Short communication

Solid-state oligomer electrolyte with amine–acid interaction for dye-sensitized solar cells

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ABSTRACT

A pair of poly(ethylene glycol) oligomers with terminal groups capable of providing amine–acid interactions are used in dye-sensitized solar cells (DSSCs) as an electrolyte that can be easily solidified at room temperature. In spite of its solidity, the oligomer electrolyte has high ionic diffusion and good permeability into the nanopores of a TiO_2 electrode. The electron diffusion coefficient and lifetime in a photoelectrode are largely affected by the adsorptive interaction between cations and the TiO_2 surface. The energy-conversion efficiency of DSSCs using the oligomer electrolyte is greater than 4.5%. Long-term storage at room temperature demonstrates that the stability of the oligomer electrolyte system is superior to that of a volatile solvent electrolyte.

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1. Introduction

During the past decade, dye-sensitized solar cells (DSSCs) have drawn much interest as promising alternatives to conventional silicon-based solar cells [1–4]. A DSSC consists of a photoelectrode with a nanoporous semiconductor film and an adsorbed sensitizer, a redox couple as an electrolyte, and a counter electrode. Extensive research has been performed on each component and, as a result, DSSCs with electrolytes in volatile solvents can yield an energy-conversion efficiency of ~11% [5]. On the other hand, poor thermal and long-term stability of liquid electrolytes have limited their performance and practical application. Accordingly, the need for stable alternatives, including a hole-transport material, an ionic liquid, or a polymer, has been stressed [6–10].

We have been investigating oligomer electrolytes as promising alternatives to liquid electrolytes for DSSCs [11,12]. Oligomers show considerable stability and ionic diffusion properties, so DSSCs employing oligomer electrolytes could exhibit long-term stability as well as a high energy-conversion efficiency [11,13]. Nevertheless, oligomer electrolytes also suffer from leakage problems and

poor mechanical properties as found with conventional liquid electrolytes. This is because oligomer electrolytes are in a liquid instead of a solid state at room temperature. Accordingly, an alternative method to enable solidification and enhancement of mechanical properties, without decrease in ion diffusivity, is in high demand.

A solid-state oligomer electrolyte, poly(ethylene glycol) with hydrogen bonding (PHB), has been introduced [14]. Through this method, the contact between the TiO_2 electrode and the oligomer electrolyte was improved and the energy-conversion efficiency of the DSSCs was increased to approximately 3.3%. This performance is high for a solid-state electrolyte, but is still much lower than in DSSCs employing common volatile solvent electrolytes.

In this study, a novel electrolyte composed of a pair of oligomers with terminal groups capable of providing secondary interactions is suggested. While the PHB system uses quadruple hydrogen bonding of the bulky terminal group to solidify, the novel oligomer electrolyte can easily solidify due to the small but strong interaction between the amine (NH_2) and acid (COOH) groups. The ion transport in the prepared oligomer electrolyte is studied through the diffusion coefficients of I^- and I_3^- when different iodide salts are employed. The effect of cations on the electron diffusion coefficient and lifetime in the photoelectrode, and performance of the DSSCs are investigated when using oligomer electrolytes.

2. Experimental

2.1. Preparation and characterization of oligomer electrolytes

Oligomer electrolytes were prepared using poly(ethylene glycol) bis(carboxymethyl) ether [PEGCME, molecular weight (MW) = 600 g mol^{-1}] and methoxypolyethylene glycol amine (MPEGA, MW = 750 g mol^{-1}) as the donor and acceptor of secondary interactions, respectively. The molar ratio of MPEGA to PEGCME in the electrolytes was fixed at 2:1. The concentrations of I$^-$ and I$_3$$^-$ were maintained at 0.85 and 0.15 M, respectively, via iodide salts with different cations such as 1-butyl-3-methylimidazolium iodide (BMII) or 1-hexyl-2,3-dimethylimidazolium iodide (HDMII) and iodine. In addition, the oligomer electrolytes contained 0.2 M N-methyl-benzimidazole (NMBI). Each electrolyte is referred to as BMII- or HDMII-electrolyte according to the source of cations.

