



## Enhancement in Performance of Dye-Sensitized Solar Cells Modified with *In Situ* Photopolymerized PDEA in TiO<sub>2</sub> Films

Seoung Hoon Kal,<sup>a</sup> James Joseph,<sup>b</sup> Jiwon Lee,<sup>c</sup> and Kang-Jin Kim<sup>a</sup>

<sup>a</sup>Division of Chemistry and Molecular Engineering, Korea University, Seoul 136-701, Korea

<sup>b</sup>Central Electrochemical Research Institute, Karaikudi 630 006, India

<sup>c</sup>Samsung SDI Company Limited, Gyeonggi-Do 449-577, Korea

Beneficial effects of *in situ* photopolymerized poly[di-(ethylene glycol)-2-ethyl hexyl ether acrylate] (PDEA) in the pores of dye-coated TiO<sub>2</sub> film on the photovoltaic characteristics of dye-sensitized solar cells (DSSCs) are reported. We have found remarkable enhancements of short-circuit photocurrent ( $J_{sc}$ ) by 39% and of open-circuit voltage ( $V_{oc}$ ) by 40 mV for the PDEA-modified DSSC compared with those of a conventional DSSC. This led to an enhancement in the overall solar energy conversion efficiency of 4.9% for the modified cell over 4.0% for a cell without PDEA at 100 mW/cm<sup>2</sup>. Moreover, the PDEA modification has led to improved long-term stability of the DSSC. Analyses of optical absorption and transient photocurrent of the cells suggest that the increased concentration of photo-injected electrons as a result of blocking of trap states in TiO<sub>2</sub> contributes to the enhancement in the  $J_{sc}$  of PDEA-modified DSSCs. The  $V_{oc}$  increase is attributed to an improved screening of the conduction band electrons from I<sub>3</sub><sup>-</sup> ions in the presence of PDEA adhered to TiO<sub>2</sub> particles.  
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DSSCs have emerged as a viable substitute to solid-state silicon solar cells over the past decade.<sup>1-4</sup> DSSCs assume importance primarily due to their low production cost and eco-friendly nature. The mesoporous TiO<sub>2</sub> film is anchored with a monolayer of sensitizing dye molecules. Highly porous structure of the TiO<sub>2</sub> film along with efficient electrolyte penetration in its pores resulted in an impressive solar conversion efficiency of 11% achieved recently in a DSSC with I<sub>3</sub><sup>-</sup>/I<sup>-</sup> electrolyte to which guanidinium thiocyanate was added.<sup>5</sup> The major disadvantages of liquid electrolytes, however, include (i) problems due to instability of sealants with long-term use; (ii) precipitation of salts at low temperatures; and (iii) solvent evaporation at high temperatures.

There have been several attempts to replace the liquid electrolytes with gel-type polymer electrolytes,<sup>6-11</sup> hole transporting materials based on p-type semiconductors such as CuSCN and CuI,<sup>12,13</sup> conducting polymers like PEDOT and polypyrrole<sup>14,15</sup> as hole transport materials, or room temperature ionic melts.<sup>16-18</sup> Polymer electrolyte matrices containing ethylene oxide moieties, poly(epichlorohydrin-co-ethylene oxide) were employed for immobilizing I<sub>3</sub><sup>-</sup>/I<sup>-</sup> in DSSCs by De Paoli *et al.*<sup>8</sup> to investigate electron transfer dynamics recently.<sup>10</sup> Yanagida and co-researchers achieved a solar conversion efficiency of 2.62% under 1 sun using DSSCs modified with *in situ* photopolymerized poly[2-(2-methoxyethoxy) ethyl acrylate].<sup>19</sup> Mao *et al.* have described *in situ* photopolymerization of di(ethylene glycol) ethyl ether acrylate in n-type GaAs(100) photocells that used ferrocene as redox electrolyte.<sup>20</sup> However, in most of the cases, efficiencies of polymer electrolyte cells were limited due to low ionic conductivities of hole conducting ions. While our work was in progress, Komiya *et al.* reported quasi-solid DSSCs using a three-dimensional polymer electrolyte prepared thermally from an oligomer having three polymerizable acrylate groups.<sup>21</sup> Their quasi-solid cells showed higher  $V_{oc}$  and smaller  $J_{sc}$  compared with those of the liquid cells.

