

Short communication

# Effect of molecular weight of oligomer on ionic diffusion in oligomer electrolytes and its implication for dye-sensitized solar cells

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## Abstract

This study measures the diffusion coefficients of  $I^-$  and  $I_3^-$  in oligomer electrolytes as a function of the molecular weight of oligomers and investigates their effect on the performance of dye-sensitized solar cells (DSSCs). The high-diffusion coefficients of ions in an oligomer electrolyte with a lower molecular weight can help to promote the redox mechanism in DSSCs and thereby increase the short-circuit current density. They can also cause a decrease in the open-circuit voltage since a high-diffusion coefficient of  $I_3^-$  is capable of reducing the lifetime of electrons in  $TiO_2$  electrodes. To offset these effects, *N*-methyl-benzimidazole is added to the oligomer electrolytes, thereby improving the open-circuit voltage and fill factor and, consequently, the overall energy-conversion efficiency, which increases to over 5%. A further test involving storage at a high temperature of 75 °C demonstrates that DSSCs employing the oligomer electrolytes show excellent thermal stability over 200 h.

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**Keywords:** Dye-sensitized solar cell; Ionic diffusion; Poly(ethylene glycol); Molecular weight; Non-volatile electrolyte

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are one of the most interesting research fields in photoelectrochemistry because they represent a potential alternative to silicon-based solar cells due to their low production costs [1]. Studies have shown that DSSCs yield an energy conversion efficiency of ~11% [2]. However, this efficiency was obtained by employing volatile liquid electrolytes, and cells incorporating such volatile liquid solvents are prone to drawbacks such as leakage and evaporation of solvent. Therefore, efforts to develop an alternative stable electrolyte are continuing in a search for practical applications [3–5].

We have been continuously investigating DSSCs employing oligomer electrolytes [6–8]. At room temperature, oligomers are commonly in a liquid state with a molecular weight in the range of 200–1000 and with little vapour pressure. Moreover, oligomers can be solidified by internal reactions or by the addition of nano-particles [7–9]. Although oligomers can be used effectively as alternative electrolytes in DSSCs, there

have been few studies of transport phenomena through the oligomer electrolytes. Accordingly, it is desirable to investigate these transport phenomena, in particular ionic and the electronic diffusion behaviour.

In this study, the diffusion coefficients of  $I^-$  and  $I_3^-$  in oligomer electrolytes as a function of the molecular weight of the oligomers are measured and their effect on the performance of DSSCs is investigated. An investigation is also made of the effect of adding *N*-methyl benzyl imidazolium to the oligomer electrolytes, as well as the thermal stability of the DSSCs with these enhanced electrolytes.

## 2. Experimental

### 2.1. Preparation of oligomer electrolytes and their characterization

Poly(ethylene glycol dimethyl ether) (PEGDME) with three different molecular weights of 250, 500 and 1000 g mol<sup>-1</sup> were used as host materials, and 1-methyl-3-propylimidazolium iodide (MPII), an ionic liquid, was used as an iodide source. The molar ratio of the oxygen atoms in ether groups of PEGDME to MPII was fixed at 20, and the content of iodine was fixed

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at 10 mol% with respect to MPII. Each electrolyte is referred to as 250, 500 or 1000. The properties of the electrolytes were characterized by using a differential scanning calorimeter (DSC, Perkin-Elmer), a rheometer (DV-III+, Brookfield) and a scanning electrochemical microscope (SECM, CHI900). To begin with, DSC measurements were conducted at a cooling rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from 100 to  $-50\text{ }^{\circ}\text{C}$  in order to confirm the phase change of the oligomers due to temperature, and a rheometer was used to measure the viscosity of the electrolytes at  $25\text{ }^{\circ}\text{C}$ . In addition, anodic and cathodic steady-state currents were determined with a SECM in order to identify each diffusion coefficient of iodide and triiodide in the electrolytes.

