Shenzhen Capchem Technology Co., Ltd.). Commercial polyethylene (PE) separators (ENTEK ET 20-26, thickness: 20 μm ; porosity: 37%) were purchased from ENTEK International Ltd. Commercial carbon-coated LiFePO_4 was from Phostech Lithium Company (average particle size: 0.2 μm ; carbon content: 2 wt.%).

2.2. Synthesis of semi-interpenetrating polymer network

The proper PVDF-HFP was dissolved in acetone and stirred continuously for 2 h to form a homogeneous solution. Then, PEGDA, VC and photo-initiator HMPP were added into the solution (the concentration of HMPP was 0.5 wt% based on curable monomer). The curable mixed solution was coated on glass surface and after 10 min of drying, it was irradiated with UV light for 90 s. Finally, the Semi-IPN membranes consisting of PVDF-HFP and cross-linked P(EGDA-co-VC) were obtained. After polymerization, the Semi-IPN membranes were washed with methanol for three times to remove the unreacted PEGDA and VC, and dried under vacuum for 12 h at 60 °C. The thickness of Semi-IPN membranes is around 100 μm . The obtained membrane shows good mechanical properties when the optimized weight ratio of PEGDA: VC: PVDF-HFP was 1:4:1.

The PVDF-HFP membrane (porosity: 35%) used as the control sample with an average thickness of ca. 97 μm was prepared by the phase inversion process [9].

2.3. Preparation of gel polymer electrolyte

The Semi-IPN and PVDF-HFP membranes were swelled in liquid electrolyte (1 M LiPF_6 in EC/DMC = 1/1, v/v) for 12 h. Finally, gel polymer electrolytes were formed and investigated.

2.4. Sample analysis

The surface morphology of the Semi-IPN membranes was observed by JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). The UV-cured reaction of the PEGDA and VC was confirmed using a FT-IR spectrometer (Spectrum 100, Perkin Elmer, Inc. USA). The DSC and TGA measurements were performed in a temperature range from -60°C to 350°C and room temperature to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. The mechanical properties of the optimized Semi-IPN membrane were measured from stress-strain tests using Instron 4465 instrument with a tensile speed of 5 mm min^{-1} .

2.5. Electrochemical measurements

To determine the uptake amount of liquid electrolyte, the optimized Semi-IPN membrane was immersed in electrolyte solution for 12 h. Subsequently, the excess solution on the surface of the membrane was slightly absorbed using filter paper. The uptake amount was calculated from the weight difference of the samples before and after the immersion step [15].

The ionic conductivity was measured by ac impedance spectroscopy using a CHI660C electrochemical analyzer in the frequency range from 100 KHz to 1 Hz at temperatures between 25 and 80 °C. Electrochemical impedance spectroscopy (EIS) was measured using a frequency response analyzer (CHI660C) with an electrochemical interface in the frequency range from 100 KHz to 0.01 Hz. Cyclic voltammetry measurements were conducted in Swagelok cell by sandwiching the GPE or PE membrane between stainless steel (SS) as working electrode and lithium metal as reference and counter electrode at 25 °C. The voltage scan rate was 10 mV s^{-1} in the potential range from -1.0 to 5.0 V . LiFePO_4 based cathode was prepared by pasting a mixture of active material, carbon black (Super-P) and PVDF as binder at a weight ratio of 80:10:10 on Al foil. Stainless steel coin cells (CR2016-type, $\phi = 16 \text{ mm}$) were assembled in glove box containing less than 10 ppm H_2O or O_2 for electrochemical evaluation. The cycling performances of $\text{LiFePO}_4/\text{Li}$ and symmetric Li/Li cells with the Semi-IPN GPE and the liquid electrolyte (1 M LiPF_6 in EC/DMC = 1/1, v/v) soaked in polyethylene (PE) separator (ENTEK ET 20-26, thickness: 20 μm ; porosity: 37%) were measured on a Land battery test system (CT 2001, Wuhan Land Electronic Co. Ltd., China) at 25 °C.

