Transport and AC Impedance Studies of Plasticized-Chitosan Based Polymer Electrolytes

A.S.A Khiar1), and A.K. Arof 2)

1) Faculty of Science and Technology, Universiti Sains Islam Malaysia, Bandar Baru Nilai, 71800 Nilai, Negeri Sembilan, Malaysia
2) Physics Department, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
e-mail:1) azwanisofia@usim.edu.my; 2) akarof@um.edu.my

Received 8 August 2011, Accepted 13 October 2011

Abstract

Dimethyl Carbonate (DMC)-plasticized chitosan-based polymer electrolytes were prepared in the present work. The sample 37.5 wt% chitosan - 37.5 wt% NH$_4$CF$_3$SO$_3$ - 25 wt% DMC showed the highest conductivity of $(1.95\pm0.15) \times 10^{-6}$ S/cm. From calculated values obtained using the Rice and Roth model, the increase in conductivity is due to the increase in the number density of mobile ions. Universal Power Law was used to analyze the AC conductivity of the sample. Arrhenius behavior was observed in the plot of hopping frequency; $\omega_P$ against temperature. The AC conductivity master curve was obtained for the highest conducting sample when scaled vertically by $\sigma_{DC}$ and horizontally by $\omega_P$.

Keywords: Chitosan; Ionic Conductivity; AC Impedance.

1. Introduction

Polymer electrolytes are materials that consist of a salt dissolved in high molecular weight polymer solvent1). There are various factors that influence ionic conductivity; the number of charge carriers, ionic mobility as well as the availability of a connecting polar domain as the conduction pathway2). Introducing additives such as plasticizer has helped to increase conductivity by increasing the amorphous content of polymer electrolytes and thus dissociates ion aggregates which are present in the polymer electrolytes which are dominant at higher salt concentrations.

Although many reports can be found in the literature on chitosan-based polymer electrolytes3,4), these reports do not give any insight on the transport mechanism of their system. In the present work, dimethyl carbonate (DMC) was introduced as plasticizer to sample of 50 wt% Chitosan - 50 wt% NH$_4$CF$_3$SO$_3$ that showed a maximum conductivity of $(8.91\pm1.38) \times 10^{-7}$ S/cm3). Rice and Roth model was applied to the conductivity data to calculate the number density, $n$; diffusion coefficient, $D$ and mobility; $\mu$ of the mobile ions5). According to the Rice and Roth model, the ionic conductivity is expressed as:

$$\sigma = \frac{Ze^2}{3kTm}ne_A A^2 \exp(-E_A/kT)$$

(1)

Here $Ze$ is charge of the conducting species, $k$ is Boltzmann constant, $E_A$ the activation energy, $T$ is temperature in Kelvin, $m$ is mass of ion and $r$ is transit time of the migrating ions. With the activation energy known from the slope and the pre-exponential term from the intercept5), $n$ could be calculated. $\mu$ and $D$ of the samples are then calculated using expression:

$$\mu = \frac{\sigma}{nq}$$

(2)

and;

$$D = \frac{kT\sigma}{n e^2}$$

(3)

2. Materials and Methods

Chitosan powder was dissolved in 1% acetic acid (1% w/v). NH$_4$CF$_3$SO$_3$ was then added to the solution with ratio of 1:1 w/w. DMC (5-30 wt%) was added to the Chitosan-NH$_4$CF$_3$SO$_3$ and the whole solution was stirred to achieve a homogenous solution. The viscous solutions were cast into plastic petri dishes and left to dry in air at room temperature.

Impedance spectroscopy was measured using HIOKI 3531 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz. Samples were mounted on conductivity holder with stainless steel electrodes having diameter of 1 cm under spring pressure. The electrical conductivity was calculated using equation:

$$\sigma = \frac{t}{R_b A}$$

(4)

Where $t$ (cm) is thickness, $A$ (cm$^2$) is cross-sectional area and $R_b$ is bulk resistance in ohms. The thicknesses of the samples were measured using a micrometer screw gauge.

3. Results and Discussions

The conductivity value at room temperature for samples prepared in the present work is listed in Table 1. The list shows a variation in conductivity with the highest conductivity obtained at $(1.95\pm0.15) \times 10^{-6}$ S/cm for sample with 25 wt% of DMC.

