Ionic conductivity and dielectric properties of LiBF₄ doped PMMA/ENR 50 filled acid modified SiO₂ electrolytes

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Abstract

Incorporation of silicon dioxide (SiO₂) filler was proven to improve phase separation and ionic conductivity of polymethyl methacrylate/50% epoxidized natural rubber (PMMA/ENR 50) electrolytes. Unfortunately, SiO₂ was found agglomerated in PMMA/ENR 50 electrolytes thus restricting surface contact between polymer electrolytes and electrodes. Therefore, in this study, SiO₂ was chemically modified using hydrochloric acid (HCl) in order to improve dispersion of SiO₂ in PMMA/ENR 50 electrolytes matrix. SiO₂ was reacted with HCl in different acid concentrations for an hour at ambient temperature then dried in an oven for 24 hours at 120 °C. The acid modified SiO₂ (HCl-SiO₂) was then blended with PMMA/ENR 50-tetrahydrofuran (THF) solutions and doped with lithium tetrafluoroborate (LiBF₄). Polymer electrolytes were obtained by solvent casting in a Teflon dish under nitrogen gas flow then further dried in an oven. The ionic conductivity of PMMA/ENR 50 filled HCl-SiO₂ electrolytes was analyzed using electrochemical impedance spectroscopy (EIS). Activation energy (Eₐ) was calculated from log ionic conductivity (σ) versus 1000/T plot using Arrhenius equation. It was found that the ionic conductivity (σ) was slightly decreased due to the acid modification SiO₂. However, further increase in HCl concentration lead to steady increase in the σ. The activation energy (Eₐ) was found inversely proportion to the σ. Dielectric constant (ε’) and dielectric loss and (ε'') were found to initially decrease upon the acid modification SiO₂. Real part modulus (M') was lower at lower frequency but increases as frequency increased. The M' peaks were observed at higher frequency. The peaks shifted to higher frequency as concentration HCl increased but still at lower frequency compared to polymer electrolytes filled with unmodified SiO₂. Nevertheless, no peak was recorded in imaginary part Modulus (M'').

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1. Introduction

Some works were conducted to explore the potential of PMMA/ENR 50 blend as polymer electrolytes in Li$^+$ ion batteries [1,2]. The studies revealed that by incorporation of few amount of ENR 50 and SiO$_2$ filler successfully improve the ionic conductivity and physical properties of PMMA/ENR 50 electrolytes. Unfortunately, SiO$_2$ is found agglomerated in PMMA/ENR 50 blend thus limit the performance of polymer electrolytes such as brittle and rough polymer surface hence lead to poor contact between polymer electrolyte and electrodes [2].

Fig. 1. Formation of hydrogen bond between silicon dioxide and water.

The structure of SiO$_2$ (Fig. 1) consists of repeating unit of Si-O-Si and known as siloxane group which all atoms are covalently bonded in tetrahedral structure. Meanwhile, on the surface of SiO$_2$, the oxygen atom which covalently bonded to silicon atom may bond to hydrogen atom resultant from reaction between SiO$_2$ with moisture and known as silanol group (Si-O-H) [3]. In the structure, the hydrogen atom on silanol group may form hydrogen bond with moisture thus encourages agglomeration of SiO$_2$ when their filled in PMMA/ENR 50 blend especially at high percentage SiO$_2$.

Based on our preliminary study, the acid modification on the surface of SiO$_2$ was able to reduce the number of silanol group (Fig. 2). The chemical and physical characteristics of HCl-SiO$_2$ and PMMA/ENR 50 blend were examined in detail. From the finding, the acid modification of SiO$_2$ reaction is proposed involve few steps in which one of the step demonstrates dehydration process where the silanol groups eliminated from the surface of SiO$_2$. Since the number of silanol groups were reduced the formation of hydrogen bonding and SiO$_2$ agglomeration may depressed.

Fig. 2. Suggested mechanism routes for modification of HCl-SiO$_2$. 
In this study, the effects of acid modification of SiO$_2$ to the room temperature and temperature dependence $\sigma$ of PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes were investigated. From these results, the $E_a$ of the polymer electrolytes was successfully calculated and discussed. Meanwhile, for the electrical properties studies, the dielectric properties ($\varepsilon'$ and $\varepsilon''$) and electric modulus ($M'$ and $M''$) of the polymer electrolytes were examined.

2. Experimental

2.1 Methodology

Acid modification of SiO$_2$ was carried out by shaking SiO$_2$ (15 nm) (Merck) in various HCl (Merck) concentrations for an hour at ambient temperature. HCl-SiO$_2$ then allowed to dried in an oven at 120 °C for 24 hours without calcination. Polymethyl methacrylate (PMMA) (Mw = 120,000) (Sigma-Aldrich, USA), 50 % epoxidized natural rubber (ENR 50) (Guthrie Polymer) and HCl-SiO$_2$ were dissolved or suspended in THF separately under continuous stirring. All constituent solutions were mixed before LiBF$_4$ was added to them and the solutions were continuing stirred for another 24 hours. Amount of ENR 50, HCl-SiO$_2$ and LiBF$_4$ were fixed at 10, 5 and 40 % (w/w) in PMMA, respectively. Thin films were obtained by casting method in Teflon petri dish under nitrogen gas flow for 12 hours. All samples were further dried in an oven at 50 °C for overnight and then kept in a desiccator.

