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Dye-sensitized solar cells employing non-volatile electrolytes based on oligomer solvent

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Abstract

The performance optimization of dye-sensitized solar cells (DSCs) employing non-volatile liquid electrolytes has been reported. Low molecular weight poly(ethylene glycol) dimethyl ether (oligo-PEGDME) was utilized as non-volatile solvent for the electrolytes. The ion transport properties of electrolytes and the influences of cations on the electron transport through photoanode have been systematically investigated. The results show that the overall efficiency of DSCs is mainly dominated by both the anion conductivity in electrolyte and the electron diffusion length in photoanode. From the analyses, the optimal composition of the non-volatile solvent-based electrolyte was successfully determined for high photon-to-electricity conversion efficiency.

Keywords: Dye-sensitized solar cells; Non-volatile solvent; Ion transport; Electron transport

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1. Introduction

Dye-sensitized solar cell (DSC) has attracted great attention over the past decade owing to its high-energy conversion efficiency and low production cost [1]. Although a respectable photon-to-electricity conversion efficiency (ca. 11% at 1 sun, AM 1.5) has been achieved for DSC employing volatile liquid electrolyte, leakage and evaporation of solvent from such cells have been suggested as one of the critical factors limiting the long-term stability [2,3].

As an alternative to volatile organic solvents, the use of room-temperature ionic liquids (RTIL) and low molecular weight organic solvents with polar ligand have received considerable attention in recent decades. RTIL have several superior properties such as the non-volatility, chemical stability, non-flammability and high-ionic conductivity at room temperature [4,5]. In addition, low molecular weight organic solvents such as ethylene carbonate (EC) and propylene carbonate (PC), or low molecular weight polyethers such as poly(ethylene glycol) derivatives (referred to as “oligomer”) also have been investigated as a promising solvent (or plasticizer) for electrolyte in secondary batteries and DSCs [6–13]. These non-volatile solvents also possess excellent physicochemical features similar to those of RTIL. The electrolytes based on the above non-volatile solvents could also be transformed into quasi-solid state electrolytes via various gelling routes [6–14].

Nevertheless, the viscosity of the non-volatile solvents is usually higher than those of conventional volatile solvents (*e.g.* acetonitrile), leading the energy conversion efficiency, which does not reach those of DSCs employing conventional volatile liquid electrolytes. The low mass transport of redox couples is a limiting factor of applicability of these solvents for DSC. Therefore, high concentration of redox couples is required to obtain considerable conductivity in the electrolyte medium. In this case, however, the dark current may be increased owing to the high concentration of triiodides near dye-attached TiO_2 and the photocurrent generation is also interrupted by the absorption of visible light into the electrolyte medium [15]. Therefore, it is believed that systematic investigations into the influence of electrolyte compositions on the photovoltaic characteristics

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of DSCs employing viscous electrolyte solvents are required to obtain more enhanced performance of long-term stable DSCs.

In this article, the characterization of the electrolytes based on non-volatile oligomer solvent for the application of DSCs has been carried out. As mentioned previously, non-volatile oligomer (*i.e.* low molecular weight polyether) could be utilized as an excellent solvent for the electrolytes employed in DSCs. In the electrolytes based on the oligomer solvent, salts are dissociated by polar ligands of oligomer matrix and transported through Lewis acid–base interactions in the free volume of the matrix, assisted by oligomer segmental motion. For more successful application of viscous electrolytes in DSCs, both high-ionic conductivity of electrolytes and excellent interfacial contact between dye-attached TiO_2 and electrolytes should be achieved [9–13]. To achieve the best efficiency of DSC employing oligomer-based electrolytes, moreover, the optimal composition of the electrolyte should be determined. The optimal condition of the electrolytes may be dominated mainly by their ion transfer ability (especially of anions (I^-/I_3^-)) and the influence of cations on the surface state of nanocrystalline semiconductor. Recently, the studies on the ion conduction in liquid electrolyte medium and the adsorptive property of specific cations on TiO_2 surface have been conducted to elucidate the influence of electrolyte on the photovoltaic characteristics of DSC [16,17]. In the case of the electrolytes based on viscous solvents, however, the detailed analyses are not sufficiently carried out yet.