3. Results and discussion

3.1. Physical properties of the gel polymer electrolytes

As illustrated in Fig. 1, the cross-linked P(EGDA-co-VC) copolymer was prepared from poly(ethylene glycol) diacrylate (PEGDA) and vinylene carbonate (VC), which is a well known electrolyte additive for lithium ion battery [16,17].

The UV-polymerization reaction of the PEGDA/VC mixtures is elucidated by measuring the change in the characteristic FTIR spectroscopy peaks assigned to C=C bonds ($1620\text{--}1640 \text{ cm}^{-1}$) of the PEGDA and VC. As shown in Fig. 2, the FTIR peaks of the C=C bonds in both PEGDA and VC disappeared after UV-cured. This indicates that the PEGDA and VC were successfully photopolymerized, leading to the formation of a self-standing film.

In order to discern the semi-interpenetrating polymer composite structure of the prepared membrane, the linear PVDF-HFP was dissolved out by acetone. Fig. 3 presents SEM images of the original Semi-IPN membrane and Semi-IPN membrane etched by acetone. The original Semi-IPN membrane in Fig. 3a shows unsmooth surface and compact structure. For the practical application, the surface evenness can be improved by hot-pressing. After acetone

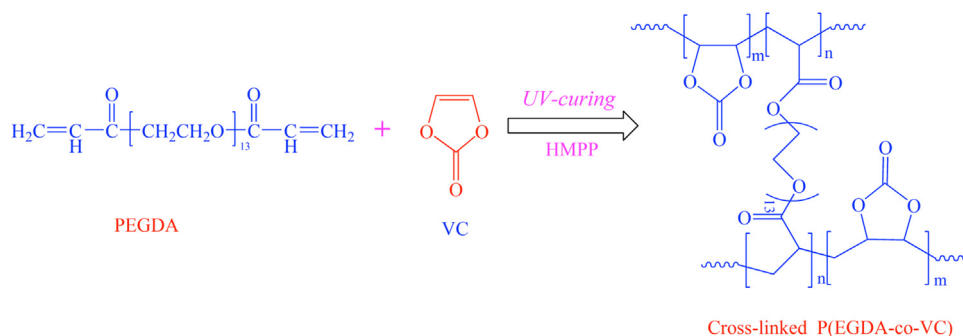


Fig. 1. Schematic synthesis procedure of the cross-linked P(EGDA-co-VC) copolymer by UV light.

etching for 12 h, PVDF-HFP is removed and a lot of pores emerge on the surface of the Semi-IPN membrane (Fig. 3b). The uniform pore distribution indicates a homogeneous PVDF-HFP dispersion in the original membrane. According to the membrane weight difference before and after the etching process, the PVDF-HFP content in the polymer membrane is estimated to be 17.9 wt.%.

Fig. 4a shows the DSC curve of Semi-IPN membrane. The glass transition temperature (T_g) of -20.9°C indicates that the Semi-IPN membrane is in a rubbery state at room temperature. The characteristic peak at around 140°C corresponds to the melting point of linear PVDF-HFP. Fig. 4b illustrates the TGA curve of Semi-IPN membrane. Before 300°C , no remarkable weight loss can be observed. It indicates that this polymer membrane could be safe for battery application at high temperature. In the temperature range from 300°C to 470°C , a continuous weight loss occurs. The early weight loss is mainly due to the decomposition of linear PVDF-HFP polymer, while the later weight loss corresponds to pyrolysis of the cross-linked P(EGDA-co-VC). However, the decomposition temperatures of the various components cannot be distinguished clearly.