In this paper, effect of *in situ* photopolymerized PDEA, which is transparent in the visible spectral region, in the pores of dye-coated TiO<sub>2</sub> on photovoltaic properties of DSSCs was studied. The I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple was flooded in the spongy polymer network, serving as an efficient charge-transporting medium. The superior performance of PDEA-filled DSSCs, in terms of better  $J_{sc}$ ,  $V_{oc}$ , overall solar conversion efficiency ( $\eta$ ), and stability over the corresponding liquid electrolyte cells without PDEA, is reported for the first time.

### Experimental

TiO<sub>2</sub> films were formed on cleaned fluorine-doped tin oxide coated glass (hereafter denoted as FTO) by the doctor blade method using P25 (Degussa) paste, dried at 70°C for 10 min, and annealed

at 450°C for 30 min according to a procedure described elsewhere.<sup>22</sup> The annealed TiO<sub>2</sub> film of about 18  $\mu$ m thickness was coated with Ru(II)L<sub>2</sub>(NCS)<sub>2</sub> (where L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, Solaronix) by immersion in 0.3 mM ethanol solution for 24 h. Chemicals of high purity were obtained from Aldrich unless otherwise specified.

A schematic setup for *in situ* polymerization is shown in Fig. 1. A dye-coated TiO<sub>2</sub> film with a geometric area of 0.25 cm<sup>2</sup> was sandwiched with another glass plate separated by a 25- $\mu$ m-thick spacer. The polymerization mixture, which consisted of di(ethylene glycol) 2-ethylhexyl ether acrylate as monomer, benzoin ethyl ether as initiator (2 wt % of monomer), 0.45 M LiClO<sub>4</sub> as electrolyte, and ethylene carbonate as plasticizer (10 wt % of monomer), was introduced into the space between the dye-coated TiO<sub>2</sub> electrode and the glass plate. Photopolymerization was carried out by illumination from the glass plate side (Oriel 300 W Xe lamp) at a light intensity of 10 mW/cm<sup>2</sup> for 3 min. After polymerization, the assembly was dismantled and the excess polymerization mixture was removed from the TiO<sub>2</sub> electrode (hereafter, PDEA/dye/TiO<sub>2</sub> electrode) by washing with anhydrous ethanol. PDEA in TiO<sub>2</sub> film was characterized with a Bomem, Hartman & Braun MB series FTIR spectrometer and with a Hitachi S-4300 microscope for FE-SEM images and energy dispersive X-ray spectra (EDX).

A DSSC was assembled using a PDEA-dye-TiO<sub>2</sub> electrode and a Pt counter electrode as described elsewhere.<sup>8</sup> The space between the two electrodes was adjusted to 25  $\mu$ m using Surlyn tape. The liquid electrolyte, composed of 0.6 M 1-hexyl-2,3-dimethylimidazolium iodide (C-TRI), 0.1 M lithium iodide, 0.05 M iodine, and 0.5 M 4-*tert*-butyl pyridine in 3-methoxypropionitrile, was injected into the cell through one of the two holes drilled on the counter electrode. The current-voltage characteristics of the cell was monitored using a Keithly M 236 source measure unit and was compared with that of the unmodified cell. An Oriel Xe lamp with an AM 1.5 filter was used for illuminating DSSCs. The optical absorption of TiO<sub>2</sub> electrodes vs. applied voltage was obtained using a three-electrode assembly with a TiO<sub>2</sub> working electrode, a Pt counter electrode, and an Ag/AgCl (0.1 M AgNO<sub>3</sub> in CH<sub>3</sub>CN) reference electrode, in acetonitrile containing 0.5 M LiClO<sub>4</sub> and 0.2 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 5 mV/s.<sup>23</sup> A Hewlett-Packard HP 8453A diode array spectrophotometer coupled with a potentiostat (EG & G model 263A) was used for the absorption measurements.