The aim of this work was the preparation of efficient and long-term stable DSCs based on oligomer solvent via the composite optimization of electron transport in the photoanode and ion transport in the electrolyte. We prepared the electrolytes consisting of low molecular weight poly(ethylene oxide) and three different types of iodide salts (*i.e.* 1,2-dimethyl-3-hexylimidazolium iodide (DMHImI), 1-propyl-3-methylimidazolium iodide (PMImI) and potassium iodide (KI)). The ion transport properties of these electrolytes had been systematically investigated by means of the measurements of ion conductivity and diffusion coefficient. In addition, the influences of cations on the electron transport occurred in photoanode had been evaluated via a laser-induced photovoltage/photocurrent transient measurement. We believe that the results of this study may provide useful information for the design of the electrolytes employing viscous solvents.

2. Experimental

2.1. DSC preparation

The oligomer electrolytes were prepared using low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME, $M_w = 250$ g/mol) and iodide salts with different cations (*i.e.* $DMHIm^+$, $PMIm^+$ and K^+). The concentration of iodides was ranged from 0.48 M to 1.80 M ($C(I^-)/C(I_3^-) = 9$). All chemicals except imidazolium iodides were purchased from Aldrich and utilized without further purification. DMHImI and PMImI were purchased from CTRI (Korea) and Solaronix (Switzerland), respectively. The properties of iodide salts employed in this work are compared in Table 1.

2.2. DSC preparation

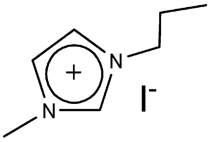
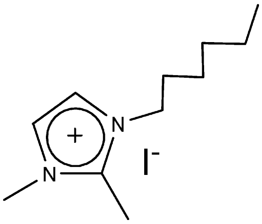
DSCs were fabricated according to the following procedure. Transparent conducting oxide glass (TCO, sheet resistance ≈7 Ω/□) was employed to prepare both the photoanode and counter electrodes. For the photoanode preparation, lab-made TiO_2 paste was cast onto TCO substrate using a doctor-blade technique and successively sintered at 450 °C for 30 min. Platinum layered counter electrode was prepared by a conventional sputtering method. The photoelectrodes (TiO_2 film thickness ≈ca. 18 μm) was sensitized with $Ru(dcbpy)_2(NCS)_2$ dye (here, dcbpy = 2,2′-bipyridyl-4,4′-dicarboxylato) solution (535-bisTBA, Solaronix, dissolved in ethanol) for one day.

2.3. Measurements of ion conductivity and diffusion coefficient

Ion conductivity of the electrolytes was measured using a lab-made four-point probe conductivity cell connected to impedance analyzer. The ion conductivity of electrolyte is based on the mobilities of both cations and anions dissolved in a solvent. The total ion conductivity can be defined by

$$\delta = \frac{l}{|Z| \cdot A} \qquad (1)$$

Table 1
Properties of iodide salts studied in this work

Criteria	Potassium iodide (KI)	1-Propyl-3-methylimidazolium iodide (PMImI)	1,2-Dimethyl-3-hexylimidazolium iodide (DMHImI)
M_w (g/mol)	166	252.1	308.2
Structure	K^+I^-		
Status	Alkali metal salt (solid)	Imidazolium molten salt (liquid)	Imidazolium salt (solid)

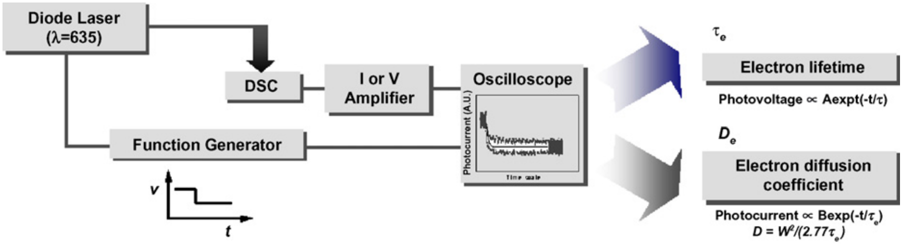


Fig. 1. Measurement setup for photocurrent or photovoltage transient induced by stepwise light intensity.

