Gel Polymer Electrolyte with Semi-IPN Fabric for Polymer Lithium-Ion Battery

Wei-Li Li, Yan-Ming Gao, Shao-Ming Wang

College of Materials and Engineering, Jiangsu Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003

ABSTRACT: A new type of semi-IPN gel electrolyte was prepared by thermal polymerization in this article. At first, the crosslinkable PEG200 (MXPEG) was prepared by condensation reaction, then the crosslinkable components were blent with PMMA and heated under vacuum to form polymer blends with semi-IPN fabric. Differential scanning calorimetry and X-ray diffraction spectroscopy were used to investigate the thermal properties and crystalline/amorphous structure of the prepared polymer blends. With semi-IPN fabric, they present amorphous absolutely. For semi-IPN gel electrolyte, the mechanical and the electrochemical properties are varied with the quantity of absorbed liquid electrolyte. Ion-conductivity behavior for semi-IPN gel electrolyte measured by means of AC impedance spectrum showed that the best data was 1.62×10^{-3} S cm^{-1} at room temperature, and Arrhenius-type relationship was obeyed in the temperature dependence of ionic conductivity. In addition, the electrochemical stability window of the semi-IPN gel electrolyte was 4.6 V. All the properties showed that the prepared semi-IPN gel electrolyte was expected to have applications of electrolyte for lithium-ion polymer secondary batteries. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1027–1032, 2012

Key words: gel polymer electrolyte; crosslinking; semi-interpenetrating network; amorphous; electrochemistry properties

INTRODUCTION

Polymer electrolytes have received considerable attention as electrolyte materials in advanced applications such as high-energy density batteries, fuel cells, and electrochemical sensors. In principle, a polymer electrolyte battery can be formed by sandwiching the electrolyte between a lithium metal (or a composite carbon) anode and a composite cathode.[1] PEO-based electrolyte is the earliest and the most extensively studied system. The complex formation of them is governed by competition between salvation energy and lattice energy of the polymer and the inorganic salt.[2] However, due to the obstacle originates from, first, the high degree of crystallinity which is unfavorable for ionic conduction in these complexes and the second, the low solubility of salt in the amorphous phase,[3] this type electrolyte commonly exhibit conductivities which range from 10^{-8} to 10^{-4} S cm^{-1} at temperature between 40 and 100°C, which excludes practical applications at ambient temperature.

After 30 years hardworking, the most striking advancement in the polymer electrolytes have attained through the incorporation of substantial amounts of plasticizers in the polymer matrix to form gel polymer electrolyte (GPE). The use of PMMA as a main body for gel polymer electrolyte was previously reported by Iijima et al.[4] and by Bohnke et al.[5] They reported ionic conductivity of the order of 10^{-3} S cm^{-1} at 25°C for a homogeneous and transparent GPE. However, all the plasticized polymer electrolytes suffer from poor, gel like mechanical property; producing freestanding film is not possible at higher plasticizer concentration. Crosslinked polymers are found to reduce the solubility of the polymers in organic solvents and also help to trap the plasticizer within the polymer matrix.[6] These merits can restrain the shortcoming of GPE effectively.

With the aim of developing high conductivity polymer electrolyte with sufficient mechanical strength, a new type of GPE with semi-IPN fabric was prepared in this article. Various means of measurements were carried out to examine which was the most important factor to impact the properties of the semi-IPN gel electrolyte.
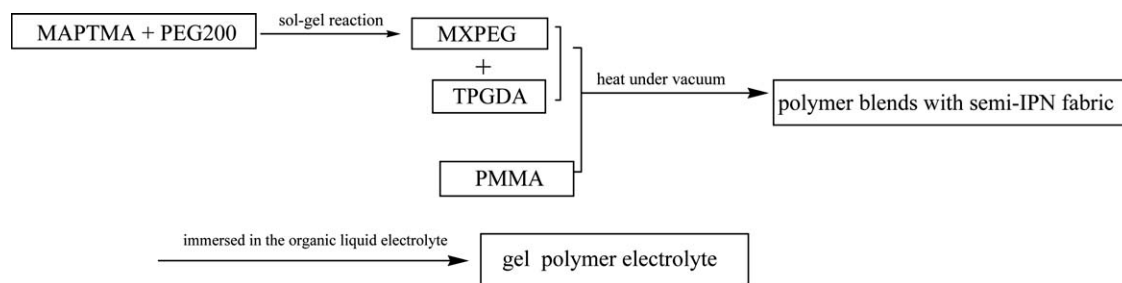
EXPERIMENTAL

