

Effect of oligomer on dye-sensitized solar cells employing polymer electrolytes

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(Received 28 January 2010 • accepted 6 May 2010)

Abstract—The effect of oligomer ($M_n=400$ –500 g/mol) on dye-sensitized solar cells (DSSC) employing polymer electrolytes consisting of poly(epichlorohydrin-co-ethylene oxide) (Epichlomer), LiI, 1-methyl-3-propylimidazolium iodide (MPII) and I_2 is investigated. Five kinds of oligomer, poly(ethylene glycol) (PEG, $M_n=400$ and 1,000 g/mol), poly(ethylene glycol) dimethyl ether (PEGDME), poly(propylene glycol) (PPG) and poly(ethylene glycol) diglycidyl ether (PEGDGE), were introduced to elucidate the role of terminal groups and chain length. The coordinative interactions and structures of polymer electrolytes were characterized by FT-IR spectroscopy and X-ray diffraction (XRD). The improved interfacial contact between the electrolytes and the electrodes by the oligomer addition was confirmed using a field-emission scanning electron microscope (FE-SEM). The electrolytes exhibited ionic conductivities on the order of 10^{-4} S/cm, but PEGDGE electrolyte showed much lower value ($\sim 10^{-8}$ S/cm). As a result, the energy conversion efficiency of DSSC was significantly affected by the oligomer. For example, the DSSC employing PEGDME with methyl terminal groups exhibited 3.95% at 100 mW/cm², which is 200-fold higher than that employing PEGDGE.

Key words: Dye-sensitized Solar Cell, Polymer Electrolyte, Oligomer, Conductivity, Titanium Oxide

INTRODUCTION

A polymer electrolyte contains polar functional moieties such as ether (–O–), ester (COO) or amide (CON) linkages in a polymer matrix. Metal salts with a low lattice energy or ionic liquid can be dissolved in a polymer matrix even in the solid state film. Dissolution process involves the coordinative interactions between the ions and the polar groups of polymer matrix. The conductive and transport properties of polymer electrolytes have led them to be intensively studied for potential applications in lithium batteries [1], fuel cells [2] and separation membranes [3].

Polymer electrolytes containing a redox couple, i.e., triiodide/iodide (I_3^-/I^-), have also been demonstrated to exhibit unique conducting properties that make them useful for solid state dye-sensitized solar cells (DSSCs) [4–7]. DSSCs, first proposed by Grätzel in 1991 [8], have attracted much interest in the last decade due to their low production cost and the low environmental impact of their fabrication. A high energy conversion efficiency ($\sim 11\%$) has been achieved in DSSCs using an organic liquid-based electrolyte [9]. The practical exploitation of DSSCs ultimately requires cheap fabrication of devices that exhibit both efficient power conversion and long operating lifetime. However, the use of liquid electrolytes poses several practical problems including leakage of the electrolyte, desorption of the sensitizing dye by the organic solvent used in the electrolyte, and toxicity of some of the organic solvents. Thus, many efforts have been made to overcome this drawback, replacing the liquid electrolytes with room temperature ionic liquids [10,11], organic and inorganic hole-transport materials [12], or gel electrolytes [13]. Another alternative approach to retain the good device properties

of the liquid electrolytes while maintaining solid-like mechanical properties is the use of quasi-solid polymer gel electrolytes [14,15].

In general, DSSCs assembled with a polymer electrolyte show lower efficiency than do cells employing a liquid electrolyte due to both the lower ionic mobility of the I/I_3 species and the poor interfacial contact of the electrolyte/electrode [16–21]. Introduction of a low molecular weight oligomer into a high molecular weight polymer can solve these two problems simultaneously [21]. In this study, various oligomers with $M_n=400$ –500 g/mol (Table 1) were introduced into high molecular weight polymer electrolytes consisting of poly(epichlorohydrin-co-ethylene oxide) (Epichlomer), LiI, 1-methyl-3-propylimidazolium iodide (MPII) and I_2 . The resultant electrolytes were characterized in terms of the interactions, structures and ionic conductivities and applied to solid-state DSSCs.

