Research Article

Preparation and Characterization of Polymer Electrolyte of Glycidyl Methacrylate-Methyl Methacrylate-LiClO$_4$ Plasticized with Ethylene Carbonate

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1. Introduction

Dye-sensitized solar cells (DSSCs) have received considerable attention due to low manufacturing cost and simple preparation technique over conventional solar cells. Dye-sensitized solar cells (DSSCs) are considered as third generation photovoltaic devices that combine high-energy conversion efficiency together with low production cost. The most important issue of the dye-sensitized cells is the stability over the time and the temperature range which occurs under outdoor conditions. A photovoltaic conversion efficiency of 12.5% has been obtained in DSSCs with organic solvent-based electrolyte [1]. Even though the high conversion efficiencies were obtained for the dye-sensitized solar cells with liquid electrolytes, potential problems caused by liquid electrolytes, such as leakage and volatilization of the liquid and possible corrosion of the counter electrode, have brought about difficulties in cell fabrication limiting the long-term performance and practical use of these dye-sensitized solar cells [2]. Several methods have been introduced to prevent electrolyte leakage. One of the strategies is to replace the volatile solvents with ionic liquids [3]. Secondly, P-type semiconductors [4], inorganic hole transport materials [5], organic hole transport materials [6], and finally polymer/redox couples blends [7] have been introduced as substitutions for traditional liquid electrolyte in all solid-state photoelectrochemical cell configurations. Nanocomposite polymer electrolyte [8, 9], polymer gel [10, 11], and solid state or quasi-solid state polymer materials [12, 13] have been utilized to replace the organic liquid electrolyte in DSSC. Replacing liquid electrolytes with solid electrolytes, the solvent-free polymer electrolytes are materials of immediate interest. The efficient DSSCs using
methacrylate compound-based solid polymer electrolytes were showing advantageous properties and sufficient efficiency [14].

The main problem associated with P(GMA-co-MMA) is its low ionic conductivity at room temperature. Adding plasticizers is a known unique approach to enhance the ionic conductivity. Nowadays, many advantageous properties of solid polymer (SPEs) based electrolytes like preventing electrolyte leakage and liquid evaporation make them suitable electrolyte for DSSCs [10]. Here, we have introduced one approach to modify polymer electrolyte system and achieve high ionic conductivity which is desirable for DSSC application. We have added plasticizer ethylene carbonate (EC) into P(GMA-co-MMA) matrix to enhance the flexibility of polymer chains and consequently improved the ionic conductivity.

2. Materials and Methods

2.1. Materials. Glycidyl methacrylate (GMA), methyl methacrylate (MMA), 2,2-dimethoxy-2-phenylacetophenone (DMPP), and lithium perchlorate (LiClO4) were purchased from Aldrich. Tetrahydrofuran (THF) was obtained from J.T. Baker. Ethylene carbonate (EC) and acetonitrile were supplied from Fluka and Dyesol, respectively.

2.2. Preparation of UV-Cured Polymer and UV-Cured Polymer Electrolyte. Copolymer was prepared by photopolymerization technique in the presence of DMPP as photoinitiator as reported in our previous work [29]. Polymer electrolyte samples containing different amounts of lithium salts were prepared by solution casting method. Tetrahydrofuran (THF) was used as a solvent. The mixture of polymer, lithium salts, and solvent was mixed and stirred for 24 hrs until a homogeneous solution was obtained. Then, the solutions were poured into Teflon mold and left to dry at ambient temperature until electrolyte films were formed. Finally, the electrolyte films of P(GMA-MMA)-LiClO4 were dried in a vacuum oven at 40°C for 2 hrs and kept inside a desiccator for their characterization and testing. Polymer electrolyte homogeneous solutions of P(GMA-co-MMA) with different concentration of lithium salts have been prepared in order to investigate the highestionic conductivity of polymer electrolyte was found to be further enhanced to maximum conductivity of 8.7 x 10^{-4} S cm^{-1}. The addition of LiClO4 in the polymer matrix tends to increase the order in amorphous state and results in higher ionic conductivity as a result of the strong interaction between polymer and LiClO4. However, when the lithium salt concentration reaches certain value, the excess dissociated Li+ and ClO4^- ions may form ion pairs or ion clusters, which reduces the free ions concentration and leads to the decrease of the conductivity [15, 16]. The mechanical property of the electrolyte film over 35% salt is not free standing, not flexible, sticky, and gelly. Moreover, the salt cannot be added into P(GMA-MMA)-EC anymore since it is overloaded. That is why we stopped at 35 wt.% LiClO4 while preparing the electrolyte.