Materials

Poly(ethylene glycol) ($M_n = 200$) (Sinopharm Chemical) and *p*-toluenesulfonic acid (AR) (Sinopharm

Scheme 1   The sketch map for the steps of preparation gel polymer electrolyte.

Chemical) were dried at 80°C under vacuum for 24 h before being used, methacryloxypropyltrimethoxysilane(MAPTMS) (Nanjing Shuguang Chemical), tripropylene glycol diacrylate (TPGDA) (Tianjin Tianjiao Chemical) PMMA(M_n, ca.10^5), THF(AR) (Sinopharm Chemical) was dehydrated using 4 Å molecular sieve before being used, liquid electrolyte LB301 (DMC : DEC : EC = 1 : 1 : 1(W/W) LiPF$_6$ 1M, Guotai-Huarong Chemical).

Preparation of gel polymer electrolyte with semi-IPN fabric

Polymer blends with semi-IPN fabric were prepared by thermal polymerization. First, MAPTMS was mixed with PEG200 at 2 : 3 molar ratio, p-toluenesulfonic acid (TPSA) was used to catalyze the reaction. The sol-gel reaction was conducted in a three-neck flask at 50°C for 12 h with magic stirring, and nitrogen gas was continuously purged to prevent oxidation. Then 2% TPGDA was added in. They were blending with PMMA at weight ratio of 1 : 1 in THF solution, AIBN (2,2'-Azobisisobutyronitrile) was added as an initiator. The crosslinking reaction was conducted at 80°C for 3 h under nitrogen gas, then the products were placed in a vacuum oven at 60°C for 24 h for complete reaction. The products present transparent and homogeneous films.

The prepared films were transferred to the glove box and immersed in the liquid electrolyte LB301 to activate. Then the gel polymer films were removed from the electrolyte solution and excess liquid electrolyte on the surface was wiped with filter article. The quantity of absorbed liquid electrolyte was controlled by means of dipping time. For conveniently, the prepared dried semi-IPN films is called SIPN-X-M and the gel polymer electrolyte is GSIPN-X-M-100 which means the S_w of GPE reaches 100.

The preparation procedure of gel polymer electrolyte was listed just like Scheme 1.

Measurements

FT-IR measurements were carried out on BRUKER VECTOR-22 spectrometer at room temperature. The spectra were collected over the range 400–4000 cm^{-1} by averaging 128 scans at a maximum resolution of 2 cm^{-1}.

DSC measurements were carried out by using a DSC Q100 (TA Instruments) (TA Instruments, USA) over a temperature of -100 to 150°C at a scan rate of 10°C/min. All the thermograms were base line corrected and calibrated using Indium metal. The experimental specimens (8–10 mg) were dried at 60°C under vacuum for 24 h before being measured. All the samples were firstly annealed at 120°C for 3 min, cooled to -100°C using liquid nitrogen and then scanned for measurement of T_g.

TGA measurement was carried out by using Perkin–Elmer Diamond TG/DTA over a temperature from 50 to 700°C.

X-ray diffractions analysis of the polymer films were performed using a D/MAX-RA X-ray diffractometer (Rigaku) with 2θ values between 5° and 50°.

Tensile properties of the semi-IPN gel electrolyte were measured through a 10 KN electromechanical tensile testing machine (CMT5104, china) at room temperature. The tensile speed was 40 mm/min.

