

# Fabrication and Characterization of a Solid Polymeric Electrolyte of PAN-TiO<sub>2</sub>-LiClO<sub>4</sub>

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**ABSTRACT:** The ionic conductivity of PAN-TiO<sub>2</sub>-LiClO<sub>4</sub> as a function of TiO<sub>2</sub> concentration and temperature has been reported. The electrolyte samples were prepared by solution casting technique. Their conductivity was measured using the impedance spectroscopy technique. The highest room temperature conductivity of  $1.8 \times 10^{-4}$  S cm<sup>-1</sup> was obtained at 7.5 wt % of TiO<sub>2</sub> filler. It was observed that the relationship between temperature and conductivity were linear, fitting well in Arrhenius and not in Vogel-Tamman-Fulcher equation. The pre-exponential factor,  $\sigma_0$  and  $E_a$  are  $1.8 \times 10^{-4}$  S cm<sup>-1</sup> and 0.15 eV,

respectively. The conductivity data have been supported by differential scanning calorimeter (DSC) analysis. DSC analysis showed that there was a significant change in glass transition temperature ( $T_g$ ) with the filler concentration. The SEM micrograph revealed that the TiO<sub>2</sub> particles are dispersed in the electrolyte, thus enhancing its conductivity. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2144–2148, 2010

**Key words:** ionic conductivity; PAN; solid polymer electrolyte; TiO<sub>2</sub>

## INTRODUCTION

Solid polymeric electrolyte containing dissolved inorganic salt and organic plasticizer has received much attention as it is a promising electrolyte material for solid state rechargeable lithium batteries and other ionic device such as dye-sensitized solar cell. The roles of plasticizer are to help the dissociation of salt into ions and associate with the ionic carriers and allow them to move faster enhancing the electrolyte conductivity.<sup>1</sup> However, the organic plasticizer such as ethylene carbonate, propylene carbonate (PC), and diethyl carbonate are costly. Furthermore, they are required in a large amount in preparing electrolyte samples. As such, many polymer electrolyte systems with different combinations of filler and salts have been developed.<sup>2–5</sup> In an earlier work on a polymer electrolyte based on PAN doped with PC plasticizer, a room temperature ionic conductivity as high as  $4.2 \times 10^{-4}$  S cm<sup>-1</sup> was obtained by Rika et al.<sup>6</sup> PAN-based solid polymeric electrolyte has been developed by a lot of groups

such as Forsyth et al., Yang et al., and Lewandowski and Stepniak.<sup>7–9</sup> Ahmad et al.<sup>10</sup> has chosen a TiO<sub>2</sub> filler to be blended into a composite solid electrolyte of PVC-LiClO<sub>4</sub> for the ionic conductivity enhancement as it is a stable semiconductor filler. Therefore, this work has chosen a solid polymeric electrolyte system of PAN-TiO<sub>2</sub>-LiClO<sub>4</sub> for a dye-sensitized solar cell development. The objective of the work is to investigate the influence of the TiO<sub>2</sub> filler and temperature on the conductivity of the electrolyte. The effect of the filler content on thermal property of the electrolyte was also investigated.

## EXPERIMENTAL

### Reagents and electrolyte film preparation

The raw materials are PAN purchased from Aldrich, which is in white powder form, TiO<sub>2</sub> in white powder form was obtained from Alfa Aesar A Johnson, Malthey Company, LiClO<sub>4</sub> purchased from Fluka, and dimethylformamide (DMF) purchased from SYSTEM ChemAR. The molecular weight of the PAN is 150,000. The molecular weight of the repeat unit of the PAN is 53.06 g mol<sup>-1</sup>. The particle size of TiO<sub>2</sub> powder is 5 μm with the purity of 99.9%. A total of 30 mL DMF solvent was poured into a measuring cylinder before being transferred to a conical flask. The flask was placed on a magnetic stirrer,