Table 1 shows that the increase in number density of charge carrier in the present system is about
of the previous system. This shows that increment of \( n \) is the main contributor to the increase in conductivity. However, \( \mu \) and \( D \) decreases. The most plausible explanation is that when number density of charge carrier increases, the migration pathway is blocked thus reducing mobility and the diffusivity of the ions, which explains the non-significant increase in conductivity in the plasticized system.

The temperature-dependent ionic conductivity measurements were taken to analyze the mechanism of ionic conduction in polymer electrolytes. Figure 1 shows the plot of \( \log \sigma \) versus \( 10^3/T \) for selected samples in the system. A linear variation observed from this plot suggests that samples are Arrhenian. As there is no sudden change in the value of conductivity with temperature it may be assumed that these complexes do not undergo any phase transitions within the temperature range investigated. Activation energy, \( E_A \) was calculated from the slope of the graph and the values are tabulated in table 1.

Tan \( \delta \) represents the value of loss tangent at any frequency. The angular frequency of the applied field \( \omega \), at which \( (\tan \delta)_{\text{max}} \) occurs, defines the relaxation time, \( \tau \) for the ionic carrier. When relaxation time was plotted as a function of temperature (Figure 2), a linear relationship was obtained and could be related to Arrhenius relationship by:

\[
\tau = \tau_0 \exp \left( \frac{E_A}{kT} \right)
\]

Here \( \tau_0 \) is the pre-exponential factor, \( E_A \) is the activation energy for the relaxation process, \( k \) is Boltzmann constant and \( T \) is absolute temperature.

The activation energy was calculated from the slope and a value of 0.65 eV was obtained. This value is close to the value of the temperature dependent activation energy (activation energy of conduction), \( E_I = 0.60 \) eV indicating that the ionic migration is responsible for the observed conductivity. The similarity of activation energy of conduction and conductivity relaxation activation energy is evidence of ionic-hopping mechanism for transport.

Figure 2. Plot of \( \ln \tau \) vs \( 1000/T \)

The universal power law (UPL) maybe simplified as:

\[
\sigma_\omega = \sigma_{DC} + A\omega^s = \sigma_{DC} \left[ 1 + \left( \frac{\omega}{\omega_p} \right)^s \right]
\]

Here \( \sigma_\omega \) is the measured AC conductivity, \( \sigma_{DC} \) is the frequency independent dc conductivity which is a thermally activated quantity, \( A \) is the pre-factor that depends on temperature and composition, \( s \) is the frequency exponent in the range \( 0 < s < 1 \), \( \omega \) is the angular frequency and \( \omega_p \) is the hopping frequency at which

\[
\sigma_\omega = \omega_p = 2\sigma_{DC}
\]

The isothermal representation of AC conductivity at different temperatures for sample 37.5 wt% chitosan - 37.5 wt% NH\(_4\)CF\(_3\)SO\(_3\) - 25 wt% DMC is shown in Figure 3.
almost frequency independent at intermediate frequencies and it is about equal to bulk conductivity. In the high frequency region the power law feature \( \sigma_\omega \propto \omega^s \) is observed. The transition from frequency independent region to frequency dependent region in the conductivity signifies the onset of conductivity relaxation. The UPL behavior observed in the sample agrees well with the prediction of the jump relaxation model\(^8\). At low frequencies, ions travel much slower and so are able to jump from one site to another vacant site, which contributes to the dc conductivity when the frequency is lower than \( \omega_P \). When frequency exceeds \( \omega_P \), \( \sigma_\omega \) increases with frequency like \( \sigma_\omega \propto \omega^s \), where \( s < 1 \). This dispersion indicates that on time scales shorter than \( 1/\omega_P \), the ionic diffusion is non-random, that is the ions perform correlated forward--backward motions.

\[
\omega_p = \omega_0 \exp\left(-\frac{E_a}{kT}\right) \tag{8}
\]

Here \( \omega_0 \) is pre-exponent and \( E_a \) is activation energy of the hopping rate. The activation energy was calculated from the slope and was found to be 0.64 eV. The value is almost the same as the activation energy from the temperature dependence conductivity plot, \( E_d = 0.60 \text{ eV} \). This shows that the charge carrier has to overcome the same energy barrier while conducting as well as relaxing.

