

# A Single Ionic Conductor Based on Nafion and Its Electrochemical Properties Used As Lithium Polymer Electrolyte

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Received: September 5, 2003; In Final Form: November 20, 2003

In an attempt to raise the transport number of  $\text{Li}^+$  to nearly unity in solid polymer electrolytes, commercial perfluorinated sulfonate acid membrane Nafion 117 was lithiated and codissolved with copolymer poly-(vinylidene fluoride)hexafluoropropylene. The effect of fumed silica on the physical and electrochemical properties of the single ion conduction polymer electrolyte was studied with atom force microscopy, fourier transform infrared spectroscopy, differential scanning calorimetry, and electrochemical impedance spectroscopy. It was confirmed that the fumed silica has an obvious effect on the morphology of polymer electrolyte membranes and ionic conductivity. The resulting materials exhibit good film formation, solvent-maintaining capability, and dimensional stability. The lithium polymer electrolyte after gelling with a plasticizer shows a high ionic conductivity of  $3.18 \times 10^{-4}$  S/cm.

## 1. Introduction

Polymer electrolytes have received considerable attention in advanced material applications such as high-energy density batteries.<sup>1,2</sup> Recently, gel polymer electrolytes with high ionic conductivity of about  $10^{-3}$  S/cm at room temperature have been reported.<sup>3–5</sup> Particularly, polymer electrolytes based on poly-(vinylidene fluoride)hexafluoropropylene copolymer (PVDF–HFP) have received much attention<sup>6–8</sup> since Gozdz et al. proposed that the PVDF–HFP film was prepared by solution casting and then reswollen in Li salt electrolyte solution. High ionic conductivity can be obtained this way while maintaining good mechanical properties at room temperature.<sup>9,10</sup> However, a disadvantage is that both anions and cations are mobile in these bi-ionic systems, which implicates the low cationic transport number. In view of applications, a single ionic conductor with high ionic conductivity would be more preferred to employ. Recently, many research interests were put on finding some new single ion electrolytes, for instance, using carboxylate or sulfonated anions bonded to a polymer matrix in combination with mobile cations.<sup>11–13</sup>

Commercial Nafion 117 film is a perfluorinated sulfonate ionomer, which is used in a large variety of electrochemical and chemical applications with excellent temperature and chemical stability. Methods for recasting films of Nafion have been reported during the past few years.<sup>14–16</sup> Dissolution at high temperature under high pressure is the major procedure to introduce. But the recasting film is brittle and dissolves readily in many polar solvents at room temperature.<sup>14</sup> To settle the problem, a polar solvent with a high boiling point can be added.

This work is to report the results of ionic conductivity measurements of a single ionic conductor based on recasting Nafion film. The procedure comprises dissolving Nafion–Li film, codissolving a block copolymer in an organic media, and then casting the films. Replacing the lithium salt with a polyelectrolyte offers performance advantages related to the

prevention of salt depletion and ionic aggregation. Since the group  $\text{SO}_3^-$  is covalently bound to a polymer backbone chain and cannot freely migrate in polymer electrolyte, the polymer electrolyte system is expected to be a single ionic conductor. PVDF–HFP was added into Nafion as a preeminent candidate to form the eutectic mixture, which could enhance the flexibility and toughness properties for the composite system. In the composite polymer electrolyte, fumed silica was also used as an addition. Many related works have testified that fumed silica used as filler could noticeably improve mechanical strength, ionic conductivity, and interfacial stability.<sup>17–21</sup> The mechanical and electrochemical properties of the composite polymer electrolyte were investigated with atom force microscopy (AFM), fourier transform infrared (FTIR), differential scanning calorimetry (DSC), and electrochemical impedance spectroscopy (EIS).

## 2. Experimental Section

**2.1. Materials and Pretreatment.** Nafion 117 film (Du Pont), propylene carbonate (PC), and lithium perchlorate (99%) were obtained from Aldrich. Kynar 2801, a copolymer of PVDF–HFP with 12% HFP, was purchased from Elf-Atochem. The fumed silica ( $\text{SiO}_2$ , 12-nm primary particle size) was purchased from Fluka Chemika. Dimethyl sulfoxide (DMSO, analytical reagent) and dibutyl phthalate (DBP, analytical reagent) were purchased from Beijing Chemical Reagent Factory, China. PVDF–HFP and  $\text{SiO}_2$  were dried at 70 °C under vacuum for 48 h,  $\text{LiClO}_4$  dried under vacuum at 120 °C for 48 h, and PC kept for 6 days on a fresh molecular sieve (4 Å) prior to use, respectively.

**2.2. Preparation of the Nafion–Li Solvent.** To obtain reproducible results, Nafion films were cut into little grains and boiled in 3%  $\text{H}_2\text{O}_2$  at 70–80 °C, washed with distilled water, immersed into 0.5 M  $\text{H}_2\text{SO}_4$  at 70–80 °C, and washed with distilled water. Each step was 1 h long. Then the grains were immersed into 1 M  $\text{LiOH}$  for 24 h to transform the grains into Nafion–Li form at room temperature. The lithiating grains were dried at 70 °C for 48 h under vacuum after they were rinsed with distilled water thoroughly.