2.2 Electrochemical Impedance Spectroscopy Measurement

The impedance of thin film samples were measured using a Hioki 3532-01 LCR High Tester. The instrument was interfaced to a computer and set to measure the impedance in a frequency range of 100 Hz – 1 MHz from 298 up to 353 K. From the Cole-Cole plot obtained, the bulk resistance can be determined hence, the electrical conductivity of the sample can then be calculated using the following equation;

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

where $\sigma$ is the ionic conductivity, $t$ is the thickness of the sample, $A$ is the contact area between sample and electrodes and $R_b$ is bulk resistance.

3. Result and discussion

The effects of HCl-SiO$_2$ on the $\sigma$ and $E_a$ of PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes are presented in Table 1. The result shows that the $\sigma$ is reduced to one order of magnitude for the polymer electrolytes filled HCl-SiO$_2$ compared to polymer electrolytes filled unmodified SiO$_2$. This may due to reduce in number of silanol groups from acid modification of SiO$_2$. Although, the silanol groups is expected to be the key of the agglomeration of SiO$_2$, but the groups may important to the filler in order to facilitate ionic conduction in the polymer electrolytes. This is because the ability of silanol groups acts as alternative pathways to form temporary hydrogen bonding between Li$^+$ ions from dissociation of LiBF$_4$. In other words, oxygen atoms in silanol groups on the surface of SiO$_2$ may act as Lewis base in which allow Li$^+$ ions to be conducted throughout SiO$_2$ surface [4].

Further increase in HCl concentration from 1 to 7 M shows steady increase in the $\sigma$. This may relate to enhancing in well dispersed of HCl-SiO$_2$ in PMMA/ENR 50 electrolytes. Even though the number of silanol groups decreases with concentration of HCl increased but remaining silanol groups on the surface of SiO$_2$ are still available to facilitate the movement of Li$^+$ ions. Dispersion of HCl-SiO$_2$ in PMMA/ENR 50 electrolytes getting better with concentration of HCl increased. As results, the particles of HCl-SiO$_2$ get closer and interconnected each other’s thus form links of ionic conduction pathways. Unfortunately, $\sigma$ dropped when SiO$_2$ was modified with 9 M HCl. This may due to HCl-SiO$_2$ may well disperse in PMMA/ENR 50 electrolytes and may get too close between each other’s. This may create blocking effect to conduction of ions in the polymer electrolytes and may cause the polymer chains become immobilized hence reduce the $\sigma$ [5].
The $E_a$ values were calculated from the slope of $\sigma$ versus 1000/T plot at temperature range of 25 to 50 °C. These temperatures were used after considering irregular trend of the temperature dependence $\sigma$ plot corresponding to PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes as presented in Fig. 3. The $\sigma$ of all samples initially increases as temperature increased up to 50 °C. The increases in $\sigma$ as temperature increased may attribute to the expansion of polymer matrix during heating. This may create free volume and unoccupied space to allow Li$^+$ ions to be conducted freely [6]. However, the $\sigma$ of polymer electrolytes is found decreases as temperature increased start from 60 up to 80 °C. Meanwhile, the $E_a$ values were found increases dramatically as SiO$_2$ modified using 1 M HCl. Further increase in concentration of HCl in acid modification of SiO$_2$ increase the $E_a$ values. The results show that the $E_a$ values are inversely proportion to the $\sigma$ values. This support the $\sigma$ results in Table 1 where the modification of SiO$_2$ using HCl may hinder the movement of ionic conducting in polymer electrolytes [7]. This may attribute to the reduction of silanol groups on the surface of SiO$_2$ as alternative conducting pathway for conduction of Li$^+$ ions.

<table>
<thead>
<tr>
<th>Concentr. of HCl (moldm$^{-3}$)</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma \times 10^{7}$ (Scm$^{-1}$)</td>
<td>52.60</td>
<td>5.95</td>
<td>7.71</td>
<td>8.75</td>
<td>12.17</td>
<td>2.69</td>
</tr>
<tr>
<td>$E_a$ (kJmol$^{-1}$)</td>
<td>0.76</td>
<td>15.50</td>
<td>15.57</td>
<td>20.50</td>
<td>17.23</td>
<td>33.63</td>
</tr>
</tbody>
</table>

Fig. 3. Temperature dependence ionic conductivity corresponding to PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes (○: 0, □: 1, △: 3, ×: 5, *: 7 and ◆: 9 M HCl).