In order to understand the dynamics of the mobile ions, the conductivity spectra at different temperatures may be presented in terms of a scaling law, which is a suitable tool for comparing ion dynamics\(^9,10\). Several parameters can be used to scale the frequency axis\(^11\). In the present work, a scaling approach using the hopping frequency, \( \omega_P \), as characteristic frequency to scale the frequency axis and the dc conductivity as the scaling parameter for the conductivity axis was used. This type of conductivity scaling is expressed as follows:

\[
\frac{\sigma_\omega}{\sigma_{\text{DC}}} = F\left(\frac{\omega}{\omega_P}\right) \tag{9}
\]

Where

\[
F\left(\frac{\omega}{\omega_P}\right) = \left(1 + \left(\frac{\omega}{\omega_P}\right)^n\right)^{-1} \tag{10}
\]

This is a scaling based on the Almond-West conductivity formalism\(^12,13\). According to them, the ability to scale at different data sets to collapse into a single master curve indicating that the process can be separated into a common physical mechanism modified only by thermodynamics scale. This kind of process is called the “Time-temperature superimposition principle” (TTSP).

Figure 5 represents the scaled conductivity spectra for sample 37.5 wt% chitosan - 37.5 wt% \( \text{NH}_4\text{CF}_3\text{SO}_3 \) - 25 wt% DMC at different temperatures. The figure shows that all the data collapse almost perfectly into one single master curve. This implies that the relaxation mechanism is independent of temperature and indicates the TTSP nature.

4. Conclusions

Dimethyl Carbonate plasticized chitosan-based polymer electrolytes was prepared and the highest conductivity obtained in this work was \((1.95 \pm 0.15) \times 10^{-6} \text{ S/cm}\) for sample 37.5 wt% chitosan - 37.5 wt% \( \text{NH}_4\text{CF}_3\text{SO}_3 \) - 25 wt% DMC. Using calculated value from the Rice and Roth model, the increase in conductivity could be due to the increase in the number density of mobile ions. The similarity of \( E_D \) and \( E_d \) indicates that ion migration is due to hopping mechanism while the identical values of \( E_\omega \) and \( E_d \) could infer that samples has to overcome the same barrier while conducting as well as relaxing. The AC conductivity master curve was obtained for the highest conducting sample when scaled vertically by \( \sigma_{\text{DC}} \) and horizontally by \( \omega_P \).
Acknowledgement

A.S.A. Khiar would like to thank University of Malaya for providing the facilities to carry out this work.

References


Table 1. Transport data of Chitosan-NH4CF3O3-DMC polymer electrolyte system

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>$\sigma x 10^{-7}$ (S/cm)</th>
<th>$E_A$ (eV)</th>
<th>$\tau x 10^{-14}$ (s)</th>
<th>$\mu x 10^{-8}$ (cm²/Vs)</th>
<th>$D x 10^{-10}$ (cm²/s)</th>
<th>$n x 10^{-19}$ (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 wt% Chitosan – 50 wt% NH4CF3SO3</td>
<td>(8.91±1.38)</td>
<td>0.78</td>
<td>8.02</td>
<td>1.61</td>
<td>4.14</td>
<td>34.5</td>
</tr>
<tr>
<td>47.5 wt% Chitosan – 47.5 wt% NH4CF3SO3 – 5 wt% DM (B1)</td>
<td>(0.29±1.05)</td>
<td>0.85</td>
<td>7.67</td>
<td>1.69</td>
<td>4.33</td>
<td>4.73</td>
</tr>
<tr>
<td>45 wt% Chitosan – 45 wt% NH4CF3SO3 – 10 wt% DMC (B2)</td>
<td>(0.88±1.67)</td>
<td>0.67</td>
<td>8.67</td>
<td>1.49</td>
<td>3.84</td>
<td>35.70</td>
</tr>
<tr>
<td>42.5 wt% Chitosan – 42.5 wt% NH4CF3SO3 –15 wt% DMC (B3)</td>
<td>(0.37±0.95)</td>
<td>0.82</td>
<td>7.81</td>
<td>1.66</td>
<td>4.26</td>
<td>23.90</td>
</tr>
<tr>
<td>40 wt% Chitosan – 40 wt% NH4CF3SO3 –20 wt% DMC (B4)</td>
<td>(0.28±1.09)</td>
<td>0.86</td>
<td>7.01</td>
<td>1.84</td>
<td>4.74</td>
<td>2.25</td>
</tr>
<tr>
<td>37.5 wt% Chitosan – 37.5 wt% NH4CF3SO3 – 25 wt% DMC (B5)</td>
<td>(19.5±0.15)</td>
<td>0.60</td>
<td>9.11</td>
<td>1.42</td>
<td>3.65</td>
<td>69.6</td>
</tr>
</tbody>
</table>