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The dissolution of films was briefly described as follows. The solvent (DMSO) with the dried polymer grains was stirred for 2 h under a nitrogen atmosphere at 170–180 °C. The resulting solution (Nafion–Li) was then cooled to 60–70 °C, filtered, and kept in seal. The Li<sup>+</sup> ion content in the Nafion–Li was detected with atomic absorption spectrometry (PekinerElmer AA 800, USA).

**2.3. Preparation of Nafion–Li and PVDF–HFP Copolymer Polymer Electrolyte.** The Nafion–Li polymer electrolyte membranes and their derived polymer electrolyte blended with PVDF–HFP copolymer were prepared by a solvent-casting method.<sup>9,10</sup> PVDF–HFP copolymer, silica, DBP, and Nafion–Li solution were stirred in specific weight ratios for 6–8 h at 60 °C. All percentages for the additives were normalized with respect to the weight of the copolymer. The resulted viscous slurry was doctor bladed onto a glass plate. After the membrane dried at 130 °C under vacuum for about 30 min, the wet membrane became dry, flexible, and translucent. Then the membranes were punched into circular pieces and immersed in a methanol solvent to extract DBP (if there were) at room temperature. When the extraction was finished, these regular-shaped membranes were dried at 60 °C for 24 h and stored in a vacuum.

All preparations and measurements of samples were made in a drybox (M. Braun, GmbH, Germany) filled with nitrogen, in which moisture condition was lower than 1 ppm.

**2.4. AC Impedance Measurement.** Ionic conductivity of the composite polymer electrolyte was determined from complex impedance spectra measured using Autolab with PGSTAT 30 (Eco Chemie, The Netherlands) with the help of frequency response analysis (FRA) system software under an oscillation potential of 10 mV over a frequency range of 1 MHz–0.1 Hz. A laboratory-built Teflon cell holder with a stainless steel electrode (SS 304) was used (the design of the holder is shown in Figure S1 in Supporting Information). AC impedance experiments were performed on the holder in the temperature range of 20–85 °C. Before the experiment, the holder was subjected to heat treatment at 80 °C for 24 h and then cooled slowly to room temperature. The cell was left about 1 h to reach thermal equilibrium before each experiment. The temperature of the entire setup was adjusted by Superthermostat (Chongqing Experimental Instrument Factory, P. R. China), which with calibration gave the samples' temperature within  $\pm 0.25$  °C. The thickness of the composite membrane was about 100  $\mu\text{m}$ , and the area was about 0.785 cm<sup>2</sup>. For comparison, some samples were activated with PC within regular time and dried with filter paper before being subjected to the conductivity measurements.

**2.5. FTIR Measurements.** Samples were prepared on a KBr substrate for FTIR study by solvent casting. Infrared spectra were obtained with a FTIR spectrophotometer (Nicolet FTIR-520FT) and recorded by averaging 64 scans with a wavenumber resolution of 2 cm<sup>-1</sup>.

**2.6. DSC Measurements.** Thermal behavior of perfluorinated sulfonate Li ionomer and its blend of polymer electrolyte films were studied by means of DSC using PERKIN-ELMER-7 Series Thermal Analysis System. Samples were loaded in sealed aluminum pans, and measurements were taken within the –70–150 °C temperature range at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere.

**2.7. AFM Measurements.** AFM imaging was carried out in a contact mode (Digital Instruments Nanoscope III), using a 14- $\mu\text{m}$  scanner along with Si cantilevers and a silicon nitride tip (Digital Instruments model NP). Each image was composed of 256 pixels in each direction in the place of the surface.

**TABLE 1: Properties of Nafion–Li/PVDF–HFP SPEs**

| sample | Nafion–Li/PVDF–HFP (w/w) | Li <sup>+</sup> (wt %) | conductivity (S/cm)   | T <sub>g</sub> (°C) |
|--------|--------------------------|------------------------|-----------------------|---------------------|
| 1a     | 100/0                    | 0.574                  | $1.12 \times 10^{-6}$ | 81.0                |
| 2a     | 62.5/37.5                | 0.359                  | $5.09 \times 10^{-6}$ | 29.7                |
| 3a     | 45.5/54.5                | 0.262                  | $3.82 \times 10^{-6}$ | 22.1                |
| 4a     | 21.8/78.2                | 0.125                  | $8.19 \times 10^{-7}$ | 18.0                |
| 5a     | 5.7/94.3                 | 0.033                  | $1.07 \times 10^{-8}$ |                     |

**TABLE 2: Properties of Nafion–Li/PVDF–HFP/SiO<sub>2</sub> SPEs**

| sample | Nafion–Li/PVDF–HFP/SiO <sub>2</sub> /DBP (w/w) | Li <sup>+</sup> (wt %) | conductivity (S/cm)   | T <sub>g</sub> (°C) |
|--------|--|------------------------|-----------------------|---------------------|
| 1b     | 60.3/36.1/3.6/0                                | 0.347                  | $3.82 \times 10^{-6}$ | 33.2                |
| 2b     | 43.2/51.6/5.2/0                                | 0.248                  | $3.67 \times 10^{-6}$ | 24.2                |
| 3b     | 20.2/72.7/7.3/0                                | 0.116                  | $1.02 \times 10^{-6}$ | 20.0                |
| 4b     | 5.7/85.7/8.6/0                                 | 0.033                  | $6.59 \times 10^{-8}$ | 39.1, 100.4         |
| 5b     | 3.1/4 6.1/4.6/46.1                             | 0.033 <sup>a</sup>     | $6.59 \times 10^{-9}$ |                     |

<sup>a</sup> After methanol extraction of DBP.