FT-IR spectra of the raw oligomers including PEGCME, MPEGA, and a blend were investigated with a FT-IR spectrometer (Nicolet). The spectrum of the BMII-electrolyte was monitored at various temperatures. The viscosities of the oligomer electrolytes as a function of temperature were determined using a rheometer (DV-III+, Brookfield). Anodic and cathodic steady-state currents were measured using a scanning electrochemical microscope (SECM, CHI900) to identify the diffusion coefficients of I$^-$ and I$_3$$^-$ in the electrolytes.

2.2. Fabrication of DSSCs with oligomer electrolytes

The preparation methods for the photo and counter electrodes have been described previously [11,12]. Both electrodes employed transparent, fluorine-doped, tin oxide glass (SnO$_2$:F, FTO, sheet resistance 8 Ω cm^{-1}). After doctor-blade coating of TiO$_2$ paste on the FTO glass, the substrate was sintered at 500 °C for 15 min. Platinum-layered counter electrodes were prepared by spin-coating and successive annealing at 400 °C for 20 min. The photoelectrodes were sensitized with 0.5 mM of purified (Ru(dcbpy)$_2$(NCS)$_2$ (535-bisTBA, Solaronix)) in an ethanol solution. A solution of the oligomer electrolytes in acetonitrile was placed drop-wise on the sensitized photoelectrode, allowing the electrolyte to penetrate the TiO$_2$ nanopores. The solvent in the drops was completely removed by vaccum drying, and the surplus electrolyte on the substrate was wiped off. The space between the photo and counter electrode was sealed by a thermal adhesive film with a thickness of 25 μm and filled with oligomer electrolytes by capillary force at 50 °C to effect thorough infiltration.

2.3. Measurement of electron transport in photoelectrode

The electron diffusion coefficient and lifetime in the TiO$_2$ electrode were determined by stepped, light-induced, transient measurements of the photocurrent and the voltage (SLIM-PCV) [15,16]. For SLIM-PCV, a diode laser (λ = 635 nm) was modulated with a function generator and ND filters were used to verify the laser intensity. To obtain reliable data, the thickness of the TiO$_2$ layer was fixed at 6.5 ± 0.1 μm, as measured by a surface profiler (P-10, Tencor), and the active area of the cells was 0.112 ± 0.004 cm^2, as calculated by an image analyzer. The operating principle and other conditions have been previously described [15].
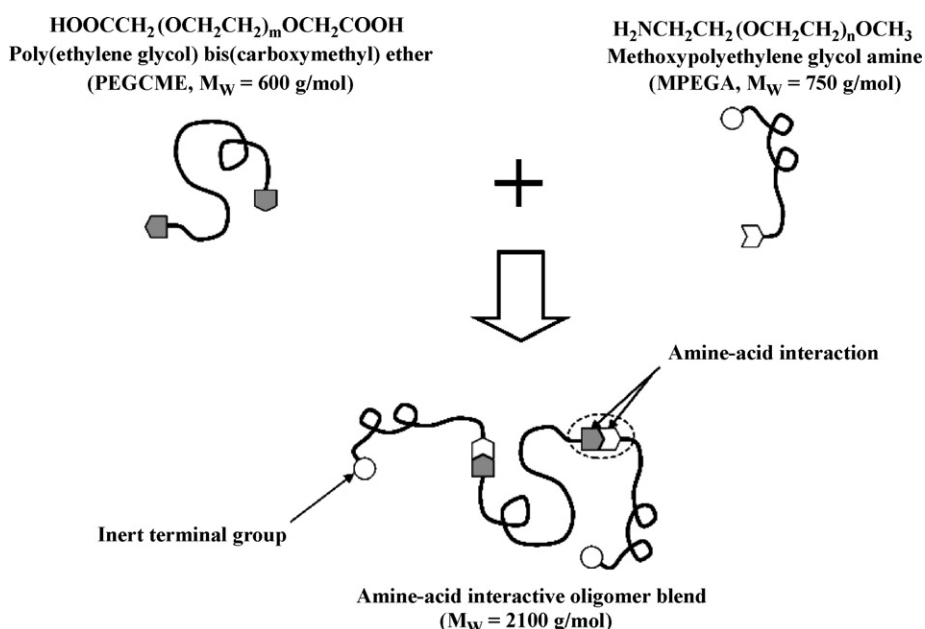
2.4. Photovoltaic performances of DSSCs

The photovoltaic performances of the prepared DSSCs, including open-circuit voltage (V_{OC}), short-circuit photocurrent density (J_{SC}), fill factor (FF), and overall energy-conversion efficiency (η) were examined. The J–V curves were measured under 1 sun condition (100 mW cm^{-2}, AM 1.5) monitored with a standard silicon solar cell using a Keithley Model 2400 and 1000 W Xenon lamp (91193, Oriel). The thickness of the TiO$_2$ layer in the DSSCs was approximately 12.0 μm and the active area of the cells was 0.24 ± 0.01 cm^2.