where δ is the total conductivity, $|Z|$ the impedance, l and A are the dimensions of the conductivity cell (length and area, respectively). To reveal the influence of ions on the photovoltaic characteristics of DSC, however, the investigation of individual ion transport may be more meaningful than that of total ion transport. The total conductivity can also be expressed as the summation of those of individual ion species, *i.e.*

$$\delta(T) = \sum_i |Z_i|\, Fc_i\mu_i = \sum_i \frac{|Z_i|^2 Fc_i e D_i}{K_\mathrm{B} T} \qquad (2)$$

where Z_i, c_i, μ_i and D_i are the charge, the mobility and the diffusion coefficient of the ith ionic species, e the electronic charge, T the absolute temperature, K_B the Boltzmann constant and F the Faraday constant. To estimate the conductivity of individual ions from Eq. (2), the diffusion coefficients of ion species should also be determined. The apparent diffusion coefficients (D_app) of I^- and $\mathrm{I_3}^-$ ions can be evaluated from anodic and cathodic steady-state current (I_ss) according to the following equation:

$$D_\mathrm{app} = \frac{I_\mathrm{ss}}{4ncaF} \qquad (3)$$

where n is the electron number per molecules, c the bulk concentration of ionic species, a the Pt-microelectrode radius (5 μm) and F the Faraday constant [18].

2.4. Measurements of electron lifetime and diffusion coefficient

Electron transfer performances of the photoelectrodes (*i.e.* electron diffusion coefficient and lifetime) were evaluated via laser-induced photocurrent/photovoltage transient measurement using a diode laser source (Coherent, LabLaser, λ = 635 nm) modulated with a function generator (UDP-303, Unicorn, Korea) [16]. The simplified experimental scheme is depicted in Fig. 1. The principle and the experimental details of the measurement were described in the original papers written by Nakade *et al.* [16,19].

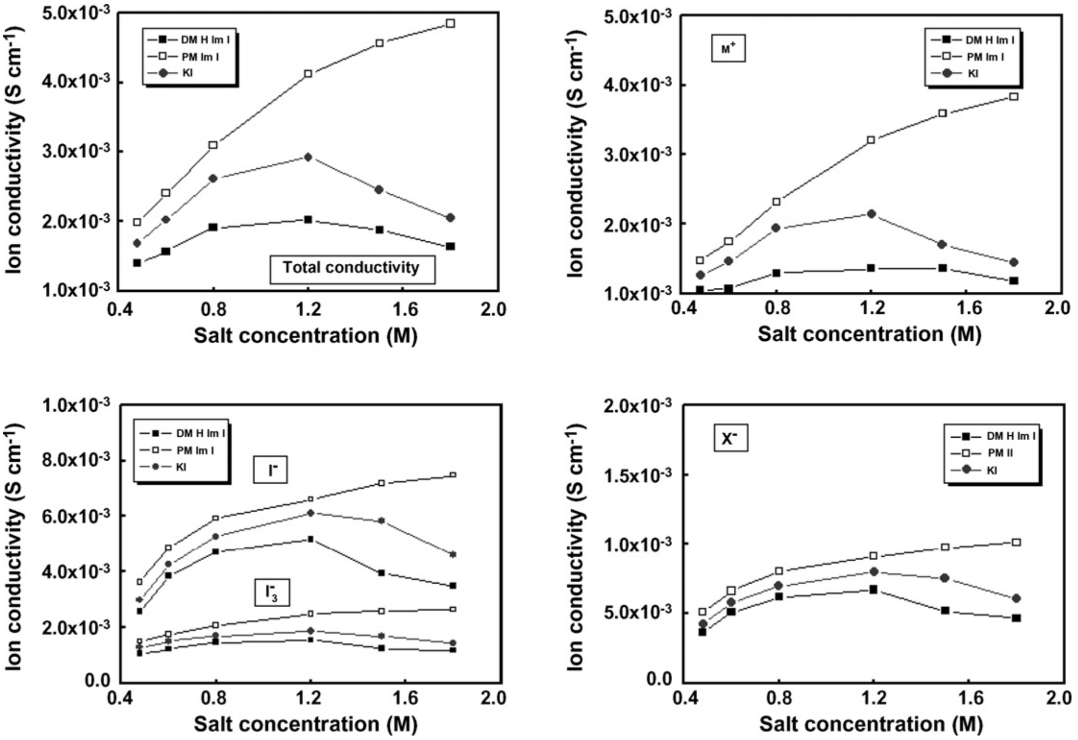


Fig. 2. Total conductivities and specific ion conductivities of the oligomer electrolytes (PEGDME(250)/[DMHImI, PMImI, KI]/$\mathrm{I_2}$) at different salt concentrations.

2.5. Characterization of photovoltaic performances of DSCs

The photovoltaic characteristics of the prepared DSCs (short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (ff) and overall energy conversion efficiency (η)) were evaluated under 1 sun light-intensity (100 mW cm^{-2}, AM 1.5) checked with an NREL-calibrated Si-solar cell (PV Measurements Inc.).