### 3. Results and Discussion

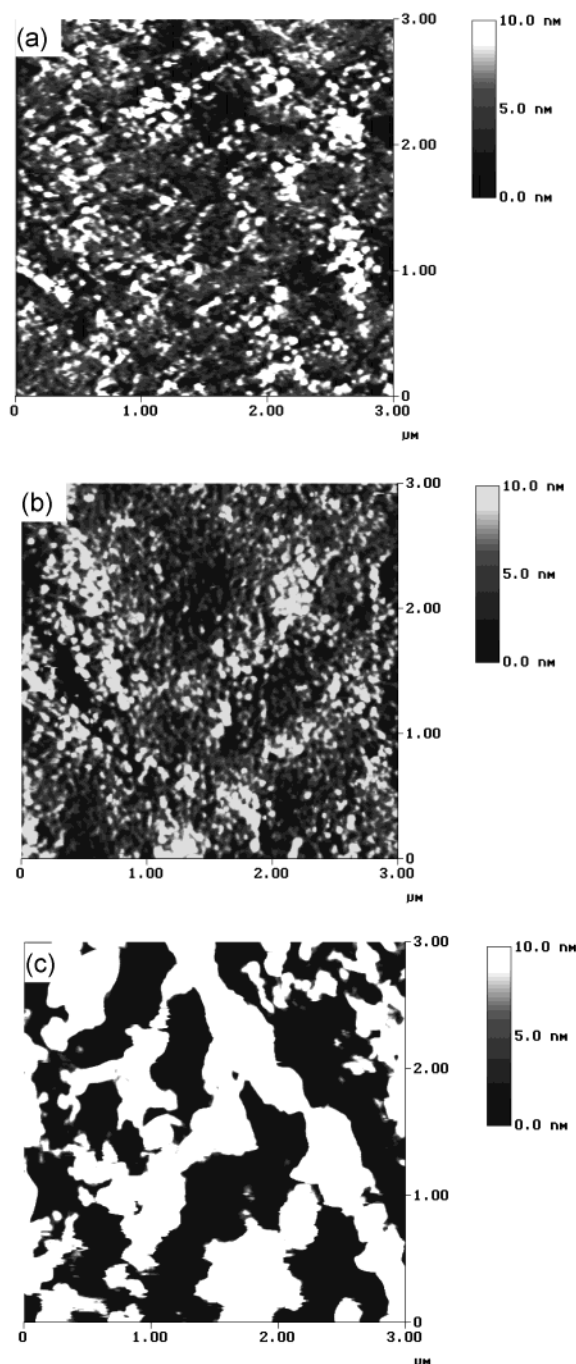
**3.1. Composition and Surface Morphology of the Blend Polymer Electrolyte.** In the present article, we have successfully prepared the solution of Nafion–Li with DMSO as mentioned above and then codissolved the solution with the PVDF–HFP copolymer. The Nafion–Li/PVDF–HFP blend polymer was used as the matrix of lithium polymer electrolyte, in which PC was added as a plasticizer and SiO<sub>2</sub> as an inorganic filler. The compositions of various polymer electrolytes based on the copolymer were listed in Tables 1 and 2. A porous Nafion–Li/PVDF–HFP/SiO<sub>2</sub>/DBP blend polymer electrolyte, which is similar to the Bellcore formulation,<sup>10</sup> was also made for comparative purposes (sample 5b in Table 2).

AFM was used to characterize the solid polymer electrolytes (SPEs) film surface morphology.<sup>6–8,22</sup> Figure 1 shows the AFM images under three conditions: (a) without SiO<sub>2</sub>; (b) with SiO<sub>2</sub>; and (c) with SiO<sub>2</sub> using extraction of DBP, respectively. When SiO<sub>2</sub> was added, SPEs show a smooth film with sparse pores (compare parts a and b of Figure 1). By comparison of part c of Figure 1 with parts a and b, it was observed that its surface is rougher and many submicron pores appear after DBP extraction. This can be considered that the addition of nanoparticles helps the formation of micropores.<sup>21</sup>

