

Conductivity and Dielectric Properties of Proton Conducting Poly (Vinyl) Chloride (PVC) Based Gel Polymer Electrolytes

(Kekonduksian dan Sifat Dielektrik Proton Menjalankan Poli (Vinyl)

Klorida (PVC) Berdasarkan Gel Polimer Elektrolit)

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ABSTRACT

Poly (vinyl) chloride (PVC)-NH₄I-EC films have been prepared by the solution cast technique. The sample containing 30 wt.% NH₄I exhibited the highest room temperature conductivity of $4.60 \times 10^{-7} \text{ S cm}^{-1}$. The conductivity increased to $1.08 \times 10^{-6} \text{ S cm}^{-1}$ when 15 wt.% of ethylene carbonate (EC) was added to 70 wt.% PVC - 30 wt.% NH₄I. The effects of ethylene carbonate (EC) addition on the frequency dependent dielectric properties of PVC based electrolytes were investigated by electrochemical impedance spectroscopy (EIS), in the temperature range of 300 K to 373 K. The dielectric properties and ac conductivity of the samples prepared have been analyzed. The values of dielectric constant were found to increase with increasing conductivity of the samples. Analysis of the ac conductivity data revealed the electrolytes to be of the non-Debye type with conduction mechanism of the overlapping-large-polaron-tunneling (OLPT) model.

Keywords: Dielectric properties; gel polymer electrolyte; non-Debye type; proton conductivity

ABSTRAK

Poli (vinil) klorida (PVC)-NH₄I-EC filem telah disediakan dengan teknik larutan tuangan. Sampel yang mengandungi 30 berat.% NH₄I mempamerkan kekonduksian suhu bilik tertinggi sebanyak $4.60 \times 10^{-7} \text{ S cm}^{-1}$. Kekonduksian meningkat kepada $1.08 \times 10^{-6} \text{ S cm}^{-1}$ apabila 15% berat etilena karbonat (EC) telah ditambah kepada 70 PVC % berat - 30% berat. NH₄I. Kesan etilena karbonat (EC) ke atas sifat dielektrik kekerapan bergantung kepada elektrolit berasaskan PVC telah dikaji oleh spektroskopi impedans elektrokimia (EIS), dalam julat suhu 300 K hingga 373 K. Sifat dielektrik dan kekonduksian ac sampel yang disediakan telah dianalisis. Nilai-nilai pemalar dielektrik didapati meningkat dengan meningkatnya kekonduksian sampel. Analisis kekonduksian data ac menunjukkan elektrolit untuk jenis bukan Debye dengan mekanisme pengaliran model yang bertindih besar-terowong polaron (OLPT).

Kata kunci: Gel polimer elektrolit; jenis bukan-Debye; proton kekonduksian; sifat dielektrik

INTRODUCTION

A proton conductor is an electrolyte, typically a solid electrolyte, in which movable ions like H⁺, H₃O⁺ or NH₄⁺ are the primary charge carriers. Proton conductors are interesting materials due to their potential application as solid electrolytes in ionic devices such as fuel cells, batteries and electrochromic glasses (Appleby 1995; Kreuer 1996). A few groups of researchers have studied proton conducting electrolytes using strong inorganic acids such as H₃PO₄, H₂SO₄ and HCl as the doping salts (Bozkurt & Meyer 2001; Lassegues et al. 2001). However, the electrolytes containing inorganic acids suffer from chemical degradation and mechanical integrity and thus are unsuitable for practical applications (Hema et al. 2008).

Other than complexation with inorganic acids, proton conducting polymer electrolytes can also be prepared by complexation with ammonium salts which are considered as good proton donors to polymer matrices (Ali et al. 1998; Ramya et al. 2007). In such systems, the charge carriers may come from ammonium ions and H⁺ ions. The conduction of H⁺ ions occur via the Grotthus mechanism,

where conduction occurs through exchange of ions between complexed sites (Hashmi et al. 1990; Kadir et al. 2010).

PVC has been studied as a host polymer for the development of lithium ion conducting electrolytes (Mary Sukeshini et al. 1996; Rajendran & Uma 2001; Rajendran et al. 2008; Subban & Arof 2004). However, no studies employing this host polymer for proton conducting electrolytes have been done. Therefore, in this paper, PVC based proton conducting polymer electrolytes were prepared employing NH₄I as the doping salt. The samples were characterized by EIS and the dielectric properties of the electrolytes are presented and discussed.