3. Results and discussion

3.1. Ion conduction properties

The ion conductivities of individual ionic species (*i.e.* I^-, I_3^- and M^+ (cations)) were evaluated as shown in Fig. 2. Among the iodide salts, PMImI (molten-state at ambient temperature) shows the highest ion conductivity. The conductivity were shown to be in the order of PMImI > KI > DMHImI. The total conductivities increased with an increase in the bulk concentration below the concentration of approximately 1.2 M. However, the ion conductivities of the electrolytes dissolving DMHImI and KI were reduced after the maximum behavior at high-salt concentrations. It is believed that the result is mainly due to a decreasing ability of the oligomer to solvate the salt and to produce free ions as the salt levels are increased [20]. As revealed in Fig. 2, the total conductivities of the oligomer-based electrolytes were dominated by the mobility of cations (*i.e.* $\sigma(M^+)$). The transport numbers of cations were shown to be 0.69, 0.78 and 0.72 for DMHImI, PMImI and KI electrolytes, respectively. Although the molecular size of PMIm$^+$ is much larger than that of K^+, the molten nature of this salt may induce the high mobility of cations. Note that the order of molecular weight of cations is DMHIm$^+$ (181.3 g/mol) > PMIm$^+$ (125.2 g/mol) > K^+ (39.1 g/mol). Meanwhile, since cations are not involved in the redox reactions occurred in DSC, the mobility of anions (*i.e.* $\sigma(X^-) = \sigma(I^-) + \sigma(I_3^-)$) may dominate the photovoltaic performance of the device. The anion conductivities were also shown to be in the increasing order of PMImI > KI > DMHImI. If the anion mobility is the only factor of electrolyte affecting the photovoltaic performance of DSC, the overall conversion efficiency may be determined by the magnitude of anion conductivity. However, the cations can also affect the electron transfer in photoanode and therefore the effect of cations on the electron transport in TiO_2 film should be considered simultaneously. The steady-state voltammograms of the oligomer electrolytes (PEGDME/PMImI/I_2) are shown in Fig. 3. The I_{ss} values were largely dependent upon both the bulk concentration and the nature of cation species (data not shown).

3.2. Electron transport properties

Electron transport in DSCs can be characterized by two major parameters of electron diffusion coefficient (D_e) and electron lifetime (τ_e). Electron diffusion coefficient was derived by a time constant (τ_c) determined by fitting the decay of the photocurrent transients with a single exponential and the TiO_2 film thickness by $D_e = w^2/2.77\tau_c$ (here, w is the film thickness) [16]. Electron lifetime is the parameter related to the electron recombination. This parameter can also be determined by fitting the decay of the photovoltage transients with a single exponential [16].

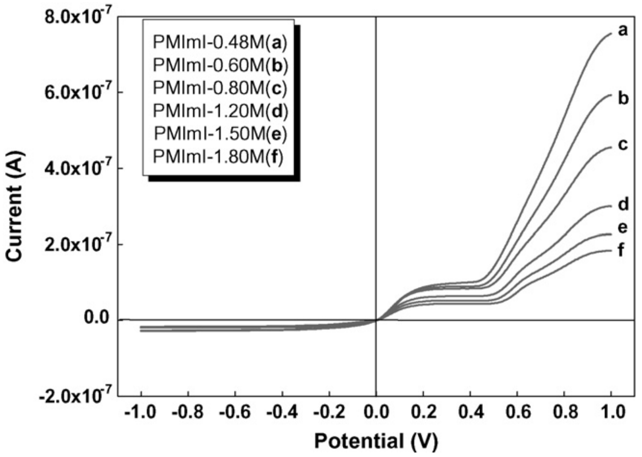


Fig. 3. Steady-state voltammograms of the oligomer electrolytes (PEGDME (250)/PMImI/I_2) with a Pt ultramicroelectrode (scan rate: 10 mV/s).