**3.2. The Solvent Uptake Ability of the Blend Polymer Electrolyte.** Adding high-permittivity molecules PC to SPEs as a plasticizer to form gel polymer electrolytes (GPEs) is one successful approach to increase the amorphous nature and ionic conductivity.<sup>23</sup> Related studies have reported that the presence of high-permittivity molecules can elevate the ionic conductivity but also bring side effects of reduced dimensional stability, mechanical strength, and poor film formation.<sup>24</sup> In this work, SiO<sub>2</sub> (10 wt %) was added to the Nafion–Li/PVDF–HFP composite polymer electrolyte to overcome the shortcomings. The reason for the mechanical strength enhancement is clearly due to the formation of an interpenetrating network, a well-known property of the silica nanoparticle.<sup>17,21</sup> At the same time, the uptake of PC for the film with SiO<sub>2</sub> has been enlarged. Figure 2 shows the relationship of PC uptake with the time for the different films and the corresponding simulated curves. The amount of uptake ( $\eta$ ) is calculated as eq 1

$$\eta = \frac{(W_t - W_0)}{W_0} \times 100\% \quad (1)$$

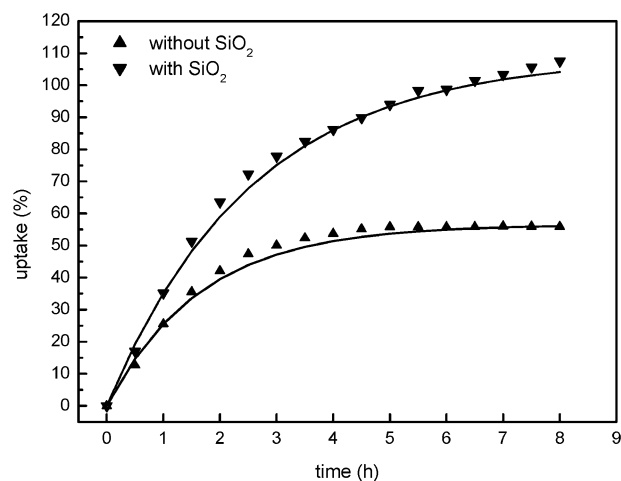
where  $W_0$  and  $W_t$  are the weight of films before and after absorbed PC.



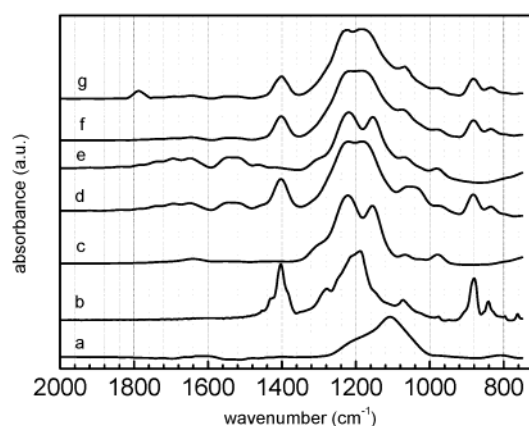
**Figure 1.** Three-dimensional AFM images of different films: (a) Nafion-Li/PVDF-HFP blends without SiO<sub>2</sub>; (b) Nafion-Li/PVDF-HFP blends with SiO<sub>2</sub>; and (c) Nafion-Li/PVDF-HFP blends with SiO<sub>2</sub> after extraction of DBP.

The results illustrate the amount of PC uptake was increased to nearly 40 wt % immediately after SiO<sub>2</sub> was added into the film. It suggests that nano-SiO<sub>2</sub> can facilitate the uptake of PC. So the amount of PC uptake in all GPE samples is fixed at about 40 wt % within regular time in this work.

**3.3. FTIR Study.** Figure 3 presents the FTIR spectra of PVDF-HFP, SiO<sub>2</sub>, Nafion-Li, and the complexes, respectively. The main bands that occur in these spectra are listed in Table 3.<sup>17,21,25–28</sup> The characteristic vibration bands of PVDF-HFP are at about 1402 cm<sup>-1</sup> for CF groups and about 1200 cm<sup>-1</sup> for CF<sub>2</sub> groups (Figure 3b).<sup>29,30</sup> The absorption band at 840 cm<sup>-1</sup> is assigned to the characteristic frequency of vinylidene groups. When Nafion-Li is mixed with PVDF-HFP, the doublet bands



**Figure 2.** The relationship of PC uptake with the time for different polymer blend films: (▲) without SiO<sub>2</sub> and (▼) with SiO<sub>2</sub>. Simulated curves are shown as solid lines.



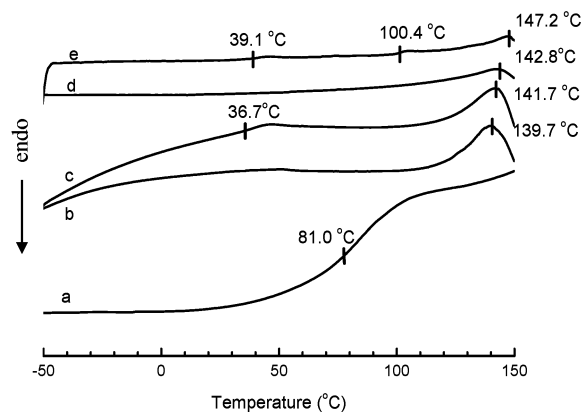
**Figure 3.** The FTIR spectra of (a) SiO<sub>2</sub>, (b) PVDF-HFP, (c) Nafion-Li, (d) Nafion-Li/PVDF-HFP (1:11), (e) Nafion-Li/SiO<sub>2</sub> (9:1), (f) Nafion-Li/PVDF-HFP/SiO<sub>2</sub> (1:11:1.1), (g) and Nafion-Li/PVDF-HFP/SiO<sub>2</sub>/PC (about 25.9:30.96:3.1:40).