3. Results and discussion

3.1. Amine–acid interaction

The hydrogen bonding of PHB is a key factor for self-solidification and the interaction between terminal groups has been previously reported [17,18]. Since, however, the PHB contains bulky terminal groups to form hydrogen bonds, the poly(ethylene glycol)

HOOCCH$_2$(OCH$_2$CH$_2$)$_m$OCH$_2$COOH
Poly(ethylene glycol) bis(carboxymethyl) ether
(PEGCME, M$_W$ = 600 g/mol)

H$_2$NCH$_2$CH$_2$(OCH$_2$CH$_2$)$_n$OCH$_3$
Methoxypolyethylene glycol amine
(MPEGA, M$_W$ = 750 g/mol)

Amine-acid interaction

Inert terminal group

Amine-acid interactive oligomer blend
(M$_W$ = 2100 g/mol)

Scheme 1. Oligomers with different terminal groups and schematic drawing of amine–acid interactive oligomers.
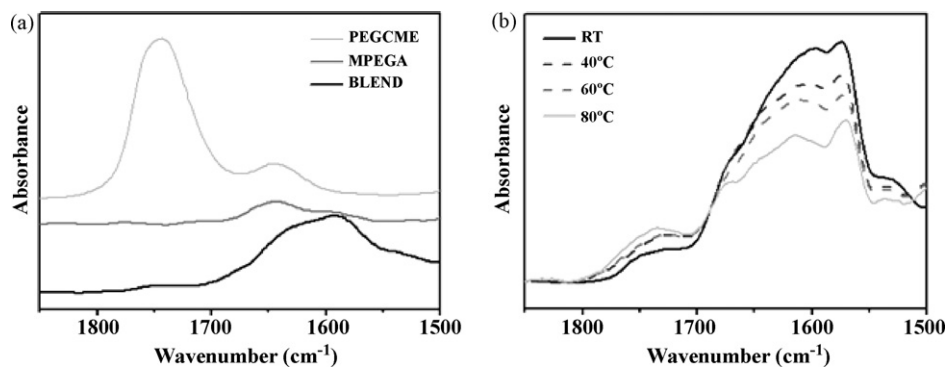
Fig. 1. FT-IR spectra of (a) raw oligomers and their blend and (b) BMII-electrolyte at various temperatures.
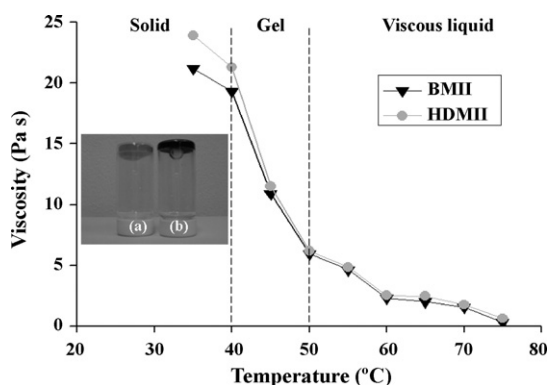

Fig. 2. Viscosities of oligomer electrolytes as function of temperature and images of (a) oligomer blend of PEGCME and MPEGA and (b) BMII-electrolyte at room temperature.

chain motion requisite for ion transport and the contact between the TiO$_2$ electrode and electrolyte are significantly hampered and thereby results in a low energy-conversion efficiency.

The interaction between NH$_2$ and COOH groups has been widely used where non-covalent bonding is required due to its high bonding-strength and small size [19–21]. To this end, another combination of functional groups capable of providing amine–acid interactions is selected, replacing the bulky groups in the PHB. A representation of the amine–acid interactive oligomers is shown in Scheme 1. The FT-IR spectra of both raw oligomers and their blend indicate well-constructed, secondary bonding between PEGCME and MPEGA. The free C=O peak of PEGCME at approximately 1740 cm^{-1} disappears and the peaks from both the ammonium and carboxylate ions in the region between 1650 and 1550 cm^{-1} emerge, as shown in Fig. 1a [21]. To investigate the durability of the amine–acid interaction as a function of temperature, FT-IR measurements of the BMII-electrolyte at various temperatures were

also performed. As shown in Fig. 1b, the interaction decreases with increasing temperature; nevertheless, most interactions are maintained up to 60 °C. In addition, more than half of the interactions remain when the temperature increases up to 80 °C.

