



Short communication

Quasi-solid-state dye-sensitized solar cells employing ternary component polymer-gel electrolytes

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ABSTRACT

Ternary component polymer-gel electrolytes are designed to facilitate ion transport in a highly viscous medium and utilize incident light more efficiently in dye-sensitized solar cells (DSSCs). Polyethers with multiple molecular size distributions are employed as solvents and TiO₂ nanoparticles as a filler to prepare the polymer-gel electrolytes. The ion transport properties of the electrolytes are systematically investigated using electrochemical analyses such as ion conductivity and diffusion coefficient measurements. The influences of the electrolyte components on the electron transport in photoanodes are also investigated by measuring the laser-induced photovoltage and photocurrent transient response, incident photon-to-current efficiency (IPCE), and current–voltage (*J*–*V*) curves. The optimized polymer-gel electrolyte results in greatly enhanced energy conversion efficiency (*i.e.*, 7.2% at 1 sun) due to the significantly improved ion transport and good light-scattering effect of the nanofillers.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are of great interest due to their attractive features of high energy-conversion efficiency and low production cost [1–3]. Recently, DSSCs employing quasi-solid polymer electrolytes have been investigated because of their intrinsic advantages such as no solvent leakage and evaporation [4–19]. To date, however, DSSCs employing polymer-based electrolytes have exhibited low cell efficiency. This is mainly attributed to the inferior mass-transfer rates of the redox couples (I^-/I_3^-) in the highly viscous medium and to high electron-transfer resistance at the electrolyte|electrode interfaces. Therefore, it is necessary to increase the ion mobility in the polymer medium to improve cell efficiency. Although many efforts have been made through using new polymers [4,8,9,11,18], inorganic nanofillers [5,10,12,14,19] and small molecule plasticizers [7,9,13,14,17] to increase the ion conductivity, a better understanding of polymer-type electrolytes is required.

In this work, an efficient polymer-gel electrolyte is fabricated to achieve high energy-conversion efficiency with quasi-solid-state DSSCs. The polymer-gel electrolyte is designed to facilitate ion transport in the highly viscous medium and utilize incident light

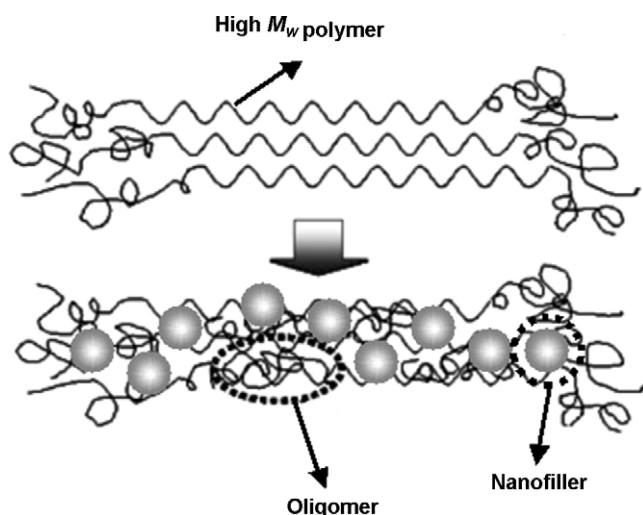
more effectively in the cell. Polyethers with multiple molecular size distributions and nanofillers (*i.e.*, nano-sized TiO₂ particles) are used to prepare the polymer-gel electrolytes. Scheme 1 is a schematic drawing of the ternary component polymer-gel electrolyte proposed here. High molecular weight polyethylene oxide (PEO, $M_w = 10^6 \text{ g mol}^{-1}$) is used as a framework to provide mechanical stability to the gel polymer electrolyte. An oligomer (*i.e.*, poly(ethylene glycol) dimethyl ether (PEGDME), $M_w = 250 \text{ g mol}^{-1}$) is added to PEO to enhance the ion mobility and facilitate penetration of electrolyte into the nanopores of a *nc*-TiO₂ photoanode [14,17]. TiO₂ nanoparticles are added to the electrolyte as a nanofiller, which can decrease the crystallinity of the polymer and build a transfer channel for the redox couples [20] that results in enhanced ion conductivity and anion transport [5]. In addition, aggregation of the nano-particles in the polymer medium may lead to a light-scattering effect. These effects are systematically evaluated by characterizing ionic conductivity, diffusion coefficients, electrochemical cell impedance, light scattering, and electron transport of the photoanode.