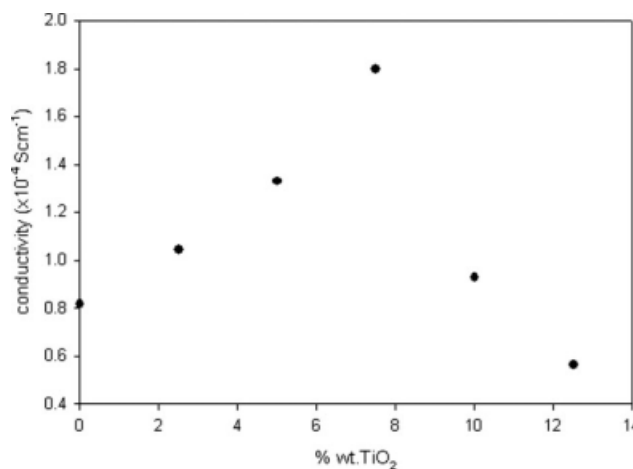
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and it was set at 70°C. The sample preparation was carried out at this temperature. A total of 80 wt % of PAN (2 g) was dissolved very slowly into the DMF and stirred for 24 h by the magnetic stirrer. A total of 20 wt % of LiClO<sub>4</sub> (0.5 g) was then dissolved in the stirred solution and then stirred for another 12 h. A total of 2.5 wt % of TiO<sub>2</sub> (0.05 g) was added into the solution and stirred efficiently with a magnetic bar for another 24 h to achieve a homogenous mixture. The solution was cast onto a glass petri-dish and allowed to evaporate completely at room temperature to solidify. Residual solvents were further removed in vacuum oven for 24 h at 60°C. The sample was stored in a desiccator containing silica gel before impedance spectroscopy, differential scanning calorimeter (DSC), and scanning electron microscopy (SEM) analysis. This procedure was repeated to prepare the electrolyte sample with 0, 5, 7.5, 10, and 12.5 wt % TiO<sub>2</sub> filler. The dried samples were then punched into circular shaped samples with diameter of 16 mm for impedance spectroscopy testing.

### Sample characterization

The alternating current (ac) impedance spectroscopy measurement was carried out at room temperature using high frequency response analyzer (HFRA Solartron 1255, Schlumberger) in the frequency range of 100 Hz–1 MHz. We have not started the impedance measurement at 1 Hz because of the limitation of our frequency resonance analyzer (FRA); we measured the frequency only within the range of 100 Hz–1 MHz instead of 1 Hz–1 MHz. The electrolyte sample was sandwiched between two stainless steel, blocking electrodes with surface area of 2.0 cm<sup>2</sup>. The bulk resistance ( $R_b$ ) data were determined from the equivalent circuit analysis by using FRA software. The conductivity values ( $\sigma$ ) have been calculated from the equation  $\sigma = t/(R_b/A)$ , where  $t$  is the thickness and  $A$  is the area of the sample. There are no error bars indicated to the experimental conductivity results because the impedance measurement was performed twice. The sample that shows the highest room temperature conductivity was chosen to investigate the temperature dependence on ionic conductivity. The measurements were done in a temperature range of 30–100°C at 10°C interval. The temperature dependence on the electrolyte conductivity was modeled by Arrhenius and Vogel-Tamman-Fulcher (VTF) equation. The thermal measurements were performed by differential scanning calorimetry DSC 8822<sup>e</sup> Mettler Toledo model in the temperature range of –60°C to +150°C at a scanning rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. Pure indium and tin were used for temperature and enthalpy calibration of the calorimeter.