The variation in electron diffusion coefficients may be explained by the different adsorptive interaction of the cations

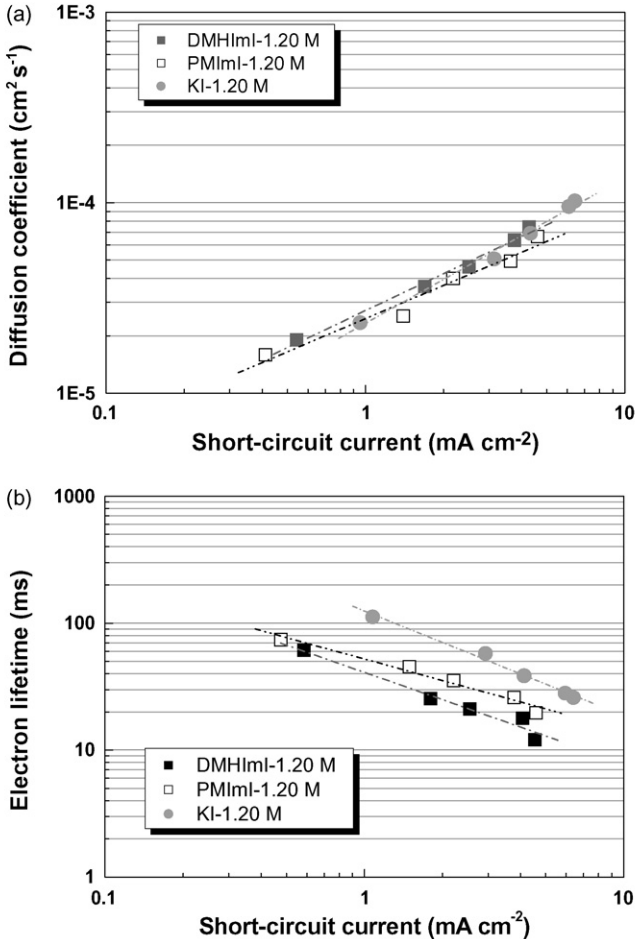


Fig. 4. Electron diffusion coefficients (a) and lifetime (b) in the TiO_2 electrodes immersed in the oligomer electrolytes (PEGDME(250)/[DMHImI, PMImI, KI]/I_2).

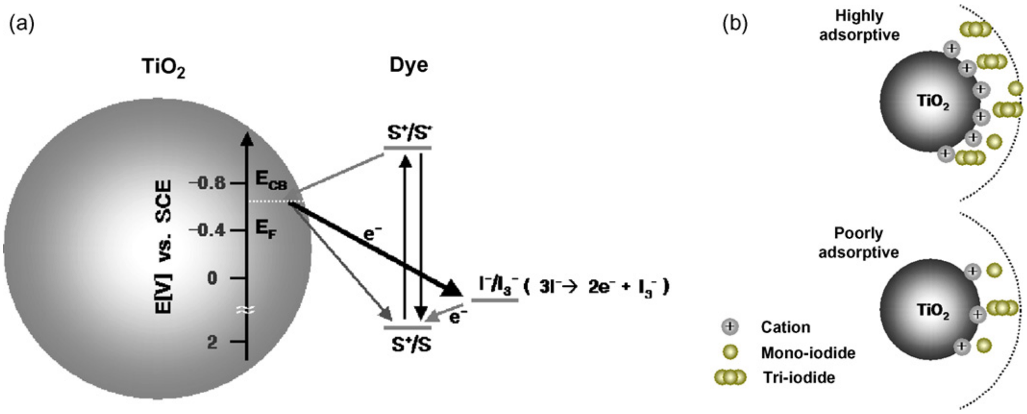


Fig. 5. Schematic presentations of (a) key reactions taking place in a dye-sensitized solar cell and (b) ionic atmosphere near TiO_2 particles (in diffusion boundary layer).

with TiO_2 surface affecting strongly ambipolar diffusion in mesoporous TiO_2 as commented by Kambe *et al.* [17]. They suggested that highly adsorptive cations (such as Li^+ and $DMHIm^+$) could induce high-electron diffusion coefficient by increasing the local cation density on the TiO_2 surface. In our case, however, there is no significant difference in the electron diffusion coefficients by the change in the cations as shown in Fig. 4(a). In the case of electron lifetime, the clear difference among the cations was observed, showing that K^+ ion resulted in the highest value in the salt concentration ranges considered and the electron lifetime increased in the order of KI > PMImI > DMHImI (as shown in Fig. 4(b)). It was also reported that the shorter lifetime is found with more adsorptive cations [21]. Moreover, the electron lifetimes decreased with an increase in the salt concentration for all kinds of cation, indicating the increasing electron recombination. These results can be interpreted with the change of the surface concentration of $I_3{}^-$, which depends on the profile of the electrical double layer formed by the cations. Fig. 5 shows the schematic drawing of the reactions taking place near *nc*-TiO_2 particles and the ionic atmosphere in the diffusion boundary layer with different cations.