2. Experimental

2.1. Preparation of polymer-gel electrolytes

A liquid oligomer electrolyte (*i.e.*, ‘Oligomer’, E1) consisting of low molecular weight poly(ethylene glycol) dimethyl ether

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Scheme 1. Schematic drawing of ternary component polymer-gel electrolyte.

(PEGDME, $M_w = 250 \text{ g mol}^{-1}$), 1-propyl-3-methylimidazolium iodide (PMImI) and iodine was prepared as the reference electrolyte. The contents of PMImI and iodine were 1.20 M and 0.12 M, respectively. A polymer-gel electrolyte (*i.e.*, ‘Oligomer/Polymer’, E2) was prepared by adding poly(ethylene oxide) (PEO, $M_w = 10^6 \text{ g mol}^{-1}$, 10 wt.%) to the liquid oligomer electrolyte.

In addition, TiO_2 nanoparticles (NP, average diameter \approx ca. 22 nm) were added as a nanofiller so that a ternary component polymer-gel electrolyte (*i.e.*, ‘Oligomer/Polymer/NP’, E3) was prepared, in which the nano-particles were completely dispersed in the electrolyte by paint shaking for 2 h followed by ultrasonication for 1 h. All chemicals, except imidazolium iodide and TiO_2 powder, were purchased from Aldrich and utilized without further purification. PMImI and TiO_2 powder were obtained from CTRL (Korea) and Ishihara Sangyo Kaisha (ST-21, Japan), respectively.

2.2. DSSC preparation

The fabrication of DSSCs using solvents with different molecular size distribution was as follows: fluorine-doped SnO_2 (FTO) glasses (sheet resistance $\approx 8 \Omega \text{ sq}^{-1}$) were used as substrates. Lab-made TiO_2 paste was coated on to the FTO substrate using a doctor-blade method, followed by sintering at 450°C for 30 min [21]. The platinum counter electrode was prepared by magnetron sputtering. The TiO_2 photoelectrodes (film thickness $\approx 15 \mu\text{m}$) were then sensitized by treatment overnight with $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ dye (here, $\text{dcbpy} = 2,2'$ -bipyridyl-4,4'-dicarboxylato) solution (535-bisTBA, Solaronix, dissolved in ethanol). For excellent interfacial contact between the TiO_2 and the electrolyte, the liquid oligomer electrolyte (E1) was dropped on to the photoelectrode. Then, the polymer-gel electrolyte films (\sim ca. $80 \mu\text{m}$ thickness, E2 and E3) were introduced between the photoelectrode and counter electrode and hot pressed for sealing (pressing conditions: $80^\circ\text{C}/7 \text{ s}$; sealant: Surlyn[®], $60 \mu\text{m}$ thickness).

2.3. Measurements of ion conductivity and diffusion coefficient

The ion conductivities of the electrolytes were measured using a lab-made four-point probe conductivity cell connected to an impedance analyzer (1260A, Solartron, UK). The ion conductivity depends on the mobilities of both cations and anions in the solvent.

The total ion conductivity is defined as follows:

$$\sigma = \frac{l}{|Z| \cdot A} \quad (1)$$

where: σ is the total conductivity, $|Z|$ is the impedance, l and A are the cell dimensions (length and area, respectively). Individual ion transports are required to understand the influence of each ion on the cell performance. The total conductivity can also be expressed by the following equation:

$$\sigma = \sum_i |Z_i| F c_i \mu_i = \sum_i \frac{|Z_i|^2 F c_i e D_i}{K_B T} \quad (2)$$

where: Z_i , c_i , μ_i and D_i are the charge, the concentration, the mobility and the diffusion coefficient of the i th ionic species, respectively; e is the electronic charge; T is the absolute temperature; K_B is the Boltzmann constant; F is the Faraday constant. To estimate the conductivity of each ion from the Eq. (2), the diffusion coefficients (D_{app}) of ion species (I^- and I_3^-) should be determined. These are calculated by the anodic and cathodic steady-state currents (I_{ss}) according to:

$$D_{\text{app}} = \frac{I_{\text{ss}}}{4ncaF} \quad (3)$$

where: n is the electron number per molecule; c is the bulk concentration of ionic species; a is the Pt-microelectrode radius ($5 \mu\text{m}$); and F is the Faraday constant [22].