Photocurrent transients under open-circuit conditions were measured with a homemade chopper attachment, which turned the light on-off at regular intervals. The incident photon-to-electron conversion efficiency (IPCE) was measured using a photon-counting spec-

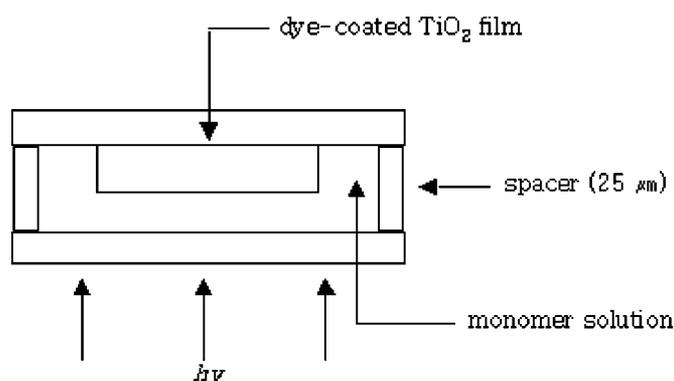


Figure 1. Schematic diagram for *in situ* photopolymerization.

trofluorometer (ISS PC1) equipped with a 350 W Xe lamp light source with a motorized monochromator. Incident light intensity was calibrated using a photodiode detector (Newport 818UV) and optical power meter (Newport 1830-C).

### Results and Discussion

FE-SEM, IR, and EDX characterized the growth of PDEA in TiO<sub>2</sub> film. On dismantling the polymerization cell, the polymer film could be seen visually on the top of the TiO<sub>2</sub> electrode. FE-SEM images in Fig. 2a and b clearly show that uniform spherical particles with an average diameter of 25 nm with a porous structure on the TiO<sub>2</sub> film are covered with the polymer. The cross-sectional FE-SEM images showed that the PDEA film grew up to 2 μm above the TiO<sub>2</sub> film. IR absorption peaks at 1738 and 1119 cm<sup>-1</sup> assigned to C=O and ether functionalities, respectively, were identified along with other stretching and bending modes of C-H bonds and C=C groups of the polymer. An analysis of EDX data measured at the cross section of the PDEA-filled TiO<sub>2</sub> films (a rectangular portion of Fig. 2c, an area of 20 μm width × 10 μm length starting at a height of about 4 μm vertically from the FTO substrate) revealed a large atomic percentage of carbon, 23%, ensuring the formation of PDEA inside the mesoscopic structure of TiO<sub>2</sub>. To avoid confusion in the characterization of the polymer by EDX and IR analyses, we polymerized PDEA in TiO<sub>2</sub> film without dye coating. It was observed, however, that the dye coating after the polymerization in the pores of TiO<sub>2</sub> film was not possible. On a separate polymerization

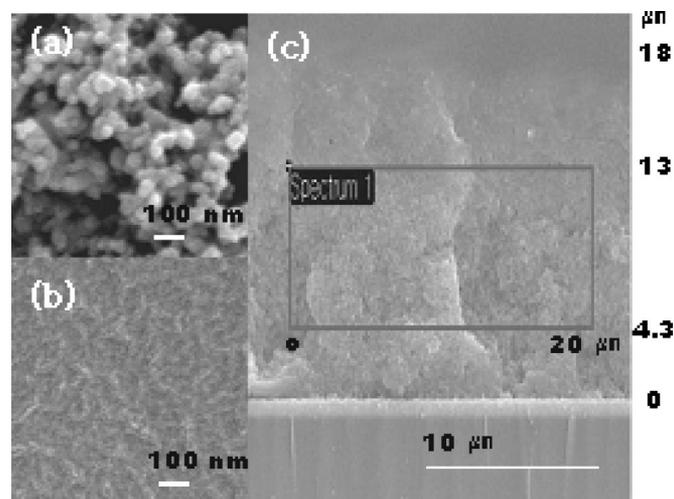


Figure 2. FE-SEM images of TiO<sub>2</sub> films: top views of the film modified (a) without and (b) with PDEA, and (c) cross-sectional view of the PDEA-modified film.