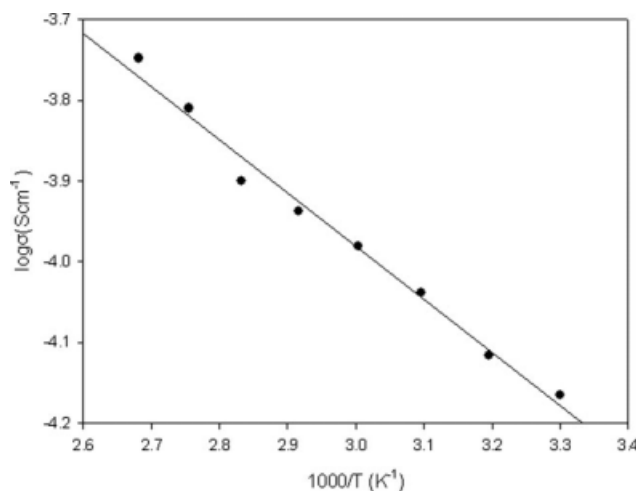


**Figure 1** Variation of conductivity with TiO<sub>2</sub> concentration.

Approximately 1 to 3 mg of the electrolyte specimens were tested. The morphology of the electrolyte with and without TiO<sub>2</sub> filler were studied by SEM. SEM model LEO 1450 VP with 20 kV voltage was performed on the electrolyte samples. Top view micrograph was taken on the surface of the sample.

## RESULTS AND DISCUSSION

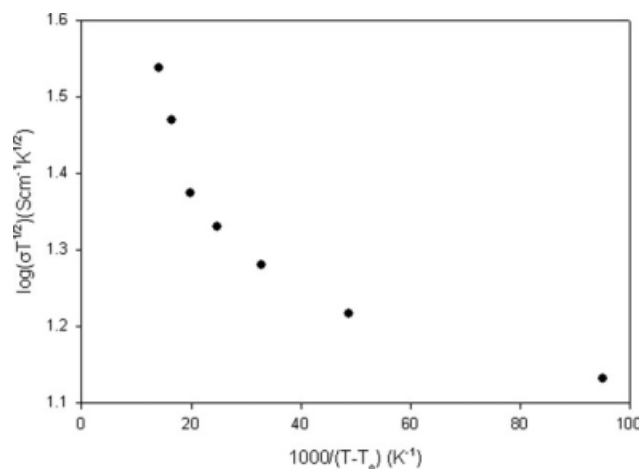
Figure 1 shows the relationship between the conductivity of PAN-TiO<sub>2</sub>-LiClO<sub>4</sub> and TiO<sub>2</sub> concentration at room temperature. The data shown in Figure 1 are the average conductivity. It was observed that the highest conductivity obtained is  $1.8 \times 10^{-4}$  S cm<sup>-1</sup> at TiO<sub>2</sub> concentration of 7.5 wt %. This result is comparable with the electrolyte with PC plasticizer showing a maximum room temperature conductivity of  $4.2 \times 10^{-4}$  S cm<sup>-1</sup> obtained at 10 wt % of LiClO<sub>4</sub> by Rika et al.<sup>6</sup> The result is also comparable with the maximum room temperature conductivity of PVdF-LiClO<sub>4</sub>-TiO<sub>2</sub> that was  $7.1 \times 10^{-4}$  S cm<sup>-1</sup> obtained at 10 wt % TiO<sub>2</sub>.<sup>11</sup> The lowest value of conductivity is  $5.6 \times 10^{-5}$  S cm<sup>-1</sup> at TiO<sub>2</sub> concentration of 12.5 wt %. Other samples with concentration of TiO<sub>2</sub> of 0, 2.5, 5.0, and 10 wt % show the conductivity of  $8.2 \times 10^{-5}$  S cm<sup>-1</sup>,  $1.0 \times 10^{-4}$  S cm<sup>-1</sup>,  $1.3 \times 10^{-4}$  S cm<sup>-1</sup>, and  $9.3 \times 10^{-5}$  S cm<sup>-1</sup>, respectively. The highest conductivity is at TiO<sub>2</sub> concentration of 7.5 wt % might be caused by the filler at this concentration produces more amorphous regions within the electrolyte and allowing more ions to be transferred. Therefore, the conductivity of the electrolyte could be improved. The results are in a good agreement with those reported by Croce et al.<sup>12</sup> and Scrosati et al.<sup>13</sup> who introduced inorganic fillers such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> in enhancing the conductivity of the polymer electrolyte. The obtained results imply that the migration of ions may occur through



**Figure 2** Arrhenius plot for the electrolyte with 7.5 wt %  $\text{TiO}_2$ .

the free volume or space between the molecules of the polymers, which can be represented by a resistor. In contrast, the immobile polymer chains become polarized in the alternating field and can be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, therefore the portion of the semi-circle can be observed at high-frequency.<sup>14</sup>

