Ionic Liquid Incorporated PVC Based Polymer Electrolytes: Electrical and Dielectric Properties
(Cecair Ionik Diperbadankan dengan Polimer Elektrolit Berasaskan PVC: Sifat Elektrik dan Dielektrik)

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ABSTRACT
This paper is focused on conductivity and dielectric properties of Poly (vinyl) chloride (PVC)- ammonium triflate (NH₄CF₃SO₃) - butyltrimethyl ammonium bis (trifluoromethyl sulfonyl) imide (Bu₃MeNTf₂N) ionic liquid, electrolyte system. The electrolyte is prepared by solution cast technique. In this work, the sample containing 30 wt. % NH₄CF₃SO₃ exhibits the highest room temperature conductivity of 2.50 × 10⁻² S cm⁻¹. Ionic liquid is added in various quantities to the 70 wt. % PVC-30 wt. % NH₄CF₃SO₃ composition in order to enhance the conductivity of the sample. The highest conductivity at room temperature is obtained for the sample containing 15 wt. % Bu₃MeNTf₂N with a value of 1.56 × 10⁻¹ S cm⁻¹. The effects of ionic liquid addition on the frequency dependent dielectric properties of PVC based electrolytes is investigated by electrochemical impedance spectroscopy (EIS) at room temperature. The values of dielectric constant were found to increase with increasing conductivity of the samples. Analysis of the ac conductivity data showed the electrolytes to be of the non-Debye type.

Keywords: Dielectric properties; EIS; ionic liquid; non-Debye type

ABSTRAK
Kertas ini memberi tumpuan kepada kajian konduktiviti dan dielektrik Poli (vinil) klorida (PVC)- ammonium triflat (NH₄CF₃SO₃) - his butyltrimethyl ammonium (Sulfonyl trifluoromethyl) imide (Bu₃MeNTf₂N), cecair ionik, sistem elektrolit. Elektrolit telah disediakan dengan teknik cast penyeleseian. Dalam penyelidikan ini, sampel yang mengandungi 30 %bt NH₄CF₃SO₃ dipamerkan pada suhu bilik tertinggi kekonduksian 2.50×10⁻² S cm⁻¹. Cecair ionik kemudiannya ditambah dalam kuantiti yang pelbagai 70 %bt PVC-30 %bt NH₄CF₃SO₃, komposisi dalam usaha untuk meningkatkan kekonduksian sampel. Kekonduksian tertinggi diperoleh pada suhu bilik 1.56×10⁻¹ S cm⁻¹ untuk sampel yang mengandungi 15 %bt Bu₃MeNTf₂N. Kesan sampingan cecair ionik pada sifat frekuensi dielektrik bergantung kepada elektrolit berasaskan PVC telah dikaji oleh spektroskopi impedans elektrokimia (EIS) dalam suhu bilik. Nilai pemalar dielektrik didapati telah meningkat dengan peningkatan kekonduksian sampel. Analisis ac kekonduksian data menunjukkan elektrolit adalah bukan dari jenis Debye.

Kata kunci: Cecair ionik; EIS; jenis bukan-Debye; sifat dielektrik

INTRODUCTION
In recent years, addition of ionic liquid to polymer electrolytes have been adopted as a means to increase the conductivity of polymer electrolytes (Hu et al. 2007). Room temperature ionic liquids (RTILs) that consist of bulky cations, due to their excellent properties such as high ionic conductivity, good thermal and electrochemical stability, negligible vapor pressure and non-flammability (Noda et al. 2001; Tokuda et al. 2004), are considered to be suitable electrolyte salts for polymer-in-salt system. Ionic liquids meet the requirements of plasticizing salts and offer improved thermal and mechanical properties to flexible polymers. Different polymer electrolytes containing RTILs including ionic liquid–polyelectrolyte systems and gel polymer electrolytes containing hydrophilic and hydrophobic ionic liquids have been reported to possess high conductivity suitable for application in electrochemical devices (Noda et al. 2000; Shin et al. 2005). The incorporation of RTILs into polymer electrolytes distinctively improve their electrochemical stability and increases their ionic conductivity at room temperature.