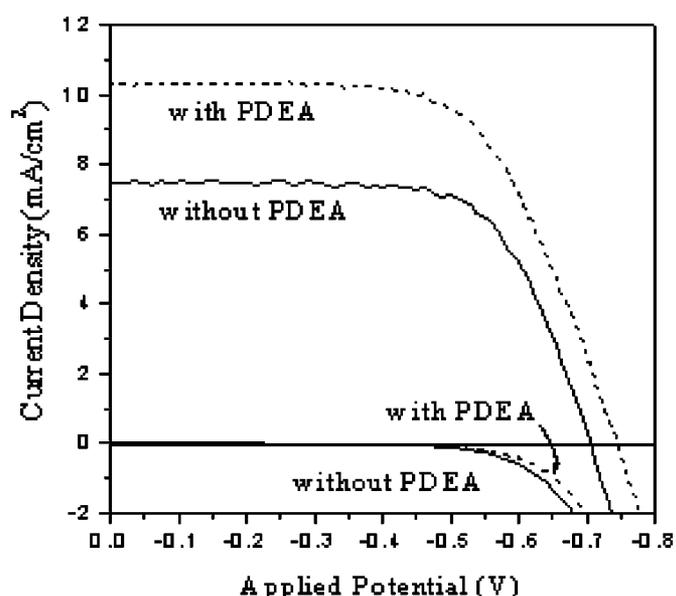


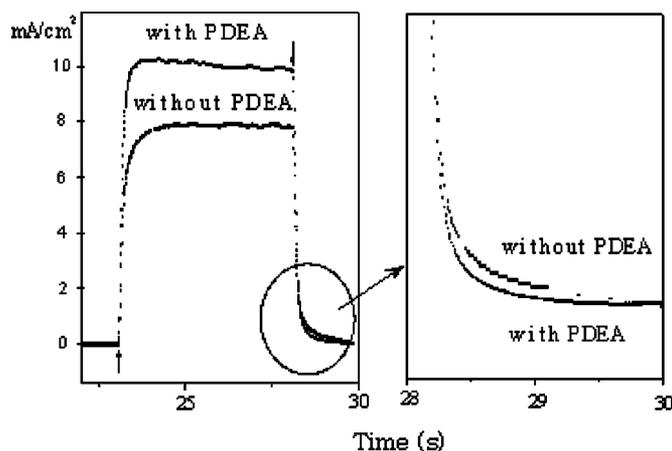
Figure 3. *J-V* curves of DSSCs modified with and without PDEA at 100 mW/cm<sup>2</sup>.

experiment on FTO without TiO<sub>2</sub> film, we have found that PDEA grows directly on the surface of the conducting substrate.

The effect of the modification of dye-coated TiO<sub>2</sub> film with PDEA on *J-V* curves was investigated. It is emphasized that the modification has enhanced both *J*<sub>sc</sub> and *V*<sub>oc</sub> as noted in Fig. 3. The figure shows enhancements in the *J*<sub>sc</sub> of about 39% and the *V*<sub>oc</sub> of 40 mV in the PDEA-modified DSSC compared with a cell without PDEA in the pores of the TiO<sub>2</sub> film. This results in a better conversion efficiency  $\eta$  of 4.9% based on the based on the *J*<sub>sc</sub>, *V*<sub>oc</sub>, and fill factor (FF) of 10.4 mA/cm<sup>2</sup>, 0.75 V, and 0.63, respectively, compared with 4.0% of the latter cell.

