

Semi-Interpenetrating Network-Structured Single-Ion Conduction Polymer Electrolyte for Lithium-Ion Batteries

Xiu Shen,^[a] Longqing Peng,^[a] Ruiyang Li,^[a] Hang Li,^[b] Xin Wang,^[a] Boyang Huang,^[a] Dezhi Wu,^[c] Peng Zhang,^{*[b]} and Jinbao Zhao^{*[a, b]}

A novel quasi solid single-ion polymer electrolyte with semiinterpenetrating network (semi-IPN) structure has been prepared. The lithium-ion conduction membrane is composed of both the cross-linked lithiated poly-2-acrylamido-2-methylpropane sulfonic acid (PAMPS-Li) as a polyanionic single-ion lithium salt source and the high molecular weight polyethylene oxide (PEO) as a polymer matrix, in which the two components show great compatibility due to the special semi-IPN structure. For such quasi-solid electrolyte system, we have particularly studied the crystallinity variety and ionic conductivity change

1. Introduction

Since the introduction in the 1990s, the lithium ion batteries (LIBs) have been widely used in the energy storage area due to their advantages of long life, no memory effect, high energy density and low self-discharge.^[11] The LIBs are composed of three main components: cathodes, anodes and electrolytes. In spite of no contribution to the capacity, the electrolytes have a great influence for modulating the performance of batteries. However, the traditional liquid electrolyte exists internal unsafe defects due to its potential leakage, high volatile and flammability, which bring underlying safety issue into the LIBs, hindering its further development in the electric vehicles (EVs) and hybrid electric vehicles (HEVs) application.

Since Wright reported the polyethylene oxide (PEO) and alkali salt ionic conductive system in 1973,^[2] the solid state polymer electrolytes (SPEs) have aroused wide attention for their high safety insurance, excellent flexibility, easy design and good formability, as well as the improved resistance to the

[a]	X. Shen, L. Peng, R. Li, X. Wang, B. Huang, Prof. J. Zhao State Key Lab of Physical Chemistry of Solid Surfaces, Collaborative Innovation Centre of Chemistry for Energy Materials, Engineering Research Center of Electrochemical Technology, Ministry of Education, State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P.R.China F-mail: ibzhao@xmu edu.cn
[b]	H. Li, Dr. P. Zhang, Prof. J. Zhao
	College of Energy, Xiamen University,
	Xiamen 361005, P.R. China
	E-mail: pengzhang@xmu.edu.cn
[c]	D. Wu
	School of Aerospace Engineering,
	Xiamen University, Xiamen 361005, China
	E-mail: wdz@xmu.edu.cn
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with a series of polymer salt concentration. The results show that the electrolyte has an appropriate mechanical stability, minimal crystallinity, and acceptable ionic conductivity of 1.34×10^{-5} S/cm at 60 °C. Furthermore, the lithium-ion conduction membrane shows the lithium-ion dominating conductive property and high transport number of 0.77. Moreover, the LiFePO₄/Li batteries' cycle results show a high discharge capacity of 140.0 mAh/g and a retention of 90.4% after 100 cycles at the rate of 0.2 C.

volume change of the electrodes during the charge and discharge process.^[3-10] The SPEs consisted usually by a lithium salt mixed with polymer matrix are mostly formed with the dual-ion lithium salt and the polymer matrix with low glass transition temperature (T_g) to gain a high ionic conductivity. However, the Li-ion transference number ($t_{i,i}^+$), which means the ratio of Li⁺ part in the all ionic conduction, is only around 0.3 in the dual electrolyte system. Actually, the movement of anions may cause a polarization, and lead to the deterioration of cycle performance.^[11] As a result, single ion polymer electrolytes (SIPEs) have aroused wide research interests.^[12]