2.4. Measurements of electron diffusion coefficient and lifetime

The electron transport properties (*i.e.*, electron diffusion coefficient and lifetime) of the TiO_2 photoanodes were evaluated by means of laser-induced photocurrent/photovoltage transient measurements. The diode laser source ($\lambda = 635 \text{ nm}$, LabLaser, Coherent, USA) was modulated with a function generator (UDP-303, Unicorn, Korea) [23]. Scheme 2 shows the simplified experimental set-up; a detailed description of the measurements has been reported by Nakade et al. [23,24].

2.5. Characterization of photovoltaic performances of DSSCs

The photovoltaic characteristics (short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (ff), and overall energy conversion efficiency (η)) were measured under 1 sun (100 mW cm^{-2} , AM1.5) that confirmed by a NREL-calibrated Si-solar cell (PV Measurements Inc., USA). The incident photon-to-current conversion efficiency (IPCE) (PV Measurements Inc., USA) was also measured to analyze the light-scattering effect in the long wavelengths. The a.c. impedance measurements were carried out at open-circuit voltage (OCV) using an impedance analyzer (1260A, Solartron, UK).

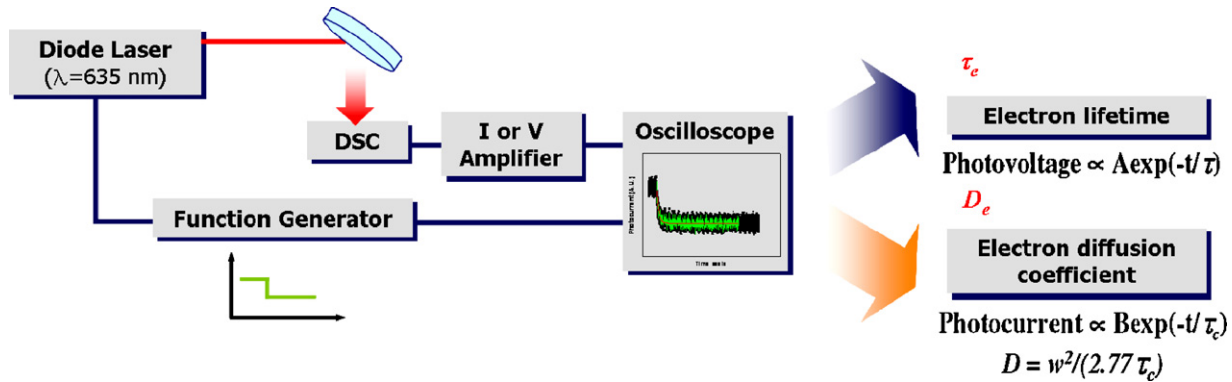
3. Results and discussion

3.1. Preparation of polymer-gel electrolyte films

Fig. 1 shows a photograph of the polymer-gel electrolyte films prepared in this work. The opacity of the electrolytes was strongly affected by the inorganic TiO_2 nanoparticles. This suggests that the aggregated nanoparticles may lead to light scattering in the electrolyte medium.

3.2. Current–voltage (J – V) characteristics

The J – V curves of the DSSCs with the oligomer-based electrolytes are presented in Fig. 2. The DSSC solely with the oligomer electrolyte exhibits an efficiency of approximately 7% at 1 sun. The cell



Scheme 2. Measurement set-up for photocurrent and photovoltage transients induced by stepwise light intensity.