**TABLE 3: Assignations of the Vibrational Bands in the FTIR Spectrum of Nafion-Li, SiO<sub>2</sub>, PVDF-HFP, and Their Complexes**

| wavenumbers/cm <sup>-1</sup> | vibration                                       |
|------------------------------|---|
| 1402                         | V <sub>s</sub> (CF <sub>2</sub> ) in PVDF-HFP   |
| 1160–1320                    | CF <sub>2</sub> -vibrations in PVDF-HFP         |
| 1300                         | V <sub>a</sub> (SO <sub>3</sub> ) in Nafion-Li  |
| 1210                         | V <sub>a</sub> (CF <sub>2</sub> ) in Nafion-Li  |
| 1187                         | CF <sub>2</sub> -vibrations in PVDF-HFP         |
| 1140                         | V <sub>s</sub> (CF <sub>2</sub> ) in Nafion-Li  |
| 1000–1100                    | V (–Si–O–Si–) in SiO <sub>2</sub> nanoparticles |
| 960, 980                     | V (C–O–C) in Nafion-Li                          |
| 1060                         | V <sub>s</sub> (SO <sub>3</sub> ) in Nafion-Li  |
| 880                          | V (C=CH <sub>2</sub> ) in PVDF-HFP              |

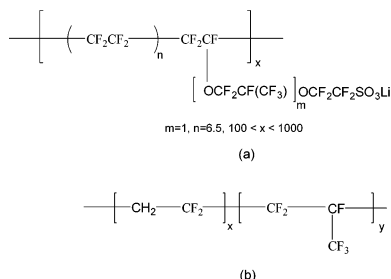
at about 1140 and 1210 cm<sup>-1</sup> (CF<sub>2</sub> symmetric and asymmetric stretching vibration in Nafion-Li) transform into a wide band (Figure 3d). The disappearance of doublet bands and shifting of bands indicate that the interaction between Nafion-Li and PVDF-HFP exists. Vibrational bands associated with the SO<sub>3</sub><sup>-</sup> groups can give information about the cationic transport mechanism and the coordination behaviors.<sup>26,31,32</sup> Unfortunately, the asymmetric stretching vibrations of the SO<sub>3</sub><sup>-</sup> groups are masked by the strong CF<sub>2</sub> bands vibrations at 1300 cm<sup>-1</sup>. A weak band at about 1060 cm<sup>-1</sup> is assigned to the symmetric stretching vibration of SO<sub>3</sub><sup>-</sup>, which shows that the Li<sup>+</sup> ions are bonded asymmetrically in Nafion.<sup>24</sup> When Nafion-Li is mixed with PVDF-HFP and/or SiO<sub>2</sub>, increments of the intensity and





**Figure 4.** DSC curves of (a) Nafion-Li, (b) PVDF, (c) PVDF-HFP/SiO<sub>2</sub> (1:9) complex, (d) Nafion-Li/PVDF-HFP (1:11), (e) and Nafion-Li/PVDF-HFP/SiO<sub>2</sub> (1:11:1.1), with a scan rate of 10 °C min<sup>-1</sup>.

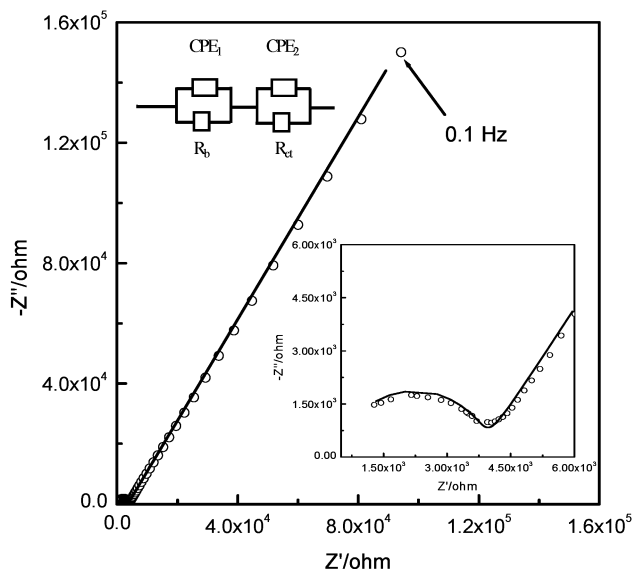
### CHART 1. Structural Formulas (a) of Nafion-Li Polymer and (b) PVDF-HFP Copolymer



upshift for the  $V_s$  ( $\text{SO}_3^-$ ) band have been observed in parts e and f of Figure 3. The results mean that more and more free  $\text{Li}^+$  ions emerge.<sup>33,34</sup> When plasticizer PC was introduced into the system, higher free ions and aggregates could be observed in Figure 3g. The peak at about 1788  $\text{cm}^{-1}$  is assigned to the carbonyl characteristic absorption peak of PC.<sup>15,28</sup> The above analysis proved the evidence for the formation of polymer complexes.

