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Short Communication

Electrical properties of composite polymer electrolytes based on PEO-SN-$LiCF_3SO_3$

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A composite polymer electrolyte (CPE) composed of poly (ethylene oxide) (PEO), succinonitrile (SN) and lithium trifluoromethanesulfonate ($LiCF_3SO_3$) was prepared to improve the ionic conductivity and electrochemical stability of the PEO based solid state electrolyte. The dependence of conductivity of CPEs on temperature was measured, and a maximum room temperature (293 K) ionic conductivity of 7.0×10^{-4} S cm^{-1} was obtained for membrane, which is composed of PEO-SN-25wt% $LiCF_3SO_3$ and dried at 30℃. Moreover, this CPE showed a high electrochemical stability potential of more than 5.0 V versus Li.

Keywords: composite polymer electrolyte; ionic conductivity; electrochemical stability window

1. INTRODUCTION

Composite polymer electrolytes (CPE) shave been widely studied in recent decades ever since the ionic conductivity of poly (ethylene oxide) (PEO) was discovered and become a promising materials for electrolytes by Fenton [1] and Wright [2]. Among the polyelectrolyte materials, PEO is mostly studied as a host for ions because of its flexible macromolecular structure and good ability of the ion dissociation. However, ascribed to the high degree of crystallization, the ionic conductivity of these PEO-based CPEs at room temperature is still too low to meet the expected value (above 10^{-4} S cm^{-1}) for practical applications [3]. Extensive studies of PEO electrolytes have revealed that the ionic conductance mainly occurs in the amorphous domains of the polymer [4]. Therefore, several approaches have been developed to increase the amorphous content in the PEO-based CPEs to achieve higher ionic conductivity at room temperature [3, 5-6]. As a non-ionic plastic material, succinonitrile (SN) [7, 8-10] has been widely used as a versatile additive to enhance the Li^+ conductivity of CPEs, since the presence of the impurity ‘trans’ isomer stabilizes the plastic crystal phase of SN [10,11]. It has been reported that in the plastic crystalline phase of highly polar SN, various salts can be dissolved to endow solid electrolytes with high ionic conductivity in a wide temperature range, and the ionic conductivity at 25℃ can reach 3×10^{-3} S cm^{-1} [10]. $LiCF_3SO_3$ is a bulky lithium salt, which exhibits great charge delocalization favorable to ionic dissociation in solvating polymers such as PEO. Besides, it presents several significant advantages such as good mechanical stability and "plasticizing" effect (decreases the crystallinity of the host polymer and facilitates the transportation capability of ions) [12, 13]. Moreover, the PEO-$LiCF_3SO_3$-based CPEs showed broad electrochemical window [14]. Lizhen Fan et.al [7-8, 15] investigated PEO-based system with SN as plasticizer, and they have done some preliminary job on the effect of $LiCF_3SO_3$ on PEO-SN systems.

Herein, we investigated the influence of $LiCF_3SO_3$ concentration on the structure, morphology, and conductivity of the PEO: SN: $LiCF_3SO_3$ polymer electrolyte, and a high room temperature ionic conductivity of 7.0×10^{-4} S cm^{-1} was obtained when the CPEs was dried at 30℃.

2. EXPERIMENTAL

The polymer electrolytes were prepared by a solution casting technique. Prior to use, PEO (Mw=1.0×10^{6}) and $LiCF_3SO_3$ (Aldrich) was vacuum-dried for 24 h at 50℃ and 120℃, respectively. SN (Aldrich) was used without further purification. Anhydrous acetonitrile from Shanghai Chemical Regent Company were used as solvents.

The molar ratio of EO segments (repeating unit of PEO) to SN was fixed at 16:10 as the composites got suitable strength and flexibility [15]. Predetermined amount of $LiCF_3SO_3$, SN and PEO were added into acetonitrile in sequence under intense stirring to form a uniform mixture at 30℃. And then, the mixture was cast onto a Teflon plate followed by the evaporation of the solvent in a dry box for 1 day. The final CPEs were obtained by further drying the as-prepared films in vacuum at 30℃ for 48 h. These procedures yielded translucent homogenous films of thickness of about 180 um, and the area of the sample is 1.55 cm^2. The as-prepared CPEs were denoted as PEO-SN-x% (wt) $LiCF_3SO_3$, in which "x" stood for the percentage of $LiCF_3SO_3$ to PEO (wt), which ranged from 0 to 30.

X-ray diffraction (XRD) patterns were recorded by a Rigaku-D/max 2400. Advance instrument equipped with Cu kα radiation (λ=1.5406 Å) performed at 40 kV and 40 mA. A scan rate of 5.0° min^{-1} in the range of 10-60° (2θ) was used to detect the crystallinity of CPEs.