To examine the state of the oligomer electrolytes as a function of temperature, the viscosities of BMII- and HDMII-electrolytes were measured at various temperatures. The electrolytes are in a solid state at room temperature and phase transition of the electrolytes occurs in the range of 40–50 °C, as demonstrated in Fig. 2. The HDMII-electrolyte exhibits a slightly higher viscosity than the BMII-electrolyte due to its iodide salt being in a solid state. In spite of the high viscosity, field-emission scanning electron microscopy (FE-SEM) images (Fig. 3) clearly confirm the successful infiltration of HDMII- as well as BMII-electrolytes into the TiO$_2$ electrode.

3.2. Ionic diffusion in oligomer electrolyte

An ultra-microelectrode technique using SECM has frequently been used to measure ionic diffusion coefficients [22,23]. The coefficients can be evaluated from the steady-state current (I_{SS}) according to:

$$I_{ss} = 4nFDCr$$

where n is the electron number per molecule, F is the Faraday constant, D is the ionic diffusion coefficient, C is the bulk concentration of electroactive species, and r is the radius of the Pt ultra-microelectrode (5 μm).

Steady-state voltammograms of the oligomer electrolytes are shown in Fig. 4. The steady-state current of the BMII-electrolyte is larger than that of the HDMII-electrolyte, which implies that I$^-$ and I$_3^-$ in BMII-electrolyte diffuse more rapidly (Table 1). A higher viscosity of the electrolyte causes a lower diffusion coefficient, so the low ionic diffusion coefficients of the HDMII-electrolyte are due to its high viscosity.
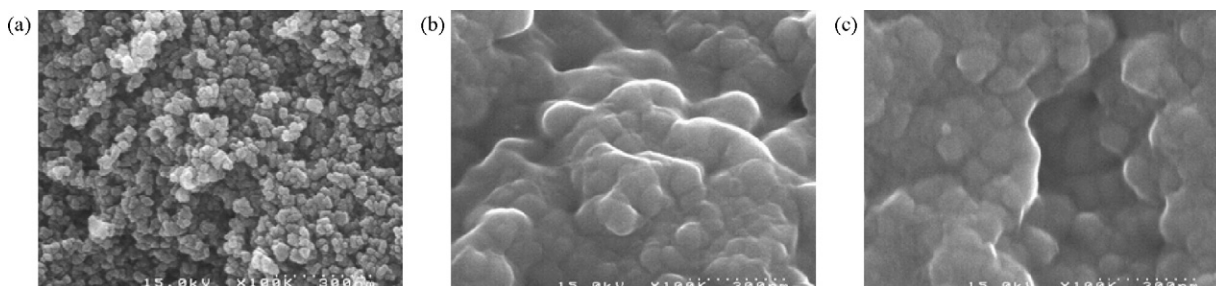

Fig. 3. Cross-sectional FE-SEM images of (a) nanocrystalline TiO$_2$ films and those cast with (b) BMII- and (c) HDMII-electrolyte.

Table 1
Diffusion coefficients of the active species in oligomer electrolytes and photovoltaic characteristics of DSSCs with oligomer electrolytes

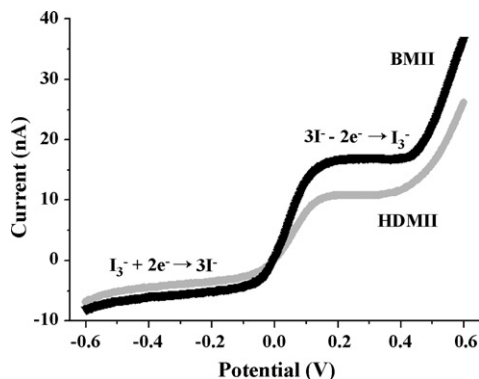| Electrolyte	Diffusion coefficient (10^{-7} cm^2 s^{-1})		Cell performance			
	I^-	I_3^-	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	η (%)
BMII	1.56	0.85	0.69	9.20	0.71	4.51
HDMII	0.99	0.61	0.67	8.41	0.68	3.82