The ionic conductivity (σ) of the semi-IPN gel electrolyte were determined by AC impedance spectroscopy (EG and G Model 273A potentiostat). It was sandwiched between two parallel stainless steel (SUS) discs (Φ: 1 cm) and mounted in a sealed coin cell to prevent contamination of the sample. The frequency ranged from 100 KHz to 10Hz at a perturbation voltage of 5 mV. The ionic conductivity (σ) was then calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and the electrode area (A) according to the equation $\sigma = 1/AR_b$.

The electrochemical stability window of the semi-IPN gel polymer electrolyte was measured by linear sweep voltammetry (LSV) at a scanning rate of 0.05 V/s. Three electrode-laminated cell was assembled inside a glove box. Stainless steel (SS) was used as working electrode and lithium metal was used both as a counter and as a reference electrode. LSV measurement was carried out using CHI660A (CH Instruments. Inc).
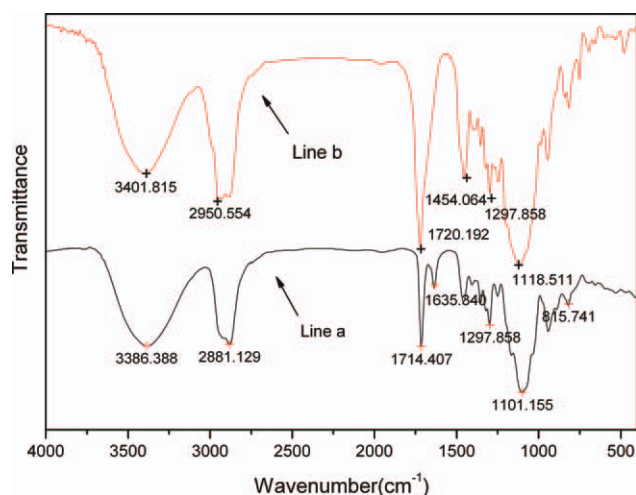
Figure 1 FTIR spectra for (a) MXPEG; (b) SIPN-X-M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 TGA measurement for SIPN-X-M. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

FTIR spectra of the semi-IPN samples

The FTIR spectra of MXPEG, which is the condensation product of MAPTMS and PEG200, and the prepared semi-IPN film SIPN-X-M are present in Figure 1 line(a) and line(b), respectively.

As is seen from line(a), the appearance at 1635 cm^{-1} indicates that C=C bond remains in the MXPEG, which will react when TPGDA is added. The absorption peak at round 1101 cm^{-1} is the superposed absorption of C—O—C and Si—O—C. In addition, the presence of residual silanols in the silica networks, which are capable of hydrogen bond formation, is evidenced in the hybrids by the appearance of the hydroxyl peaks at the 3100–3600 cm^{-1}. While from line(b), it can be seen that
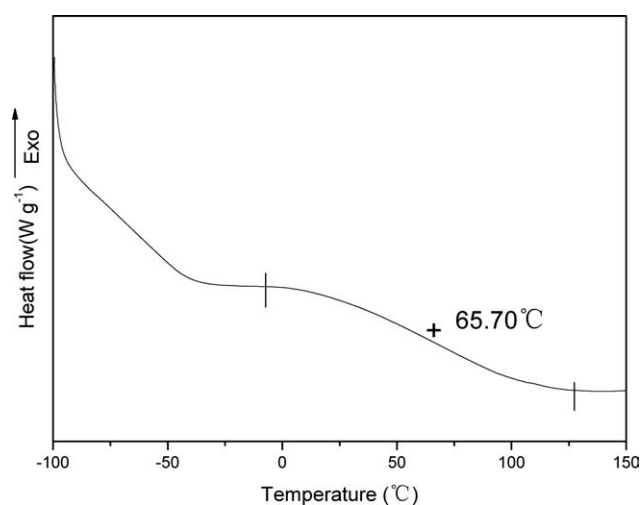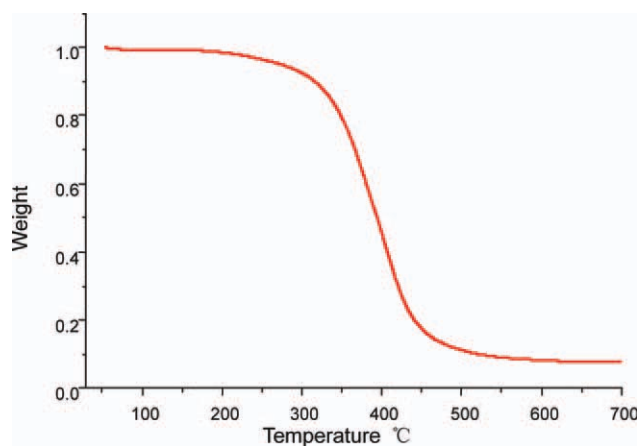
the intensity of absorption peak at around 3400 cm^{-1} decreased with further condensation reaction. The disappearance of absorption peak at 1635 cm^{-1} indicates no unreacted present in the products.