The conflicting contribution of diffusion coefficient and lifetime can be combined and expressed by means of the diffusion length (L_d). Diffusion length of electrons is denoted as $L_d = (D_e \tau_c)^{1/2}$ [22]. The diffusion length was also shown to increase in the order of KI > PMImI > DMHImI and decreased with an increase in the salt concentration as shown in Fig. 6.

3.3. Electron performance parameter

To integrate the contributions of the two major parameters related to electrolytes (*i.e.* anion conductivity ($\sigma(X^-)$) and electron diffusion length (L_d)), we have defined the electrolyte performance parameter (*i.e.* $L_d \sigma(X^-)$ [Ω^{-1}]). The results are plotted as a function of salt concentration in Fig. 7. The performance parameter shows the maximum behavior near 1.2 M concentration and the magnitude order is KI ≈ PMImI > DMHImI. Similarly, the overall conversion efficiencies of the DSCs also increased as the salt concentration increases up to approximately 1.2 M. At the higher concentration range, the efficiencies leveled off or even decreased. The variation tendency in the overall efficiency is very similar to that in the electrolyte performance parameters (*i.e.* η(KI) ≈ η(PMImI) > η(DMHImI)), demonstrating both

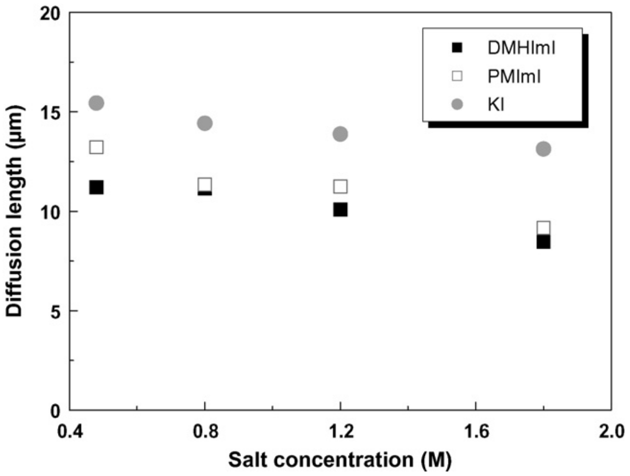


Fig. 6. Average diffusion lengths of the DSCs employing the oligomer electrolytes (PEGDME(250)/[DMHImI, PMImI, KI]/I_2).

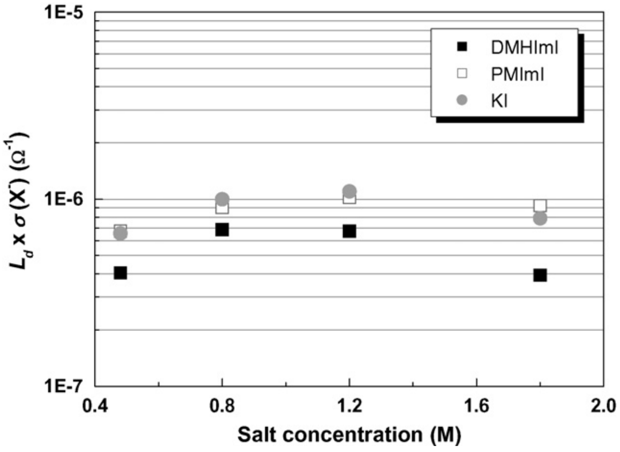


Fig. 7. Electrolyte performance parameters ($L_d \sigma(X^-)$) measured at different salt concentrations.

Table 2
Photovoltaic characteristics of the DSCs employing two different photoanodes

Photoanode	J_{sc} (mA cm^{-2})	V_{oc} (V)	ff (−)	η (%)	L_d (μm)
Modified[a]	19.38	0.64	0.61	7.52	12.28
Normal	15.24	0.62	0.62	5.88	10.25

[a] Nb_2O_5 thin layer on the TiO_2 film + TiO_2 interlayer between TCO and mesoporous TiO_2 film.

the anionic conductivity in electrolyte and the electron diffusion length in photoanode are the major factors dominating the device efficiency. For example, although PMImI-based electrolyte shows the highest ion conductivity among the tested electrolytes, the electron-harvesting efficiency is not superior to that of KI-based electrolyte owing to the relatively poor electron diffusion length.