MATERIALS AND METHODS

PVC and NH₄I of required mass were dissolved separately in tetrahydrofuran (THF) after which they were mixed and stirred for several hours at room temperature. Appropriate amounts of EC were added to form solutions which were later cast into petri dishes and left to dry by evaporation

at room temperature to form films. The films were further dried in a vacuum oven at 40°C for 24 h. PVC and NH_4I weight ratios was maintained at 70:30 since this weight formed the highest conducting polymer-salt film while the amount of EC dispersed was expressed as a weight percent (wt.%) with respect to the total weight present in the system. Complex impedance measurements were carried out using HIOKI 3532-50 LCR hi tester in the frequency range of 100 Hz to 1 MHz. The prepared electrolyte films were sandwiched between two stainless steel electrode with diameter 2.0 cm and conductivity measurements were carried out in the temperature range from 300 to 373 K.

RESULTS AND DISCUSSION

Figure 1 depicts the room temperature conductivity as a function of weight percent of NH_4I for the salted polymer electrolytes. It is apparent from the figure that the conductivity increased rapidly from $1.55 \times 10^{-10} \text{ S cm}^{-1}$ for pure PVC system to $4.60 \times 10^{-7} \text{ S cm}^{-1}$ for PVC - NH_4I system when 30 wt.% of NH_4I was added and decreased slowly with further increase in NH_4I content. The maximum conductivity achieved was $4.60 \times 10^{-7} \text{ S cm}^{-1}$ for the system containing 70 wt.% PVC - 30 wt. % NH_4I . This system was chosen to be added with EC. Figure 2 shows the variation of room temperature conductivity with weight percent EC for the plasticized proton conducting electrolytes. In the case of plasticized electrolytes, the conductivity increased to a maximum of $1.08 \times 10^{-6} \text{ S cm}^{-1}$ when 15 wt.% of EC was added to 85 wt.% (PVC - NH_4I). This means that the conductivity increased by one order of magnitude when EC was added to PVC - NH_4I system. At higher plasticizer concentration a decrease in conductivity was observed. These results are in agreement with those described in the literature (Buraidah et al. 2009; Choi & Shin 1996; Subban 2003). According to these reports, the initial increase in conductivity is attributed to increase in the number of mobile ions upon addition of plasticizer. The plasticizer acts as an agent to cause more salt to be dissociated. As the amount of ions increases so does the conductivity.

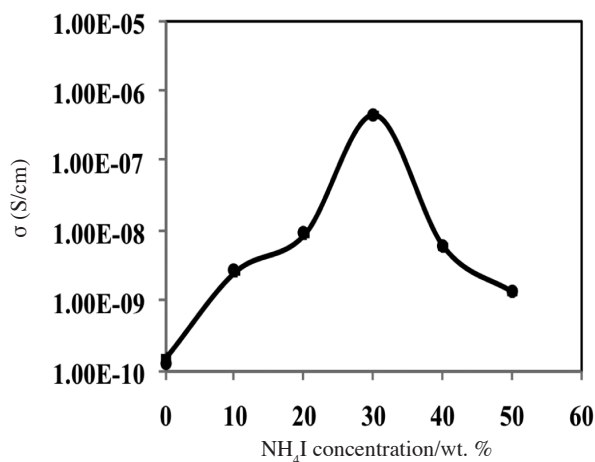


FIGURE 1. Variation of room temperature conductivity

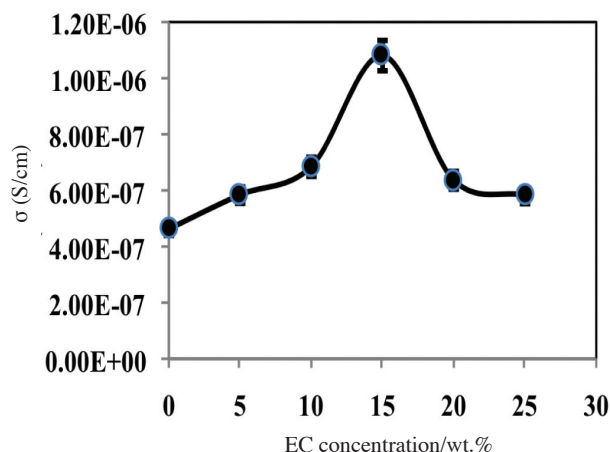


FIGURE 2. Variation of room temperature with weight percent NH_4I conductivity with weight percent EC

Beyond 15 wt.% EC, addition of more plasticizer caused aggregation of ions which impedes the movement of mobile ions consequently reducing conductivity (Buraidah et al. 2009).