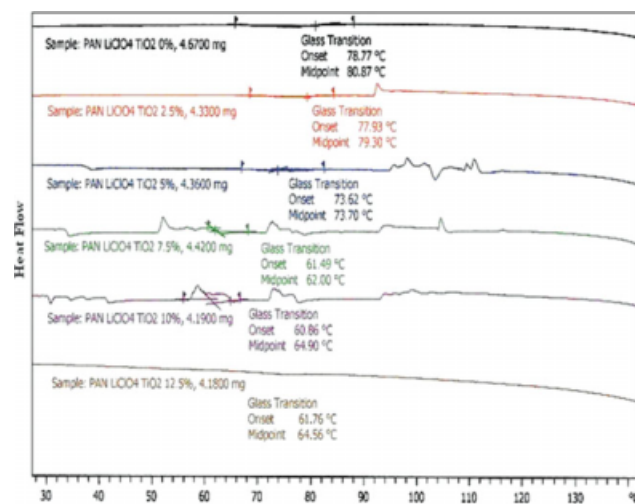
Figure 2 shows Arrhenius plot of the electrolyte. In its original form, the pre-exponential factor  $A$  and the activation energy  $E_a$  are considered to be temperature-independent. The variation of the conductivity with temperature is linear, indicating that the conductivities of the electrolyte are thermally assisted and Arrhenian.<sup>1</sup> The correlation factor of the linear adjustment is 0.9872. The value of pre-exponential factor ( $\sigma_0$ ) and activation energy ( $E_a$ ) were estimated from the y-axis intersection and the slope of the graph of  $\log \sigma$  against  $1000/T$  that was plotted. The value of  $\sigma_0$  and  $E_a$  are  $1.8 \times 10^{-4} \text{ S cm}^{-1}$  and 0.15 eV, respectively. These values are accurate because the correlation factor of the linear adjustment is very close to 1. Those obtained from the electrolyte system with PC plasticizer were  $2.0 \times 10^{-4} \text{ S cm}^{-1}$  and 0.46 eV.<sup>6</sup> The  $\sigma_0$  is comparable but not for  $E_a$ . The activation energy is a combination of energy of charge carrier creation and the energy of ion migration. Therefore, it can be suggested that the value of  $E_a$  is because of the energy that is required to provide a conductive condition for the migration of ions. It can be concluded that the energy required to dissociate cations from anions in the electrolyte of PAN- $\text{TiO}_2$ - $\text{LiClO}_4$  is smaller than the electrolyte of PAN-PC- $\text{LiClO}_4$ . From the value of  $\sigma_0$ , it can be concluded that the mobility of charge carrier of PAN- $\text{TiO}_2$ - $\text{LiClO}_4$  is smaller than PAN-PC- $\text{LiClO}_4$ . From the results that were obtained, it can be seen that the conductivity of the electrolytes increases when the temperature is increased. As the tempera-



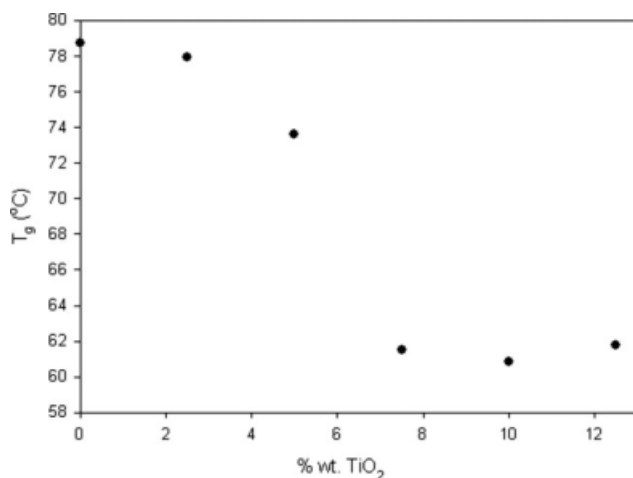
**Figure 3** VTF plot for the electrolyte with 7.5 wt %  $\text{TiO}_2$ .

