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THE INVESTIGATION OF THE SOLVENT EFFECT ON THE CONDUCTION BEHAVIOR OF IONIC LIQUID COMPOSITES ELECTROLYTES

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ABSTRACT

Ionic liquid/PVDF-HFP based electrolyte is one of the promising solid state electrolyte for energy storage devices. It is known that additional amount of propylene carbonate (PC) or Ethylene carbonate (EC) can improve the conductivity of the electrolyte though the ion concentration is diluted. Both dielectric spectroscopy and time domain method are employed to characterize the segmental dynamics of the polymer matrix and the charge dynamics of ionic in the electrolyte over a broad temperature range. It is found the both conductivity and mobility of the electrolyte are improved due to the acceleration of the PVDF-HFP chains by the additional solvents. Also the mobile ion concentration was of the sample with PC or EC is higher than that without solvent even the total ion concentration of the ionic liquid salt is diluted.

Keywords: Electrolyte, Ionic Liquid, Conductivity, Mobility, Ion Concentration

I. INTRODUCTION

Ion transport and storage in solid state polymer matrix films is of great interest for energy storage devices and transducers, such as actuators, sensors, fuel cells, and supercapacitors [1-5]. Under electric field, ions with opposite polarity are transported through the polymer membrane, and the accumulation of ions near the two electrodes results in the charge storage and the electroactive strain of these electroactive devices[6]. Despite the huge practical importance of ionic liquid containing membranes, after decades of research, many aspects of ion transport of ionic liquids in the polymer matrix are not fully understood.

Room temperature ILs are a class of salts composed of large cations and anions in liquid form at room temperature, and are highly advantageous compared with aqueous electrolytes because of their prominent properties, including high ionic conductivity, negligible vapor pressure, broad electrochemical window, and high thermal stability[7]. It has been demonstrated that compared with aqueous solutions, the use of ILs as electrolyte can increase the life time of the electroactive devices dramatically. Furthermore, their broad electrochemical windows allow for higher applied voltages. Among various ILs, EMI-TFSI is one of the ideal ILs for energy storage devices because of its high conductivity, low viscosity, and large electrochemical window at room temperature [7].

Poly(vinylidene fluoride-co-hexafluoropropylene) PVDF-HFP consists of poly(vinylidene fluoride) main chains and hexafluoropropylene side chains and is well known for its chemical inert properties and is compatible with various kinds of ionic liquid electrolytes which make it suitable for the polymer matrix for solid state electrolyte[8]. The dielectric behavior in response to AC stimuli of PVDF-HFP have been intensively investigated by impedance approach. The relaxation peak at low frequency is usually referred to the long range segmental relaxation of the main chains while that at higher frequency is usually referred to the shorter range relaxation of the side chains. When blended with ionic liquid, the conductivity of the electrolyte is decrease dramatically when compared to that of the neat ionic liquid. One of the effective way to improve the conductivity of the solid state electrolyte composted is to have additional solvent into composite. Propylene carbonate (PC) melting point ~48.8 OC and Ethylene carbonate (EC), MP~34 OC, are commonly used solvents and it have been found that with additional amount of solvent in the ionic system the conductivity of the electrolytes increase dramatically. However, the charge transport mechanism is not clear yet.

Here we employ the impedance approach, to estimate how the ionic liquid and solvent affect the polymer chain relaxation behavior and hence the ion conductivity of the solid electrolyte composites. On the other hand, the conductivity, mobility and mobile ion concentration of the composite was also estimated by a newly developed time domain model[6]. Based on the modified Poisson-Nernst-Planck relation, the conductivity can be separated into the contribution of mobility and mobile ion concentration. In this work, ion conduction occurs in the polymer matrix, it is inevitable to exam the correlation between the ionic conduction and the segmental dynamics of the polymer chains. Here, we explore the dielectric spectroscopy as well as transient current responses of the EMI-TFSI/PVDF-HFP membranes with different solvent over a broad temperature range to investigate the how the ion transport behavior of ionic liquid was affected by the solvent.