On the other hand, sufficient electrolyte uptake of a polymer membrane is necessary for a GPE to offer a high ionic conductivity. The liquid electrolyte uptake behavior of the Semi-IPN and PVDF-HFP membranes is shown in Fig. 5a. The uptake process is basically completed within 1 h. The Semi-IPN membrane exhibits a high electrolyte uptake up to 188%, which leads to the high ionic conductivity of the GPE. The Semi-IPN GPE membrane exhibits the ionic conductivity of $1.49 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , which is adequate for rechargeable lithium battery. The good electrolyte uptake can be ascribed to the unique co-polymer structure. There is a strong interaction between ethylene oxide (EO) of cross-linked P(EGDA-co-VC) and Li^+ . Moreover, the structure of polymerized VC is similar to ethylene carbonate solvent. The high polarity of VC unit leads to

good affinity to organic solvent in the electrolyte solution and, at the same time, can function as a solvent to promote the lithium salt dissociation and solvate lithium ions. All of these are favorable for the electrolyte uptake and ionic conduction. In contrast, the PVDF-HFP membrane soaked in the same liquid electrolyte shows a lower electrolyte uptake of 151.8% after 1 h (also no excess liquid electrolyte outside the membrane), and exhibits the ionic conductivity of $1.07 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C . It should be mentioned that liquid electrolyte is mainly accommodated in the pores of a PVDF-HFP membrane, rather than in its bulk polymer. Therefore, the ionic conductivity of the PVDF-HFP membrane is dependent on its porosity. Fig. 5b illustrates the temperature dependence of ionic conductivity of Semi-IPN GPE and PVDF-HFP. The ionic conductivity increases with the temperature in accord with Arrhenius relationship.

Another important physical property of battery separator is its mechanical performance. Fig. 6 presents the stress-strain curves of the Semi-IPN and PVDF-HFP membrane at room temperature. The tensile strength of the PVDF-HFP membrane is 6.22 MPa with an elongation-at-break value at 20%, while the tensile strength of the Semi-IPN membrane reaches 10.7 MPa with an elongation-at-break value at 312.6%. The Semi-IPN membrane shows better toughness than the PVDF-HFP. The good toughness will reduce the risk of the flexural deformation of the membrane, which is favorable for battery application. The cross-linked P(EGDA-co-VC) copolymer provides good mechanical properties for the Semi-IPN membrane, while the penetrated PVDF-HFP improves its toughness. Eventually, a good compromise is made between ionic conductivity and mechanical properties in this Semi-IPN GPE.

3.2. Electrochemical behaviors of the gel polymer electrolytes

Fig. 7 demonstrates the electrochemical stability windows of the prepared Semi-IPN GPE and liquid electrolyte at 25°C . In a potential range between -1.0V and 1.0V (vs. Li/Li^+), distinct reduction and oxidation peaks are observed, corresponding to the reversible plating and stripping of metallic lithium. In Fig. 7b, the oxidative degradation of the prepared Semi-IPN GPE takes place at around 4.2V vs. Li/Li^+ , which is mainly attributed to oxidative decomposition of the PEO chains of cross-linked P(EGDA-co-VC). For the Li/PE -liquid electrolyte/SS cell (Fig. 7a), in the anodic direction, the current emerges at about 4.5V vs. Li/Li^+ for the liquid electrolyte, indicating the oxidative decomposition of the liquid electrolyte, especially solvent molecules inside. A stability window up to 4.2V for the GPE would be sufficient for application in rechargeable lithium batteries with some types of cathodes, such as LiFePO_4 and sulfur-based composites.

The lithium deposition and stripping cycle stability was examined by designing symmetric Li/PE -liquid electrolyte/ Li and $\text{Li}/\text{Semi-IPN GPE}/\text{Li}$ cells. Fig. 8 exhibits cycle performance of lithium electrode in both the electrolyte systems at 25°C , using a

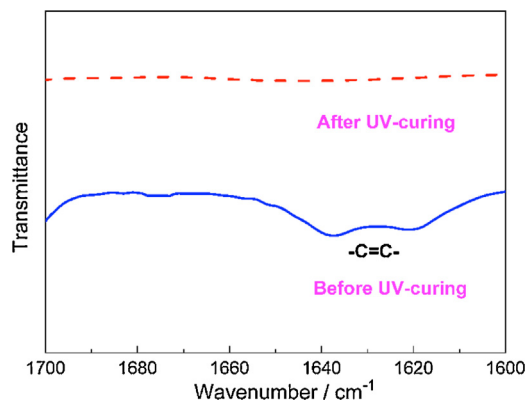


Fig. 2. Variation in FT-IR spectra of C=C double bonds of PEGDA and VC before and after UV-irradiation.