Ohno et al. (2004) reported that polymerized ionic liquids have high ionic conductivity with their polymer brushes and crosslinked polymers forming flexible and transparent films with excellent ionic conductivity of 1.1×10⁻⁴ S cm⁻¹. Shin et al. (2005) have shown that by adding 1-butyl-1-methyl pyrrolidinium TFSI to PEO resulted in a marked increase in ionic conductivity between 1 and 2 orders of magnitude. However, the upper limit of conductivity achievable in the polymer electrolyte is still one order less than the conductivity of the neat ionic liquid. Additionally the large ratio of ionic liquid to polymer in Shin’s optimized electrolyte has adverse effects on the transference number, thus limiting the capacity that can be delivered by lithium with each cycle (Cheng et al. 2007; Sun et al. 2002). This led to interest in novel ionic liquid
scaffolds that could overcome these observed limitations while mimicking the preferred method of Li+ conduction through the polymer chains (Stallworth et al. 1999; Tarascon & Armand 2001).

Fuller et al. (1997) reported the synthesis of gel electrolytes prepared from ionic liquid and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF(HFP)). High-temperature proton conducting membranes based on perfluorinated membrane-ionic liquid composites have also been described (Bennett & Leo 2004; Doyle et al. 2000). Md Abu et al. (2005); Noda et al. (2000) and Shobukawa et al. (2005) have reported on free radical cross-linking of certain vinyl monomers in ionic liquid, resulting in mechanically strong and highly conductive polymer electrolyte films. Shin et al. (2005, 2003) have reported flexible solid polymer electrolytes based upon ternary mixtures of ionic liquids with classical PEO/lithium salt binary blends and their use in lithium metal-polymer electrolyte batteries.

In this work, a new ionic liquid comprising of butyltrimethyl ammonium (cation) and bis (trifluoromethyl sulfonyl) imide (anion) incorporated PVC into based polymer electrolytes were prepared. The conductivity and dielectric properties of the gel polymer electrolytes have been studied and presented in this paper.

MATERIALS AND METHODS

The proton conducting polymer electrolytes were prepared by solution-cast technique. PVC (molecular weight 2.33×10^5 g mol⁻¹) and NH₄CF₃SO₃ from Aldrich were mixed with Bu₃MeNTf₂N from Fluka in various weight fractions. Solution cast films were obtained by pouring the solution of PVC, NH₄CF₃SO₃ and Bu₃MeNTf₂N in tetrahydrofuran (THF) from Aldrich into glass petri dishes which were subsequently dried at room temperature (300 K). The films formed were further dried in a vacuum oven at 313 K with a pressure of 10⁻³ Torr for 24 h. The polymer films obtained were stored in a desiccator. The impedance of the samples was measured using HIOKI 3532-50 LCR Hi Tester interfaced to a computer with frequency ranging from 100 Hz to 1 MHz. The samples were mounted on a conductivity holder with blocking stainless steel electrodes of diameter 2 cm. The conductivity was calculated using (1):

\[ \sigma = \frac{t}{R_b A} \]  

(1)

where \( t \) (cm) is the thickness of the sample, \( A \) (cm²) is the electrode - electrolyte contact area which is 3.142 cm² and \( R_b \) is the bulk resistance in Ohms (Ω).

RESULTS AND DISCUSSION

Figure 1 shows a typical complex impedance plot for the highest conducting PVC-NH₄CF₃SO₃: Bu₃MeNTf₂N (85:15) proton conducting polymer electrolyte film at room temperature (300 K). It consists of a high frequency semicircle and a low frequency spike. The semicircle corresponds to bulk resistance while the spike corresponds to interfacial impedance of the electrolyte. The semicircle can be represented by a parallel combination of a capacitor, which is due to the immobile polymer chain and a resistor which is due to the mobile ions inside the polymer matrix (Ramesh & Arof 2001). If the electrodes and electrode/electrolyte interface were ideal, vertical spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end should have been obtained.