II. EXPERIMENTAL AND THEORY

2.1 Sample preparation

PVDF-HFP, EMI-TFSI, Propylene carbonate (PC) and Ethylene Carbonate (EC) are purchased from Aldrich. PVDF-HFP and EMI-TFSI are dried in vacuum oven at 80 C for 12 hrs before process. 400mg of PVDF-HFP are dissolved in 3 ml acetone solvent and stirred for at least 4 hrs. After the polymer is dissolved in acetone, 280mg of ionic liquid EMI-TFSI was then added and stirred for another 2 hrs. For the sample with PC solvent, an amount of 3.5 mole of additional PC and EC are added respectively. The solution was casted on a Teflon coated glass to from the PVDF-HFP/EMI-TFSI and PVDF-HFP/EMI-TFSI/PC composite films. The thickness of these samples are at around 50 microns. For the electrical measurement, gold leaf are employed as electrodes on both side of the membranes.

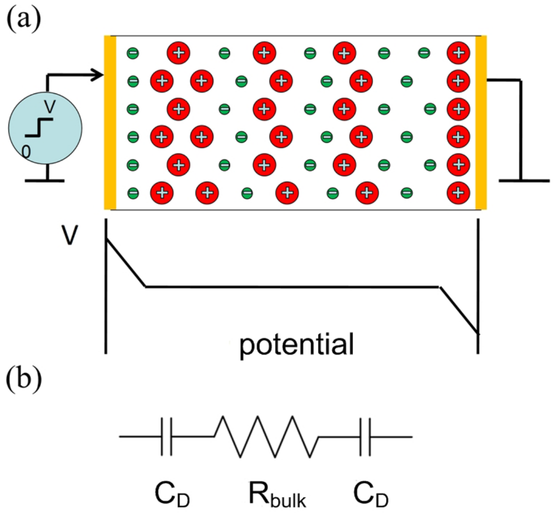
2.2 Measurement methods

In general, charge transport is a result of drift and diffusion and can be described by Poisson-Nernst-Planck equations[6],

$$\varepsilon\varepsilon_0 \frac{\partial E}{\partial x} = \rho \qquad (1)$$

$$\psi_\pm = \pm \mu n_\pm \mathrm{E} - \mathrm{D}\frac{\partial n_\pm}{\partial x} \qquad (2)$$

where ρ is the charge concentration, ε the dielectric constant of the medium, □ $\square_\square$ the vacuum permittivity, ψ □ is the ion flux density (current density J=qψ □ □ □ □ □ is the ion mobility, n is the ion concentration (the subscripts + and – indicate positive and negative charges, E electric field, D diffusion coefficient. For the ionic liquids studied here, we assume $n_+=n_-$. □ □ and D are related by the Einstein equation, $D = \mu KT / q$. [6]



Figur 2-1 The Plot Shows the Charge Process of Electric Double Layer Capacitors

For the ionomer membrane in figure 2-1(a) under a step voltage (from 0 at t<0 to V volts at t>0), the initial current density before the screening of electric field occurs is I_0==□ V S/d, where □ (=qn□) is the conductivity, d is the membrane thickness, and S is the electrode area. When the applied voltage is not high (in the order of 10kT, where k is the Boltzmann's constant), the initial transient current follows the charging of an electric double layer capacitor C_D in series with a bulk resistor R, [6]

$$I(t) = I_0 \exp(-t/\square_{DL}) \qquad (3)$$

Where $\square_{DL}$ = d $\square_{DL}$/2D = RC_D, describes the typical charging time for the electric double layer which has a thickness $\square_{DL}$, the Debye length,

$$\lambda_{DL} = (\varepsilon\varepsilon_0 kT / Z^2 q^2 n)^{1/2} \qquad (4)$$

Where Z is the mobile ion charge (=1 for EMI-Tf), and q=e, electron charge. It was further shown that at longer time, the charge diffusion from the bulk to the double layer region leads to a power law decay of the diffusion current (in which the initial current fits well by eq. (3), followed by a power law decay of the diffusion current, having a typical time constant □ ~ d^2/(4D)). Therefore, by fitting experimental transient current I(t) with eq. (3), □ , n, and □ can be obtained if □ of the ionomer membrane (with ILs) is known.[6]

$$\sigma = \frac{I_0 d}{VS} \qquad \mu = \frac{qVS\varepsilon\varepsilon_0 d}{4kT{\tau_{DL}}^2 I_0} \qquad n = \frac{4kTI_0^2\tau_{DL}^2}{\varepsilon\varepsilon_0 q^2 V^2 S^2}$$

mpedance spectroscope is employed to determine □ , Besides □ □ □ □ □ (= d/(SR), where d is the thickness and S the surface area of the membrane), can also be determined from the Nyquist plot.