EXPERIMENT

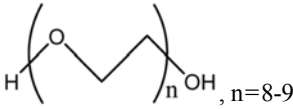
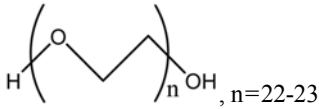
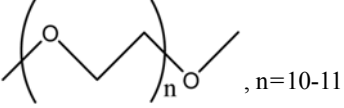
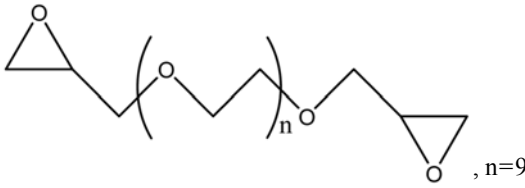
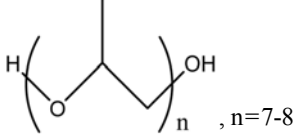
1. Materials

Poly(epichlorohydrin-co-ethylene oxide) (Epichlomer, epichlorohydrin content: 64–69 wt%), poly(ethylene glycol) (PEG, $M_n=400$ and 1,000 g/mol), poly(ethylene glycol) dimethyl ether (PEGDME, $M_n=500$ g/mol), poly(propylene glycol) (PPG, $M_n=425$ g/mol) and poly(ethylene glycol) diglycidyl ether (PEGDGE, $M_n=526$ g/mol), lithium iodide (LiI), iodine (I_2) and all other solvents were purchased from Aldrich and used as received without further purification.

Conductive glass substrates (fluorine-doped tin oxide overlayer (FTO glass)) with a sheet resistance of 8 Ω /square were purchased from Pilkington. Sensitizing organometallic dye, *cis*-dithiocyanate-*N,N'*-bis-(4-carboxylate-4-tetrabutylammonium carboxylate-2,2'-bipyridine) ruthenium(II) (N719), TiO_2 colloidal paste (Ti-Nanoxide D20), and 1-methyl-3-propylimidazolium iodide (MPII) were purchased from Solaronix S.A. All solvents and chemicals were

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Table 1. Names and chemical structures of oligomer used in this study

Name	M_n (g/mol)	Structure
PEG	400	
PEG1000	1,000	
PEGDME	500	
PEGDGE	526	
PPG	425	

reagent grade and were used as received without further purification.

2. Preparation of Polymer Electrolytes

Predetermined amounts of Epichloromer, oligomer, salt and I_2 (10 wt% of salt) were dissolved in acetone to make up 5 wt% polymer solutions. Two salts, metal salt (LiI) and ionic liquid (MPII), were used to prepare the polymer electrolytes. The solutions were cast onto Teflon-glass plates and dried in an N_2 environment at room temperature. The films were further dried in a vacuum oven for two days at 40 °C.

3. Fabrication of DSSCs

DSSCs with an active area of 0.4 cm² were constructed according to the following procedure. To prepare the photoelectrodes, conductive FTO glasses (1.5 cm×2 cm) were coated by titanium (IV) bis(ethyl acetoacetato) diisopropoxide solution (1 wt% in butanol). After drying at 50 °C for 30 min, the photoelectrodes were heated to 450 °C for two hours, held at 450 °C for 30 min, and then cooled to room temperature over eight hours. The nanocrystalline TiO_2 electrodes were fabricated by depositing TiO_2 colloidal paste onto the photoelectrodes using a simple doctor-blade technique. The layer was sintered at 450 °C for 30 min to obtain a mesoporous TiO_2 film. After sintering, the TiO_2 electrodes were immersed in a solution of an amphiphilic dye (N-719) in absolute ethanol for 24 hours at room temperature. Afterward, the electrodes were washed with absolute ethanol and dried in a moisture-free atmosphere. The Pt counter electrodes were prepared by spin coating a H_2PtCl_6 solution (2 wt% in isopropyl alcohol) onto the FTO glasses, followed by heating to 450 °C for two hours. The polymer electrolyte solutions were directly cast onto dye-adsorbed TiO_2 electrodes. Finally, the photoelectrodes and the Pt counter electrodes were assembled in a sandwich arrangement and sealed with epoxy resin.

The photoelectrochemical performance characteristics, including short-circuit current (J_{sc} , mA/cm²), open-circuit voltage (V_{oc} , V), fill factor (ff), and overall energy conversion efficiency (η , %), were measured with a Keithley Model 2400 and a 1,000 W xenon lamp (Oriel, 91193) upon masking a cell. The light was homogeneous up to an 8×8 in² area, and its intensity was calibrated with a Si solar cell (Fraunhofer Institute for Solar Energy System, Mono-Si+KG 3filter, Certificate No. C-ISE269) to a 1 sun light intensity (100 mW/cm²), which was double-checked with an NREL-calibrated Si solar cell (PV Measurements Inc.).