Ionic conductivity of the CPEs was determined by electrochemical impedance spectroscopy (EIS). The film was sandwiched between two stainless steel (SS) electrodes to form a symmetrical SS/electrolyte/SS cell. The cell was placed into a high and low temperature test chamber. For each temperature, at least 1 hour were waited to reach the thermal equilibrium of the CPE before the impedance response was recorded. The impedance tests were carried out in the frequency range of 100 KHz to 10 Hz at the amplitude of 5 mV from 0 to 60℃ on IMe6 electrochemical interface software.

Electrochemical stability window of the CPEs was determined by running linear voltammetry sweep in a three-electrode cell using stainless steel as the working electrode, lithium as both the counter and the reference electrode with the CPE film (or a Celgard 2300 membrane with 1M

$LiCF_3SO_3$/(DOL+DME) (1:1, vol) electrolyte) sandwiched between. An IMe6 Electrochemical Interface was used to run the voltammetry at a scan rate of 5 mV s^{-1}.

3. RESULTS AND DISCUSSION

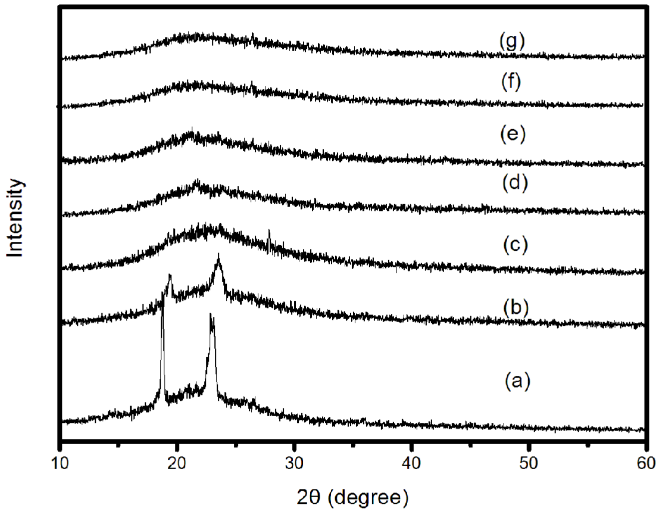

Figure 1. XRD pattern of (a-g) PEO-SN-x wt% $LiCF_3SO_3$ (x=0, 5, 10, 15, 20, 25, 30)

The XRD patterns of CPEs at room temperature are shown in Fig.1. The patterns of PEO-SN-x% (wt) $LiCF_3SO_3$ (x=0, 5, 10, 15, 20, 25, 30) membranes are presented by line a to g. It shows typical XRD pattern of crystalline PEO (2θ=19 and 23.5°) [16] in line a and b. It can be observed that, in line c to g, with the concentration of $LiCF_3SO_3$ increasing, the intensity of the diffraction peaks becomes weaker and broader, suggesting the decreasing in crystallinity of PEO, which may attribute to the coordination interactions between the ether O atoms of the PEO and Li^+ which rooted in the dissociation of $LiCF_3SO_3$ into PEO-SN environment. Meanwhile, it also can be observed in the XRD pattern that for the concentration of the $LiCF_3SO_3$ ranging from 10 to 30 wt%, there are no peaks corresponding to $LiCF_3SO_3$ or PEO, which indicates the complete dissolution of salt in the amorphous region of polymers and inhibit the crystallization of PEO-SN-x% (wt) $LiCF_3SO_3$ complexes. From Fig.1, it can be seen that the samples with even 20-30 % (wt) of $LiCF_3SO_3$ have no diffraction peaks in the XRD patterns, which is different from the previous work about the PEO-$LiCF_3SO_3$ system [17]. This is probably due to the uniform disperse of both PEO and $LiCF_3SO_3$ into the composite system, and the interaction between O atoms in PEO and Li atoms from the salt greatly reduced the crystallinity of them.

Fig.2 shows the comparison of conductivity of CPEs with different contents caused by the variation of salt concentration. It has been noticed in Fig.2 that the conductivity increases with the increasing content of $LiCF_3SO_3$ in the range of 5 % to 25 %. However, the conductivity declines when the percentage of $LiCF_3SO_3$ keeps on increasing. The amount of $LiCF_3SO_3$ deeply affects the ionic conductivity of these hybrid films. The increasing of ionic conductivity is due to the enhancement of the ionic mobility and number of carrier ions when the lithium salt content is relatively low, as works have been reported [18, 19].