Dielectric relaxation studies are a vital tool to show the relaxation of dipoles in polymer electrolyte. The real part (ϵ_r') and imaginary part (ϵ_r'') of dielectric permittivity curves for unplasticized and plasticized samples are shown in Figures 3 and 4, respectively. The conductivity enhancement with addition of EC to PVC- NH_4I could be substantiated by the dielectric constant values, both real and imaginary as displayed in Figures 3 and 4, respectively. Dielectric constant is a measure of the amount of charge stored. Since the dielectric constant value is high for the sample with 15 wt.% EC, this means that the number of charge stored is high giving rise to higher conductivity in this sample. The graph does not display any relaxation peaks indicating that the increase in conductivity is due to

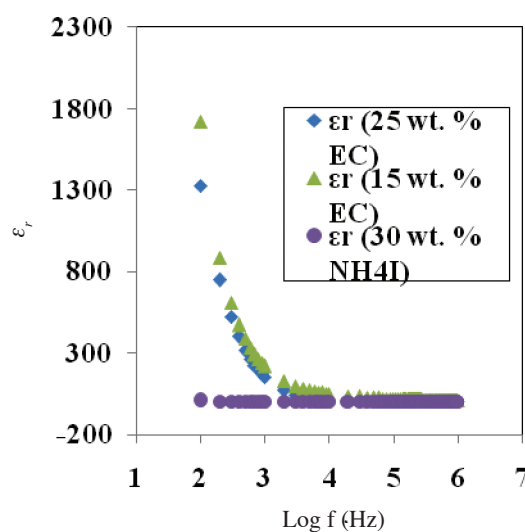


FIGURE 3. Variation of the real part of dielectric constant with frequency for selected unplasticized and plasticized samples at 303 K

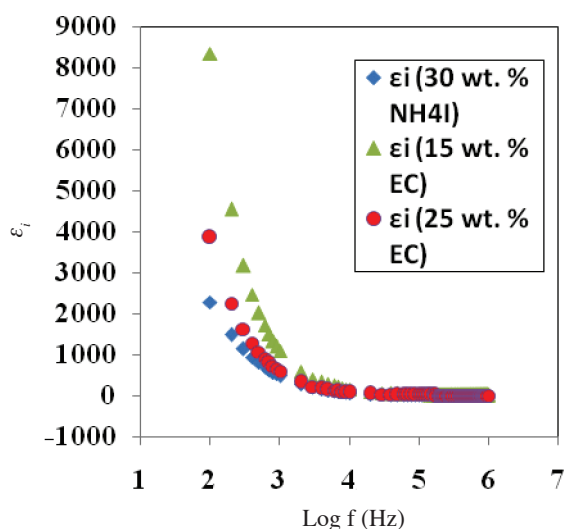


FIGURE 4. Variation of the imaginary part of dielectric constant with frequency for selected unplasticized and plasticized samples at 303 K

increase in the concentration of mobile ions. This in turn implies that EC causes the salt to dissociate giving rise to more mobile ions. This reflects that EC which has a high dielectric constant value has good plasticizing properties by reducing the Coulombic interaction between ions which in turn reduced ion-pairing (Tobishima & Yamaji 1984). The observed variation in ϵ_r with frequency could be attributed to the formation of a space charge region at the electrode and electrolyte interface at the low frequency region. This behavior is known as the non-Debye type of behavior, where diffusion of ions occurs in the space charge regions (Baskaran et al. 2006). The low frequency dispersion region corresponds to the contribution of charge accumulation at the electrode–electrolyte interface. The highest value of ϵ_r for 15 wt.% EC is due to the enhanced charge carrier density at the space charge accumulation region, which causes equivalent capacitance to be enhanced (Ramesh & Ong 2010). At high frequencies, the periodic reversal of the electric fields occurs so fast that there is no time for ion to build up at the interface. Hence, the polarization due to the charge accumulation decreases, which caused the decrease in the value of ϵ_r .