III. RESULTS AND DISCUSSION

Figure 3-1 plots the dielectric relaxation loss peak of PVDF-HFP with EMI-TFSI over a broad temperature from -40 to 80 ^{O}C. As can be seen, the relaxation peak at -30 ^{O}C (the black square symbol) is at ~10 Hz and that at 30 ^{O}C (pink star) is at ~4kHz. Above 30 ^{O}C the relaxation peak did not move forward further with increasing the temperature. This means that the peak represents the relaxation frequency of the HFP side chains shit to high frequency progressively from ~10 Hz to the highest frequency and gradually saturate with temperature at an ultimately frequency at 3x10^{3} Hz. Above that temperature, the relaxation frequency is approximately fixed and did not increase further with increasing temperature.

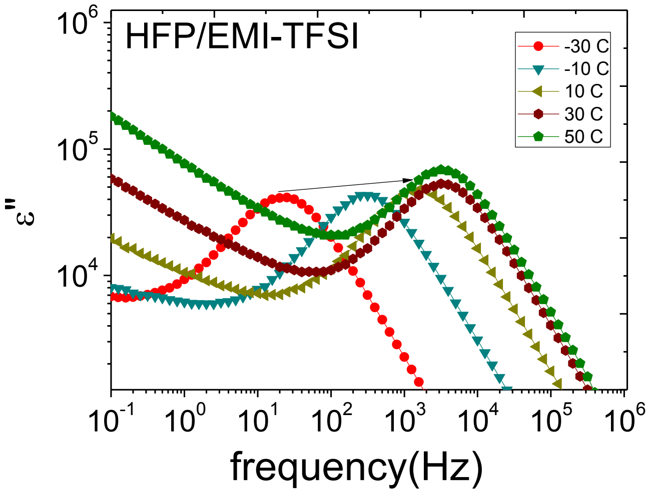


Figure 3-1 The dielectric relaxation loss of PVDF-HFP/EMI-TFSI.

Figure 3-2 plots the dielectric loss response of the PVDF-HFP/EMI-TFSI with 3.5 mole of additional solvent PC. The result indicated that the relaxation peak at low temperature -30 OC is at ~ 500Hz while that at 10 OC is at ~3kHz and above which the frequency is almost identical. This indicated that the similar phenomena as that observed at figure 3-1, that is the relaxation peak frequency increases with increasing temperature. However, when compared to figure 3-1, the relaxation frequency of the sample with PC at -30 OC (500 Hz) is much higher than that sample without PC solvent at the same temperature. This result implies that the additional of PC solvent accelerates the segmental motion of the HFP side chains and this could provide the reasonable clue to answer the question why the conductivity of the sample with PC is much higher than that without PC over all the measured temperature range.

On the other, it seems that the saturation of relaxation frequency of both samples is almost the same but the one without PC solvent saturated at 40C and that without PC saturated at 10 ^{O}C. This implies that though at the same temperature, solvent PC accelerate the relaxation frequency of the PVDF-HFP side chains, it does not change the ultimate relaxation frequency of the chains much.

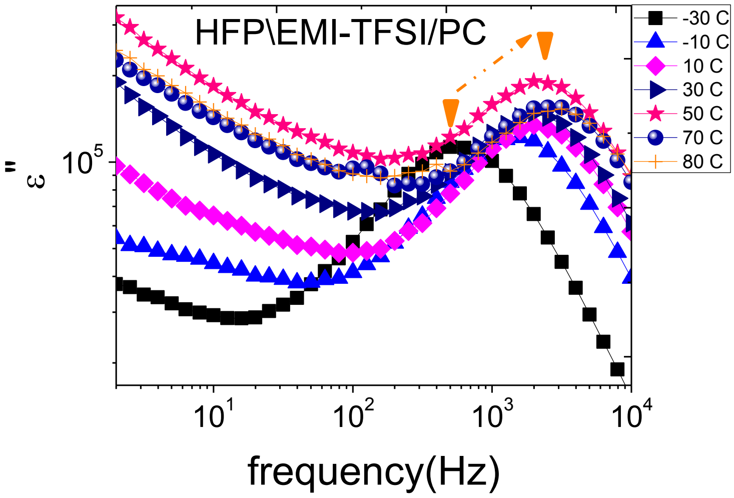


Figure 3-2 The dielectric relaxation loss of PVDF-HFP/EMI-TFSI/PC.