4. Characterization

FT-IR spectra of the samples were collected using an Excalibur Series FTIR (DIGLAB Co.) instrument in the frequency range of 4,000 to 600 cm⁻¹ with an ATR facility. X-ray diffraction (XRD) measurements were performed with a Rigaku D/max-RB apparatus (Tokyo, Japan). Data were collected from 5° to 60° at rate of 2°/min. Ionic conductivity was measured under a dry atmosphere using an impedance analyzer (IM6, ZAHNER, Germany) and a lab-made four-probe conductivity cell. The morphologies of the TiO_2 electrodes were observed with a field-emission scanning electron microscope (FE-SEM, SUPRA 55VP, Germany, Carl Zeiss).

RESULTS AND DISCUSSION

To investigate the coordinative interactions between salt and polymer, the FT-IR spectra of neat Epichloromer, Epichloromer/PEGDME blends and Epichloromer/PEGDME/(LiI+MPII) electrolyte were measured, as presented in Fig. 1. The ratio of Epichloromer:oligomer was 7 : 3 wt and the content of salt was fixed at $[EO] : [salt] = 10 : 1$. The salt mixture of LiI+MPII was always 1 : 1 wt ratio throughout the

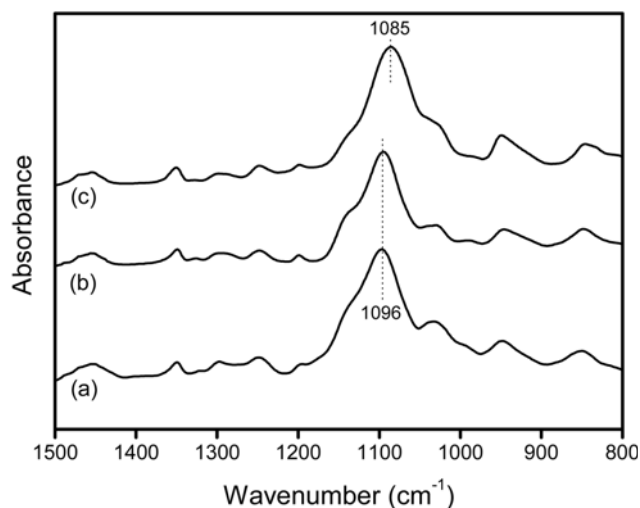


Fig. 1. FT-IR spectra of (a) Epichlomer, (b) Epichlomer/PEGDME and (c) Epichlomer/PEGDME/(LiI+MPII).

paper. The ether [-O-] stretching band of pristine Epichlomer appeared at $1,096\text{ cm}^{-1}$ and was not changed by the introduction of PEGDME because of similar chemical structures. Upon the addition of salt into Epichlomer/PEGDME, the ether stretching band shifted to a lower wavenumber of $1,085\text{ cm}^{-1}$. The shift to a lower wavenumber originated from the loosening of the C-O-C bond by the electron donation to cation [22,23]. Similar behaviors were also observed for other oligomer systems.

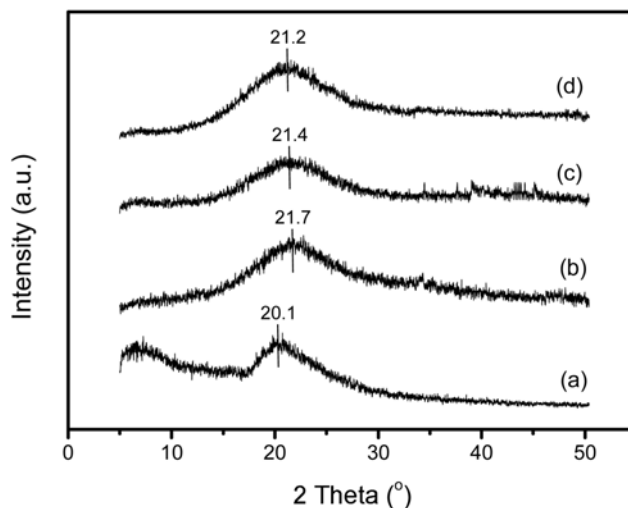


Fig. 2. XRD patterns of Epichlomer/(LiI+MPII)/I₂ electrolytes containing (a) PEG, (b) PEGDGE, (c) PEGDME and (d) PPG.