The SIPEs can be fabricated by following methods: 1) linking anions onto the polymer chain via polymerization of lithium salts monomer^[13] or modification of existing macromolecule polymer,^[14] 2) grafting polyanions onto organic backbone,^[15] 3) using anions trapping agents in dual-ion systems to decrease the mobility of anions based on the Lewis acid-base theory.^[12] It is reported that various SIPEs can improve the lithium ion transference number and decrease polarization.^[12,16] Also, the lithiated nafion film has been used as a single ion conductor^[17,18] and the functional coating layer of separator^[19-22] for LIBs. Armand et al. reported the SIPE of "BAB" triblock copolymers composed of polystyrene segment and PEO segment which obtain the high conductivity of 1.3×10^{-5} at 60 °C with t_{1i}^{+} of 0.85.^[4] Besides, by replacing the hydrogen atom of LiAlH₄ with polyethylene glycol (PEG) via a mild approach, the LiAI-PEG/PEO-based single Li-ion conductor has been prepared $(4.0 \times 10^{-5} \text{ S/cm} \text{ at } 30^{\circ}\text{C})$, and the molecular dynamics simulation has verified the hopping ion transport mechanism.^[23]

The interpenetrating network (IPN) structure^[24] has been widely used to enhance the compatibility of polymer electrolyte. On one hand, the IPN can reduce the crystallinity of crystalline polymer matrix by breaking the orderly arrangement of polymer chain segment, thus increasing the ion conduction amorphous phase region. On the other hand, it also can show



Figure 1. (a) Synthesis route diagram of cross-linked PAMPS-Li and final $(SI)^2PE$ membrane; (b) diagram of the semi-IPN structure of linear PEO and network shape PAMPS-Li; (c) interaction of Li⁺ with Lewis alkali O atom and $-SO_3^-$.

good compatibility and dimensional stability based on the tight twisted 3D networks ensuring the good entanglement of the two components and reducing the phase separation.^[25-27] Choosing proper combination of the well mechanical polymer and good lithium conductor, a stable dual phase interpenetrating structure can be obtained.^[28,29]

In this work, we have developed a novel guasi solid polymer electrolyte by combining the single lon conduction strategy with the semi-Interpenetrating polymer network structure. This quasi solid polymer electrolyte can be abbreviated as the (SI)²PE, and has been thoroughly studied. The semi-IPN single ion conductor is based on the network shape lithiated poly-2acrylamido-2-methylpropane sulfonic acid (PAMPS-Li) as the first component and the high molecular weight linear PEO as the second component. The interpenetrating structure can ensure the close contact between the polyanionic lithium source and the lithium ion conduction polymer matrix, and, at the same time, sharply decrease the crystallinity of the matrix. It should be pointed out that the 2-acrylamido-2-methylpropane sulfonic acid (AMPS) is water-soluble, and widely used in the proton exchange membrane for the biomimetic machine,^[30] sensor,^[31] and fuel cells.^[32] The AMPS possess the following advantages. It contains both double bond to be polymerized and functional group of sulfonic acid which can be further lithiated as lithium ion source. Besides, the AMPS-based Li single lithium ion conductor is prolific, cheap and easy to manipulate, which is beneficial to its further application.^[33]

2. Results and Discussion

The synthetic route is given in Figure 1a, in which the N, N'methylene bisacrylamide (MBA) is used as the cross-linker, and the polymerization is based on a free radical polymerization process. Figure 1b shows the diagram of (SI)²PE matrix structure. The network shape PAMPS-Li and linear PEO are entangled and interpenetrated with each other. Figure 1c shows the diagram of the interactions between Li⁺ with Lewis alkali (O atom and $-SO_3^-$), in which the Li⁺ can be well conducted while the immobility of poly-anions is maintained. The cross-linked PAMPS-Li bonds into one whole molecular by covalent bonding, which leads to the high weight-average molecular weight (Mw = $1.3 \pm 0.35 \times 10^7$ g/mol, see the Figure S1).