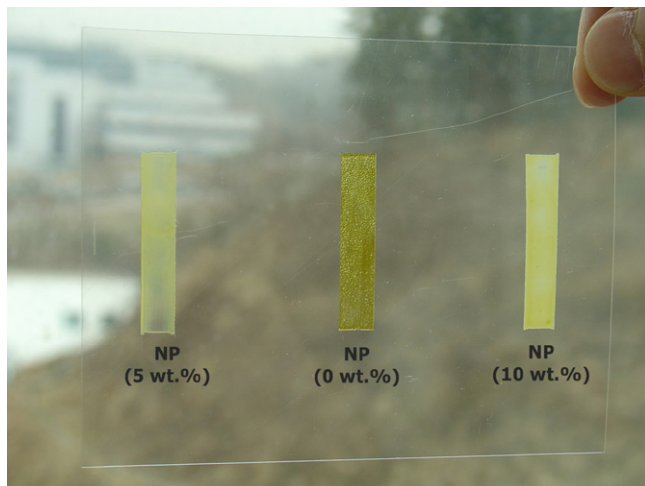


Fig. 1. Photograph of polymer-gel electrolytes.

performances are reduced, however, by the addition of polymer into the oligomer electrolyte due to the considerably decreased J_{sc} . The addition also markedly increases the open-circuit voltage of the cell. It is worth noting that the short-circuit current is significantly recovered by the nano-particles used as a nanofiller without a significant change in the V_{oc} . As a result, the DSSC with the ternary component polymer-gel electrolyte (E3) gives the best cell efficiency (*i.e.*, 7.19%).

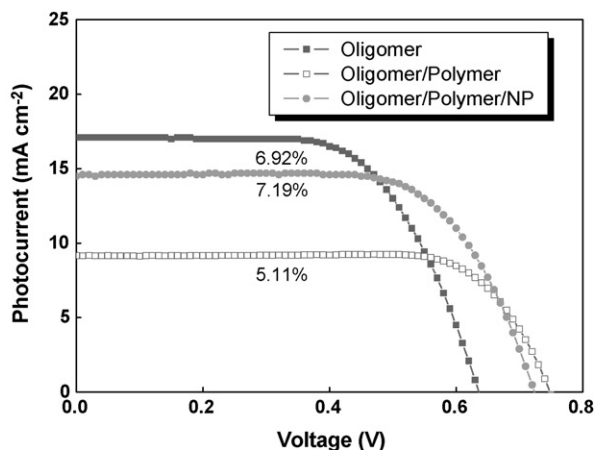


Fig. 2. J - V curves of DSSCs employing oligomer-based electrolytes measured under 100 mW cm^{-2} illumination.

The dark current of the cells was also measured (Fig. 3). The dark current is significantly decreased by introducing the polymer into the oligomer electrolyte. This indicates that the recombination rate is effectively suppressed due to the reduced accessibility of ions to the dye-attached TiO_2 surface, that results in a greatly increased V_{oc} . Fig. 3 also shows that the nanofillers in the electrolyte cause an even greater reduction in the dark current. This may be due to the lower concentration of free tri-iodide ions near the dye-attached TiO_2 surfaces because the surfaces of nanofillers can immobilize the ions. Although the dark current of 'Oligomer/Polymer/NP' is smaller than that of 'Oligomer/Polymer', the results for V_{oc} under illumination might be inconsistent with those of the dark current owing to the high electron concentration at the TiO_2 surface of 'Oligomer/Polymer/NP' (as shown in Fig. 2).

3.3. Ion transport performance in electrolytes

The diffusion coefficients and the total ion conductivities were measured to elucidate the ion transport in electrolytes. The diffusion coefficients of the anion species were evaluated from a steady-state voltammogram, as shown in Fig. 4. The charge transport in the electrolyte medium is effectively facilitated by adding nano-particles to the polymer-gel electrolyte. The enhanced ion mobility of the ternary component polymer-gel electrolyte may be explained by an ion-exchange mechanism with the formation of an electron transport path. Usui et al. [25] recently reported that adsorbed imidazolium cations on the TiO_2 surface can align the anion species by electrostatic interaction, facilitating electron transport by the ion-exchange mechanism depicted in Scheme 3 [20,25].