The enhancement in the *J*<sub>sc</sub> of the PDEA-modified cell is intriguing because of the expectation that ionic mobility would be relatively low in the PDEA-filled TiO<sub>2</sub> film.<sup>7,8</sup> The low ionic mobility may retard the kinetics of the dye cation reduction by I<sup>-</sup> ions, resulting in a decrease in photocurrent. Furthermore, the variance of *J*<sub>sc</sub> vs. light intensity has shown that *J*<sub>sc</sub> increases linearly with an increase of light intensity up to 100 mW/cm<sup>2</sup> regardless of the PDEA modification. This linearity implies that the light intensity-dependent photocurrent is not limited by diffusion of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> in the spongelike PDEA-filled TiO<sub>2</sub> film. The increase in *J*<sub>sc</sub> with PDEA modification is consistent with the recent report by De Paoli *et al.*<sup>7</sup> They noted that the Lewis base nature of diethylene glycol in a polymer electrolyte would minimize the electron occupancy in the TiO<sub>2</sub> trap states. The decrease in the trap states is supported by transient photocurrent response of DSSCs.

Figure 4 demonstrates that modification with PDEA facilitates the rise and fall of photocurrent, recorded during on-off cycles of illumination at 100 mW/cm<sup>2</sup>. The time required for both the rise and the fall to 90% of the total photocurrent change of the PDEA-modified DSSC is measured to be faster by about 0.15 s than that of the unmodified DSSC. Blocking of the TiO<sub>2</sub> trap states with PDEA is responsible for the faster responses.<sup>21,24,25</sup> The 20% increase in the transient photocurrent observed for the PDEA-modified DSSC over that for unmodified cell is consistent with the *J*<sub>sc</sub> increase in Fig. 3. The blocking may be the result of the adherence of PDEA molecules to TiO<sub>2</sub> particles. The adherence is understood to occur mainly due to the hydrogen bonding interaction between OH groups on the dye-coated TiO<sub>2</sub> surface and oxygen atoms of ethylene oxide

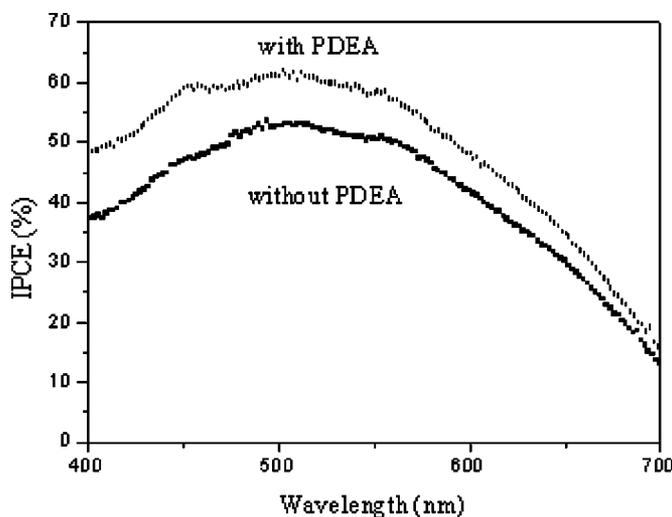


**Figure 4.** Transient  $J_{sc}$  of DSSCs with and without PDEA at  $100 \text{ mW/cm}^2$ . Arrows  $\uparrow$  and  $\downarrow$  indicate when the light was turned on and off, respectively.