It is observed from the optical photograph that the (SI)²PE membrane is semi-transparent (Figure 2a), flexible and well



Figure 2. (a) Morphology, (b) flexibility, (c) surface SEM images of the $(SI)^2PE$ membrane; (d) cross section element mapping of C, O, S atom of the $(SI)^2PE$ membrane.



withstands mechanical bending (Figure 2b). And the flexibility provides good processability when the membrane is applied in the LIBs. The scanning electron microscopes (SEM) image of the (SI)²PE membrane (Figure 2c) shows that it has a compact surface morphology without detectable porous structure, which provides an assurance for the continuous Li-ion conduction pathway. As seen from the cross section of the elemental mappings graph, the membrane is homogeneous, and the C, O, and S elements are evenly distributed through the whole membrane, indicating a uniform two components mixing of network shape PAMPS-Li and linear PEO segment and fine semi-IPN structure construction. Even more, this also demonstrates a sustainable Li-ion conduction pathway, verifying the semi-IPN structure without dual polymer phase separation problem.

In order to determine the molecular structure, the Fourier transform infrared spectroscopy (FT-IR) spectra of AMPS monomer, cross-linked PAMPS and cross-linked PAMPS-Li are measured and shown in Figure 3. The absorption peaks (curve a) at



Figure 3. FT-IR spectra of (a) AMPS monomer; (b) cross-linked PAMPS-H; (c) cross-linked PAMPS-Li. The spectra are shifted in ordinate for convenience.

1610 cm^{-1} (C=C stretching vibration), 982 cm^{-1} and 947 cm^{-1} (=C-H out-of-plane bending vibration) in Figure 3a disappear after polymerization due to the C=C double bond reaction, indicating the success of the polymerization. Besides, the infrared absorption peaks may be affected by the environment around the chemical bond.^[34] As we can see, from the AMPS monomer to PAMPS (Figure 3a, 3b), the stretching vibration of C–S decrease form 627 cm^{-1} to 623 cm^{-1} . This is due to the intermolecular hydrogen bonding which may decrease the electron cloud density, making the equalization of stretching vibration frequency.[35] From Figure 3b, 3c, due to the interaction of Li⁺ and O atom, the peak of C–S shows a blue shift^[36] from low frequency of 623 cm^{-1} to high frequency of 630 cm^{-1} because of the effect of counter ion when exchanging proton to metal ion, indicating the successful lithiation process for AMPS-Li lithium salt monomer.^[37] Moreover, the asymmetric stretching vibration of O=S=O shifts from 1240 cm⁻¹ to 1220 cm⁻¹ and become broader, and the symmetric stretching vibration of O=S=O shifts from 1090 cm⁻¹ to 1049 cm⁻¹ after the polymerization.

Figure 4 shows the differential scanning calorimetry (DSC) curves of pure PEO and (SI)²PE membranes ((SI)²PE-x-y) containing different complex ratio (x-y is the mass ratio of PEO : PAMPS-Li, and it is 8–2, 7–3, 6–4, 5–5, and 4–6, respectively). In the Figure 4a, with the increase of the cross-linked PAMPS-Li proportion within the membrane, the melting points decrease from 69.5 °C (pure PEO) to 63.5 °C ((SI)²PE-6-4), hence adding of the cross-linked PAMPS-Li decreases the melting point of the PEO. Besides, the area of the melting endothermic peaks of PEO also decrease. The enthalpy and crystallinity change of PEO in the (SI)²PE with varying cross-linked PAMPS-Li ratio (Figure 4b) have been calculated according to the integration of the corresponding endothermic peaks in Figure 4a. The crystalline calculation equation (Equation [1]) is as follows:

$$\chi_{c} = \frac{\Delta H_{exp}}{\Delta H} \times \frac{1}{w_{f}} \times 100\%$$
⁽¹⁾

where χ_c is the membrane crystallinity, ΔH_{exp} is the melting enthalpy integral value, ΔH is the melting enthalpy of 100% crystallized PEO (213.7 J/g),^[38] and w_f is the weight ratio of the PEO. It can be concluded that with the increase of the crosslinked PAMPS-Li, the absolute value of the enthalpy change (heat absorption) decreases, and the crystallinity of PEO with respect to the enthalpy change also decreases which is in accordance with lowering of melting point. This is due to the semi-IPN structure dramatically reduced the crystallinity region by interpenetrating with the linear segment of PEO.