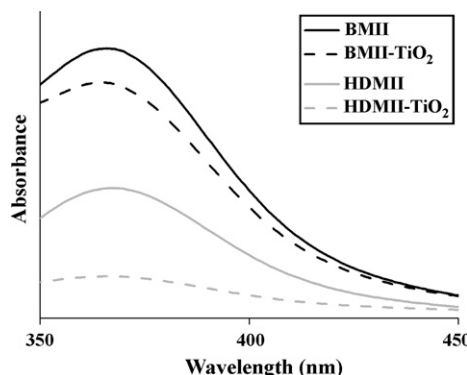**Fig. 4.** Steady-state voltammograms of oligomer electrolytes measured at scan rate 3 mV s^{-1}.

Fig. 6. UV–vis absorption spectra of 0.1 M BMII and HDMII solutions in PEGDME (MW 500 g mol^{-1}) and centrifuged solution after addition of TiO$_2$ nanoparticles (30 mg for 5 ml of the BMII and HDMII solutions).

As shown in a recent study [11] ionic diffusion coefficients in oligomer electrolytes decrease with increasing MW of the oligomers [11]. If the amine–acid interaction has the same effect on ionic diffusion as increasing the MW, then the ionic diffusion coefficients of the oligomer electrolytes will be much lower than those of the poly(ethylene glycol dimethyl ether) (PEGDME) electrolytes with a MW of 1000 (10^{-8} cm^2 s^{-1}), and may be similar to those of PEGDME electrolytes with a MW of 2100. The values of the oligomer electrolytes, however, are in the range of approximately 10^{-7} to 10^{-8} cm^2 s^{-1}. Consequently, in spite of the viscosity increase, the amine–acid interaction does not significantly decrease the ionic diffusion coefficients. Considering this phenomenon, the amine–acid interaction can be one of the most effective ways to solidify oligomer electrolytes without critically decreasing the ionic diffusion rate.

3.3. Electron transport in photoelectrode

The electron transport in the TiO$_2$ mesoporous film of DSSCs was characterized by electron diffusion coefficients and lifetime. The decay of photocurrent and photovoltage transients was measured by SLIM-PCV and the obtained data were fitted with an exponential function [15]. Fig. 5 shows the electron diffusion coefficient and lifetime as a function of electron charge density of cells employ-

ing BMII- and HDMII-electrolytes. The electron charge density was calculated using a published equation [24].

While the electron diffusion coefficient of the cells employing the HDMII-electrolyte is greater than that of the cells employing the BMII-electrolyte, the reverse is observed for the electron lifetime. This behaviour can be explained by the effect of different adsorptive interactions between the cations and TiO$_2$ surface. Electron diffusion coefficients may be largely affected by the cation adsorption on TiO$_2$ mesoporous films due to the ambipolar diffusion in a photoelectrode [25]. As confirmed in Fig. 6, the absorbance of the 0.1 M BMII solution in PEGDME with a MW of 500 decreases by approximately 13% after adding TiO$_2$ nanoparticles (30 mg for 5 ml of the solutions) and centrifuging. By contrast, the absorbance of the 0.1 M HDMII solution decreases by approximately 68% after addition of the nanoparticles, that is, over five times more than the reduction seen in the BMII solution. Based on this result, it is confirmed that HDMI$^+$ cations are more adsorbed on to the TiO$_2$ surface than BMI$^+$ cations. A highly adsorptive cation could induce a high electron diffusion coefficient and a short electron lifetime due to the increase of local cation density as well as local concentration of I$_3^-$ [25,26]. This interpretation corroborates the higher electron diffusion coefficient and shorter lifetime of cells employing HDMII-electrolyte.
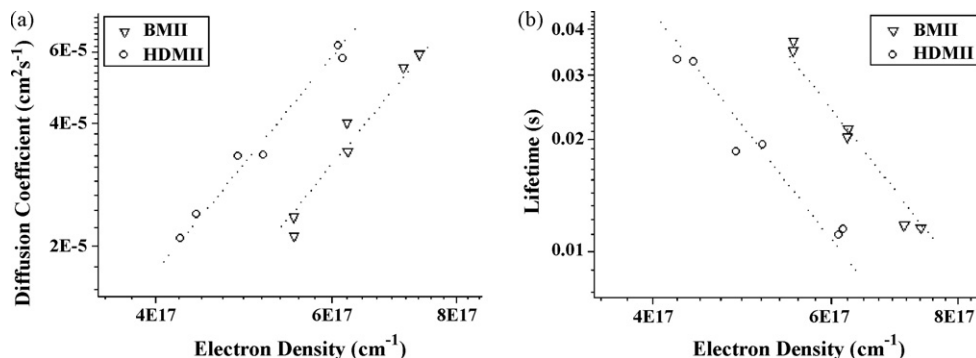