The P(GMA-co-MMA) with LiClO4 based polymer electrolyte with optimum ionic conductivity was mixed as function of concentration of EC. Figure 3 shows the ionic conductivity of P(GMA-co-MMA)-25 wt.% LiClO4 with various EC content at room temperature. As can be seen from
Figure 1: Appearance of P(GMA-co-MMA)-LiClO₄-EC.

Figure 2: Ionic conductivity of P(GMA-co-MMA)-LiClO₄ based polymer electrolyte as a function of LiClO₄ content.

Figure 3: Variation of ionic conductivity of P(GMA-co-MMA)-EC-LiClO₄ based polymer electrolyte as a function of EC content.

Figure 3, the conductivity increases with the addition of EC content. The film with the composition higher than 80 wt.% EC was mechanically unstable; hence the conductivity was difficult to measure. The conductivity increases slowly from $1.4 \times 10^{-6}$ S cm$^{-1}$ to $3.0 \times 10^{-4}$ S cm$^{-1}$ for P(GMA-co-MMA)-25 wt.% LiClO₄-80 wt.% EC. This conductivity is higher than that of P(GMA-co-MMA) reported in [17] for which the conductivity of $2.7 \times 10^{-5}$ S cm$^{-1}$ was achieved at 30 wt.% LiClO₄. Generally, the enhancement of ionic conductivity in plasticized solid polymer electrolyte can be explained by the interaction between polymer LiClO₄ and EC. There are three main interactions among them (i) ion-ion interaction between Li$^+$ cations and ClO$_4^-$ anions, (ii) ion-dipole interactions between Li$^+$ cations and chlorine in polymer, and (iii) ion-molecule interactions between Li$^+$ and EC [18]. These interactions are important to form polymer-LiClO₄-EC polymer electrolyte, in which three different compounds of polymer-Li$^+$, polymer-Li$^+$-EC, and Li$^+$-EC exist. The oxygen of C=O in EC is an electron donor which participates in competition with ClO$_4^-$ and polymer. The Li$^+$-EC interactions exist not only between Li$^+$ and oxygen atoms of C=O group, but also between Li$^+$ and another two oxygen atoms in the ring structure of EC. Besides that, Li$^+$-EC interaction plays an important role in the conductivity of polymer-LiClO₄-EC system. The addition of EC leads to the formation of Li$^+$-EC complex and enhances the flexibility of polymer chains by decreasing the crystalline fraction of polymer-Li$^+$ complex. The high dielectric constant of EC ($\varepsilon_r = 85.1$) effectively reduces the inter-ion coulomb interactions; hence, more Li$^+$ contributed to the conductivity of the complexes [19–21]. Furthermore, EC molecules are relatively small in size compared to polymer host molecule and therefore can easily transfuse into the polymer matrix, causing an interaction between plasticizer molecule and polymer chain molecules. This reduces the cohesive forces operating between the polymer chains resulting in an increase in the
chain segment mobility [18]. The increase in chain segmental mobility facilities ion transport leads to enhancement of conductivity. The conductivity decreases at 70 wt.% EC since it is a saturated level for EC addition into P(GMA-co-MMA)-LiClO4. This results in less space for Li+ ions to move within the matrix of P(GMA-co-MMA)-EC.

3.2. Fourier Transforms Infrared (FTIR). The FTIR spectra of the polymer system change according to their composition and may be able to show the occurrence of complexation and interaction between the various constituents. The possible mechanism of dissociation of lithium salt and plasticizer in polymer host has been proposed in [22] as shown in Figure 4. EC can introduce a new ionic pathway along which the Li+ ions can hop through the polymer.