The structural properties of polymer electrolytes were characterized by XRD analysis. Fig. 2 shows the XRD patterns of Epichlomer/(LiI+MPII)/I₂ electrolytes containing various oligomers. All the electrolytes exhibited broad amorphous XRD halos, indicating the lack of crystalline parts in the films. It represents that the crystalline inorganic materials such as LiI and I₂ are completely dissolved in the polymeric matrix due to coordinative interactions between the polymer and the salt. Bragg d-spacing of polymer electrolytes

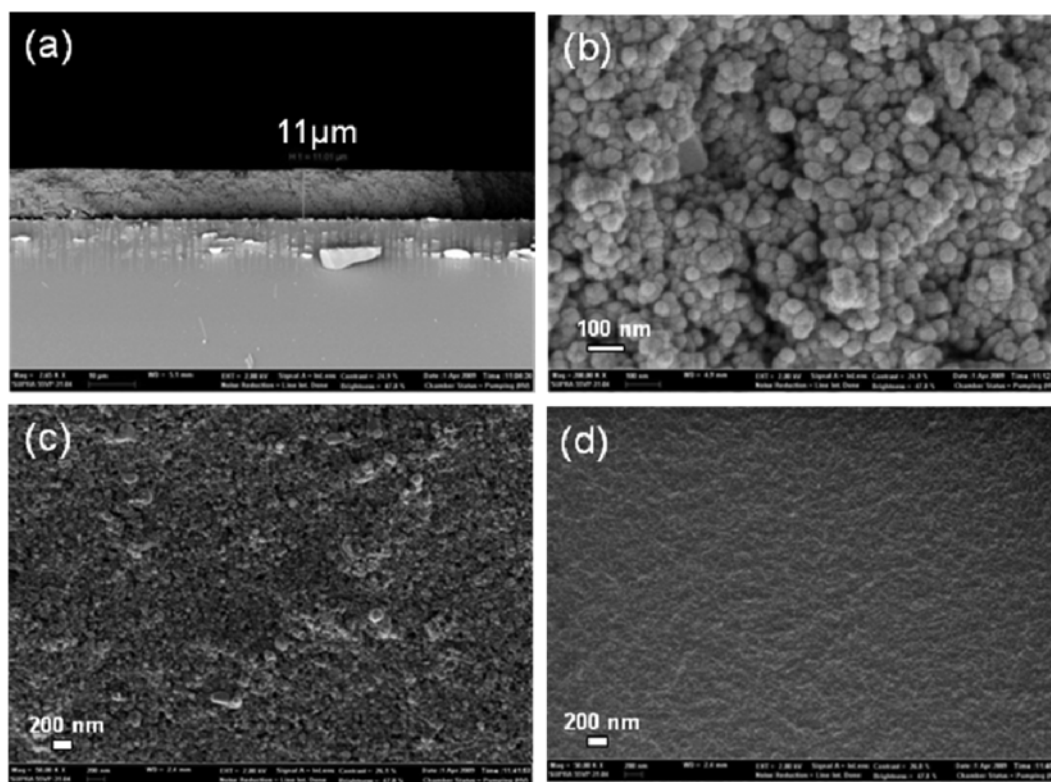


Fig. 3. Cross-sectioned FE-SEM images of (a) pristine TiO₂ (×2,650), (b) TiO₂ (×200,000), (c) TiO₂ (×50,000) and (d) TiO₂ with Epichlomer/PEGDME/(LiI+MPII)/I₂ electrolytes.

was determined from the maximum position in the broad peak using Bragg relation. The d-spacing of PEG-based polymer electrolyte was the highest as 4.4 Å (from 20.1°), whereas that of PEGDGE was the lowest as 4.1 Å (from 21.7°). It demonstrates that the chain contraction and densification of PEGDGE-based polymer electrolytes was the most significant, which may be related to the additional interactions/or reactions. These interactions and structural properties of the PEGDGE-based electrolyte will be characterized by FT-IR spectroscopy and directly related to ion conducting properties and solar cell performances.