DSC and TGA measurements for the semi-IPN film

Figure 2 presents the DSC thermograms for the dried semi-IPN film. There is no fusion peak present in the temperature range from −100 to 150°C. This contrasts strongly with conventional PEO-based electrolytes which normally display an endothermic melting peat at around 60°C.[7] The absence of a peak is taken as evidence of a fully amorphous structure in the PEO-like crosslinked polymer network. The MATPMS unit is thought to act as an irregular pair in PEG chain and hinders its crystallization. The crosslinked structure also prevents the PEO like
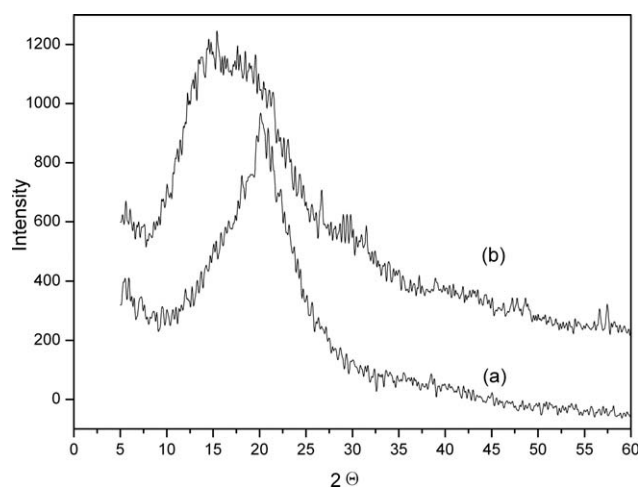

Figure 2 DSC thermograms for SIPN-X-M.