ture increases, the polymer expands more easily to produce more free volume or space between the molecules. The mobility and the dissociation rate of  $\text{Li}^+$  ion also increased. As a result, the ion can move more freely between the free volumes. The resulting conductivity represented by the overall mobility of ion and polymer is determined by the free volume around the polymer chains. According to Figure 2, the conductivity was from  $6.5 \times 10^{-5}$  to  $1.8 \times 10^{-4} \text{ S cm}^{-1}$  corresponding with the temperature range from 30 to  $100^\circ\text{C}$ . On the other hand, the obtained conductivity at room temperature is  $1.8 \times 10^{-4} \text{ S cm}^{-1}$ . This is because the room temperature conductivity measurement was not performed not on the same day as the temperature varying conductivity measurement.

Figure 3 shows Vogel-Tammann-Fulcher plot of the electrolyte. With the glass transition temperature ( $T_g$ ) obtained from Figure 4 and the ionic



**Figure 4** DSC thermographs of the electrolyte with different  $\text{TiO}_2$  weight percentage. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** Variation of glass transition temperature of the electrolyte with TiO<sub>2</sub> content.

conductivity that were calculated at each interval of temperature, VTF model was introduced and applied whereby a plot of  $\log(\sigma T^{1/2})$  against  $1000/(T - T_0)$  was presented in Figure 3. In polymer electrolyte, VTF-type behavior is generally observed for the temperature dependence of the ionic conductivity, where  $A$  and  $B$  are constants related to the charge carrier density and the activation energy, respectively.

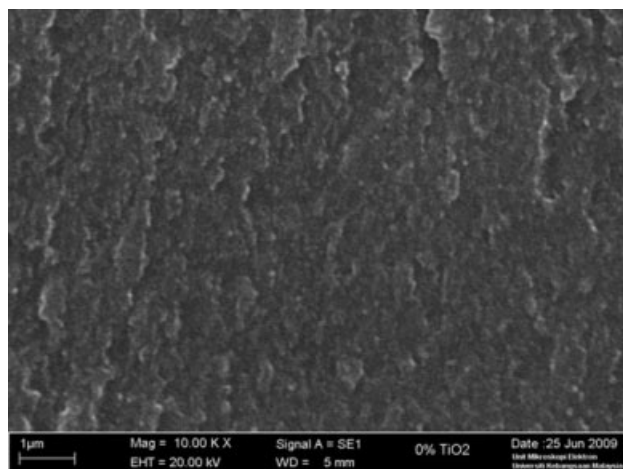
$$\sigma(T) = AT^{(-1/2)}e^{[-B/(T-T_0)]}$$

The glass transition temperature ( $T_g$ ) obtained from DSC analysis was used in determining  $T_0$ , whereby  $T_0 = T_g - 50$  K. By plotting a graph of  $\log(\sigma T^{1/2})$  against  $1000/(T - T_0)$ , a nonlinear graph is obtained for the concentration of TiO<sub>2</sub> of 7.5 wt %. The linear adjustment cannot be done because the correlation factor is only 0.7525. Therefore, the value of the constant  $A$  and  $B$  cannot be computed from the plot. Thus, the information of the charge carrier density and the activation energy of the electrolyte can be obtained.

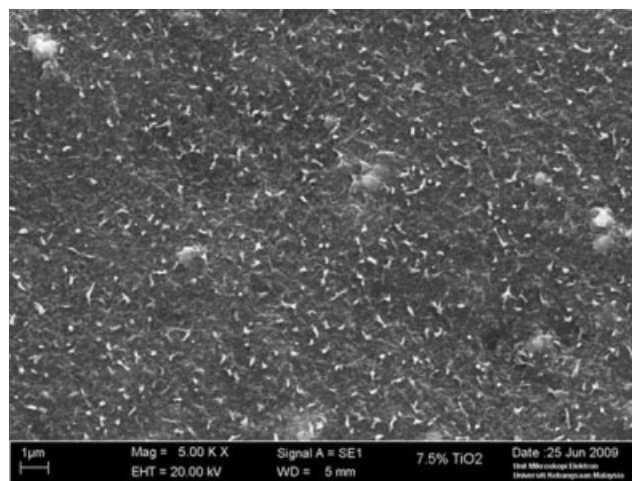
Figure 4 shows the DSC thermographs for the electrolyte with different wt % of TiO<sub>2</sub>. The glass transition temperature for each sample was taken at the onset of the endothermic peak. The variation of  $T_g$  with TiO<sub>2</sub> content is shown in Figure 5. It was noticed that the content of TiO<sub>2</sub> filler affects the value of  $T_g$  because a significant difference in  $T_g$  was observed from the figure. This suggests that the presence of TiO<sub>2</sub> filler lowers the main chain mobility resulting in the decrease in the electrolyte glass transition temperature.<sup>15</sup> This is in a good agreement with the results obtained by the other researchers. Ahmad et al.<sup>15</sup> reported that the introduction of