## 2.2. Fabrication of DSSCs employing oligomer electrolytes

A photoelectrode consisted of a  $\text{TiO}_2$  blocking layer and a nanocrystalline  $\text{TiO}_2$  on transparent fluorine-doped tin oxide glass ( $\text{SnO}_2\text{:F}$ , FTO) (sheet resistance  $8\ \Omega\ \square^{-1}$ , Pilkington). To prepare the  $\text{TiO}_2$  blocking layer, a Ti(IV) bis(ethyl acetoacetato)-diisopropoxide solution (5% (w/w) in 1-butanol) was spin-coated on the FTO glass, and then the electrode was annealed at  $500\text{ }^{\circ}\text{C}$  for 15 min. To control the thickness of the nanocrystalline  $\text{TiO}_2$ , the substrate was covered on two parallel edges with tape.  $\text{TiO}_2$  paste (18NR-T, STI) was then cast with a doctor-blade and sintered at  $500\text{ }^{\circ}\text{C}$  for 15 min. The thickness of the  $\text{TiO}_2$  layer was around  $12.0\ \mu\text{m}$ , as measured by a surface profiler (P-10, Tencor). A sensitizer ( $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  (535-bisTBA, Solaronix)) was purified to enhance the performance of the cells [10]. The  $\text{TiO}_2$  electrodes were dipped in a solution consisting of  $0.5\ \text{mM}$  of the purified sensitizer in absolute ethanol for 24 h. A Pt counter electrode was prepared by spin-coating the  $\text{H}_2\text{PtCl}_6$  solution ( $0.007\ \text{mol dm}^{-3}$  in isopropanol) onto FTO glass and then sintering at  $400\text{ }^{\circ}\text{C}$  for 20 min. The space between the photo and counter electrode was sealed by means of thermal adhesive film with a thickness of  $25\ \mu\text{m}$ , and then filled with oligomer electrolytes by capillary force at  $50\text{ }^{\circ}\text{C}$  to infiltrate thoroughly. After preparing the DSSCs using oligomer electrolytes, the performance of the cells was examined. Their current density–voltage ( $I$ – $V$ ) curves were measured at 1 sun ( $100\ \text{mW cm}^{-2}$ , AM 1.5) using a Keithley Model 2400 and a 1000 W xenon lamp (91193, Oriel). The active area of the DSSCs was about  $0.20\ \text{cm}^2$ .

## 2.3. Electron lifetime in $\text{TiO}_2$ electrode

The electron lifetime in the  $\text{TiO}_2$  electrode of the cells was measured by means of stepped, light-induced, transient measurements of the photocurrent and voltage (SLIM-PCV) [11]. Only when the  $\text{TiO}_2$  electrode was thinner than the diffusion length of the electrons in the  $\text{TiO}_2$  electrode was the measurement reliable. Therefore, the thickness of the  $\text{TiO}_2$  layer was fixed at approximately  $6.9\ \mu\text{m}$ . For SLIM-PCV, a diode laser ( $\lambda = 635\ \text{nm}$ ) was operated at a voltage of  $3.00\ \text{V}$  and then stepped down to  $2.70\ \text{V}$ . ND filters were used to verify the laser intensity. Other conditions have been explained in detail at a previous publication [11].

Table 1  
Properties of oligomer electrolytes according to molecular weight of oligomer

Oligomer electrolyte	Viscosity (cP)	Diffusion coefficient ( $\times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}$ )	
		$\text{I}^-$	$\text{I}_3^-$
250	14	9.10	4.27
500	55	2.58	2.41
1000	490	0.27	0.15

## 3. Results and discussion

### 3.1. Properties of oligomer electrolytes

The properties of the oligomer electrolytes as a function of molecular weight of oligomer were characterized (Table 1). As a result of DSC measurements (Fig. 1), it is confirmed that an oligomer with a lower molecular weight had a lower crystallization temperature. In the case of 250 oligomer, a crystallization temperature is not found even down to  $-50\text{ }^{\circ}\text{C}$ . By contrast, the 500 and 1000 oligomers displayed crystallization at temperatures of around  $-6$  and  $20\text{ }^{\circ}\text{C}$ , respectively. Therefore, for the purpose of measuring the photovoltaic performance of DSSCs, it is important to note that the 250 and 500 oligomers are in a liquid state at room temperature in the range of  $20$ – $30\text{ }^{\circ}\text{C}$ , while the 1000 oligomer is in a gel state. The viscosity of the oligomer electrolytes at  $25\text{ }^{\circ}\text{C}$  was tested with a rheometer. As expected, the viscosities of 250 and 500 samples, being liquid-state, are relatively low, whereas 1000, being gel-state, has a high viscosity. This phenomenon is consistent with the DSC measurements.