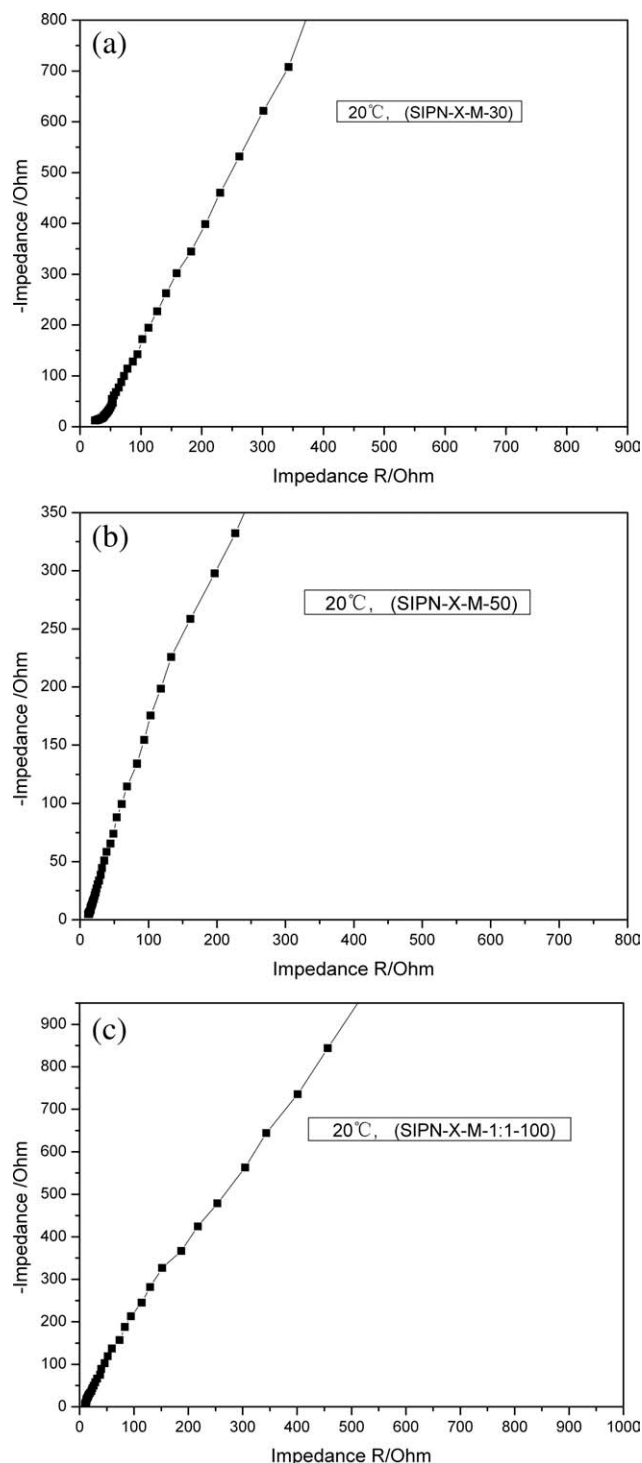**Figure 4** XRD patterns for (a) SIPN-X-M, (b) GSIPN-X-M-100.

Figure 5 AC impedance spectra of semi-IPN gel polymer electrolyte (a) G-SIPN-X-M-1 : 1–30. AC impedance spectra of semi-IPN gel polymer electrolyte (b) G-SIPN-X-M-1 : 1–50 (c) G-SIPN-X-M-1 : 1–100. AC impedance spectra of semi-IPN gel polymer electrolyte.

segments from freely packing into a long-range ordered crystalline structure.[8]

Besides, it can be seen from DSC measurement that there is only one board glass transition temperature for the dried film. With the semi-IPN fabric, the

two polymer segments are tended to entangle with each other, it displays only one board temperature transition ($T_g = 65.70°C$) corresponding to the amorphous region.

To study whether the unreacted remained after being heated under vacuum, TGA measurement was carried out to measure the products, SIPN-X-M. The blending polymer hosts were still stable up to 250°C, and no significant weight loss was observed up to that temperature. After under being heated under vacuum for such a long time, the reaction could be carried on thoroughly, and the unreacted would be volatilized under vacuum.

XRD measurements

XRD measurements have been carried out for the semi-IPN films and the semi-IPN gel electrolyte to examine its nature of the crystallinity.

It can be seen from line (a) and (b) in Figure 4 that there is no sharp crystal diffraction peak for the semi-IPN film and the semi-IPN gel electrolyte. The semi-IPN structure can break the orderly arrangement of polymer chain segments and the two systems show only amorphous phase. This result can be interpreted by considering the Hodge et al. criterion,[9] which establishes a correlation between the height of the peak and the degree of crystallinity. The result of XRD measurement consists to DSC.

In addition, when liquid electrolyte is absorbed, it is seen from line (b) that no peaks corresponding to pure Li salts of the liquid electrolyte appeared in the gel polymer electrolyte which indicates the complete dissolution of liquid electrolyte in the semi-IPN host.

Swelling and electrical measurements of semi-IPN gel polymer electrolyte

Typical AC impedance spectrums for the semi-IPN gel electrolyte varied with the absorption liquid electrolyte using SS blocking electrodes are shown in Figure 5.