Figures 5, 6, and 7 show the FTIR spectra of P(GMA-co-MMA)-25 wt.% LiClO4 with varying percentage of EC plasticizer. If the shift in peak is above 1 cm⁻¹, it is considered significant. 1 cm⁻¹ difference is the uncertainty of the FTIR spectrum. The identified peaks of polymer electrolyte complex and their changes are listed in Table 1. From Figure 5, the C=O stretching of EC is not observed in the spectrum of the EC free sample. With the addition of 20 wt.% EC into the system, C=O a doublet peak was observed at 1802 and 1773 cm⁻¹. The doublet peaks shift to lower wavenumbers at the addition of 40 wt.% EC. Further addition of 80 and 80 wt.% EC has shifted the doublet peaks to even lower wavenumber at 1801 and 1772 cm⁻¹. The shift phenomena are due to the interaction between the Li+ ions from LiClO4 and the oxygen atoms of the ring group of EC including the C=O band [23]. In [24], the shift of the C=O bending in pure EC was reported due to the interaction between Li+ salt and C=O group of the EC molecules and their results are in a good agreement with those reported in [25, 26]. However, there are no significant changes in the C=O peak of the polymer host. According to the result reported in [18], there was only physical interaction that appeared among EC, polymer host, and salt. The interaction of Li+ and O=C of coordination GMA competes with Li+ and O=C of EC in plasticized samples. This is because P(GMA-co-MMA) has a larger molecule size in comparison to EC molecule; hence, the interaction between (GMA-co-MMA) and lithium salt was stronger as compared to EC-lithium salt.

After the addition of EC, the band for C–O–C stretching of film was found to shift from 1252 to 1249 cm⁻¹, and the bands of these group peaks disappear as shown in Figure 7. The C=O bending band belonging to EC is observed in FTIR spectrum after the addition of EC into system. This is assigned to the interaction between Li+ of the salt after the addition of EC into the system. This result is in good agreement with the one that has been reported in [25]. Due to the increase in amount of EC, the physical interaction between EC, polymer, and salt was established, as the signal around 906 and 850 cm⁻¹ which belong to epoxy group shifted to 803 and 896 cm⁻¹ and enhanced lithium ion mobility. An interaction between salt and plasticizer leads to reduction in the coulombic interaction between the cation and anion of salt thus dissociating the salt to produce more mobile ions.

The interaction between plasticizer and salt may reduce salt-polymer interaction, which could increase chain flexibility [27]. This interaction is expected to occur between the Li+ ions with the oxygen atoms on C–O–C and C=O in the EC ring structure as proposed in [19]. However, Li+ ions prefer C–O rather than C=O [28]. It can be seen from Table 1 the band belonging to C–O–C is shifted farther than C=O upon the addition of salt. However, these changes in peak intensity and shape revealed that complexation exists between lithium salt and oxygen atoms in the polymer host.

3.3 X-Ray Diffraction (XRD). Figure 8 shows the XRD patterns of P(GMA-co-MMA)-25 wt.% LiClO4 complexed with various EC contents. This figure displays three humps in the region between 10°–25°, 25°–35° and 35°–40° in the spectra which could be attributed to the amorphous nature of P(GMA-co-MMA). The peaks pertaining to LiClO4 [29] are
### Table 1: Vibrational mode assignments of P(GMA-co-MMA)-25% LiClO₄ based polymer electrolyte with different percentage of EC.

