**Ionic Conductivity of PEMA-LiClO₄ Polymer Electrolytes**

(Kekonduksian Ion dalam Elektrolit Polimer PEMA-LiClO₄)

S. N. AMIR, R. OTHMAN, R. H. Y. SUBBAN & N. S. MOHAMED*

**ABSTRACT**

Solid polymer electrolytes comprised of various weight percent ratios of poly(ethyl methacrylate) (PEMA) and lithium perchlorate (LiClO₄) salt were prepared via solution casting technique using N,N-dimethylformamide (DMF) as the solvent. The conductivity values of the electrolytes were determined via impedance spectroscopy. The conductivity of the PEMA-LiClO₄ electrolytes increased with increasing salt concentration and the highest conductivity obtained was in the order of 10⁻⁶ S cm⁻¹ at salt concentration of 20 wt%. The conductivity decreased for higher salt concentration. In order to understand the conductivity behavior, XRD and dielectric studies were done. The results showed that the conductivity was influenced by the fraction of amorphous region and number of charge carriers in the system. The transference number measurement was also performed on the highest conducting electrolyte systems. The result of the measurement indicated that the systems were ionic conductors.

Keywords: Dielectric constant; impedance spectroscopy; Scherrer length

**EXPERIMENTAL DETAILS**

The samples for this work were prepared by employing the solution casting technique. Various weight percent of LiClO₄ was dissolved in solutions containing 1 g of PEMA (M₁ = 125000) and 40 mL of DMF. The mixtures were stirred for 24 h using digital magnetic stirrers. After thoroughly dissolved, each sample was cast into petri dishes and let to dry at room temperature. The conductivity values of the electrolytes were measured utilizing Solatron 1260. Structural properties of the electrolytes were investigated by X-ray diffraction employing LabX XRD 6000 equipment. Transference number for the film with highest conductivity was determined using D.C. polarization method. The sample was placed between carbon electrodes and then polarized by applying a potential of 1.0 V. The variation of current with time was recorded. The ionic conductivity transference number was calculated using the equation,
where \( i_t \) and \( i_r \) are the total and residual current, respectively.

**RESULTS AND DISCUSSION**

Figure 1 shows that the conductivity increases until it reaches a maximum value of \( 2.34 \times 10^{-6} \) S cm\(^{-1} \) at 20% LiClO\(_4\). Beyond this maximum value, the conductivity decreases with the increase in the wt% of LiClO\(_4\). In order to explain the prior conductivity variation with the percentage of LiClO\(_4\), structurally, XRD was performed.

Figure 2 depicts the X-ray patterns of PEMA-LiClO\(_4\) films. The XRD pattern for pure PEMA obtained in this work is similar to that obtained by Rajendran et al. (2008) where a small peak appeared at \( 2\theta \approx 29.5^\circ \). Almost all peaks of LiClO\(_4\) are not observed indicating that complexation between PEMA and LiClO\(_4\) has occurred. At \( 2\theta \approx 29.5^\circ \), the intensity of the peak decreases from 10% LiClO\(_4\) up to 20% LiClO\(_4\). Exceeding 20% LiClO\(_4\), the height of the peak tends to increase.

The Scherrer length, \( L \), for every sample was determined using the equation,

\[
L = \frac{0.9A}{\Delta 20_{\text{within}} \sin\left(\frac{20_{\text{max}}}{2}\right)}
\]

\[ L = \frac{0.9\lambda}{\Delta 20_{\text{within}} \sin\left(\frac{20_{\text{max}}}{2}\right)} \]  

**FIGURE 1.** Variation of conductivity at room temperature with concentration of salt

**FIGURE 2.** X-ray pattern of PEMA with (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 25 and (g) 30 wt% LiClO\(_4\)**
where $\lambda = 1.5418 \text{ Å}$ and $\Delta 2\theta$ is the width at half maximum. In this work, Scherrer length was calculated using the peak at 29.5°. The plot of the variation of $L$ with salt concentration is presented in Figure 3. According to Hashmi et al. (1998), the smaller the value of $L$, the more amorphous the sample is. Hence, from Figure 3 it can be inferred that the amorphicity of the electrolyte films studied increases with increasing salt concentration up to 20 wt% of LiClO$_4$. However, the amorphicity decreased when salt concentration is greater than 20 wt%. This observation is opposite to the variation of conductivity with salt concentration shown in Figure 1. This shows that the conductivity was affected by the amorphicity of the films. The most amorphous film was the film with PEMA:LiClO$_4$ wt% ratio of 80:20.

Graph of $\varepsilon_r - \log \omega$ for all films are shown in Figure 4. The dielectric constant rose sharply at low frequencies. According to Mohamed and Arof (2004), this behaviour indicates that electrode polarization and space charge effects have occurred. The variation of dielectric constant with salt concentration follows the same trend as the variation of conductivity with salt concentration. Since $\varepsilon_r$ represents the number of charge carrier in the system, it can be inferred that the increase in conductivity was due to the increase in the number of charge carriers.

In the attempt to study the relaxation times of the PEMA-LiClO$_4$ films, the curves of the variations of imaginary part of electric modulus with frequency were plotted (Figure 5). The relaxation times determined from the curves are listed in Table 1. The variation of relaxation time with salt concentration was consistent with the variation of conductivity with salt concentration. That is, the relaxation time decreased with increasing conductivity and vice versa. Table 1 also reveals that the ions travel...
fastest in the film of PEMA with 20 wt% salt. This is another factor that contributed to its high value of conductivity.

From Figure 6, the ionic transference number, $t_i$, and electronic transference number, $t_e$, were determined to be 0.938 and 0.062, respectively. According to Linford (1988), when $t_i > t_e$, the majority charge carriers are ions. Thus, the results of the transference number measurement confirm that the majority charge carriers in the PEMA+20% LiClO$_4$ film are ions.

**Table 1. Relaxation times for PEMA-LiClO$_4$ films**

<table>
<thead>
<tr>
<th>Film</th>
<th>Relaxation time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEMA + 10 wt% LiClO$_4$</td>
<td>0.0170</td>
</tr>
<tr>
<td>PEMA + 15 wt% LiClO$_4$</td>
<td>0.0072</td>
</tr>
<tr>
<td>PEMA + 20 wt% LiClO$_4$</td>
<td>0.0014</td>
</tr>
<tr>
<td>PEMA + 25 wt% LiClO$_4$</td>
<td>0.0018</td>
</tr>
<tr>
<td>PEMA + 30 wt% LiClO$_4$</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

The highest conductivity achieved in this work was $2.34 \times 10^{-6}$ S cm$^{-1}$ for the ratio of PEMA to LiClO$_4$ of 80:20. The transference number measurement suggests that the majority charge carriers are ions. The results from this work showed that PEMA is another potential host for polymer electrolytes. Work on improving the conductivity of PEMA based electrolytes is being carried out in the authors’ laboratory.
REFERENCES


S.N. Amir
Department of Engineering
Centre for Foundation Studies
International Islamic University of Malaysia
46350 Petaling Jaya, Selangor, Malaysia

R. Othman
Department of Sciences, Kuliyyah of Engineering
International Islamic University of Malaysia
Jalan Gombak
53100 Kuala Lumpur, Malaysia

R.H.Y. Subban
Faculty of Applied Sciences
Universiti Teknologi MARA
40450 Shah Alam, Selangor, Malaysia

N.S. Mohamed*
Centre for Foundation Studies in Science
University of Malaya
50603 Kuala Lumpur, Malaysia

*Corresponding author; email: nsabirin@um.edu.my

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