![Figure 1](image-url)  

**FIGURE 1.** Complex impedance plot for the highest conducting PVC-NH₄CF₃SO₃: 15 wt. % Bu₃MeNTf₂N polymer electrolyte film at 300 K
dissociation of salt leading to an increase in the number of charge carriers. The incorporation of Bu$_3$MeNTf$_2$N into this polymer-salt system has produced more mobile ions and has also lowered the viscosity that led to increase in ionic mobility which consequently led to increase in conductivity (Baskaran et al. 2006).

In order to better understand the ionic transport phenomenon of any polymer electrolyte system, its dielectric relaxation is further studied (MacCallum & Vincent 1989). The complex permittivity ($\varepsilon^*$) or dielectric constant of a material is defined as,

$$\varepsilon^* = \varepsilon_r - j\varepsilon_i$$

(2)

where $\varepsilon_r$ is the real part of dielectric constant and $\varepsilon_i$ is its imaginary component which basically represents the storage and loss of energy in every cycle of the applied electric field, respectively (Dutta & Biswas 2002).

Figures 3 and 4 show the dielectric constant ($\varepsilon_r$) and dielectric loss ($\varepsilon_i$) as a function of frequency for selected samples at 300 K. From Figure 3, it can be seen that the values of $\varepsilon_r$ rises very sharply at the low-frequency region. This can be explained on the basis of electrode polarization effects (Mishra & Rao 1998). This low-frequency dispersion region is basically attributed to the high contribution of charge accumulation at the electrode – electrolyte interface (Armstrong et al. 1974; Hodge et al. 1976; Howell et al. 1974). In the high-frequency region, it is found that the value of $\varepsilon_r$ is almost constant with frequency. This happens because the periodic reversal of the electric field occurred so fast that the charge carriers did not get sufficient time to orient themselves in the field direction. Hence, there is no excess ion diffusion in the direction of the field which led to the decrease in the values of dielectric constant (Adachi & Urakawa 2002). From Figure 4, it can be seen that the dielectric loss ($\varepsilon_i$) becomes very large (~$10^4$) towards low-frequency region. This is due to the motion of free charge carriers within the material (Kyritsis et al. 1995). The values of dielectric loss did not correspond to the bulk dielectric processes but were due to the free charges that were built up at the interface between the materials of electrolyte and electrode. When the values of frequency were very low, charge carriers received sufficient time to build up at the electrode-electrolyte interfaces before the field changes its direction, and this contributes to the large values of dielectric loss. This phenomenon is called

FIGURE 3. Variation of the real part of dielectric constant with frequency for selected samples at 300K
‘conductivity relaxation’ (Dyre et al. 1991). The increase in the values of dielectric constant and dielectric loss for the highest conducting polymer electrolytes as observed can be attributed to the increase in charge carrier density due to the increase in dissociation of ion aggregates. A further analysis of dielectric behavior for the polymer gel electrolyte system may be achieved using dielectric modulus analysis, which suppresses the effects of electrode polarization (Shastry & Rao 1991) as shown in Figures 5 and 6.

Analysis of modulus spectroscopy have shown that the bulk properties of the material is complementary to impedance spectroscopy which basically highlights electrode and grain boundaries effect. Electrical modulus $M^*$ may be defined as the reciprocal of the complex relative permittivity $\varepsilon^*$ as

$$M^* = \frac{1}{\varepsilon^*} = M_r + jM_i.$$  (3)

Figures 5 and 6 show the real part ($M_r$) and imaginary part ($M_i$) of electrical modulus as a function of frequency for selected samples at 300 K. Both $M_i$ and $M_r$ were observed to increase in the high-frequency region and to give a long tail at lower frequencies. The peaks in the modulus formalism at high frequencies show that the polymer electrolyte films are predominantly ionic conductors (Richert & Wagner 1998). The peak curves at higher frequencies with increased conductivity. This may be due to bulk effects. It is observed from the plots that $M_r$ and $M_i$ decreases towards low frequencies. This is due to electrode polarization phenomenon which makes a negligible contribution and its effect seems to be clearly vanishing towards low-frequency domain. The presence of this long tail in the low-frequency region is probably due to their large capacitance values associated with the electrodes (Ramesh & Arof 2001). The increasing peak of Figure 5 can be assumed to be related to the translational ion dynamics and mirrors the conductivity relaxation of the mobile ions.