The dependence of ionic conductivity on temperature for $(SI)^2PE$ is shown in Figure 4c. It can be found that the conductivity change behavior of the $(SI)^2PE$ electrolyte follows Arrhenius law within the measuring temperature range of $30 \sim 90$ °C. The $(SI)^2PE-6-4$ is the best ratio of $(SI)^2PE$ system with the highest conductivity of 1.34×10^{-5} S/cm at 60 °C and 2.29×10^{-5} S/cm⁻¹ at 90 °C. Cross-linked PAMPS-Li itself as a polyanionic lithium salt has its intrinsic ionic conductivity, but it is not self-supporting, so we didn't get the specific value. The conductivity-temperature change trend follows Arrhenius Equation (Equation, [2] [3]):

$$\sigma = \sigma_0 exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

$$\log\sigma = \log\sigma_0 - \frac{E_a}{2.303RT}$$
(3)

where σ and σ_0 refers to the ionic conductivity and preexponential factor, respectively, E_a is the activation energy, and R is the molar gas constant (8.314 J/mol/K). E_a of different ratio has been calculated and presented in Table 1. The results

Table 1. Energy activation of membranes with varying PAMPS-Li ratio.						
	(SI) ² PE-8- 2	(SI) ² PE-7- 3	(SI) ² PE-6- 4	(SI) ² PE-5- 5	(SI) ² PE-4- 6	
<i>E</i> _a (kJ mol ⁻¹)	21.76	22.44	17.81	18.76	22.36	



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Figure 4. (a) DSC curves of (SI)²PE-x-y membranes with different ratio of PEO. (b) Enthalpy change and degree of crystallization corresponding to (SI)²PE-x-y membranes with different ratio. (c) Arrhenius behavior of (SI)²PE-x-y membranes with different PAMPS-Li ratio (from 20%–60%, marked with colors) at elevated temperature from 30 to 90 °C. The inside plot is the conductivity of different complex ratio at 60 °C. (d) EIS plots of the best ratio (SI)²PE-6-4 from 30 to 90 °C.

indicate that the (SI)²PE-Li-6-4 shows the lowest activation energy of 17.81 KJ/mol, revealing the lowest energy barrier among the (SI)²PE membrane system. The ionic conductivity trend with different cross-linked PAMPS-Li ratio (Figure 4c inset plot) could be explained by the following equation (Equation [4]):

$$\sigma = \sum_{i} n_{i} q_{i} \mu_{i} \tag{4}$$

where σ is the ionic conductivity, n_i is the carrier number related to ion concentration, q_i is the charge number, μ_i is the ion mobility, *i* refers to the ion species. The lithium ion conductivity is the synergistic effect of the carrier number and ion migration velocity, and the former is related to the lithium salt concentration and degree of dissociation, while the latter is affected by the ion conduction ether segment motion in this work. As the amount of the cross-linked PAMPS-Li increases, the total number of charge carriers, Li⁺, increases. And the high ionic conductivity of those semi-IPN SIPE system is mainly due to the nature of the ionic dissociation, reassociation, and competitive mechanism.^[39] However, since the PAMPS-Li is a rigid polymer, the film-forming and ion conduction are dependent on the ether segment of PEO. As a result, further increase of polymer salts decreases the amount of PEO, thus decreasing the ether segment motion, therefore, the curve of the relationship between the ratio of two polymers with the ionic conductivity exhibits a volcano form, and there exists a peak in the plot (Figure 4c inset plot). Figure 4d shows the EIS plots of the $(SI)^2PE-6-4$ at elevated temperature from 30 °C to 90 °C. The increase of the $(SI)^2PE$ conductivities along with temperature is due to the decrease of tight ion pairing^[40,41] and the enhancement of the segment motion.