Fig. 4 shows the frequency dependence of the dielectric constant ($\varepsilon'$) corresponding to PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes. All samples shows similar characteristic in which the $\varepsilon'$ is higher at lower frequency due to orientation of polar groups, ions and space charges polarization at these frequencies. However, when the frequency is increased, dipoles are failed to align with the applied field and thus they oscillating begins to lag behind and the $\varepsilon'$ start to decreases [8]. This phenomenon is known as an electrical relaxation process [9]. Meanwhile, samples filled with HCl-SiO$_2$ show decrease in $\varepsilon'$ indicated that significant influence of acid modification of SiO$_2$ on the $\sigma$ [10]. It is important to note that the amount of Li$^+$ ions and filler are same for every sample. However, the number of silanol groups on the surface of SiO$_2$ may vary due to the acid modification of SiO$_2$ using different concentrations of HCl as proposed in Fig. 2. Thus, the polarization of charge in the polymer electrolytes may reduce due to reduce in number of interaction side for temporary hydrogen bonding between for Li$^+$ ions and oxygen atoms of silanol groups.
Besides, the figure shows that there is no segmental relaxation process observed in all sample suggesting that the LiBF₄ is homogeneous distributed in the polymer electrolytes [9].

Fig. 4. Frequency dependence of the dielectric constant ($\varepsilon'$) corresponding to PMMA/ENR 50 filled HCl-SiO₂ electrolytes ($\Phi$: 0, $\Box$: 1, $\Delta$: 3, $\times$: 5, $\ast$: 7 and $\circ$: 9 M HCl).

Fig. 5. Frequency dependence of the dielectric loss ($\varepsilon''$) corresponding to PMMA/ENR 50 filled HCl-SiO₂ electrolytes ($\Phi$: 0, $\Box$: 1, $\Delta$: 3, $\times$: 5, $\ast$: 7 and $\circ$: 9 M HCl).

Fig. 5 shows the frequency dependence of the dielectric loss ($\varepsilon''$). The figure shows similar behaviour that observed for the $\varepsilon'$ in Fig. 4. The $\varepsilon''$ are higher at low frequency due to polarization effects on the electrode and free charge motion in the system which is strongly related to the $\sigma$ of the samples [11]. However, the $\varepsilon''$ are found decreases as frequency increased may attribute high periodic reversal of the field at the interface. Thus the effect of ions to the electric modulus decreases resulting from the reduction of the diffusion of ions in polymer electrolyte [10]. Meanwhile, the acid modification of SiO₂ decrease the $\varepsilon''$ values of PMMA/ENR 50 filled HCl-SiO₂ electrolytes at the lower frequency region. This may due to the reduction of mobility of charge carrier [9] consequences from the reduction of silanol groups on the surface of HCl-SiO₂. As mentioned earlier, the HCl-SiO₂ gains its homogeneity in PMMA/ENR 50 electrolytes. Unfortunately, the number of Li⁺ ions that successfully conducted to the surface of electrodes may reduce since the number of alternative pathways for Li⁺ ion, oxygen atoms in silanol groups on the surface of HCl-SiO₂ was reduced in acid modification of SiO₂.
Fig. 6 depicts the variation of real part of modulus ($M'$) corresponding to PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes. The curves show that dispersions are found at higher frequency. The $M'$ are said free from space charge effect may separate in to two region; the electrode polarization region which found below 3 kHz and ionic conduction region which observed higher than 3 kHz. The curves revealed that the ionic conduction region shows dispersion at higher frequency [12]. The value of $M'$ is lower at lower frequency may attribute to removal of electrode/electrolyte polarization in the system [13] hence able to facilitate the migration of Li$^+$ ions in the ionic conduction [14]. The $M'$ increases as frequency increased hence the $M'$ peaks observed at the higher frequency. The $M'$ peaks are shifted to a higher frequency as HCl concentration used in acid modification if SiO$_2$ increased but still lower compared to polymer electrolyte filled unmodified SiO$_2$.

Fig. 7 shows the frequency dependence of imaginary part of modulus ($M''$) corresponding to PMMA/ENR 50 filled HCl-SiO$_2$ electrolytes. The $M''$ may use as an indicator for the energy loss under electric field. The dispersion is found at frequency of 30 kHz. The figure shows that there is no $M''$ peak observed for all samples indicated that there is no conductivity relaxation is recorded within the experimental frequency range. The figure is difficult to interpret since the behaviour of curves is not well seen especially at higher frequency. Since the $M''$ peak is not observed, the determination of exact value of ionic conductivity relaxation frequency ($f_0$) and ionic conduction relaxation time ($\tau_0$) are impossible [12].
4. Conclusion

The PMMA/ENR 50 filled HCl-SiO₂ electrolytes were successfully prepared by solvent casting method. The room temperature and temperature dependence σ of polymer electrolytes were found slightly decrease due to the acid modification of SiO₂. Dielectric properties and electric modulus revealed that the acid modification SiO₂ gives significant influence to the electrical properties of the PMMA/ENR 50 filled HCl-SiO₂ electrolytes.

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