3.4. Modification of photoanode for oligomer-based electrolytes

Based on the results of this work, it was shown that high ion concentration (of approximately 1.2 M) is recommended for the preparation of oligomer-based electrolytes having the maximum ion conductivity. At high ion concentration, on the other hand, the electron transport is suppressed by the increase in the electron recombination. To maximize the device performance, therefore, the reduction in the electron recombination rate should be achieved. Recently, several techniques for preventing the electron recombination in DSCs have been suggested. One of the techniques is the introduction of Nb_2O_5 thin layer on the TiO_2 film to form an inherent energy barrier at the electrode/electrolyte interface, leading to the reduced recombination rate [23]. We have treated the photoanode with $NbCl_5$ ethanol solution (20 mM) by spin-coating and successive sintering process (at 500 °C for 30 min). After the $NbCl_5$ treatment, both the electron diffusion coefficient and the electron lifetime were largely increased as reported by Zaban *et al.* [23,24]. Moreover, the electron recombination rate can be significantly reduced via the introduction of a blocking layer formed between TCO surface and nanocrystalline-TiO_2 layer [25]. Therefore, we have also introduced a very thin TiO_2 interlayer (thickness ≈200 nm) using a surface-templated sol–gel process prior to the formation of mesoporous TiO_2 film onto the surface [26]. As a result, the overall conversion efficiency of the DSC was largely enhanced owing to the increase both in the photocurrent and the photovoltage. It is obvious that the increase in the diffusion length (as revealed in Table 2) followed by the enhancement of electron collection yield largely improves the photovoltaic properties of the DSC. The best efficiency of the DSC employing the oligomer-based electrolyte is 7.18% at 100 mW cm^{-2} (the *J–V* curves are shown in Fig. 8).

3.5. Durability of DSCs employing oligomer-based electrolytes

We have also checked the durability of the DSCs employing the electrolytes with volatile solvent (acetonitrile) and non-volatile oligomer solvent (PEGDME(250)) for 60 days as shown in Fig. 9. In the case of the DSC employing volatile solvent, the cell efficiency was decreased over time mainly due to the solvent leakage. However, the DSC employing oligomer solvent showed the constant performance during the test.

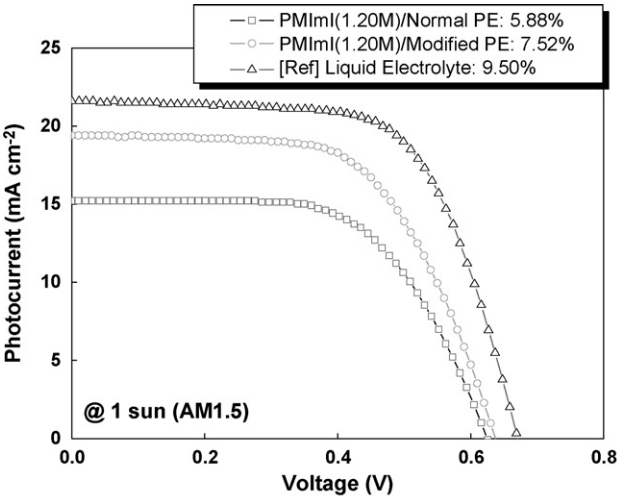


Fig. 8. *J–V* curves of the DSCs employing two different photoanodes.

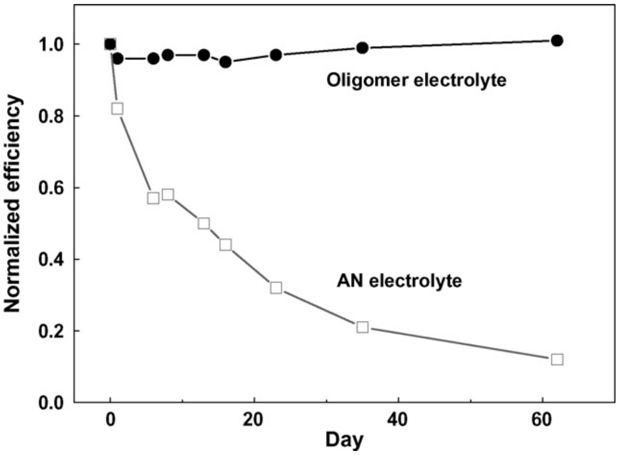


Fig. 9. Durability test of the DSCs employing volatile solvent (acetonitrile) and non-volatile oligomer solvent (PEGDME(250)).