For further studying the effect of semi-IPN structure on the PEO crystallinity, the X-ray diffraction (XRD) has been measured and analysed. In order to verify the crystallinity decreasing effect of IPN structure, we have prepared the PAMPS-Li without Semi-IPN by not adding cross-linking agent, and made the PAMPS-Li/PEO blending membrane for comparison. Figure 5 shows the XRD spectra of cross-linked PAMPS-Li and PAMPS-Li, the (SI)²PE, the directly PAMPS-Li/PEO blending membrane without Semi-IPN structure, and pure PEO membrane. The peaks of pure PEO can be indexed to the standard card (JCPDS: 49-2109). The lithium salt of PAMPS-Li and cross-linked PAMPS-Li both do not show obvious crystalline peaks, indicating their amorphous phase. However, after blending with PEO, the



Figure 5. XRD spectra of cross-linked PAMPS-Li, PAMPS-Li, (SI)²PE, the directly PAMPS-Li/PEO blending membrane and pure PEO membrane.

PAMPS-Li/PEO shows evident crystallinity peaks corresponding to (120) and (112) lattice plane of PEO, while the (SI)²PE membrane shows two greatly reduced peaks, indicating the huge crystallinity reduction of PEO by constructing the 3D interpenetrating structure. Associating with the rough surface of the prepared membrane, it is clear that the PAMPS-Li/PEO shows a distinct phase separation. The results of the two membranes with or without IPN structure are guite different in the film-forming property and crystallinity. This is due to the semi-IPN structure can achieve a tight entanglement of the network shape cross-linked PAMPS-Li and linear PEO, disturbing the organization segment region, reduce the crystallinity of PEO, and enhance the amorphous phase. It has been widely acknowledged that the Li⁺ is mainly transported through the amorphous region in polymer. The increased amorphous phase will decrease the energy barrier of segment motion among polymers, and enhance the ability of Li-ion association and dissociation, thus increasing the ionic conductivity.^[42]

The mechanical strength curves of (SI)²PE-6-4 and pure PEO are shown in Figure 6. The pure PEO shows an extremely large



Figure 6. Strain-stress curve of pure PEO and (SI)²PE-6-4.

strain of 560%, more than 5 times of its initial length but a relatively lower stress value of 8 MPa. However, with the blended cross-linked PAMPS-Li, the semi-IPN structured membrane shows a remarkable increased Young's modulus up to nearly 12 MPa and a decreased strain of 250%, indicating improved rigidness. Above results point out that the (SI)²PE membrane shows better mechanical property compared to the bare PEO membrane. This is because of the semi-IPN structure retaining good mechanics.^[26] The 3D interpenetration networks improve the morphology and mechanical stability.

Figure 7a shows the electrochemical window of the $(SI)^2PE-6-4$ membrane, which is stable below 4 V (vs. Li/Li⁺) due to the



Figure 7. (a) LSV curve with the scan rate of 0.5 mV/s and (b) transference number plots of $(SI)^{2}PE-6-4$.

oxidation of the PEO segment at further higher potential. The lithium ion transference number was calculated with parameter values from Figure 7b. And the calculated result is $t_{\rm Li}^+ = 0.77$, suggesting the Li-ion dominating conduction, because the anions are immobilized on the polymer backbones. The reason why t⁺ is less than unity may be for two main reasons: (1) The flexible space among polymer chains allows the short-range moving of the attached anions, causing the motions of negative

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charges. (2) The segmental motion of polyanionic block may happen due to the effect of quantitative amount of plasticizer on the segment activity.^[40]

Electrochemical performance of the (SI)²PE-6-4-assembled battery has been studied. The (SI)²PE-6-4 shows its superiority of a good cycle performance (Figure 8a) at high temperature of



Figure 8. (a) Cycle performance and (b) Charge and discharge curves of the 1st, 20th, 50th, 100th cycle of the LiFePO₄/Li coin cell with (SI)²PE-6-4.