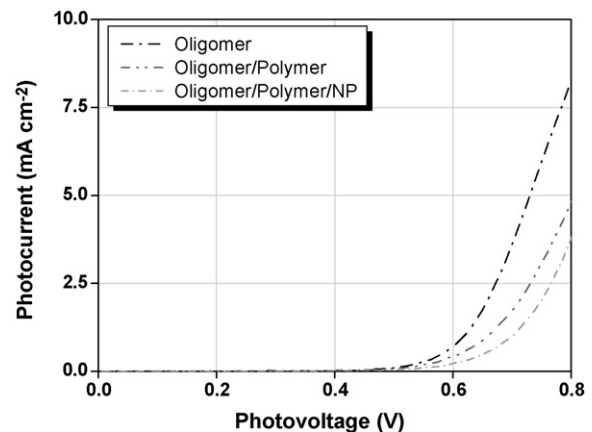
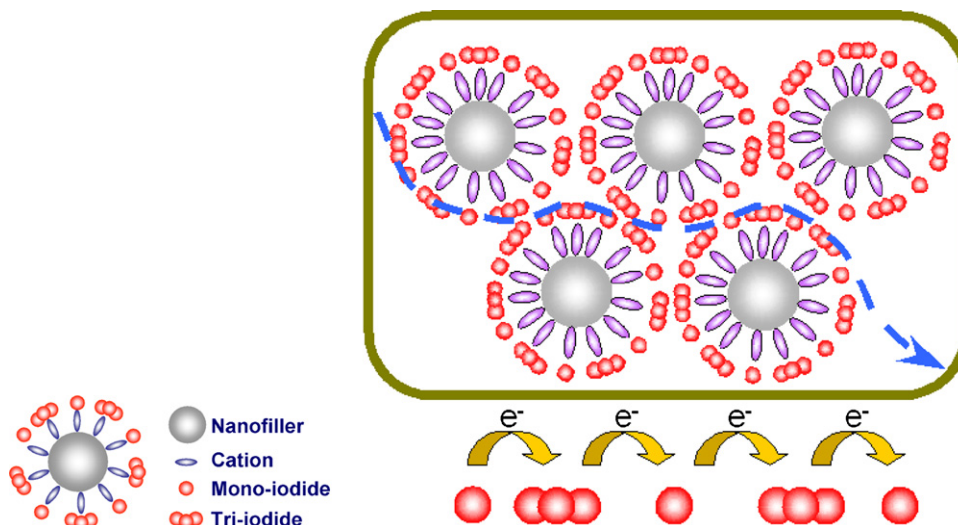


Fig. 3. J - V curves of DSSCs employing oligomer-based electrolytes measured in dark.



Scheme 3. Immobilization of cations on surface of nanofillers and electron transport path formed by nanofillers. This scheme is reproduced from Ref. [20].

Table 1
Ion transport properties of different electrolytes (ion conductivities and transport numbers)

Electrolyte	σ (t) (S cm ⁻¹)	σ (X ⁻) (S cm ⁻¹)	σ (M ⁺) (S cm ⁻¹)	t_{-}^a (-)	t_{+}^b (-)
Oligomer (E1)	1.02×10^{-3}	7.73×10^{-4}	2.47×10^{-4}	0.76	0.24
Oligomer/Polymer (E2)	2.15×10^{-4}	1.66×10^{-4}	4.92×10^{-5}	0.77	0.23
Oligomer/Polymer/NP (E3)	8.58×10^{-4}	7.83×10^{-4}	7.54×10^{-5}	0.91	0.09

^a t_{-} : transport number of anion ($= u_{-}/(u_{-} + u_{+})$, here u = mobility [26]).

^b t_{+} : transport number of cation ($= 1 - t_{-}$).

The total ion conductivities were also determined to elucidate the individual ion conductivities. Table 1 shows the ion transport properties measured. Among them, the liquid oligomer electrolyte (E1) has the highest total ion conductivity. The magnitude of the total conductivity, σ is in the order of E1 > E3 > E2. However, only anions are involved in the redox reactions occurring in the DSSC, indicating the dominant factor of the cell performance. The anion conductivities are in the order of E3 > E1 > E2. The transport numbers of anions (t_{-}) for E1, E2 and E3 are 0.76, 0.77, and 0.91, respectively. It should be noted that the transport number of the anion is greatly increased by adding nanoparticles to the electrolyte. This is attributed to the adsorbed cations on the NP surface,

as suggested in Scheme 3. As a result, the anion mobility of the ternary component polymer-gel electrolyte (E3) was much superior to that of the liquid oligomer electrolyte (E1), as shown in Table 1.