An ultra-microelectrode technique using SECM has frequently been used to measure the ionic diffusion coefficients of  $\text{I}^-$  and  $\text{I}_3^-$  [12,13]. These are directly connected with the redox mechanism in DSSCs. The diffusion coefficients were calculated from the steady-state current ( $I_{\text{SS}}$ ) using the following equation:

$$I_{\text{SS}} = 4nFDcR$$

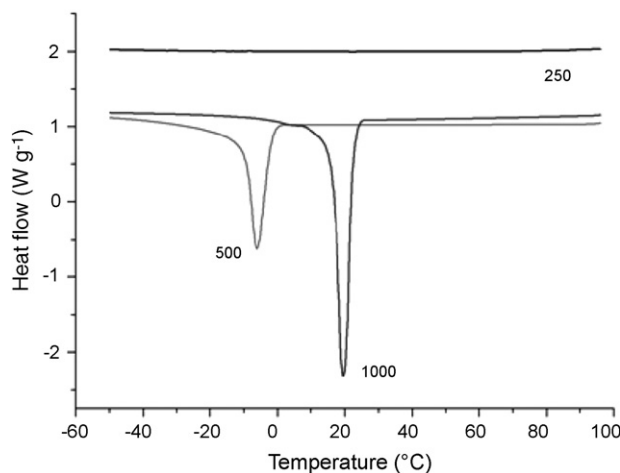


Fig. 1. DSC thermograms for oligomer electrolytes of various molecular weights.

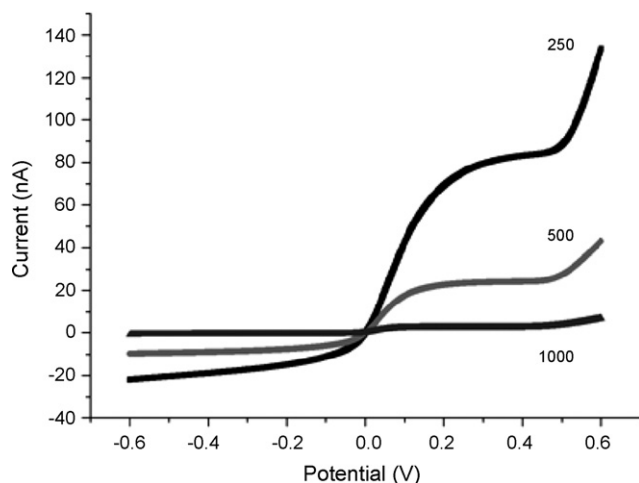


Fig. 2. Steady-state voltammograms of oligomer electrolytes measured at a scan rate  $5 \text{ mV s}^{-1}$ .

where  $n$  is the electron number per molecule, that is,  $n$  is 2 and  $2/3$  for  $\text{I}^-$  and  $\text{I}_3^-$ , respectively;  $F$  the Faraday constant;  $D$  the diffusion coefficient of  $\text{I}^-$  or  $\text{I}_3^-$ ;  $C$  the bulk concentration of electroactive species;  $r$  is the radius of the Pt ultra-microelectrode ( $5 \mu\text{m}$ ).

Steady-state voltammograms of the oligomer electrolytes are shown in Fig. 2. It is found that the steady-state currents increase with decreasing oligomer molecular weight. As noted previously, the oligomer with a lower molecular weight had a lower crystallization temperature and viscosity. Accordingly, it is considered that these properties enhance both the mobility of ions and the steady-state currents. As found in Table 1, oligomers with molecular weights of 250 and 500 show large diffusion coefficients, viz.,  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . Although the diffusion coefficients are still lower than those of common volatile liquid electrolytes, it is not considered significant enough to regenerate the sensitizers. In the case of the 1000 oligomer, however, the electrolyte has a critically low value of  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , and thus the reduction of the sensitizers might be deterred by the lack of redox couples due to the lower ionic diffusion in the electrolyte.