60 °C, with a stable coulombic efficiency of around 100%, and the first charge capacity reaches 140.0 mAh/g which maintains 90.4% after 100 cycles. Figure S2 shows comparison of the cycle performance of cells with commercial liquid electrolyte (1 mol LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC), 1:1, in volume) at 60 °C, which has low coulombic efficiency and sharply decreased capacity, fading after 65 cycles. This is due to the decomposition and side reaction of LiPF₆ within battery above 60 °C. Figure 8b shows the capacity-voltage curves of the 1st, 20th, 50th, 100th charge-discharge cycle. And at the first 20 cycle, the cell shows stable capacity, however, after a long cycle from 50 cycles to 100 cycles, the cell capacity decreases. This may due to the high temperature effect. Even so, the chargedischarge plateau does not show significant broadening, and the potential difference is almost the same, which is due to the stable IPN structure and the high t_{Li}^{+} of the single ion conductor, getting rid of the polarization problem. The discharge capacity after 100 cycles is still 126.6 mAh/g (90.4% of 1st cycle).

3. Conclusions

A new semi-IPN structured single ion conductor electrolyte system with different ratio has been developed, composing of cross-linked PAMPS-Li and linear PEO, forming an interpenetrating 3D network. On one hand, the semi-IPN structure can enhance the mechanical stability and two-phase compatibility as well as decrease the crystallinity. On the other hand, the single lithium ion conduction property contributes to the electrochemical performance, decreasing the polarization of the batteries. The (SI)²PE membrane is homogeneous and flexible. Both good mechanical and ionic conduction properties are obtained. We have studied the crystallinity variety and ionic conductivity change with a series of polyanionic salt concentration. And the optimal ion conductivity of the guasi-solid (SI)²PE system with a drop of limited quantitative plasticizer is 1.34×10^{-5} S/cm at 60 °C. The lithium ion transference number is 0.77, higher than most dual-ion conductors, showing typical single ion transport behavior. What's more, the guasi solid cells with the semi-IPN structured single lithium ion conductor membrane show a stable high-temperature cycle performance, much better than that with commercial liquid electrolyte. We have demonstrated that the combination of SIPE property and Semi-IPN structure has a synergistic effect, and the (SI)²PE membrane can be a promising candidate for future use in stable single ion conductor for the LIBs.

Experimental Section

Preparation of the Cross-Linked PAMPS-Li

The cross-linked PAMPS-Li hydrogel was fabricated by the free radical polymerization. First, the AMPS was dissolved in water to get the solution with the concentration of 1 mol/L, followed by adding equivalent Li₂CO₃ slowly into above solution to lithiate the monomer for forming AMPS-Li monomer under magnetic stirring. Then the cross-linker N, N'-Methylene bisacrylamide (MBA, 4 mol%, Sigma Aldrich) was added to the monomer and initiator ammonium persulfate (APS, 0.1 mol% molar to the monomer). The amount of crosslinker and initiator was calculated by a molar ratio to monomer. Then the mixed solution was transferred into a threenecked flask within silicon oil bath. Replace the air in the flask with nitrogen to eliminate oxygen using dual exhaust pipes and maintain the inert atmosphere. After 10 h polymerization at 70 °C, wash the bulk hydrogel with water and immerse it in water for 3 h to dissolve the unreacted monomer and other impurities. Repeat the wash procedure for three times. The cross-linked PAMPS-Li hydrogel was dried, and the agglomerate particles were obtained. The particles were milled using high energy ball mill (FRITSCH, Germany), and then the cross-linked PAMPS-Li powder was obtained.