Figures 5 and 6 show the frequency variation of the imaginary (M_i) and real (M_r) part of dielectric modulus, respectively, for the same set of samples. It shows that M_i and M_r increase towards high frequencies and give a long tail at low frequencies. The presence of some relaxation peaks in the modulus formalism at high frequencies show that the polymer electrolyte films are ionic conductors. The reason for the peak curving at higher frequencies is attributed to bulk effects (Austin Suthanthiraraj et al. 2009). It is observed from the plots that M_i and M_r have low values at low frequencies which implies that the capacitance values is high giving evidence of the non-Debye behavior in the samples (Baskaran et al. 2006; Ramesh & Chai 2007). The modulus spectral formalism has facilitated the process of identification and separation of electrode effects

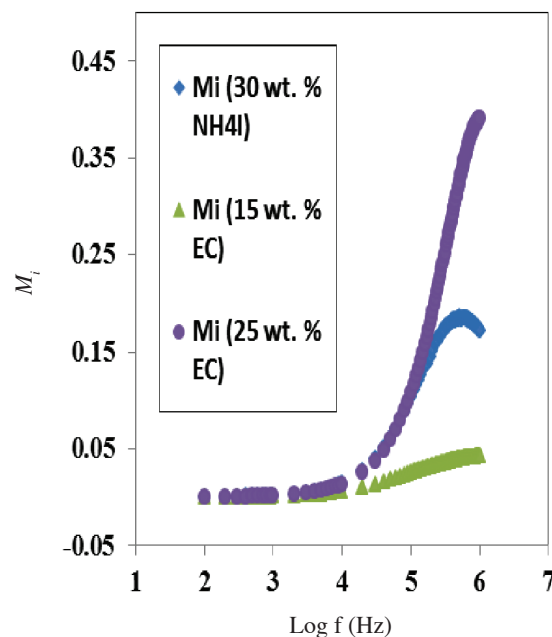


FIGURE 5. Variation of the imaginary part of modulus with frequency for selected unplasticized and plasticized samples at 303 K

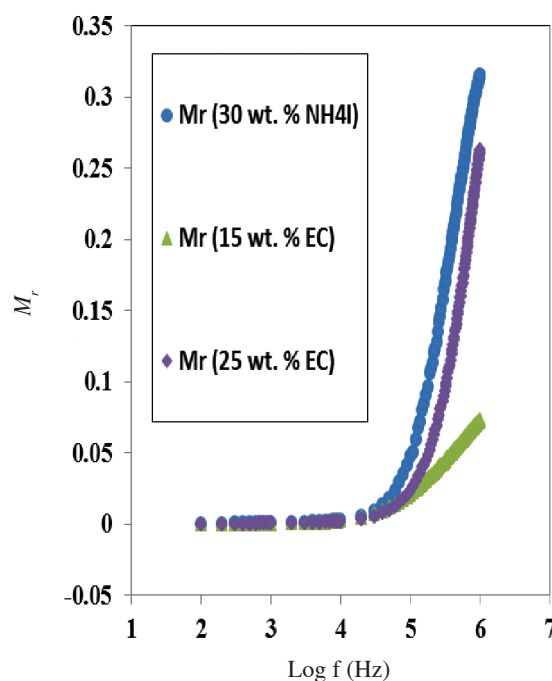


FIGURE 6. Variation of the real part of modulus with frequency for selected unplasticized and plasticized samples at 303 K

from the bulk relaxation phenomena occurring within the plasticized polymer electrolyte system with higher content of EC (Austin Suthanthiraraj et al. 2009).

A Typical plot of conductivity dependence on frequency at different temperatures for the highest conducting film is shown in Figure 7. The ac conductivity was calculated from the dielectric constant, ϵ_r and loss tangent, $\tan \delta$ according to the equation below:

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta \tag{1}$$

where ω is the angular frequency and ϵ_0 is the permittivity of free space. In general, the phenomena of ac conductivity dispersion is analyzed using the Jonsher's universal power law (Murugaraj et al. 2003),

$$\sigma(\omega) = \sigma_{dc} + A \omega^s \tag{2}$$

where the ac conductivity, σ_{dc} is the frequency-independent component, A is a parameter dependent on temperature and s is the power law exponent with value in the range of $0 < s < 1$. The values of exponent s were derived from the slope of Figure 7. It was found that that exponent

s varies between 0.17 and 0.67 as temperature varies from 300 K to 333 K. In order to identify the conduction mechanism in this electrolyte system, the exponent s is plotted as a function of temperature as depicted in Figure 8. For the highest conducting film, it was found that the exponent s decreases with increasing temperature. Thus, the temperature dependence of s could be interpreted by the overlapping large polaron-tunnelling (OLPT) model.