**3.4. Thermal Properties.** The DSC measurements were carried out to analyze the glass transition temperature and phase behavior. Figure 4 shows DSC traces for PVDF-HFP, Nafion-Li, and the blend polymer with SiO<sub>2</sub>, respectively. The glass-transition temperatures ( $T_g$ ) of the SPE samples are listed in Tables 1 and 2. The Nafion-Li and PVDF-HFP polymers have similar polymer backbone structures, as shown in parts a and b of Chart 1. For the eutectic mixture,  $T_g$  is expected to be intermediate between that of two components.<sup>7,9</sup> As shown in Figure 4a,  $T_g$  is 81.0 °C for the Nafion-Li film. In the case of PVDF-HFP that was cast from acetone,  $T_g$  is not observable by DSC for its semicrystalline (Figure 4b).<sup>27</sup> Figure 4d shows that  $T_g$  is not observable in the temperature range for the Nafion-Li/PVDF-HFP blend film. After the SiO<sub>2</sub> addition,  $T_g$  changes to 36.7 and 39.1 °C in parts c and e of Figure 4, respectively. This suggests that the interactions between the polymer chains and nano-SiO<sub>2</sub> exist and that the two polymers can be finely mixed.

**3.5. Conductivity.** EIS was used to characterize the electrochemical behavior of the single ionic conductor based on Nafion-Li/PVDF-HFP blends. Figure 5 illustrates typical EIS response for the Nafion-Li/PVDF-HFP composite polymer electrolyte membrane in a symmetry cell. As illustrated in the inset of Figure 5, the profile shows a depressed semicircle starting from the origin of the plot in the high-frequency range



**Figure 5.** Impedance plots for the Nafion-Li/PVDF-HFP/PC (27.3:32.7:40) gel polymer electrolyte. Simulated curves are shown as solid lines. Its corresponding equivalent circuit and the enlarged data in high frequency are shown in inset. Symbols  $Z'$  and  $Z''$  refer to the real and imaginary components;  $R_b$  and  $R_{ct}$  stand for the resistances of Li ion migration in electrolyte bulk and charge transfer through interface between SS electrode and electrolyte;  $\text{CPE}_1$  and  $\text{CPE}_2$  are associated with the bulk-electrolyte and the double-layer capacitances, respectively.

and a straight line inclined at constant angle to the real axis in the low-frequency range. So a single (RC)(RC) circuit may give adequate description of the ac response.<sup>35-38</sup> Nevertheless, the constant phase element (CPE) was necessarily introduced to account for the nonideality of the interface between the electrode and electrolyte in the practical impedance spectrum.<sup>39,40</sup> As shown in the inset of Figure 5, the equivalent circuit consists of a parallel circuit of  $\text{CPE}_1$  and the bulk-electrolyte resistance ( $R_b$ ) in series with a parallel circuit of  $\text{CPE}_2$  and the charge-transfer resistance ( $R_{ct}$ ). The  $\text{CPE}_1$  and  $\text{CPE}_2$  may be associated with the bulk-electrolyte and the double-layer capacitances, respectively.

The impedance of a CPE can be expressed as following

$$Z_{\text{CPE}} = A(j\omega)^{-n} \quad (2)$$

$$\alpha = (1 - n)\frac{\pi}{2} \quad (3)$$

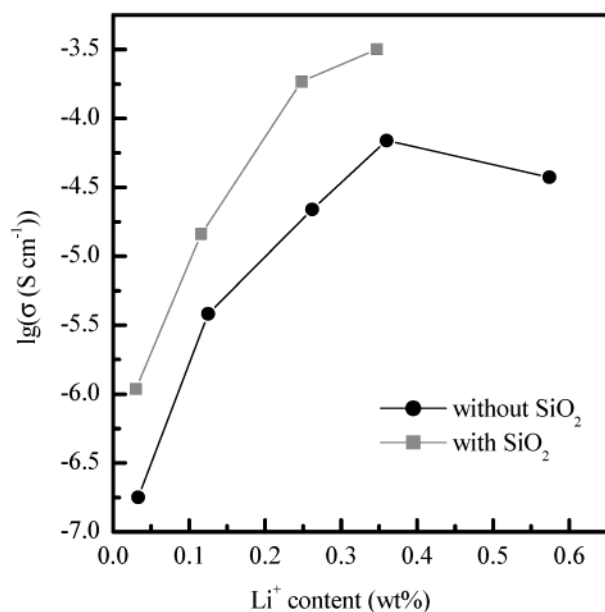
where  $A = C^{-1}$  only when  $n = 1$ , and  $n$  is related to  $\alpha$  (the deviation from the vertical of the line in the  $Z'$ - $Z''$  plot).  $n = 1$  indicates a perfect capacitance, and lower  $n$  values directly reflect the roughness of the electrode used.

Hence, with the help of the FRA system software, the equivalent circuit was used to fit the experiment data. The bulk-electrolyte resistance  $R_b$  and CPE can be estimated from this fitting procedure. The ionic conductivity  $\sigma$  of the polymer electrolyte is calculated by

$$\sigma = l/(AR_b) \quad (4)$$

where  $l$  is the thickness of the blend polymer electrolyte film and  $A$  is the area of the SS electrode.