The interfacial properties between the electrolyte and the electrodes are of pivotal importance in determining the overall conversion efficiency of solid-state DSSCs [19-21]. Thus, the morphologies of the nanocrystalline TiO₂ electrode were observed by using FE-SEM. Fig. 3 shows FE-SEM images of cross-sections of TiO₂ with and without electrolytes. The thickness of the TiO₂ layer was approximately 11 μm, as seen in Fig. 3(a). The pristine TiO₂ nanoparticles without electrolytes maintained their original shapes and sizes of 30-40 nm in diameter, as shown in Fig. 3(b) and (c). Upon introducing Epichloromer/PEGDME/(LiI+MPII)/I₂ electrolyte (Fig. 3(d)), the morphology of the TiO₂ layer was much smoother due to adequate coating of TiO₂ nanoparticles by the electrolytes. This result demonstrates good interfacial contact between the TiO₂ electrode and polymer electrolyte.

Solid-state electrolytes consisting of Epichloromer, oligomer, mixture salt (LiI : MPII=1 : 1 wt%) and iodine (I₂) were prepared and applied in a DSSC. To examine its photovoltaic performance, the photocurrent density-voltage characteristics of the DSSC were measured at 100 mW/cm², as shown in Fig. 4. The solar cell performances, including J_{sc}, V_{oc}, FF, and η, obtained from the curves are summarized in Table 2, where the ionic conductivities of electrolytes are also included. The DSSC employing the polymer electrolytes with PEGDME and PEG exhibited energy conversion efficiency of almost 4%, which was the highest among many oligomer systems. The DSSC employing PPG electrolyte showed lower efficiency (2.8%) than those of PEG and PEGDME in the similar length of

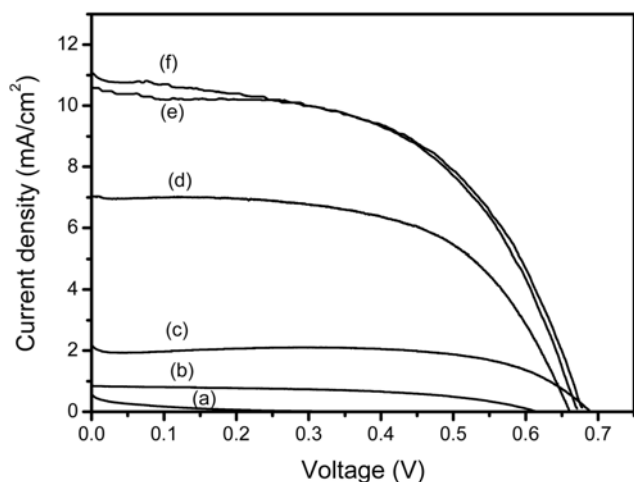


Fig. 4. Current-voltage curves of DSSC employing Epichloromer/(LiI+MPII)/I₂ electrolytes with varying oligomer; (a) PEGDGE, (b) no oligomer, (c) PEG1000, (d) PPG, (e) PEG400 and (f) PEGDME.

Table 2. Ionic conductivity and DSSC performances of Epichloromer/oligomer/(LiI+MPII)/I₂ electrolytes

Oligomer	Ionic conductivity ($\times 10^{-5}$ S/cm)	Efficiency (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF
PEGDME	61	3.95	0.68	12.9	0.45
PEG	50	3.87	0.67	13.5	0.43
PPG	12	2.82	0.65	7.3	0.60
PEGDGE	0.001	0.02	0.48	0.59	0.09
PEG1000	26	0.89	0.69	2.2	0.58
None	0.1	0.27	0.62	0.85	0.51

polymer chains. It is presumably due to lower ionic conductivity and less negative flat band potential [24]. The lower molecular weight PEG ($M_n=400$ g/mol) electrolyte exhibited higher ionic conductivity and higher cell efficiency than PEG1000 ($M_n=1,000$ g/mol), indicating the importance of the chain length of oligomer. Interestingly enough, both the ionic conductivity and the energy conversion efficiency of DSSC for PEGDGE based electrolyte was unusually lower compared to other similar systems. These values were even much lower than those of Epichloromer electrolyte without oligomer. Considering these unusual properties, there must be some unexpected interaction/or reaction in the PEGDGE electrolyte system, resulting in the deterioration of ionic conductivity and cell performance.