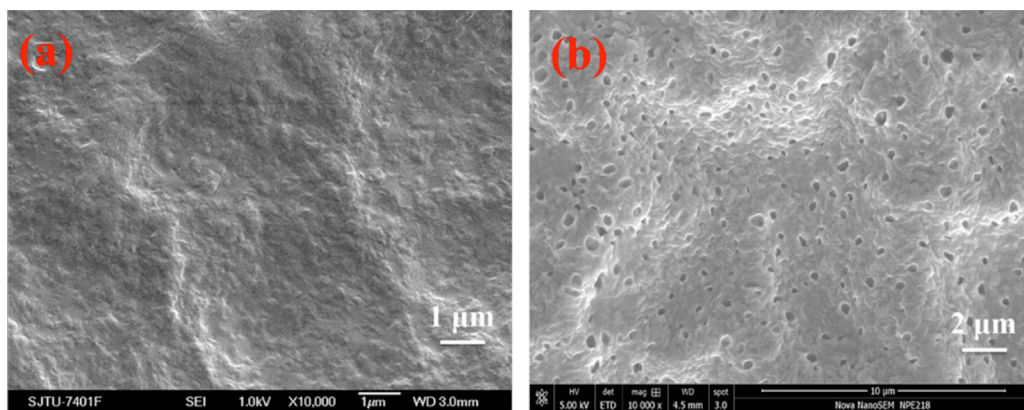


Fig. 3. (a) Physical appearance of the Semi-IPN membrane; (b) SEM images of the Semi-IPN membrane by acetone solvent etching.

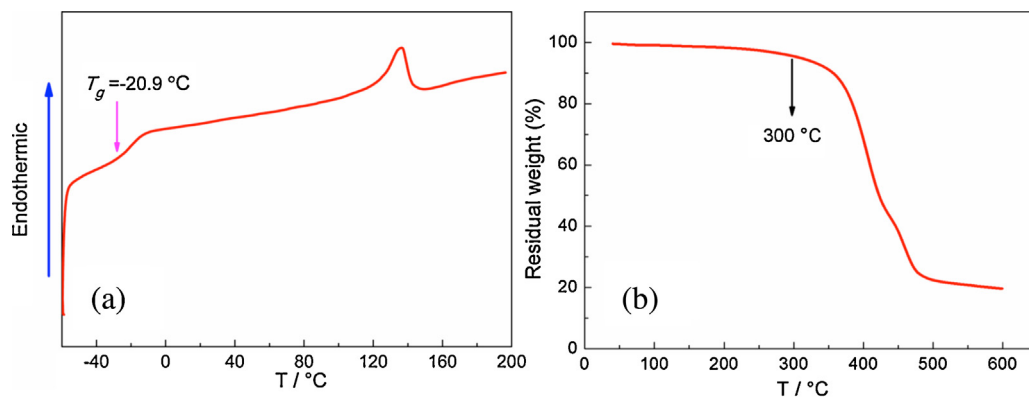


Fig. 4. (a) DSC curve of Semi-IPN membrane; (b) TGA profile for Semi-IPN membrane.

constant current density of 0.5 mA cm^{-2} . Fig. 8a shows the chronopotentiogram of the Li/PE-liquid electrolyte/Li cell holding 6 h for each process. The over-potential for deposition or dissolution of lithium metal is about 80 mV at the beginning and shows a tendency to increase quickly with the enhanced cycle number. Typically after 160 h, the potential polarization becomes extremely serious and unstable. This phenomenon may be due to the accelerated electrolyte consumption, along with the release of the gases, via the reductive decomposition of the electrolyte solution under the active lithium. On the contrary, Semi-IPN GPE provides lithium metal electrode with an excellent cycle performance under the same condition (Fig. 8b). Except the relatively high voltage polarization in the initial several cycles for the electrode activation and SEI layer formation, the deposition and

dissolution of lithium metal in Semi-IPN GPE occurred at a low over-voltage around 35 mV. After stable cycling for about 700 h, the voltage presents a gradually ascending tendency. Evidently, the Semi-IPN GPE is superior to the conventional liquid electrolyte for the lithium anode rechargeable battery.