As shown in Table 1, the ionic conductivity increases with an increase of  $\text{Li}^+$  ion content in the SPEs. But, the sample 1a has very low ionic conductivity ( $1.12 \times 10^{-6}$  S/cm), which is free of PVDF-HFP. In this work, the introduction of PVDF-HFP into Nafion-Li units is intended to enhance the flexibility

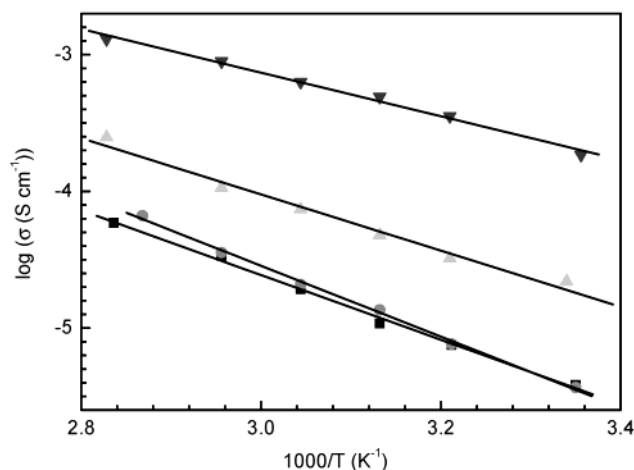


**Figure 6.** The Li<sup>+</sup> content of gel polymer electrolyte without SiO<sub>2</sub> (—●—) and with SiO<sub>2</sub> (—■—) dependence on the ionic conductivity.

and toughness properties of the eutectic mixture system. This cosolvent effect was found to have significant influences on the electrochemical behavior of the polymer electrolyte based on the ionomer.<sup>41</sup> It could induce the ionic interactions between the matrix polymer and Li<sup>+</sup> ion, which has been illustrated with FTIR and DSC in Figures 3 and 4. Thus, the charge carriers number increase as well as the ionic conductivity. Table 2 shows that the ionic conductivity increases slightly after SiO<sub>2</sub> addition. The results could be attributed to the special function surface of nano-SiO<sub>2</sub>. It is known that nanoscopic fumed silica particles aggregate to form an open three-dimensional network structure which provides for the minimally impeded ion-transport properties.<sup>17–21</sup> When dispersed in the polar Nafion–Li/PVDF–HFP blends, the fumed silica forms the three-dimensional network structure that enhances the mechanical properties of the composite system also. The porous polymer electrolyte prepared by extraction of DBP has the lowest ionic conductivity (10<sup>–9</sup> S/cm). In the same way, the CPE<sub>1</sub> about the capacity of bulk polymer electrolyte can be obtained and is available in Supporting Information (Tables S1 and S2, respectively), which is related to cationic migration and dielectric polarization.

Figure 6 illustrates the dependence of ionic conductivity on Li<sup>+</sup> ion content in GPEs (the error data are available in Supporting Information). Compared with SPEs, the GPEs have higher ionic conductivity. As shown in Figure 6, the highest ionic conductivity could get up to 3.18 × 10<sup>–4</sup> S/cm at room temperature, the typical value of ionic conductivity commercially available. The results suggest that Li<sup>+</sup> ion transportation mostly takes place in the gel region within GPEs system.<sup>42–44</sup> High ionic conductivity means the enhancement of the amount of free Li<sup>+</sup> ions, or the increasing flexibility of polymer chains to promote ion transportation. This implies that high ionic conductivity can obtain for single ionic conductor under the help of nanoparticles and reasonable molecule design. The GPEs for the sample 5b in Table 2 made with extraction have a 5.8 × 10<sup>–6</sup> S/cm ionic conductivity, which shows that the porous film structure has little positive effect to enhance the ionic conductivity in this system.

To characterize the transport properties of the electrolyte, ionic conductivity as a function of the temperature is further studied. Figure 7 shows Arrhenius representations for the



**Figure 7.** Arrhenius plot of the ionic conductivity for several investigated polymer electrolytes: (■) Nafion–Li/PVDF–HFP (45.5:54.5), (●) Nafion–Li/PVDF–HFP/SiO<sub>2</sub> (43.2:51.6:5.2), (▲) Nafion–Li/PVDF–HFP/PC (27.3:32.7:40), (▼) and Nafion–Li/PVDF–HFP/SiO<sub>2</sub>/PC (25.9:30.96:3.1:40).