The follow equivalent circuit is used to model the experimental response
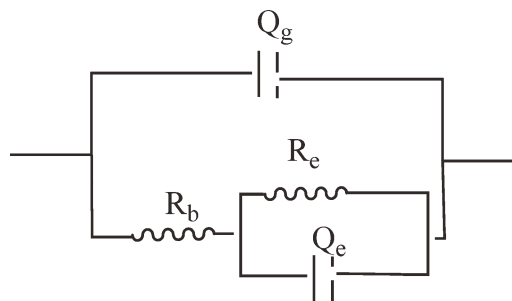
Scheme 2 The equivalent circuit for the semi-IPN gel electrolyte.

TABLE I
Properties of the Mechanical Properties and Ionic Conductivities for the Semi-IPN Gel Electrolytes

Sample	Form	Tensile strength (Mpa)	Breaking extension (%)	σ_T (S cm^{-1})[a]
GSIPN-X-M-30	Solid state film	2.48	84.1	3.7504×10^{-4}
GSIPN-X-M-50	Gel (Freestanding film)	1.72	93.2	9.143×10^{-4}
GSIPN-X-M-100	Gel (Freestanding film)	0.53	178.8	0.00162
GSIPN-X-M-150	Gel(hard to handle)	–	–	–

[a] Measured at 20°C.

In the model, Q_g and Q_e are capacitances arising from the cell geometry, and the electrode-electrolyte interface respectively. R_b and R_e correspond to the bulk resistance of the electrode and electrolyte interface. It is widely accepted that R_b is given by the intercept on the real axis at the high frequency end of the spectrum.[10,11] However, a high-frequency semicircle expected for parallel R_b and Q is not obtained, it is thought that the semi-IPN gel electrolyte is laid between the two parallel stainless steels and no electrochemical reaction has taken. Only the resistive component of the semi-IPN gel electrolyte could be considered at the high amount of plasticizing electrolyte.

The value of ionic conductivity at room temperature and the morphologies for the semi-IPN gel electrolyte varied with the value of S_w are given in Table I.

With the value of S_w increases, the morphology of semi-IPN gel electrolyte changes from self-supported solid-state form to gel-state form. The value of tensile strength decreased with the absorbed liquid electrolyte, however, the value of breaking extension increased with it. The value of ionic conductivity of the semi-IPN gel electrolyte increases with the absorption of liquid electrolyte, and its ionic conductivity reaches highest when the S_w is 100, which is possible to construct an effective local pathway for GPE in the absorbed liquid phase and in gel phase for ionic conduction. However, when the value of S_w reaches 150%, the prepared semi-IPN gel electrolyte film is so sticky and hard to handle, which makes it exclude from practical application.

To study the liquid electrolyte preserve ability, GSIPN-X-M-100 was selected to study the weight loss through evaporation after 24 h. The value of weight reservation percent (R_w) was determined as

follows: $R_w = ((W - W_0)/W_0) \times 100$, where W_0 and W are the weights of the gel polymer electrolyte and gel polymer electrolyte being heated.

It is seen from Table II that the value of R_w for semi-IPN gel electrolyte is decreased with temperature increasing. However, even in 60°C, the value is still able to achieve 85.3%. This Phenomenon may be caused by two factors, first, the high polarity of the polymer blends and similar chemical structure between the PMMA and EC/PC, which will help to absorb the liquid electrolyte in it; second, semi-IPN fabric of the polymer blends will be propitious to let liquid electrolyte be embedded in.