The reaction and interaction of PEGDGE based electrolyte was investigated by FT-IR spectroscopy, as presented in Fig. 5. Pristine PEGDGE exhibited the ether stretching band at 1,094 cm⁻¹ and the epoxy band at 885 cm⁻¹ (Fig. 5(a)). Upon the introduction of LiI and/or I₂, the epoxy stretching band at 885 cm⁻¹ was almost unobservable, implying chemical reaction between iodine and epoxy group. According to the previous work, the epoxides are readily subject to cleavage by elemental halogen or halogenated salt such as LiI even under the mild conditions, leading to the halohydrin [25]. Thus, the formation of ring opening halogenations of PEGDGE electrolyte can be illustrated as Scheme 1. It is concluded that the

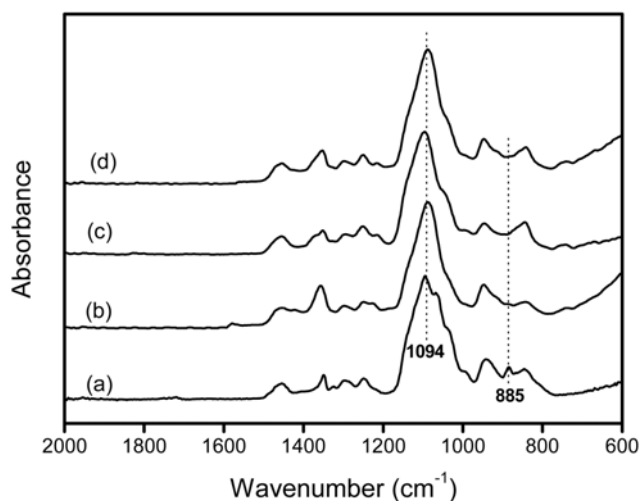
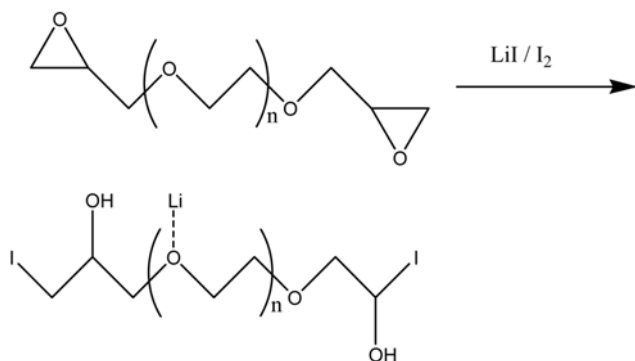


Fig. 5. FT-IR spectra of (a) PEGDGE, (b) PEGDGE/LiI, (c) PEGDGE/I₂ and (d) PEGDGE/LiI/I₂.



Scheme 1. Reaction and coordination of LiI and I₂ with PEGDGE.

formation of halohydrin in the electrolyte significantly deteriorates the ionic conductivity of electrolyte and the performance of DSSC because of lower concentrations of triiodide/iodide (I_3^-/I^-). This finding would be very important because epoxy based polymer electrolytes were successfully used in lithium batteries [26,27] but not applicable to DSSCs.

CONCLUSION

Epichloromer polymer electrolytes containing various oligomers with similar molecular weight were prepared and applied to solid-state DSSC. In particular, the effect of oligomer was investigated in terms of interactions, structures, ionic conductivity and DSSC performances. FT-IR spectroscopy and XRD analysis confirmed the coordinative interactions between the salt and the polymer matrix, leading to complete amorphous structures of polymer electrolytes. Upon the introduction of oligomer, the interfacial contact between the electrolytes and the electrodes was improved, as confirmed by FE-SEM. The ionic conductivities of polymer electrolytes were varied depending on the type of oligomer but mostly ranged in $1.2\text{--}6.1 \times 10^{-5}$ S/cm at room temperature. However, the ionic conductivity of PEGDGE based electrolyte ($\sim 10^{-8}$ S/cm) was much lower than those of other similar systems. The DSSC employing PEG and PEGDME electrolytes exhibited the highest energy conversion efficiency of almost 4% at 100 mW/cm^2 . However, the energy conversion efficiency of DSSC employing PEGDGE electrolyte (0.02%) was unusually lower compared to other similar systems, due to the ring opening halogenations of epoxy groups.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation (NRF) grant funded by the Korea government (MEST) (R01-2008-000-10112-0) and the Ministry of Knowledge Economy (MKE) and Korea Institute for Advancement in Technology (KIAT) through the Workforce Development Program in Strategic Technology. This work was also supported by New & Renewable Energy R&D program (2009T100100606) under the Ministry of Knowledge Economy.