TiO<sub>2</sub> filler with the dielectric constant of 180 into solid polymeric electrolyte assists the lithium salts to dissociate more easily than in gel polymer electrolyte utilizing propylene carbonate with the dielectric constant of 64.5. However, for composite polymer electrolyte utilizing inorganic filler, the effect induced by filler does not dominate over the dissociation of salt. The crystallization phenomena is observed in the electrolyte beyond its glass transition point. After this point, the electrolyte starts to become amorphous. There is a strong correlation between the results shown in Figures 1 and 5. As the filler content is increased, the conductivity of the electrolyte increases up to an optimum level of the filler content. On the other hand, the  $T_g$  of the electrolyte decreases. The higher the filler content, the lower crystallization of the electrolyte, thus lowering its conductivity. The conductivity will decrease when the electrolyte approaches its  $T_g$ .

Figures 6 and 7 show the SEM micrograph of the electrolytes showing the films surface morphology with and without TiO<sub>2</sub> filler, respectively. The increase in conductivity of the electrolyte with the presence of the TiO<sub>2</sub> filler might be explained by its surface morphology. With the presence of TiO<sub>2</sub> filler, the film surface becomes rough with some small aggregates compared with that without the filler. In Figure 7, the TiO<sub>2</sub> particles represented by the white grains are uniformly dispersed in the entire surface region. This result is in a good agreement with that reported in Ref. 16 It can clearly be seen from Figure 6 that there are no TiO<sub>2</sub> particles distributed in the electrolyte. The TiO<sub>2</sub> particles in the electrolyte will give a compensating effect on the transport properties of Li<sup>+</sup> ions, hence improving the conductivity of the electrolyte.<sup>16</sup>



**Figure 6** SEM micrograph of PAN-LiClO<sub>4</sub> without TiO<sub>2</sub> filler.



**Figure 7** SEM micrograph of PAN-LiClO<sub>4</sub> with 7.5 wt % TiO<sub>2</sub> filler.

### CONCLUSIONS

A solid polymeric electrolyte of PAN-TiO<sub>2</sub>-LiClO<sub>4</sub> was prepared by the solution casting technique. The effect of TiO<sub>2</sub> filler concentration and temperature on the ionic conductivity of the electrolyte has been investigated. The highest room temperature conductivity of  $1.8 \times 10^{-4} \text{ S cm}^{-1}$  was obtained at 7.5 wt % of TiO<sub>2</sub> filler. This result is comparable with the electrolyte system with PC plasticizer, indicating that TiO<sub>2</sub> is an alternative for PC plasticizer in enhancing the electrolyte conductivity. The result also implies that the electrolyte is suitable in a dye-sensitized solar cell as a medium for redox couple. It was observed that the relationship between temperature and conductivity were linear, fitting well in Arrhenius and not in VTF equation. The pre-exponential factor,  $\sigma_0$  and  $E_a$  are 0.15 eV and  $1.8 \times 10^{-4} \text{ S cm}^{-1}$ , respectively. The conductivity data have been sup-

ported by DSC analysis. DSC analysis showed there was a significant change in glass transition temperature ( $T_g$ ) with the filler concentration. The SEM micrograph revealed that the TiO<sub>2</sub> particles are uniformly dispersed in the electrolyte, thus improving its conductivity.

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