CONCLUSION

The addition of plasticizer (EC) to PVC-NH₄I polymer electrolytes increased the ionic conductivity. The increase in ionic conductivity may be due to increase in number of

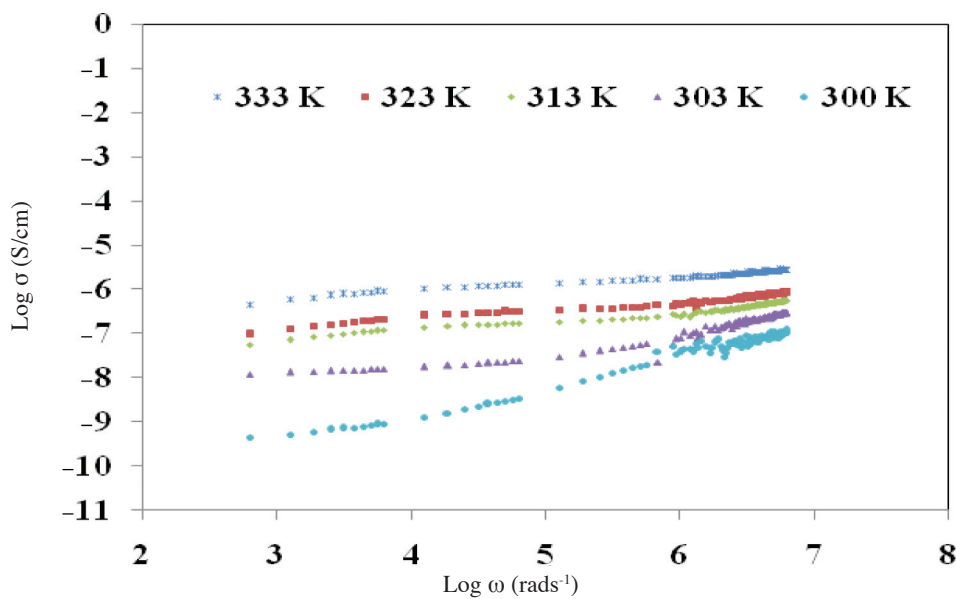


FIGURE 7. Conductivity versus frequency plot for sample with 15 wt.% EC at various temperatures

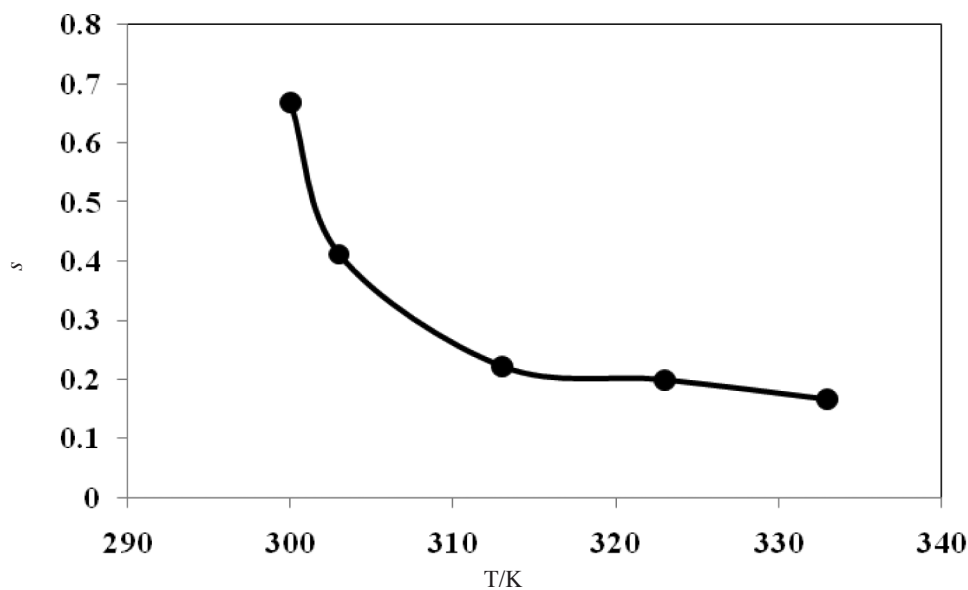


FIGURE 8. Variation of exponent s with temperature for sample containing 15 wt.% EC

ions and the decrease in conductivity beyond the optimised concentration could be attributed to lower mobility of ions due to the presence of a high concentration of ions. Analysis of the ac conductivity data revealed the electrolytes to be of the non-Debye type with conduction mechanism obeying the OLPT model.

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