The broad nature of the peaks can be understood as being the result of distribution of relaxation times. These peaks are broader than the Debye peak, which is treated as an ideal ionic conductor represented by a single parallel RC element (Isasi et al. 1995). The broad and asymmetrical shape of electrical modulus plot is generally explained by the non-exponential decay function of the electric field using the mathematical relation:

$$\phi(t) = \exp\left[-(t/\tau)^\beta\right].$$  (4)

where, $\tau$ is the relaxation time and $\beta$ is the well-known Kohlrausch parameter which decreases with an increase in the relaxation time distribution and its values lies between $0$ and $1$ for practical solid electrolyte system, indicative of departure from the Debye relaxation ($\beta = 1$) (Padmasree et al. 2006).

In this work, it was found that $\beta$ has an average value of 0.4956 for the PVC-NH$_4$CF$_3$SO$_3$ - 15 wt. % Bu$_3$MeNTf$_2$N polymer electrolyte. This shows that the relaxation phenomena in the polymer electrolyte system is non-Debye type since the values of $\beta$ obtained were less than 1 indicating deviation from the Debye-type relaxation.

Figure 7 shows the frequency dependence of loss tangent for selected samples at ambient temperature. For maximum dielectric loss ($\tan \delta_{\text{max}}$) at a particular frequency, the absorption peak is described by:

$$\tau \omega = 1.$$  (5)

Here $\tau$ is the relaxation time, $\omega$ is the angular velocity with $\omega = 2\pi f$, $f$ is the frequency value corresponding to maximum $\tan \delta$ in Hz.

Relaxation time occurred as a result of ionic charge carriers within the polymer material obeying the change in the direction of the applied field. It is observed from Figure 7 that the peak frequency shifted towards higher frequency as the conductivity increases. The shift of the peak towards higher frequency suggests quicker relaxation time. As discussed earlier, the increase in ionic conductivity was due to the enhancement in the number of carrier ions. Thus, the relatively fast segmental motion coupled with mobile...
ions enhanced the transport properties of the sample which explains the decrease in relaxation time with conductivity (Pradan et al. 2009).

Typical conductance spectra measured at 300 K for PVC-NH$_4$CF$_3$SO$_3$-Bu$_3$MeNTf$_2$N polymer electrolyte is shown in Figure 8. The spectrum consists of two distinct regions within the measured frequency range. The low-frequency spike describes electrode-electrolyte interfacial phenomena and is ascribed to space charge polarization at the blocking electrodes (Yamamoto et al. 1994). This
is followed by the frequency-independent plateau region connected to $\sigma_{dc}$ of the complexed polymer electrolyte. The extrapolation of the plateau region to zero frequency gives the value of dc conductivity at all temperatures and these were found to be consistent with that obtained from Figure 2. In the high-frequency region, the mobility of charge carriers is high, and hence the conductivity increases with frequency (Ramesh & Arof 2001). It is observed that the dc conductivity increases up to 15 wt. % $\text{Bu}_3\text{MeNTf}_2\text{N}$, which suggests that the free volume around the polymer chain increased the mobility of ions and polymer segments.

CONCLUSION

PVC- NH$_4$CF$_3$SO$_3$ - Bu$_3$MeNTf$_2$N proton conducting polymer electrolytes have been prepared by solution cast technique. Highest ionic conductivity was obtained for the electrolyte PVC-NH$_4$CF$_3$SO$_3$: Bu$_3$MeNTf$_2$N with weight ratio of 85:15 with a value of 1.56 x 10$^{-4}$ S cm$^{-1}$. The modulus spectrum and dielectric studies show non-Debye nature of the electrolyte materials which corresponds to long-time slow polarization and relaxation of hopping charges.

ACKNOWLEDGEMENTS

S.K Deraman is grateful to Research Management Institute (RMI) for Excellence Fund Grants and Universiti Teknologi MARA (UiTM) for the scholarship.

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Received: 22 March 2013
Accepted: 2 August 2013