Fig. 5. Electron (a) diffusion coefficient and (b) lifetime in TiO$_2$ electrodes of DSSCs with oligomer electrolytes.
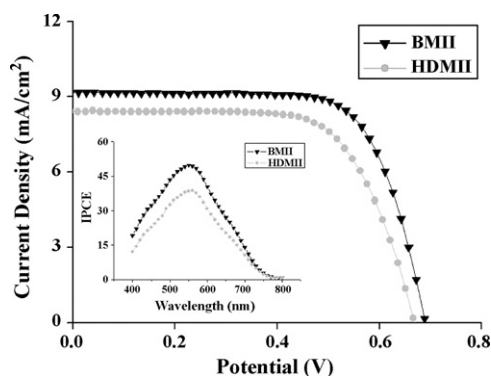
Fig. 7. *J–V* curves measured at 100 mW cm^{-2} and IPCE versus wavelength of light for DSSCs with oligomer electrolytes.
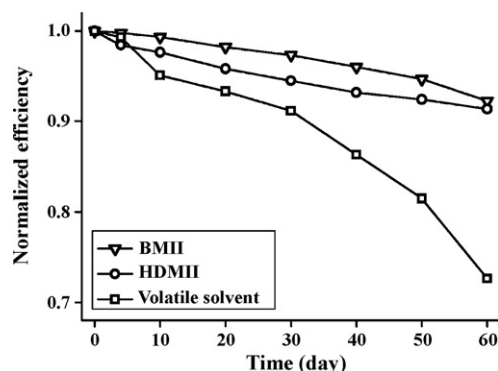

Fig. 8. Stability test of DSSCs with oligomer electrolytes and volatile solvent electrolyte (1 M BMII, 0.15 M I$_2$ and 0.2 M NMBI dissolved in 3-methoxypropionitrile) at room temperature.

3.4. Photovoltaic performance

The *J–V* and IPCE curves of DSSCs employing BMII- and HDMII-electrolytes are presented in Fig. 7. The DSSC employing the BMII-electrolyte exhibits a conversion efficiency greater than 4.5% and has a higher V_{OC} and J_{SC} than the DSSC prepared with HDMII-electrolyte. The V_{OC} of the former is expected to be greater, as a longer electron lifetime generally results in a higher V_{OC}. Furthermore in spite of the addition of NMBI to increase V_{OC}, the highly absorbed HDMI$^+$ cations on the TiO$_2$ electrode could shift the conduction band-edge of the TiO$_2$ mesoporous films downward [27]. Considering the higher ionic diffusion coefficients and thereby a more effective redox reaction at the photo and counter electrodes, it is reasonable that the DSSC with the BMII-electrolyte has a higher J_{SC} than that with the HDMII-electrolyte.

The long-term stability of the DSSCs using different oligomer electrolytes was also evaluated (Fig. 8). After room temperature storage for 60 days, the cells employing the oligomer electrolytes maintain over 91% of their initial efficiency while the cell prepared with a volatile solvent electrolyte (3-methoxypropionitrile) drops to only 73% of its initial efficiency.

4. Conclusions

Amine–acid interactions have been determined to be a promising route to prepare oligomer electrolytes that retain high ionic diffusion despite their solid state. Using the oligomer electrolyte, a DSSC with a solid-state electrolyte has been fabricated and its energy-conversion efficiency is greater than 4.5%. The influence of adsorptive interactions between the cations and TiO$_2$ surface on electron transport in the photoelectrode has also been investigated. Cells employing the oligomer electrolytes show superior stability to that prepared with a volatile solvent electrolyte.

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