The a.c. impedances of the cells were measured under the dark and illumination conditions. The a.c. impedance spectra under the dark condition are presented in Fig. 5. In the dark condition, the magnitude of the impedance depends strongly on the total conductivity of the electrolytes. Under illumination (100 mW cm^{-2}), however, the impedance of E3 is comparable with that of E1 and much smaller than that of E2, as shown in Fig. 6. The diffusion impedance in the low-frequency range (0.01–2 Hz) is

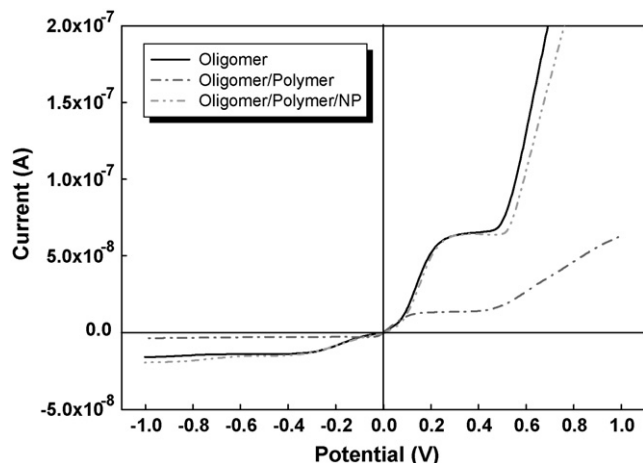


Fig. 4. Steady-state voltammograms of oligomer-based electrolytes measured with a Pt ultramicroelectrode (scan rate: 10 mV s^{-1}).

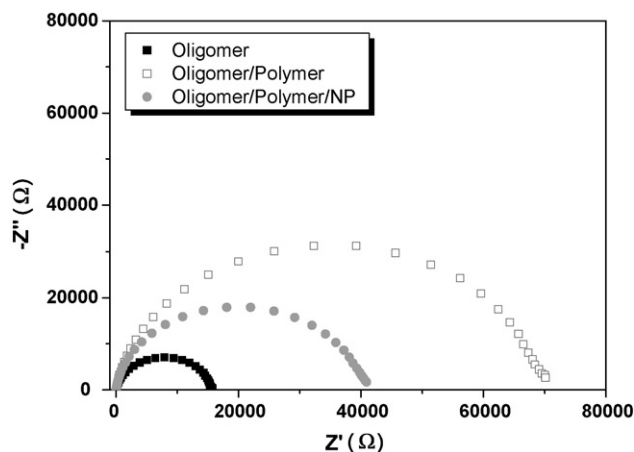


Fig. 5. a.c. impedance spectra of DSSCs employing oligomer-based electrolytes measured in dark.

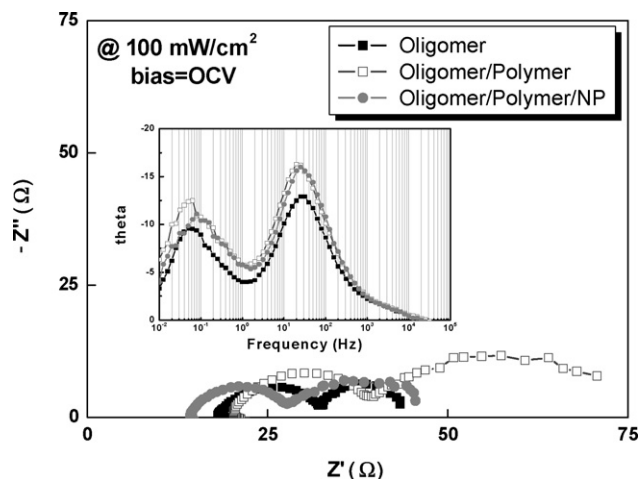


Fig. 6. a.c. impedance spectra of DSSCs employing oligomer-based electrolytes measured under 100 mW cm^{-2} illumination.