In order to explain the superior electrochemical performance of the Semi-IPN GPE, the interfacial property of lithium electrode in the different electrolytes was investigated by electrochemical ac-impedance technology. Fig. 9 exhibits the changes of the ac-impedance spectra and the interfacial resistances under storage and cycling conditions for Li/PE-liquid electrolyte/Li and Li/Semi-IPN GPE/Li cells. The real part of the impedance at the highest frequency signifies the bulk resistance of an electrolyte, and the amplitude of a semicircle is representative of the interfacial

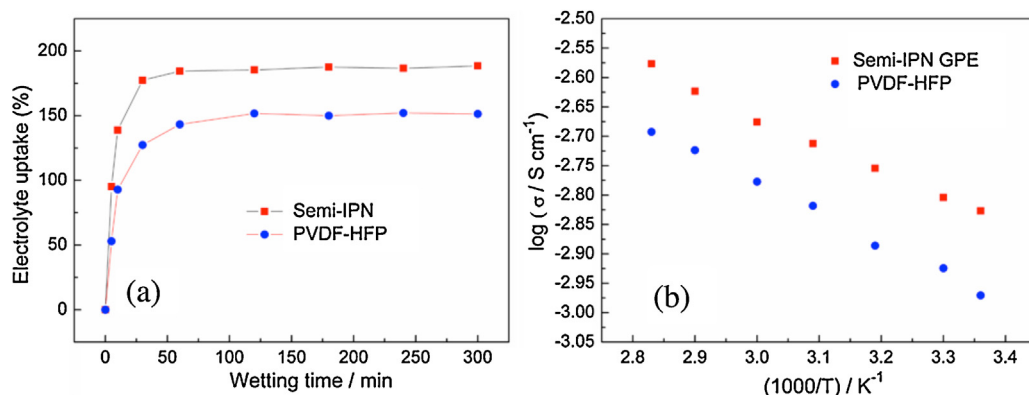


Fig. 5. (a) Electrolyte uptake of the Semi-IPN and PVDF-HFP membrane; (b) Temperature dependence of ionic conductivity for the Semi-IPN GPE and PVDF-HFP.

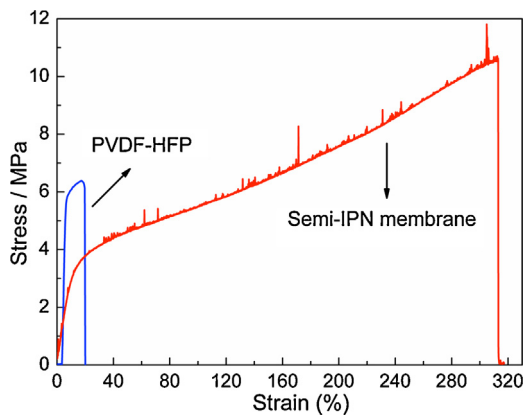


Fig. 6. The stress–strain curves for the Semi-IPN and PVDF-HFP membrane at room temperature.

resistance (R_i) between an electrode and an electrolyte [18,19]. The R_i in the Semi-IPN GPE is about $200 \Omega \text{ cm}^2$ at the 1st day, then increases with time like in the liquid electrolyte, and becomes relatively stable after 18 days (Fig. 9a). In contrast, the R_i in the liquid electrolyte increases more quickly within the first 13 days and still unstable up to 18 days (Fig. 9b). Moreover, R_i of Li/Semi-IPN GPE interface is relatively stable at about $120 \Omega \text{ cm}^2$ during cycling (Fig. 9c), while R_i of Li/liquid electrolyte interface fluctuates significantly at a higher value. These results indicate that the Semi-IPN GPE has better compatibility with lithium electrode and the SEI film formed on the lithium surface is more stable and conductive

than that in the liquid electrolyte, leading to a lower and more stable voltage polarization of the above Li/Semi-IPN GPE/Li cell.