4. Conclusion

In this work, we have characterized non-volatile oligomer electrolytes with three different types of iodide sources and carried out the systematic investigation into both the ion transport in electrolytes and the electron transport in *nc*-TiO_2 film of the DSCs. The results showed that the overall efficiency of the DSC is mainly determined by both the anionic mobility in oligomer-based electrolyte and the electron diffusion length in photoanode. It was also concluded that the use of oligomer-based electrolytes can promise both the excellent durability and the respectable energy conversion efficiency of the DSC by the optimization of the electrolyte compositions.

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References

[1] M. Grätzel, J. Photochem. Photobiol. A: Chem. 164 (2004) 3.

[2] P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, J. Am. Chem. Soc. 125 (2003) 1166.

[3] T. Kato, A. Okazaki, S. Hayase, Chem. Commun. (2005) 363.

[4] F. Mazille, Z. Fei, D. Kuang, D. Zhao, S.M. Zakeeruddin, M. Grätzel, P.J. Dyson, Inorg. Chem. 45 (2006) 1585.

[5] A.F. Nogueira, C. Longo, M.-A. De Paoli, Coord. Chem. Rev. 248 (2004) 1455.

[6] J. Wu, Z. Lan, D. Wang, S. Hao, J. Lin, Y. Wei, S. Yin, T. Sato, J. Photochem. Photobiol. A: Chem. 181 (2006) 333.

[7] V.C. Nogueira, C. Longo, A.F. Nogueira, M.A. Soto-Oviedo, M.-A. De Paoli, J. Photochem. Photobiol. A: Chem. 181 (2006) 226.

[8] B. Li, L. Wang, B. Kang, P. Wang, Y. Qiu, Sol. Energy Mater. Sol. Cell 90 (2006) 549.

[9] M.-S. Kang, J.H. Kim, J. Won, Y.S. Kang, J. Photochem. Photobiol. A: Chem. 183 (2006) 15.

[10] M.-S. Kang, Y.J. Kim, J. Won, Y.S. Kang, Chem. Commun. (2005) 2686.

[11] M.-S. Kang, J.H. Kim, Y.J. Kim, J. Won, N.-G. Park, Y.S. Kang, Chem. Commun. (2005) 889.

[12] Y.J. Kim, J.H. Kim, M.-S. Kang, M.J. Lee, J. Won, J.C. Lee, Y.S. Kang, Adv. Mater. 16 (2004) 1753.

[13] J.H. Kim, M.-S. Kang, Y.J. Kim, J. Won, N.-G. Park, Y.S. Kang, Chem. Commun. (2004) 1662.

[14] T. Kato, A. Okazaki, S. Hayase, J. Photochem. Photobiol. A: Chem. 179 (2006) 42.

[15] G. Nazmutdinova, S. Sensfuss, M. Schrödner, A. Hinsch, R. Sastrawan, D. Gerhard, S. Himmler, P. Wasserscheid, Solid State Ionics 177 (2006) 3141.

[16] S. Nakade, T. Kanzaki, Y. Wada, S. Yanagida, Langmuir 21 (2005) 10803.

[17] S. Kambe, S. Nakade, T. Kitamura, Y. Wada, S. Yanagida, J. Phys. Chem. B 106 (2002) 2967.

[18] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Gratzel, Nat. Mater. 2 (2003) 402.

[19] S. Nakade, T. Kanzaki, S. Kambe, Y. Wada, S. Yanagida, Langmuir 21 (2005) 11414.

[20] J.R. MacCallum, C.A. Vincent, Polymer Electrolyte Reviews, Elsevier Applied Science, London, 1987, p. 78.

[21] S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, J. Phys. Chem. B 109 (2005) 3480.

[22] J. Bisquert, V.S. Vikhrenko, J. Phys. Chem. B 108 (2004) 2313.

[23] S.G. Chen, S. Chappel, Y. Diamant, A. Zaban, Chem. Mater. 13 (2001) 4629.

[24] K.-S. Ahn, M.-S. Kang, J.-K. Lee, B.-C. Shin, J.-W. Lee, Appl. Phys. Lett. 89 (2006) 013103.

[25] S. Ito, P. Liska, P. Comte, R. Charvet, P. Péchy, U. Bach, L. Schmidt-Mende, S.M. Zakeeruddin, A. Kay, M.K. Nazeeruddin, M. Grätzel, Chem. Commun. (2005) 4351.

[26] K.-S. Ahn, M.-S. Kang, J.-W. Lee, Y.S. Kang, J. Appl. Phys. 101 (2007) 084312.