Synthesis and characterization of a highly cross linked PEGME and PEG for solid electrolyte and its application in dye-sensitized solar cells

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Abstract
In this paper, we were prepared a highly cross linked polymer with poly (ethylene glycol) methyl ether (PEGME) and poly ethylene glycol (PEG) in presence of inorganic salts by chemical method and used as polymer electrolyte with the addition of iodide couple. This electrolyte is showing ambient ionic conductivity of 2.35 mS/cm, it is comparably well high to reported electrolyte. Solid state dye sensitized solar were fabricated with this polymer electrolyte and achieved an open circuit voltage of 0.616 volt, short circuit current of 8.96 mA/cm\(^2\) and over all conversion efficiency of about 3% under light intensity of 100mW/cm\(^2\).

Keywords: dye sensitization, gel electrolyte, solid state dye sensitized solar cells, PEG, PEGME

Introduction
There is continuing interest in the development of high-quality and high ionic conductivity solid polymer electrolytes for the use in lithium batteries, sensors and solar cells [1-3]. The main advantage of polymer electrolytes is favorable mechanical properties, ease of fabrication of thin film of desirable size, and an ability to form effective electrode-electrolyte contacts. Generally, Polymer based electrolytes have displayed a low ionic conductivity at room temperature transport. Highly cross linked polymers have been appeared to be effective in enhancing ion conductivity, better mechanical stability and also good water absorvent, and improving the interfacial contact with electrode.

Recently, many researchers are searching an alternative candidate to replace liquid electrolyte in dye sensitized solar cells [4-5] because the use of liquid electrolyte has some limitation such evaporation and leakage of solvent in long term operation of device. A solid electrolyte has ability to solve the leakage and evaporation of liquid increase long-term stability with high performance. In spite of extensive researches, the performance of solid DSSCs is not satisfactory. This has been partially explained by imperfect contact between solid electrolytes and nanoporous TiO\(_2\) layers [6]. Many efforts have already been developed to increase the interfacial contact between electrolyte and nanoporous layers by using inorganic gel, polymer gel and organic gel electrolytes [7-9]. In this addition, we attempted to synthesize highly cross linked polymer with poly (ethylene glycol) methyl ether (PEGME) and poly ethylene glycol (PEG) in presence of inorganic salts by chemical method. In this paper, we were fabricated quasi-solid state dye sensitized solar cells by synthesized highly cross-linked polymers with iodide couple and achieved a high ionic conductivity.
Experimental

For the preparation of mesoporous TiO$_2$ nanocrystalline film, TiO$_2$ (P-25, Degussa) slurry was prepared by the incremental addition of aqueous polyethylene glycol (Fluka, average MW of 20,000) solution as binder to prevent cracking of film and control the porosity during preparation of film. Thus prepared uniform slurry was coated on FTO glass (by a doctor blade technique. After natural drying at room temperature, the thin film was calcined in static air at 450°C for 30 min.

The synthesis of acid of PEGME (A) was reported in literature [10]. Synthesized polymer (A, 5%) was dissolved in deionized water and adding different ratios of polyethylene glycol (PEG) under stirring and LiI (appropriate amount), after that the whole mixture heated up to 70°C under vacuum condition for 10 hours. Finally a solid material was obtained. For Gel electrolyte, synthesized polymer mixed LiI 0.1M, I$_2$ 0.010M in acetonitrile and then whole mixture was placed on stirrer and stirred over a period of 24 hours.

To fabricate the DSSCs, thus prepared TiO$_2$ thin film electrodes were immersed in the dye solution of 0.3 mM ruthenium dye (N-719) in dry ethanol at room temperature for 24 hrs. The dye-adsorbed electrodes were then rinsed with ethanol and dried under a nitrogen stream. Pt counter electrodes were prepared by electron beam deposition of Pt (60 nm thickness) on ITO glass. The resulting dye adsorbed film was seal with a Pt-sputtered conducting glass by a spacer (surlyn) and the gel electrolyte was introduced into the cell through one of two small holes drilled in the counter electrode.

The photoelectrochemical properties of the solar cell were studied by recording the current–voltage characteristics of the cell under an illumination of 1 Sun (100 mW/cm$^2$) using a solar simulator (Yamashita Denso, YSS-80). The area of the dye-coated TiO$_2$ electrode was 0.25 cm$^2$.

The photochemical characterization of DSSCs including photocurrent density was measured by using a scanning potentiostat (EG&G 273). The device was connected in a two-electrode configuration: the dye adsorbed TiO$_2$ film on TCO glass was connected as the working electrode and the Pt-coated TCO glass was used as the pseudo-reference (circuited with the counter electrode). Photocurrent–Voltage (I–V) curve was measured by using two computerized digital multimeters (Model 2000, Keithley) and a variable load. The light source was a 1000-W halogen lamp (Philips lighting) and its radiant power was adjusted with respect to Si reference solar cell (NERL, USA for Solar Energy System; Mono-Si + KG filter) to about one-sun light intensity (100 mW/cm$^2$).

Results and discussion

From the DSC thermograms (fig. 1) the glass transition temperature (T$_g$), the melting temperature (T$_m$) and the melting enthalpy (H$_m$) were determined. The obtained results for the pure PEG (figure not shown) and for the PEGME/PEG/I$^-$/I$_3$$^-$/I$^-$/I$_3$ composite electrolyte are differed. Before the measurements, the materials were placed in a desiccator for 2 days. Then, they were heated from $-80$ to 100°C with a rate of 10°C/min under nitrogen atmosphere. A slight decrease of melting temperature observed for the synthesized hybrid polymer which is around 57°C and lower than the pure PEG (64°C). In fact,
according to the literature, the addition of inorganic salts and organic molecules in polymer matrix causes the lowering in crystallinity and prevents the recrystallization of polymer. Synthesized polymer electrolyte shows a weak signal of $T_g$, which corresponds to high flexibility of polymer.

The current-voltage characteristics of polymer gel electrolyte based DSSCs were observed under 1 sun illumination (fig.-3). Table-1 shown the averaged data extracted from I-V curve measurements of different types of electrolyte based DSSCs.

In case of PEGME/PEG (10% w/w) based gel electrolyte cell shows the maximum efficiency (3.08%) with an $I_{SC}$ of 8.96 mA/cm$^2$, a $V_{OC}$ of 0.609 volt and fill factor 0.57 which are comparatively high in compare to only PEG gel electrolyte based cells. In the other words, the conversion efficiency of DSSCs with modified polymer based gel electrolyte increased because of the interference of acid of PEGME in the PEG matrix which provides the better interfacial contact between the electrolyte and TiO$_2$ surface. Also the high gelation supports in easy electron transport during the operation and improves the thermal stability, it gives long term life. The use of hybrid polymer materials is very effective to enhance the photocurrent and overall efficiency.
Table 1 Summary of IV data of PEGME/PEG and PEG electrolyte based DSSCs

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$V_{oc}$ (volt)</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>0.526</td>
<td>8.01</td>
<td>0.54</td>
<td>2.39</td>
</tr>
<tr>
<td>PEGME/PEG</td>
<td>0.609</td>
<td>8.96</td>
<td>0.57</td>
<td>3.08</td>
</tr>
</tbody>
</table>

**Conclusion**

A novel polymer (PEGME/PEG) is prepared by simple chemical method. The ionic conductivity of synthesized polymer is depended on the ratio of acid of PEGME and PEG. The polymer gel electrolyte shows high stability and a moderately high value of ionic conductivity about 2.35 mS/cm. Improved conductivity affects the photocurrent and performance of DSSCs with this gel electrolyte.

**References**