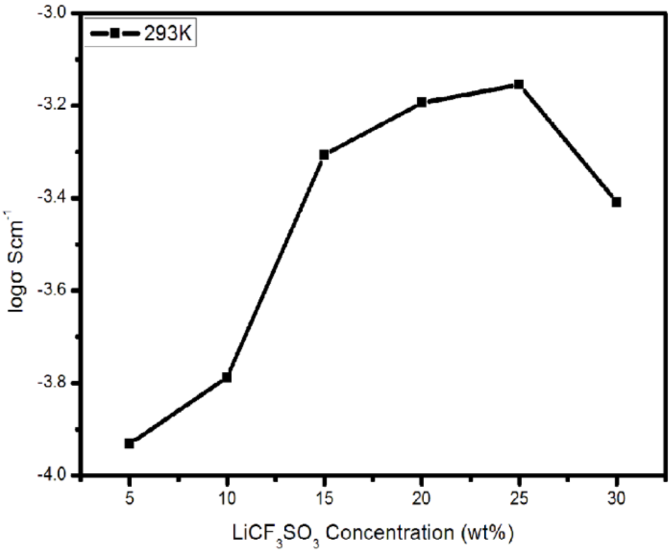

Figure 2. Effect of salt content on the conductivity of PEO-SN-x wt% $LiCF_3SO_3$ (x=5, 10, 15, 20, 25 and 30) complexes under different temperatures

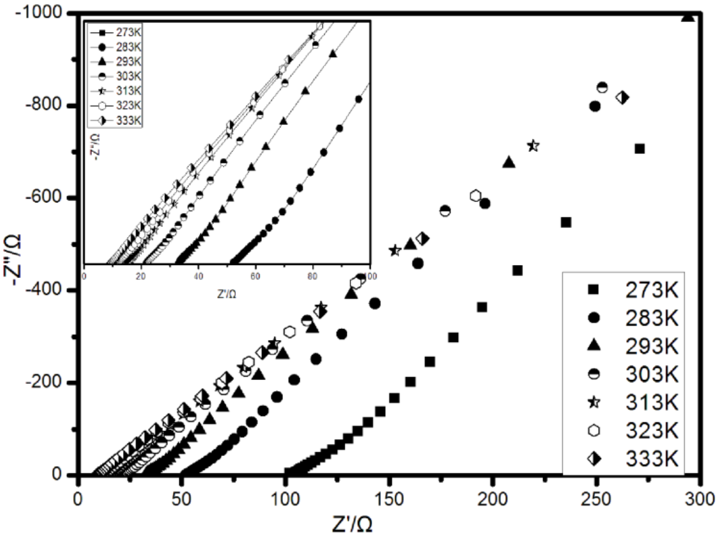

Figure 3. Impedance plots of PEO-SN-25wt% $LiCF_3SO_3$ at different temperatures

While as the content of salt keeps on increasing, the build-up of charge carriers is offset by the retarding effect of ion aggregates such as ion pairs and ion triplet formation, which causes constraints in ionic and polymer segmental mobility [20]. Therefore, the conductivity reaches a max value at 25 wt% of $LiCF_3SO_3$, which shows a balance between these two opposing forces: increasing of the number of charge-carrier ions and the formation of ion couples and multiple ions [21].

Ionic conductivities of the as-prepared CPEs under different temperature were measured, and the typical impedance plots of PEO-SN-25wt% $LiCF_3SO_3$ are shown in Fig.3. The plots show a spike at the whole frequency region under the whole temperature range. The conductivity of the polymer electrolyte can be calculated from the equation $\sigma= L/(AR)$, where A is the area of electrode, L is the thickness of the film, and R is the bulk resistance from ac impedance. Testing results show that, the PEO-SN-25wt% $LiCF_3SO_3$ exhibits an ionic conductivity (σ) of 7×10^{-4} S cm^{-1} at 293 K.

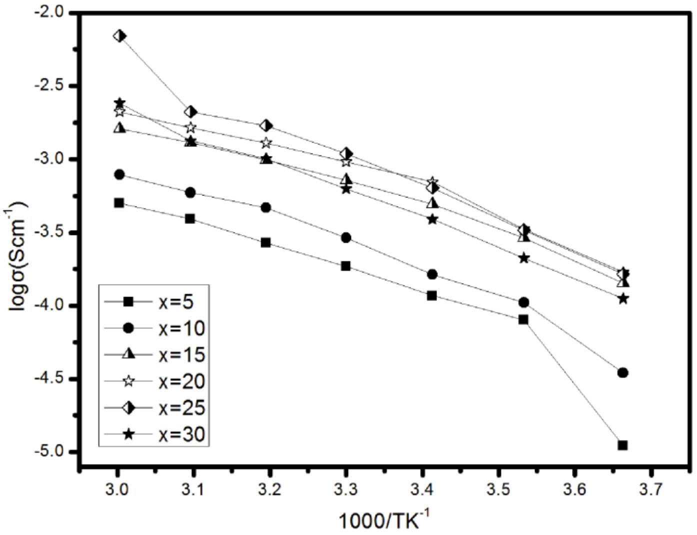

Figure 4. Temperature dependence of ionic conductivity of PEO-SN-x wt% $LiCF_3SO_3$ (x =5, 10, 15, 20, 25 and 30).