3.3. Evaluation of Li/LiFePO₄ cell

Applicability of the Semi-IPN GPE was further evaluated by assembling a full cell using metallic lithium anode and LiFePO₄ cathode. Fig. 10a shows the discharge capacities of the Li/LiFePO₄ cells with Semi-IPN GPE and liquid electrolyte during cycling at room temperature. Both the cells display good cycling performance with slight capacity loss throughout 100 cycles at 0.3 C rate. Specific capacity of LiFePO₄ cathode in Semi-IPN GPE is as high as 148.2 mAh g^{-1} after 100 cycles. Fig. 10b shows the initial and 50th cycle charge–discharge profiles. For the Semi-IPN GPE-based cell, the quite flat voltage plateaus at 3.46 V for charging and 3.38 V for discharging correspond to Fe³⁺/Fe²⁺ redox couple reaction on the cathode. Judging from the stable cycle capacity and low voltage polarization, the Semi-IPN GPE as both electrolyte and separator provides good electrochemical reversibility for the cell reactions.

Fig. 10c shows the rate performances of the cells using the PE-liquid electrolyte and Semi-IPN GPE at 25 °C. After the cell was cycled at the initial rate of 0.3 C for 5 times, the current density was gradually increased in stages until 5 C. With an enhanced discharge rate, the capacity decreased regularly. For the cell with Semi-IPN GPE, the relatively stable capacities around 154.4, 150.5, 143.9, 137.7, 132 and 125 mAh g^{-1} were obtained at current rates of 0.3 C, 1.0 C, 1.5 C, 3 C, 4 C and 5 C, respectively. As the current rate returned to 0.3 C, most of the initial capacity can be retained. The comparable results for both the electrolyte systems indicate that

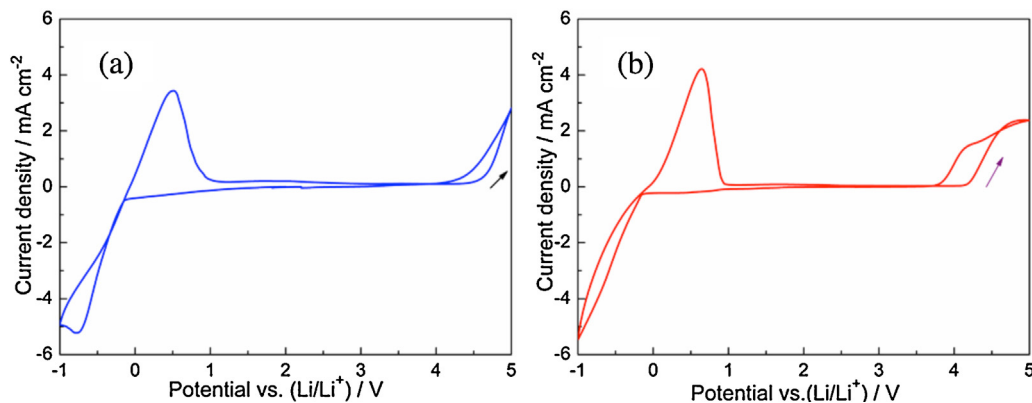


Fig. 7. Cyclic voltammograms of the liquid electrolyte (a) and Semi-IPN GPE (b) at 25 °C using Li as reference and counter electrodes and stainless steel as working electrode.