### 3.2. Photovoltaic performance

The effects of ionic diffusion in the oligomer electrolytes on the photovoltaic performance of DSSCs using the electrolytes were investigated. Table 2 summarizes the open-circuit

Table 2  
Performance characteristics of DSSCs employing oligomer electrolytes at  $100 \text{ mW cm}^{-2}$

Oligomer electrolyte	$V_{\text{OC}}$ (V)	$J_{\text{SC}}$ ( $\text{mA cm}^{-2}$ )	FF (%)	$\eta$ (%)
250	0.605	13.92	58.4	4.92
500	0.624	11.39	58.0	4.12
1000	0.497	6.40	44.1	1.40
N250	0.665	11.52	65.7	5.03
N500	0.684	10.09	65.2	4.50
N1000	0.604	6.61	46.9	1.87

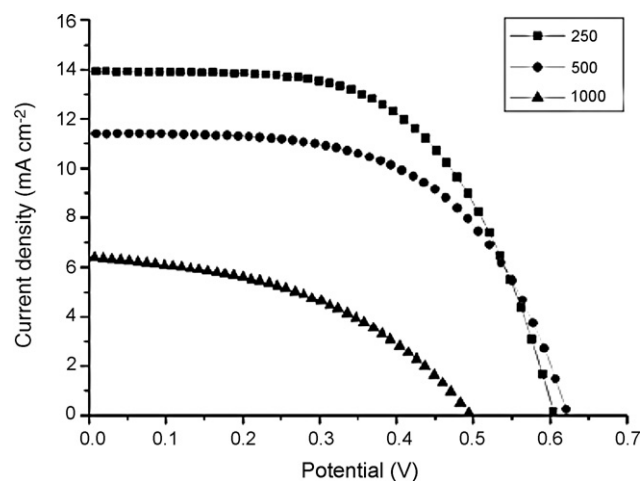


Fig. 3.  $I$ - $V$  curves measured at  $100 \text{ mW cm}^{-2}$  of DSSCs employing oligomer electrolytes of various molecular weights.

voltage ( $V_{\text{OC}}$ ), short-circuit photocurrent density ( $J_{\text{SC}}$ ), fill factor (FF) and overall energy-conversion efficiency ( $\eta$ ) of the DSSCs. The  $I$ - $V$  curves are presented in Fig. 3. The cell employing 250 electrolyte gave a high current density, viz.,  $13.92 \text{ mA cm}^{-2}$ , because of the high diffusion coefficients of the redox couples that are needed to regenerate oxidized sensitizers and smooth redox mechanisms. By contrast, in the case of the 1000 oligomer, the cell delivers a current density of only  $6.40 \text{ mA cm}^{-2}$  and has a very low fill factor and overall energy-conversion efficiency because its ionic diffusion coefficients are significantly lower, and thus the oxidized dyes cannot be readily reduced.

It is also found that the cells with 250 electrolytes have a lower  $V_{\text{OC}}$  values than that with a 500 electrolyte. This may be related to recombination between the electrons in the  $\text{TiO}_2$  electrode and  $\text{I}_3^-$  in the electrolyte. If the diffusion coefficient of  $\text{I}_3^-$  is large, the collision frequency between the electrons and  $\text{I}_3^-$  also increases, which results in an increase in the recombination rate along with a decrease in the lifetime of the electrons [11,14–16]. It is well known that a high recombination rate results in low  $V_{\text{OC}}$  [17–19]. Accordingly, DSSCs using 250 electrolytes will have a lower  $V_{\text{OC}}$ . Nevertheless, the cell employing 1000 electrolyte shows the lowest  $V_{\text{OC}}$ . The reason for this behaviour may be related to insufficient redox reactions with sensitizers and impediment of charge transfer at the counter electrode due to the small ionic diffusion coefficients.

### 3.3. Electron lifetime in $\text{TiO}_2$ electrodes

To clarify the relationship between the diffusion coefficient of  $\text{I}_3^-$  in the oligomer electrolytes and the  $V_{\text{OC}}$  of the DSSCs employing the electrolytes, the electron lifetime in the  $\text{TiO}_2$  electrodes was measured. It can be expected that the electron lifetime will increase as the oligomer molecular weight increases since results discussed above have shown that a larger molecular weight of electrolyte induces a decrease in the diffusion coefficient of  $\text{I}_3^-$ . As shown in Fig. 4, the results are as expected. The electron lifetime of the 250 electrolyte is almost half that of the