Figure 6 shows the ionic conductivity against the reciprocal absolute temperature for GSIPN-X-M varied with different liquid electrolyte absorption. A linear relationship that confirms the variation in conductivity with temperature follows an Arrhenius relationship, $\sigma = A\exp(-E/k_B T)$, where A is a constant which is proportional to the number of carrier ions, k_B represents the Boltzmann constant and E is the activation energy. This phenomenon also indicates that the charge carriers are decoupled from the segmental motion of the polymer chain and transport through the gel phase and the absorbed liquid
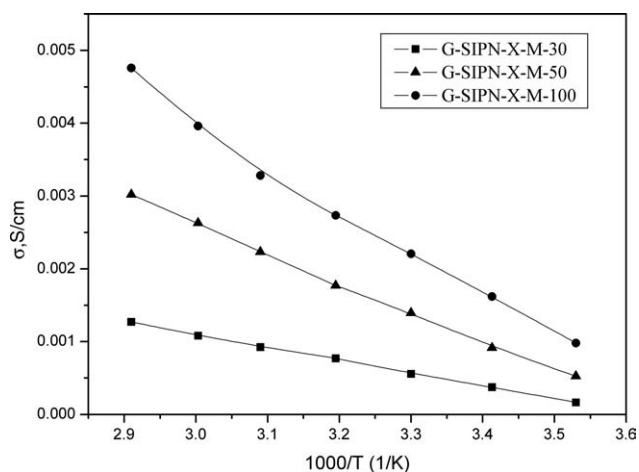
TABLE II
Weight Loss for GSIPN-X-M-100 Through Evaporation

Temperature	Reservation percent of weight
20°C	98.5%
40°C	95.4%
60°C	85.3%

Figure 6 Dependence of conductivity on the reciprocal of temperature for semi-IPN gel electrolyte with different absorption of liquid electrolyte.
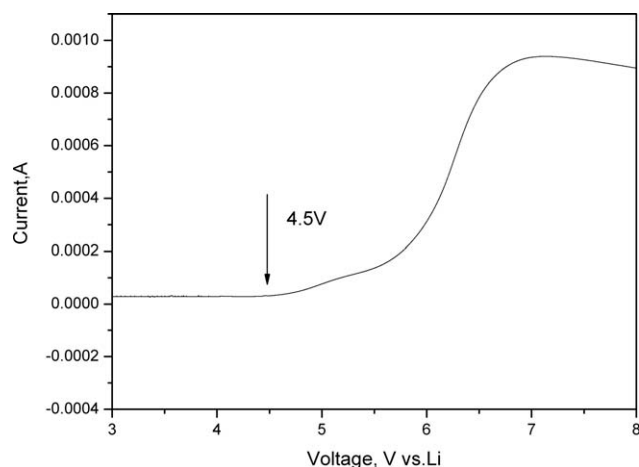
Figure 7 Electrochemical stability window of the semi-IPN gel electrolyte (GSIPN-X-M-100) by linear sweep voltammogram.

phase. The ionic conductivity follows the activated hopping mechanism,[12,13] it is typical AC impedance for gel polymer electrolyte.

Take GSIPN-X-M-100 as an example. The result of LSV is presented in Figure 7. The working electrode potential of the cell was varied from 3.0 to 7.0 V (versus Li) at a scanning rate of 0.05 V/s.

It is evident from Figure 7 that there is no electrochemical reaction in the potential range from 3.0 V to 4.6V. The onset of current flow at 4.9 V is associated with the decomposition of the electrolyte. From this result, the semi-IPN gel electrolyte is thought to be acceptable for high voltage cathode materials, such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$.[14]

CONCLUSION

The gel polymer electrolytes with semi-IPN fabric have been prepared in this article. For a polymer electrolyte battery, it is very important to select poly-

mer electrolyte with good properties, such as good mechanics, high ionic conductivity at room temperature and so on. With the semi-IPN fabric of the polymer blends, the orderly arrangement of PEO-like segments is broken and the system shows amorphous structure. Relative to the former gel polymer electrolyte, the semi-IPN gel electrolyte can not only retain the good mechanics, but also absorb a mass of liquid electrolyte to withstand a highly ionic conductivity. Their mechanical and electrochemical properties varied with the liquid electrolyte absorption. When value of S_w is 100, the prepared semi-IPN gel electrolyte shows good properties for application in lithium-ion polymer batteries, and further investigations in application are in progress.

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