REFERENCES

1. N. Yoshimoto, H. Nomura, T. Shirai, M. Ishikawa and M. Morita, *Electrochim. Acta*, **50**, 275 (2004).
2. Y. T. Goh, R. Patel, S. J. Im, J. H. Kim and B. R. Min, *Korean J. Chem. Eng.*, **26**, 518 (2009).
3. J. H. Kim, B. R. Min, J. Won and Y. S. Kang, *Macromolecules*, **36**, 4577 (2003).
4. S. Murai, S. Mikoshiba, H. Sumino, T. Kato and S. Hayase, *Chem. Commun.*, **13**, 1534 (2003).
5. J. N. Freitas, A. S. Gonçalves, M. A. Paoli, J. R. Durrant and A. F. Nogueira, *Electrochim. Acta*, **53**, 7166 (2008).
6. J.-W. Lee, K.-J. Hwang, W.-G. Shim, K.-H. Park, H.-B. Gu and K.-H. Kwun, *Korean J. Chem. Eng.*, **24**, 847 (2007).
7. J. E. Benedetti, M. A. Paoli and A. F. Nogueira, *Chem. Commun.*, **9**, 1121 (2008).
8. B. O'Regan and M. Gratzel, *Nature*, **353**, 737 (1991).
9. M. Gratzel, *Inorg. Chem.*, **44**, 6841 (2005).
10. P. Wang, S. M. Zakeeruddin, J. E. Moser, R. H. Baker and M. Gratzel, *J. Am. Chem. Soc.*, **126**, 7164 (2004).
11. T. Matsumoto, T. Matsuda, T. Suda, R. Hagiwara, Y. Ito and Y. Miyazaki, *Chem. Lett.*, **1**, 26 (2001).
12. J. Bandara and H. Weerasinghe, *Sol. Energy Mater. Sol. Cells*, **85**, 385 (2005).
13. T. Kato, A. Okazaki and S. Hayase, *J. Photochem. Photobiol. A: Chem.*, **179**, 42 (2006).
14. S. Lu, R. Koeppe, S. Gunes and N. S. Sariciftci, *Sol. Energy Mater. Sol. Cells*, **91**, 1081 (2007).
15. M. Biancardo, K. West and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, **90**, 2575 (2006).
16. V. C. Nogueira, C. Longo, A. F. Nogueira, M. A. Soto-Oviedo and M. A. De Paoli, *J. Photochem. Photobiol. A: Chem.*, **181**, 226 (2006).
17. A. F. Nogueira, J. R. Durrant and M. A. Paoli, *Adv. Mater.*, **13**, 826 (2001).
18. S. Nakade, T. Kanzaki, Y. Wada and S. Yanagida, *Langmuir*, **21**, 10803 (2005).
19. Y. J. Kim, J. H. Kim, M. S. Kang, M. J. Lee, J. Won, J. C. Lee and Y. S. Kang, *Adv. Mater.*, **16**, 1753 (2004).
20. J. H. Kim, M. S. Kang, Y. J. Kim, J. Won, N. G. Park and Y. S. Kang, *Chem. Commun.*, **14**, 1662 (2004).
21. M. S. Kang, J. H. Kim, J. Won and Y. S. Kang, *J. Phys. Chem. C*, **111**, 5222 (2007).
22. P. Basak and S. V. Manorama, *Eur. Polym. J.*, **40**, 1155 (2004).
23. A. Zalewska, J. Stygar, E. Ciszewska, M. Wiktoro and W. Wiczorek, *J. Phys. Chem.*, **105**, 5847 (2001).
24. M. S. Kang, Y. J. Kim, J. Won and Y. S. Kang, *Chem. Commun.*, **21**, 2686 (2005).
25. H. Sharghi, M. M. Eskandari and R. Ghavami, *J. Mol. Catal. A*, **55**, 215 (2004).
26. W. Klinklai, S. Kawahara, E. Marwanta, T. Mizumo, Y. Isono and Hiroyuki Ohno, *Solid State Ionics*, **177**, 3251 (2006).
27. R. Idris, M. D. Glasse, R. J. Lathan, R. G. Linford and W. S. Schlindwin, *J. Power Sources*, **94**, 206 (2001).