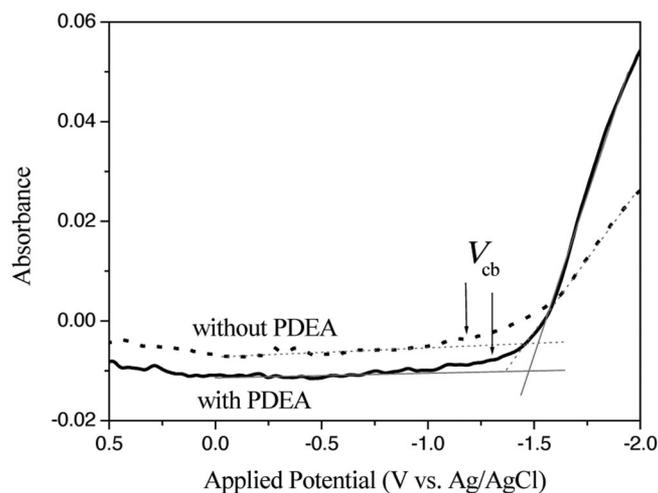
segments in PDEA. PDEA is also adhered by interaction between Ti(IV) ions on the surface and oxygen atoms in PDEA, which results in decreasing the deep trap states.<sup>7,21</sup>

The  $J_{sc}$  improvement in the PDEA-modified cells is supported by IPCE (Fig. 5) and optical absorption spectra of  $\text{TiO}_2$  electrodes vs. electrode potential (Fig. 6) in addition to the transient photocurrent (Fig. 4). The action spectra shown in Fig. 5 demonstrate unflinching increases in IPCE values in the visible region for the PDEA-incorporated DSSC along all wavelengths over those of an unmodified cell. The average increase of the IPCE values below  $550 \text{ nm}$  was found to be about 10% relative to that of unmodified cell. However, the relative increase in the IPCE values above  $550 \text{ nm}$  is much smaller for PDEA-modified electrodes. This is possibly due to the negative shift in the conduction band edge for the PDEA modified  $\text{TiO}_2$  cell. Similar decrement in the red absorption on shifting the conduction band edge negatively was observed by Boschloo *et al.*<sup>26</sup>

Figure 6 shows the absorbance measured at  $800 \text{ nm}$  vs. applied potential, illustrating the electrochromic behavior of the  $\text{TiO}_2$  film in a  $\text{Li}^+$ -containing solution. The higher absorbance below the conduction band potential ( $V_{cb}$ , indicated by an arrow) in the case of the PDEA-filled  $\text{TiO}_2$  electrode (whose graph is displaced slightly downward for clarity compared with that of the unmodified electrode) indicates the higher density of conduction band electrons for



**Figure 5.** Action spectra of DSSCs modified with and without PDEA at  $100 \text{ mW/cm}^2$ .



**Figure 6.** Absorbance at  $800 \text{ nm}$  vs. applied potential for  $\text{TiO}_2$  electrodes modified with and without PDEA in acetonitrile containing  $0.2 \text{ M TBAP}$  and  $0.1 \text{ M LiClO}_4$ . Scan rate was  $5 \text{ mV/s}$ . The arrows indicate the  $V_{cb}$ .

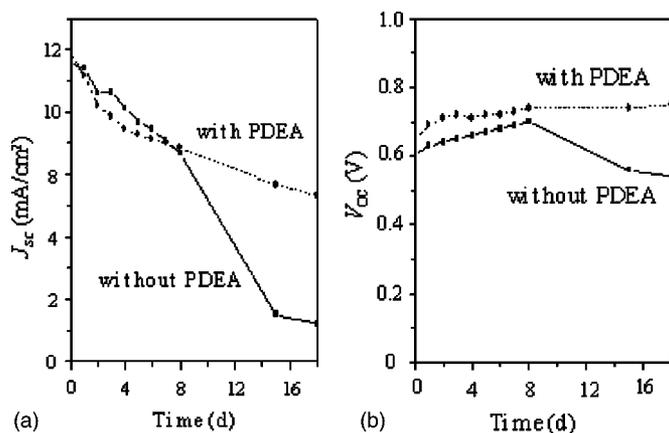
the former cell.<sup>21,24,27</sup> In our experiments we took care to have identical DSSCs except for PDEA filled in the pores of the dye-coated  $\text{TiO}_2$  films.