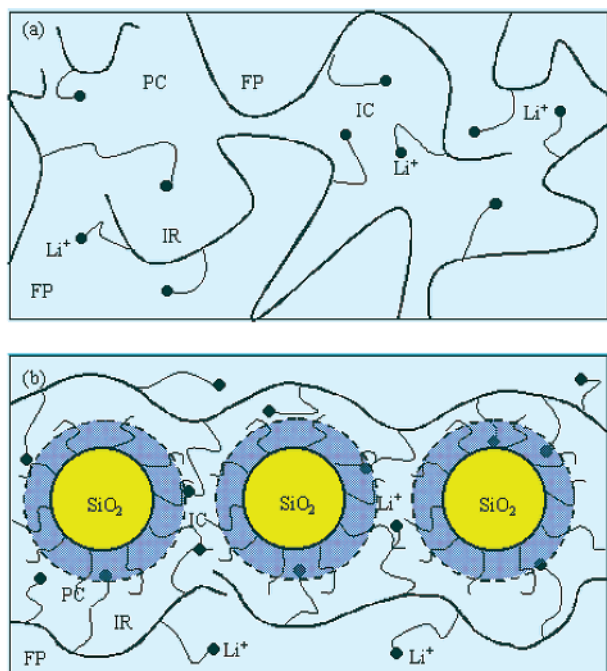
temperature dependence of the ionic conductivity. The dependence for all investigated compositions can be fitted reasonably by a straight line in this temperature range. The correlation coefficients (*R*<sup>2</sup>) are in the range of 0.98–0.99. The linear relationship suggests that the conductivity is thermally activated. The conductivity relationship can be expressed as

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where  $\sigma_0$  is the pre-exponential factor and  $E_a$  is the activation energy.

The activation energy values  $E_a$  calculated from eq 5 are 19 and 20 kJ/mol for SPE films without and with SiO<sub>2</sub>, and 16 and 15 kJ/mol for GPE films without and with SiO<sub>2</sub> (error < 5%), respectively. It suggests that SiO<sub>2</sub> does not sharply change the mechanism for ion conduction in Nafion–Li/PVDF–HFP blends. After gelling with PC, the GPEs have low activation energies for ionic transport. The relatively low active energies suggest that its conductivity mechanism is similar to that in low molecular weight electrolyte.<sup>15</sup> The different activation energies for the SPEs and GPEs suggest the local dynamics of lithium ion transport is somewhat different. From the linear behavior seen in Figure 7 and the discussion related to Tables 1 and 2 and Figure 6, it can be concluded that the lithium ion conductivity mechanism is directly related to the fraction of PVDF–HFP and plasticizer present in the composite system and not so much to the dynamics of the polyelectrolyte chains.

A schematic diagram was used to explain the important effects of SiO<sub>2</sub> and PVDF–HFP on ionic conductivity of composite polymer electrolyte as shown in Figure 8. From the figure, we can see that the fluorocarbon phase, interfacial region, and ionic clusters regions coexist in the polymer blends. The fluorocarbon phase consists of the polymer backbone. The interfacial region is mixed with side chains, PC, and sulfonate groups that are not active as exchange sites. The ionic clusters region is where most of the absorbed PC resides. Adding SiO<sub>2</sub> into the blends could have two effects on ionic conduction with its special function. One is to modify the polymer blends microstructure at the interfacial region through the interactions between the polymer chain and electronegative SiO<sub>2</sub>, and the other is to offer a large surface to absorb more high-permittivity plasticizer PC, which forms a facilitated passage for ionic transport on the nanoparticles surface. The results could be



**Figure 8.** The two models proposed for the interaction between polymer and PC in the Nafion-Li/PVDF-HFP blend polymer electrolyte membrane (a) without SiO<sub>2</sub> and (b) with SiO<sub>2</sub>. The fluorocarbon phase (FP), interfacial region (IR), and ionic clusters (IC) are shown in it.

supported by the FTIR and DSC measurements. These locally induced structural modifications result in the increase of the number of free Li<sup>+</sup> ions, which can move fast throughout PC on the SiO<sub>2</sub>-extended surface as illustrated in Figure 8b. To provide further support for our hypothesis, electrochemical measurements for the blend polymer electrolyte are currently in progress.

#### 4. Conclusions

In this work, we present a composite polymer electrolyte system where conductivity is based on the single ionic conductor principle. Nafion film was lithiated, codissolved with the copolymer PVDF-HFP with addition SiO<sub>2</sub> or not, and then cast as polymer electrolyte films. SPEs and GPEs prepared in this way show perfect electrochemical behavior while keeping good mechanical properties. EIS study illustrates that the ionic conductivities of the SPEs and GPEs depend on the Li<sup>+</sup> ion content and the addition of SiO<sub>2</sub>, and the GPEs especially have a higher ionic conductivity that rises rapidly up to 10<sup>-4</sup> S/cm. The results could be attributed to SiO<sub>2</sub> having an effect on morphology and a positive enhancement in ionic conductor, which has been supported by FTIR and DSC measurements. The polymer electrolyte investigated in this work shows Arrhenius behavior, indicating that the lithium ion motion is depended on factors to influence the perfluorinated sulfonate Li ionomer dissociation degree of the composite system in the investigated temperature. A model was proposed for the interaction between ionic groups and polymer backbone in the Nafion-Li/PVDF-HFP blend polymer electrolyte.

**Acknowledgment.** The work has been supported by the National Natural Science Foundation of China (Nos. 20075028 and 20275036). The authors thank Miss HuaLan Zhou for her help in AFM measurement.

**Supporting Information Available:** A schematic diagram of the laboratory-built Teflon cell holder, tables relating lithium

ion content to CPE dependence, and a figure relating lithium ion content of the gel polymer electrolyte to the dependence on the average ionic conductivity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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