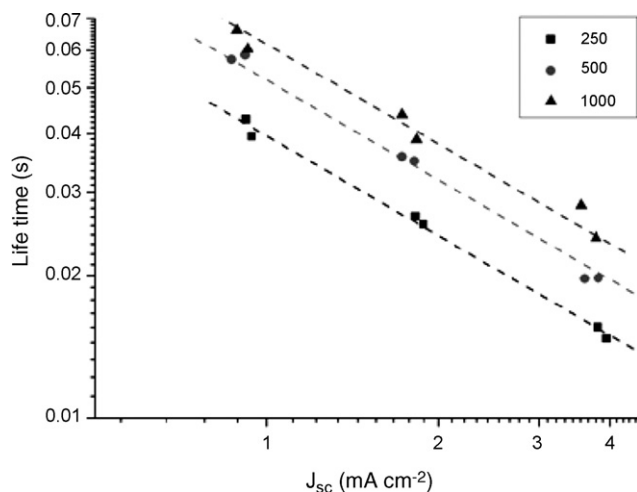


Fig. 4. Electron lifetime in  $\text{TiO}_2$  electrodes of DSSCs employing oligomer electrolytes of various molecular weights.

other oligomer electrolytes. Consequently, it is confirmed that the  $V_{OC}$  of cells employing oligomer electrolytes decrease with increasing diffusion coefficient of  $\text{I}_3^-$  because of the enhanced recombination process between the electrons in the  $\text{TiO}_2$  electrode and  $\text{I}_3^-$ .

#### 3.4. Addition of *N*-methyl-benzimidazole

The DSSCs employing the oligomer electrolytes give relatively lower values of  $V_{OC}$  than those obtained with common liquid electrolytes (Table 2). In general, the low  $V_{OC}$  has been improved by adding 4-*tert*-butylpyridine (TBP) into the electrolyte [19]. However, TBP can introduce problems such as leakage or evaporation of electrolyte as is often found in DSSCs employing volatile liquid electrolytes when the vapour pressure is not negligible at room temperature. To eliminate this volatility, *N*-methyl-benzimidazole (NMBI) has frequently been used in ionic liquid electrolytes because it is in a solid state at room temperature [12,16]. In light of this experience, NMBI was chosen as an additive to improve the  $V_{OC}$ . The composition of MP11 and iodine in the oligomer electrolytes was fixed according to the previously reported conditions, and NMBI of 50 mol% with respect to MP11 was added. The doped electrolytes are now referred as N250, N500, and N1000.

DSSCs using oligomer electrolytes with NMBI were prepared, and their photovoltaic performance was then characterized. As shown in Fig. 5, the addition of NMBI into the oligomer electrolytes results in improvements in both the  $V_{OC}$  and the FF that lead to improved overall energy-conversion efficiency (over 5%) while the  $J_{SC}$  decreased. Of particular note, the  $V_{OC}$  of each of the cells is enhanced significantly by over 60 mV. To confirm this effect of NMBI on  $V_{OC}$ , electron lifetime in the  $\text{TiO}_2$  electrode was measured (Fig. 6). Comparing Figs. 4 and 6, it can be seen that the oligomer electrolytes containing NMBI reflected similar or slightly shorter electron lifetimes than in the case of electrolytes without NMBI. This result is inconsistent with an assessment of photovoltaic per-

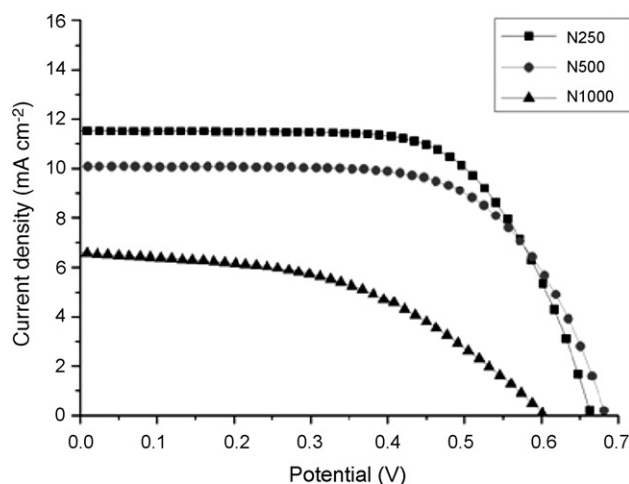


Fig. 5.  $I$ - $V$  curves measured at  $100 \text{ mW cm}^{-2}$  of DSSCs employing oligomer electrolytes with NMBI.