$V_{oc}$  in DSSCs depends on the concentration of free electrons in the conduction band of  $\text{TiO}_2$  at open circuit. The increase in  $V_{oc}$  for a PDEA-modified DSSC (Fig. 3) is indicative of a lower degree of back electron transfer (Eq. 1),<sup>28,29</sup> compared with an unmodified DSSC



The  $V_{oc}$  increase is manifest in the decrease of dark current shown in Fig. 3. Apparently, PDEA grown directly on the surface of the conducting substrate screens  $\text{I}_3^-$  more effectively from the FTO/ $\text{TiO}_2$  interface and retards back electron transfer from the FTO compared with the case in an unmodified cell.<sup>7,23</sup> The role of the PDEA layer on the FTO is therefore analogous to that of a  $\text{TiO}_2$  buffer layer formed by treatment of FTO with titanium(IV) butoxide in conventional DSSCs.<sup>30</sup> The  $V_{oc}$  increase of the PDEA-modified cell is consistent with the IPCE data in Fig. 5 and the negative shift of the electrochromic graph in Fig. 6. The interaction between the ethylene oxide moieties of PDEA and the  $\text{TiO}_2$  surface is responsible for the shifting of the conduction band edges ( $V_{cb}$ ) of  $\text{TiO}_2$  toward a more negative value compared with an unmodified cell. The negative shift of the electrochromic graph, estimated by the shift of the points where absorption begins to increase, is supported by a small but consistent negative shift of intersection points determined from the tangents of the base line and the rising portion of the graphs, as shown in Fig. 6.

The average FF of 0.63 observed for PDEA-modified cells was found to be lower than that of 0.69 of unmodified DSSCs. However, series resistance of the PDEA-modified cell is considered to remain essentially the same because the slopes of the  $J$ - $V$  curves around the  $V_{oc}$  in Fig. 3 are nearly independent of the PDEA modification.<sup>31</sup> This implies that the decrease of the FF can be ascribed to an increase in the ohmic drop over the series resistance in the PDEA-modified cell owing to the higher photocurrents. Finally, after everyday evaluation of the cells for 18 days at  $100 \text{ mW/cm}^2$ , we observed that the stability of the PDEA-modified cell is improved. It is evident from Fig. 7 that the  $V_{oc}$  of the modified cell remains nearly identical, whereas there is a considerable decrease in its value in the case of the unmodified cell. Decrement of  $J_{sc}$  of the unmodified cell is also much more pronounced compared with that of the



**Figure 7.** Time dependence of (a)  $J_{sc}$  and (b)  $V_{oc}$  of DSSCs modified with and without PDEA.  $J$ - $V$  curves were recorded everyday at  $100 \text{ mW/cm}^2$ .

PDEA-filled cell. The reason for the failure of the unmodified cell is at present not very clear and may be due to the evaporation of electrolyte.

### Conclusion

Photovoltaic properties of DSSCs with *in situ* photopolymerized PDEA in the dye-anchored  $\text{TiO}_2$  films were investigated. FE-SEM, EDX, and IR spectra clearly showed the formation of PDEA in the pores of the dye-coated  $\text{TiO}_2$  films. The PDEA-filled DSSCs exhibited superior  $J_{sc}$ ,  $V_{oc}$ , overall conversion efficiency, and long-term stability compared with the corresponding values of the unmodified DSSCs. The enhanced  $J_{sc}$  is attributed to the increased concentration of photo-injected electrons due to the blocking of surface trap states in  $\text{TiO}_2$  by the interaction between Ti(IV) states on the surface and the Lewis base nature of ethylene oxide segments in PDEA. This interaction can also result in an increase of the barrier for the back electron transfer to  $\text{I}_3^-$  ions, formed at the  $\text{TiO}_2$ /electrolyte interface, leading to the  $V_{oc}$  increase. Further studies are underway toward improvement of the efficiency by reducing  $\text{TiO}_2$  film thickness, in addition to the use of pure ionic liquids.

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