Figure 3-3 plots the dielectric loss response of the PVDF-HFP/EMI-TFSI with 3.5 mole of additional solvent EC. As can be seen in the figure, the segmental relaxation frequency increase with increasing temperature from ~300Hz to ~10kHZ(-40 to 0 ^{O}C) and suddenly the frequency jump to ~3Khz at above 10 ^{O}C and then the relaxation frequency saturated gradually with temperature. This abrupt increase on relaxation frequency may because the melting process of the EC solvent as it melting point is at around 34 ^{O}C.

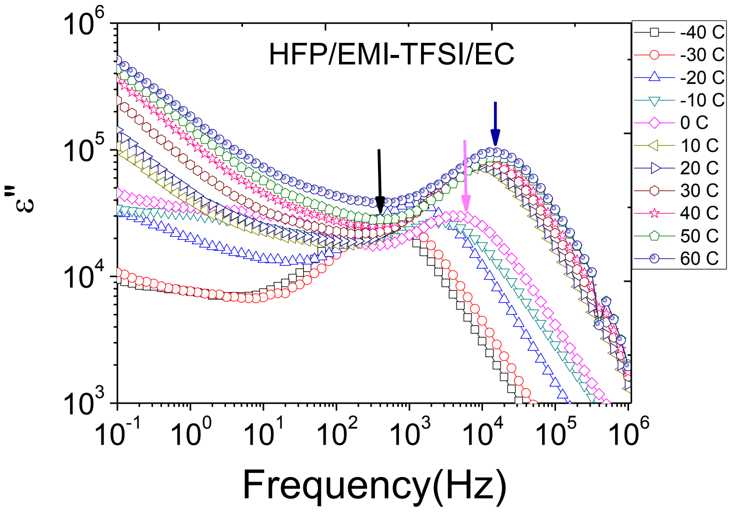


Figure 3-3 The dielectric relaxation loss of PVDF-HFP/EMI-TFSI/EC.

Figure 3-4 plots the conductivity versus temperature of the samples. As can be seen the conductivity of these all samples do not linearly dependent on the temperature in the log plot implying that the ionic conduction in these two samples is coupled to the segmental motion of the polymer chains. Obviously, both samples with PC or EC solvent have a much higher conductivity over the temperature range, though the sample was diluted by the PC or EC solvent. On the other hand, a sudden drop of conductivity was observed at 246 K for the PVDF-HFP composite. This dramatic decrease on conductivity might be attributed to the solidify process of the EMI-TFSI near the same temperature. On the other hand, in the sample with PC, the sudden decrease on conductivity was not observed even at the lowest measured temperature (243K) implying that the EMI-TFSI did not solidify due to the additional PC solvent as the melting point of the PC solvent is at 225K. Therefore, it is not surprise that the sample with PC has a higher conductivity than that without PC solvent especial at lower temperature region. In addition, as can be seen the sample with EC solvent also has a high conductivity than that without solvent especially at high temperature region. As the melting point of the EC solvent is at around 320K, it can be expected that the effect of the EC solvent will occur at higher temperature region (>320K). Hence the abrupt drop of the conductivity of the sample with EC can be attributed to the solidification of the EC solvent that slows down the ion conduction.

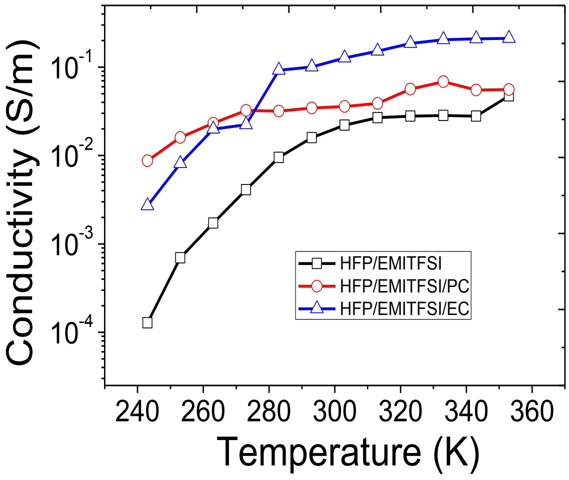


Figure 3-4 The conductivity versus temperature for PVDF-HFP/EMI-TFSI with and without PC solvent.