Fig.4 shows the temperature dependence of ionic conductivity of PEO-SN-x wt% $LiCF_3SO_3$ (x =5, 10, 15, 20, 25 and 30). The ionic conductivity of PEO-SN-x wt% $LiCF_3SO_3$ is measured from 0 to 80 °C, as outlined in Fig.4. The overall conductivity increases with the increasing content of $LiCF_3SO_3$ in the range of 5% to 25%, especially under room temperature, while such effects were rather limited at higher temperatures. Particularly, for x=25 and x=30, the conductivity shows a sharp increase from 323 to 333 K, which may cause by the melt of SN [10]. PEO-SN-25wt% $LiCF_3SO_3$ features ionic conductivity of 7.0×10^{-4}S cm^{-1} at 20°C, increased almost by one order of magnitude compared to the PEO-SN-5wt% $LiCF_3SO_3$ system. At 60 °C, we can see from Fig.4 that the PEO-SN-25wt% $LiCF_3SO_3$ CPEs has conductivity greater than 10^{-3}S cm^{-1}, showing an enhancement of about 10 times that of PEO-SN-5wt% $LiCF_3SO_3$.

Electrochemical stability window of the polymer electrolyte was obtained by linear voltage sweep. Fig.5 displays the linear voltage sweep curves of Celgard 2300 membrane doped liquid electrolyte and PEO-SN-25wt% $LiCF_3SO_3$ CPE at room temperature. The irreversible onset of the current determines the electrolyte breakdown voltage, which in the case of the liquid electrolyte only extends to about 4.5 V versus Li. However, the irreversible onset of the current of the PEO-SN-25wt% $LiCF_3SO_3$ exceeds 5.2 V versus Li. The decomposition voltage of PEO-SN-x wt% $LiCF_3SO_3$

decreases with $LiCF_3SO_3$ content and exceed 4.8 V vs. Li even though the content of $LiCF_3SO_3$ is 10 wt%.

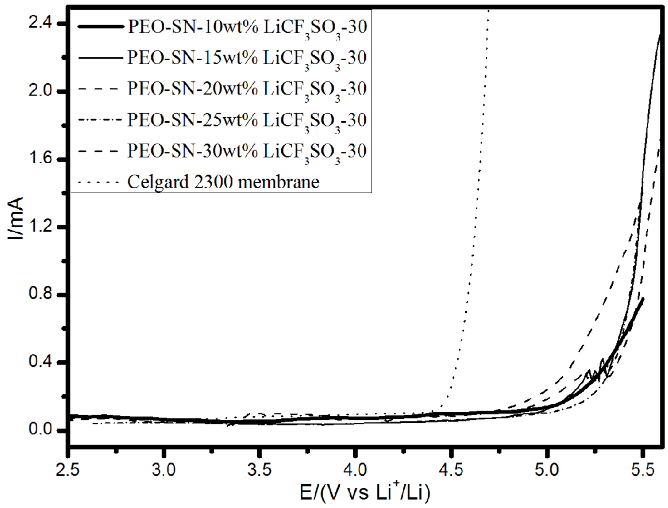

Figure 5. Current–voltage response of Celgard 2300 membrane and PEO-SN-x wt% $LiCF_3SO_3$ (x=10, 15, 20, 25, 30) composite polymer electrolyte obtained at room temperature.

The as-prepared PEO-SN-$LiCF_3SO_3$ CPE shows a wider electrochemical stable window than $LiPF_6$/EC+DEC (1:1, vol) electrolyte with Celgard 2300 membrane, therefore, it may be able to be used as candidate electrolyte in rechargeable lithium batteries whose working voltage is higher than 4.5 V versus Li.

4. CONCLUSION

The PEO-SN-$LiCF_3SO_3$ CPEs films were prepared with various compositions by solution casting method. The addition of $LiCF_3SO_3$ can reduce the crystallinity of the composites effectively. A maximum conductivity of 7.0×10^{-4} S cm^{-1} at 293 K was obtained for the PEO-SN-25wt% $LiCF_3SO_3$, and it increased with increasing measuring temperature. The electrochemical stability window of the PEO-SN-25wt% $LiCF_3SO_3$ exceeds 5.2 V versus Li. The high decomposition voltage enables the present CPEs as candidate electrolyte materials for solid-state rechargeable lithium batteries.

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