formance, especially as regards the  $V_{OC}$  of the cells, because the longer electron lifetime generally means higher  $V_{OC}$ . Therefore, it is considered that NMBI do not help to enhance electron lifetime, but make the conduction band of the  $\text{TiO}_2$  electrode more negative because it is a basic material and thus can prevent adhesion of small cations such as  $\text{H}^+$  to the  $\text{TiO}_2$  particles, thereby causing a potential reduction of  $\text{TiO}_2$  electrode. This speculation can be indirectly supported in light of the slowdown in the decrease of  $J_{SC}$  due to the addition of NMBI. This slowdown occurs because the conduction band of the  $\text{TiO}_2$  electrode shifts to become more negative, and thus, the amount of electrons transferred from excited sensitizer to the conduction band of the  $\text{TiO}_2$  electrode is reduced. Interestingly,  $J_{SC}$  of the cell employing 1000 electrolytes increased when NMBI was added. A possible reason for this increase is that the addition of NMBI decreases the crystallization temperature of the electrolyte from 20 to 17 °C, so the diffusion coefficients of redox species increase, consequently facilitating the redox reaction in DSSCs.

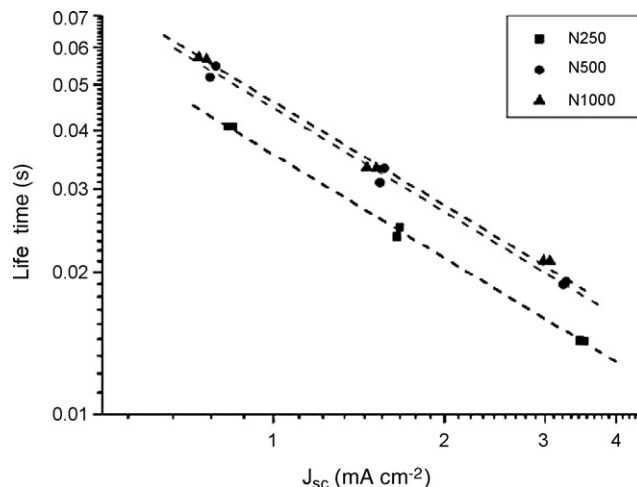


Fig. 6. Electron lifetime in  $\text{TiO}_2$  electrodes of DSSCs employing oligomer electrolytes with NMBI.

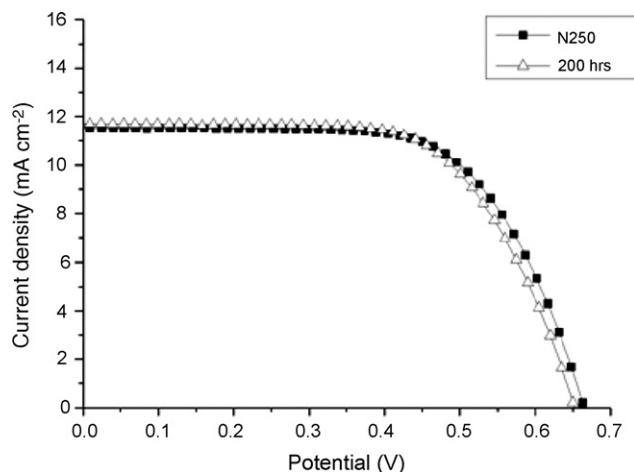


Fig. 7. Variation of photovoltaic performance after storage at 75 °C for 200 h of DSSC employing an oligomer electrolyte (molecular weight of 250) and NMBI.

### 3.5. Thermal stability

The DSSCs employing oligomer electrolytes were stored at high temperature to confirm their thermal stability. Following storage of the cells employing the 250 electrolyte with NMBI, at 75 °C for 200 h, cell performance was measured again. This test confirms that the  $V_{OC}$ ,  $J_{SC}$ , and FF of the DSSCs change very little, and the energy-conversion efficiency of the DSSCs decreases by only 2% (Fig. 7). Moreover, after 300 h, the cell still maintained 91% of its initial efficiency. Therefore, it can be concluded that DSSCs employing oligomer electrolytes have excellent thermal stability.

## 4. Conclusions

It is found that the diffusion coefficients of ions in the oligomer electrolyte are largely influenced by the molecular weight of the oligomer. As a result, not only the redox mechanism in DSSCs and electron lifetime in the  $TiO_2$  electrode,

but also the overall performance of the DSSCs is significantly affected. It is also confirmed that the addition of NMBI to the oligomer electrolyte enhances the  $V_{OC}$ , FF and overall energy-conversion efficiency of the cells. Cells prepared with oligomer electrolytes show excellent thermal stability.

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