To reveal the fundamentals beneath the increased conductivity, we employed the time domain model to separate the conductivity into the contribution of mobility and mobile ion concentration. Figure 3-5 represents the ion mobility of the PVDF-HFP/EMI-TFSI samples with and without PC solvent. The nonlinear temperature dependent behavior implying that the ion mobility is coupled to the segmental motion of the PVDF-HFP chains. A sudden drop on mobility is also observed on ion mobility at 240 K indicating the solidification of the EMI-TFSI salt in the PVDF-HFP matrix. On the contrary, the mobility drop is not observed on the sample with PC over the measured temperature range. This may be due to that the PC solvent help the dissociation of the EMI-TFSI salt and keep it from solidification at low temperature range. On the other hand, the mobility of the sample without PC drop dramatically at high temperature range while the data of the sample with PC was not plotted due to the consideration of the evaporation of solvent PC at high temperature region which might affect the PC content in the sample. The mobility of the EC sample drop quickly at below 280 K, this is reasonable as the EC melting point is at 320 K. Over all it seems that the EC effect occurs at high temperature region while the PC effect occurs at a lower temperature region.

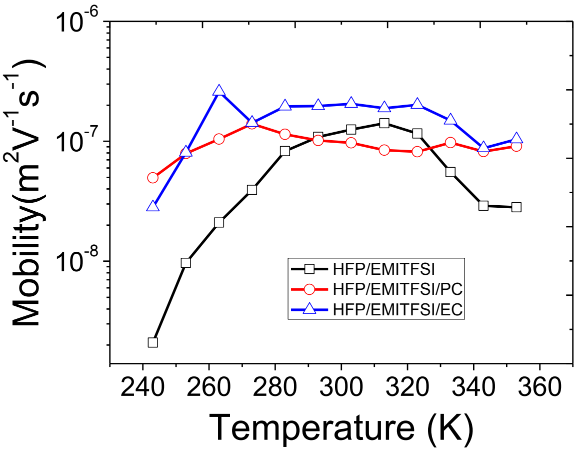


Figure 3-5 The ion mobility versus temperature for PVDF-HFP/EMI-TFSI with and without PC solvent.

Figure 3-6 plots the mobile ion concentration of the both composites. The sample with PC or EC solvent has a higher mobile ion concentration than that without solvent even the sample was diluted by the Solvent. This implies that both PC and EC assistant the dissociation of the ions in the composted. As can be seen, the concentration of the sample without solvent drop at ~240K as the solidification of the EMI-TFSI. Moreover at above 320K the slop of the temperature dependence of concentration of all samples increases. As the mobile ion concentration is high at high temperature, the probability for ions to collide each other increases and thus reduces the ion mobility as shown in figure 3-5.

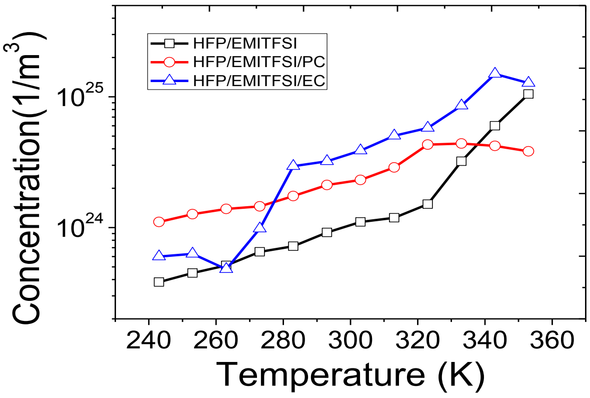


Figure 3-6 The mobile ion concentration versus temperature for PVDF-HFP/EMI-TFSI with and without PC solvent.

IV. CONCLUSION

The Ionic liquid based PVDF-HFP solid state electrolyte was investigated. It is found that with additional amount of solvent PC or EC, the conductivity of the electrolyte can be improved. The conductivity was separated into the contribution of mobility and mobile ion concentration. The dielectric spectroscopy results indicated that the segmental relaxation frequency is accelerated by the additional amount of PC solvent. Besides, the mobility of the mobile ions was also increased due the existence of PC or EC solvent at the same temperature. Moreover, even it was diluted, the mobile ion concentration of the electrolyte with additional solvent was higher than that without solvent.

V. ACKNOWLEDGMENTS

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