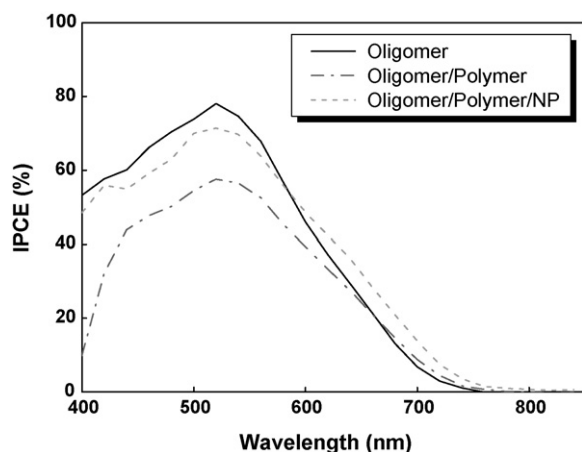


Fig. 7. IPCE spectra of DSSCs employing oligomer-based electrolytes.

greatly reduced by the nanoparticles (E3) due to the improved ion mobility.

3.4. Incident photon-to-current conversion (IPCE) efficiencies

The IPCE curves of the cells with different oligomer-based electrolytes are given in Fig. 7. Upon the addition of polymer to the electrolyte (E2), the IPCE is decreased mostly due to the reduced ion conductivity. By contrast, the introduction of nanofillers (E3) induces a significantly increased maximum IPCE and a better IPCE in the long wavelength region. This suggests that the enhanced cell performance of the cell with E3 is due to the improved ion conductivity and light-scattering effect of the nanoparticles in the long wavelength region [27].

3.5. Electron transport performances

The electron transport properties of TiO_2 are represented by the electron diffusion coefficient (D_e) and the lifetime (τ_e), which were estimated by means of stepped laser-induced photocurrent and photovoltage transient measurements [23]. The value of D_e was calculated by fitting the decay of the photocurrent transients with a single exponential and the TiO_2 film thickness by $D_e = w^2/2.77\tau_c$ (w = film thickness) [23]. Similarly, τ_e was calculated by fitting the decay of the photovoltage transients with a single exponential [23].

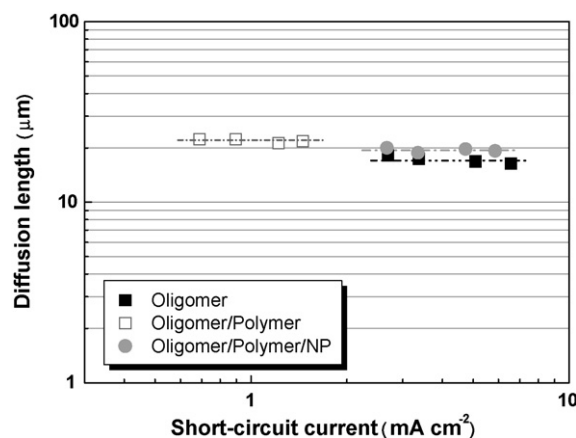


Fig. 8. Electron diffusion lengths of TiO_2 electrodes immersed in oligomer-based electrolytes.

The overall electron transport property was evaluated in terms of the electron diffusion length, $L_d = (D_e \cdot \tau_e)^{1/2}$ [28]. Fig. 8 shows the electron diffusion lengths in the TiO_2 electrodes. The cell with the ternary component polymer-gel electrolyte (E3) has a longer diffusion length than that with the liquid electrolyte (E1), mostly due to the reduction in dark current as evidenced by the results of J - V curves.

4. Conclusions

One of the most important issues with DSSCs is to use quasi-solid electrolytes because they provide moderate ion conductivity as well as excellent long-term stability. Different polymer-gel electrolytes have been prepared and compared in order to facilitate ion transport in the highly viscous medium and utilize incident sunlight effectively. A liquid-state oligomer has been employed as a main solvent to improve the interfacial contact between dye-attached TiO_2 and electrolyte, and to increase ion mobility in the electrolyte. The addition of a high molecular weight polymer to the liquid electrolyte (E2) leads to a solidified electrolyte and a reduced dark current, whereas the short-circuit current of the cell is significantly decreased due to the inferior ion mobility. This disadvantage can be overcome by using inorganic nanoparticles as a filler, which induces greatly enhanced ion transport and effective light scattering. A DSSC with the ternary component polymer-gel electrolyte (E3) exhibits the best energy conversion efficiency (7.2% at 1 sun), compared with the other electrolyte-type cells (E1 and E2). It is expected that these findings should provide good insight into the design of DSSCs with highly efficient polymer-gel electrolytes.

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