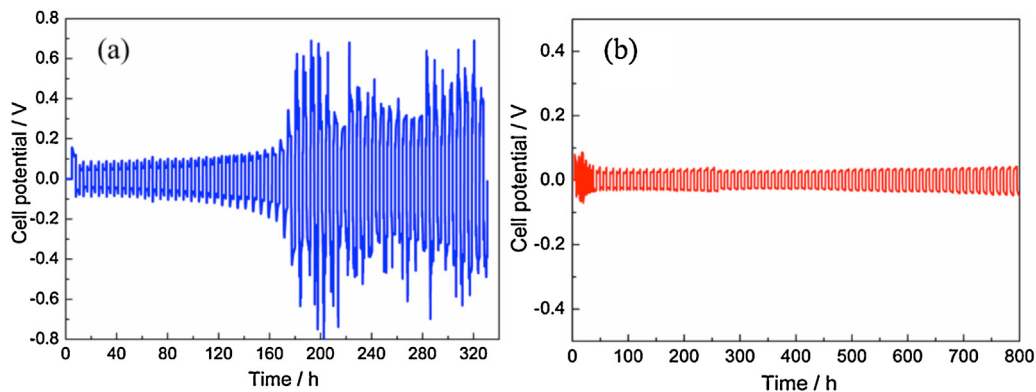


Fig. 8. The cycle performance of lithium deposition and stripping processes in (a) symmetric Li/PE-liquid electrolyte/Li and (b) Li/Semi-IPN GPE/Li cells at 25 °C, using a constant current density of 0.5 mA cm^{-2} .

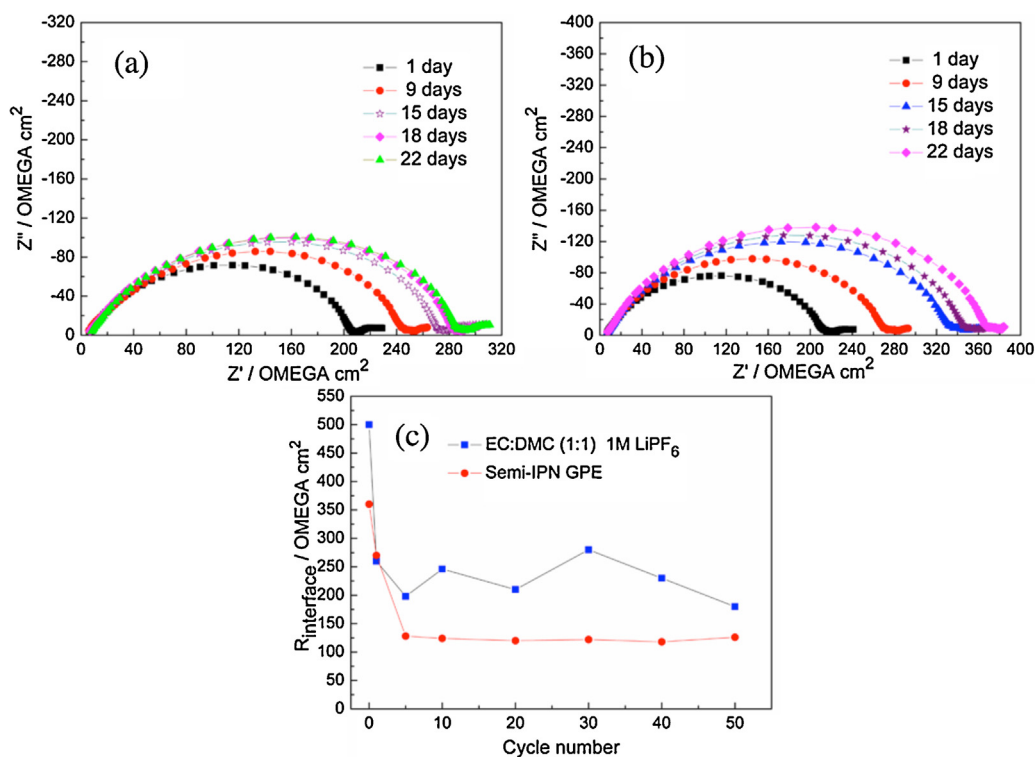


Fig. 9. The ac-impedance spectra of (a) Li/Semi-IPN GPE/Li and (b) Li/PE-liquid electrolyte/Li cells at different storage time; (c) R_i change during cycling.