Preparation of the (SI)²PE Membrane

Disperse the gradient ratio of PEO (Mn = 600,000, EKEAR, Shanghai, China) and cross-linked PAMPS-Li powder into the ethyl alcohol, and then add water slowly to form the 3D semi-IPN structured mixture, followed by magnetic stirring for 4 h to obtain uniform and viscous hydrogel. Then scrape the gel on the glass plate with bird applicator. Air-dry and then peel the ion-conductor membrane



off, and store at 60 °C in vacuum oven for 3 days to ensure full drying due to that water in PEO is not easy to remove.^[43] Then the solid $(SI)^2PE$ with different complex ratio $((SI)^2PE-x-y)$ membranes were obtained (x-y is the mass ratio of PEO: PAMPS-Li, 8–2, 7–3, 6–4, 5–5, 4–6).

Assemble of the Batteries

The coin cells were assembled with spinel-type LiFePO₄ cathode and Li metal anode. The cathode was composed of LiFePO₄, acetylene black (AB) and polyvinylidene fluoride (PVDF) binder with weight ratio 8:1:1. The dry (SI)²PE membrane was sandwiched between the cathode and the anode. And to make the lithium ion transport in cathode and improve the interface compatibility, a drop of plasticizer was added between the (SI)²PE and cathode interface to assemble the quasi solid battery. And the plasticizer (quantitative amount of 5 ul using pipette) was consisted of ethylene carbonate (EC) and propylene carbonate (PC) (1:1, in volume ratio).

Characterization

The surface morphology of the (SI)²PE membrane was observed by the field emission scanning electron microscopes (FE-SEM, Hitachi, S-4800). The energy dispersive X-ray spectroscopy (EDS) elemental mapping was taken to observe the element distribution of the (SI)²PE membrane's cross section. The weight-average molecular weight (Mw) was determined by a normal laser light scattering (LLS) spectrometer. The differential scanning calorimetry (DSC) curves were measured on a Model STA 449 instrument (NETZSCH Machinery and Instruments Co., Ltd) to investigate the enthalpy change of the membrane. Fourier transform infrared spectroscopy (FTIR, Thermo Fisher Scientific Inc) study was used to study the molecular information in the wavenumber range of 400~ 4000 cm⁻¹. The X-ray diffraction (XRD) results were taken on the Rigaku X-ray diffractometer (XRD, Miniflex600). The mechanical strength was detected and calculated by the Universal Material Measuring Machine (UTM-4000) with a strain rate of 1.66 mm/s.

The ionic conductivity (σ) was tested by electrochemical impedance spectroscopy (EIS) on an electrochemical Solartron workstation. The EIS testing frequency range of $0.1 \sim 10^5$ Hz. The ionic conductivity was calculated by the following equation :[5]

$$\sigma = L/(R_b \times A) \tag{5}$$

where *L* is the thickness of the membrane, R_b is the resistance of the (SI)²PE bulk and A is the area of the stainless steel (SS). Linear Sweep Voltammograms (LSV) was applied to do a study on the electrochemical window, for which the asymmetric cell of Li| (SI)²PE|SS was assembled. The scan rate is 0.5 mV/s.

The symmetric cell of $Li | (SI)^2 PE | Li$ was assembled for the lithium ion transference number (LTN). And the LTN was tested by chronoamperometry methods by an electrochemical workstation (Autolab), and calculated by following equation:[6]

$$t^{+} = \frac{I_{s}(V - I_{0}R_{0})}{I_{0}(V - I_{s}R_{s})}$$
(6)

where t⁺ stands for the transference number, V stands for the polarization voltage of 10 mV applied in this work; I_{0r} , I_{sr} , R_0 , R_s represents the initial and final polarization current and initial and final impedance of the Li/Li symmetric cell, respectively.

To research the electrochemical performance, the CR2016 coin cells were assembled. A battery testing system (NEWARE) was used to achieve the battery charge and discharge. Battery cycle performances at a current rate of 0.2 C in the voltage range of $2.5 \sim 3.7$ V at 60 °C was measured for 100 cycles.

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Conflict of Interest

The authors declare no conflict of interest.

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