<table>
<thead>
<tr>
<th>Vibrational mode of P(GMA-co-MMA)</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O stretching of EC</td>
<td>1802, 1773</td>
</tr>
<tr>
<td>Carboxyl group stretching</td>
<td>1719</td>
</tr>
<tr>
<td>Symmetric stretching of epoxy and ester group</td>
<td>1253, 1071, 566</td>
</tr>
<tr>
<td>Stretching C–O–O of ester group</td>
<td>1153</td>
</tr>
<tr>
<td>Asymmetric stretching of epoxy</td>
<td>903</td>
</tr>
<tr>
<td>C–H blending vibration of epoxide ring</td>
<td>748</td>
</tr>
<tr>
<td>C=O bending</td>
<td>718</td>
</tr>
</tbody>
</table>

**Figure 6:** FTIR spectra of PGMA-25 wt.% LiClO₄-EC based polymer electrolyte as a function of EC in the wavenumber region 1500–1000 cm⁻¹. **Figure 7:** FTIR spectra of PGMA-25 wt.% LiClO₄-EC based polymer electrolyte as a function of EC in the wavenumber region 1000–700 cm⁻¹.

absent in the complexes. This indicates complete dissolution of the salt in the polymer matrices. These observations are similar to the work reported in [30] However, upon the addition of EC into P(GMA-co-MMA), the intensity of the peaks decreases and a noticeable broadening of the area under the peaks is observed. This implies that the amorphous nature of the film increases with concentration of the plasticizer. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. The increase of amorphous area will improve ionic mobility and thus enhance the ionic conductivity of polymer electrolyte at room temperature. Similar findings were reported in [31, 32]. Higher degree of amorphous phase was observed in host polymers-LiClO₄ with 80 wt.% EC in the total plasticizer content; hence ionic conductivity at this particular ratio was the highest. In [33], it was reported that the incorporation of polar carbonate groups into a polymer chain did not only reduce the crystallinity of the polymer, but also increased the dielectric constant relative to polymer with the same molecular weight, thereby providing the high flexibility necessary to promote ion mobility. The amorphous nature produces greater ionic diffusivity leading to high ionic conductivity.

3.4. Cyclic Voltammetry (CV). Polymer electrolytes intended for practical applications in commercial devices must supply high lithium ion mobility to provide elevated power densities in device. Moreover, electrolytes must also be chemically stable to enable devices to attain extensive shelf lives in high voltage devices and they must be able to withstand the range of potential of the electrode couple. Figure 9 presents the cyclic voltammetry curves of P(GMA-co-MMA)-LiClO₄ with various EC contents. The stability of the polymer complexes at interface with stainless steel (SS) as electrode is limited by the potentials of +3.8 V on anodic side and of −3.8 V at the cathode side for P(GMA-co-MMA)-25 wt.% LiClO₄-EC. This could be due to noninteraction of the lithium ions in the polymer electrolyte with the SS electrodes. The cathodic peak at about 3.8 V has been attributed to the reduction of polymer electrolyte on cathode is the key reason for safety problem of lithium ion battery, which can be understood by their electrochemical stability on stainless steel electrode [34]. Polymer
electrolytes with plasticizer show higher electrochemical stability compared to polymer electrolyte without EC. However, the current density of electrolyte after breakdown potential is still low at low concentration of EC and it increases with EC concentration. In all polymer electrolytes, the current densities increase with increasing amount of EC. On the other hand, the electrochemical stability of polymer electrolytes is slightly affected by plasticizer concentration. The anodic stability is usually limited by the decomposition of polymer and lithium salt. In contrast, the situation with cathodic stability is more complicated as reported in [35]. Based on the obtained result, there is no oxidation peak related to the decomposition of polymer electrolytes in the scanning range, indicating that the electrolytes are suitable enough for the application.

4. Conclusions

We have prepared the plasticized polyglycidyl methacrylate P(GMA) copolymerized with polymethyl methacrylate P(MMA)-LiClO$_4$ polymer electrolyte via solution casting technique. The conductivity was improved about six orders upon the addition of LiClO$_4$ salt into the P(GMA-MMA) and about two orders upon the addition of EC to the P(GMA-MMA)-LiClO$_4$. Upon the addition of LiClO$_4$ salt, the band belonging to C–O–C is shifted farther than C=O. Upon the addition of EC, the band for C–O–C stretching is shifted to lower wavenumber. Upon the addition of EC into P(GMA-co-MMA)-LiClO$_4$, the crystallinity degree of the electrolyte increases. The cyclic voltammetry analysis reveals that the electrolyte is suitable for dye-sensitized solar cell application.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References