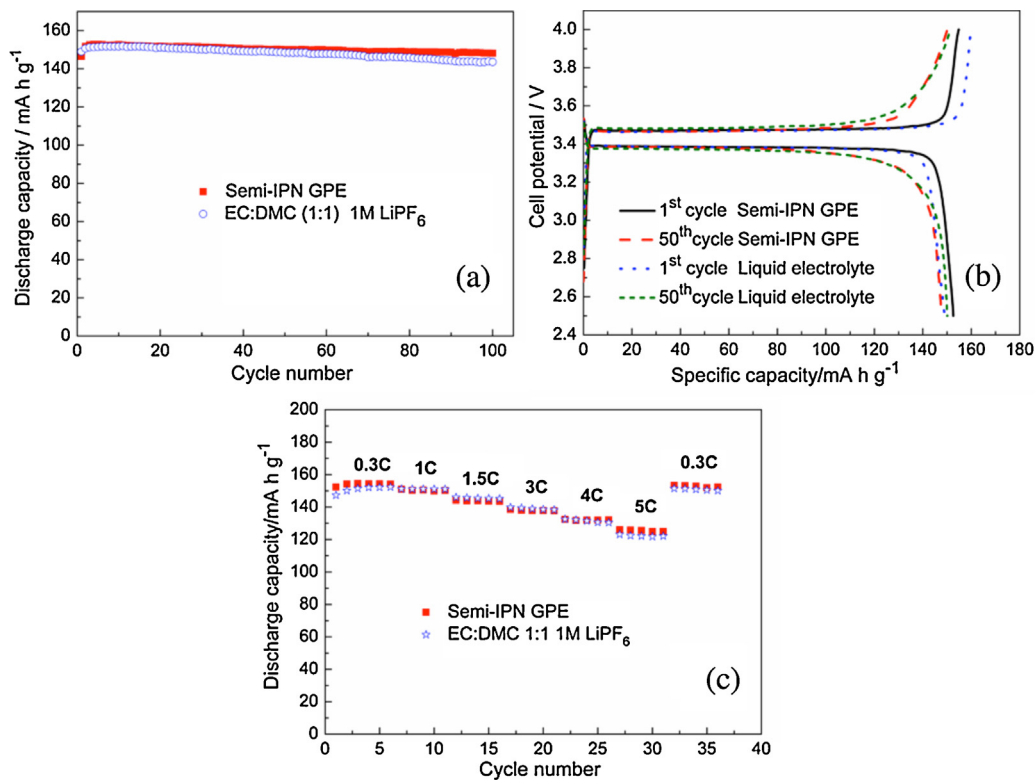


Fig. 10. (a) Discharge capacities of the Li/LiFePO₄ cells with Semi-IPN GPE and PE-liquid electrolyte during cycling at room temperature; (b) the initial and 50th cycle charge-discharge profiles of the cells using PE-liquid electrolyte and Semi-IPN GPE; (c) Rate performances of the cells using the PE-liquid electrolyte and Semi-IPN GPE at 25 °C.

the Semi-IPN GPE membrane might be used for power lithium ion batteries.

4. Conclusions

We have reported the preparation, electrochemical characterization and full cell tests of a new Semi-IPN GPE for secondary lithium batteries. This polymer membrane can accommodate a large amount of electrolyte solution, which assures its high ionic conductivity of $1.49 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C. In its composite structure, the cross-linked P(EGDA-co-VC) copolymer reinforces the mechanical properties and linear PVDF-HFP polymer improves the toughness and flexibility. The Semi-IPN GPE demonstrates superior thermal stability, mechanical properties and excellent interface stability to lithium metal electrode. Li symmetric cell with the above electrolyte displays lower voltage polarization and longer valid cycle life than that using the conventional liquid electrolyte. Moreover, the Li/LiFePO₄ cell using the Semi-IPN GPE exhibits superior cycling stability and rate performance comparable to the cell based on conventional liquid electrolyte. All these positive effects indicate that the Semi-IPN GPE could be a promising candidate for rechargeable lithium batteries with higher safety.

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