

Origin of high open-circuit voltage in solid state dye-sensitized solar cells employing polymer electrolyte



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ABSTRACT

Herein, the energy level alignment and electron recombination kinetics in solid state dye-sensitized solar cells (DSCs) employing a solid polymer electrolyte (SPE) have been quantitatively characterized. In order to determine the microscopic origin of the enhanced characteristics in polymer electrolytes, we carried out an extensive study of the photovoltaic properties with respect to the electrolyte type and composition, including a liquid electrolyte (LE) and various salt types and concentrations. We observed a smaller downward shift in the conduction band energy of the TiO₂ layer upon contact with the SPE as well as a retarded electron recombination rate. These led to an increase in the V_{oc} for DSCs with an SPE, which is mostly attributable to the coordinative interactions of the ethylene oxide (EO) units in poly(ethylene oxide) (PEO) and poly(ethylene glycol) dimethyl ether (PEGDME) with metallic Li⁺ ions and Ti atoms. Such coordinative interactions induce 1) the capture of Li⁺ cations in the bulk of the polymer electrolyte, thereby reducing their effective concentration and 2) the facile formation of a PEO passivation layer on top of the TiO₂ layer. Therefore, it was concluded that the high V_{oc} in solid state DSCs employing a polymer electrolyte is attributable to the coordinative properties of the EO units in PEO and PEGDME in the SPE.

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1. Introduction

Polymer electrolytes, which are comprised of redox mediators dissolved in a polymeric matrix, are ionically conductive and possess the requisite mechanical properties needed for applications in many electrochemical devices [1–3]. For instance, all solid state dye-sensitized solar cells (DSCs) that employ solid polymer electrolytes (SPEs) have the advantages of prolonged durability and flexible device applications, as compared to liquid or gel-state electrolytes, at the expense of their energy conversion efficiency (up to 9% at 1 sun conditions) [4].

Representative solid polymer electrolytes (SPEs) are based on poly(ethylene oxide) (PEO) and its derivatives [5–13]. The unique

functionality of PEO are primarily attributed to its repeating ethylene oxide (EO) units, which readily interact and coordinate with electron-deficient atoms such as Ti atoms in the TiO₂ layer surface and Li⁺ in the electrolyte. For instance, the interactions between EO units and Ti atoms help form a PEO-adsorbed layer on the TiO₂ surface, which can influence the conduction band shift as well as electron recombination. In addition, the EO units interact with cations, such as Li⁺ in the electrolyte, to capture and reduce the effective concentration in the bulk electrolyte and in the nanopores of the TiO₂ layer. Therefore, it is anticipated that the interactions between EO units and metallic atoms and cations can seriously affect the solar cell performance (particularly the V_{oc}). However, the high performance of all solid state DSCs with PEO/PVdF (poly(vinylidene fluoride))/TiO₂ nanoparticles is claimed to be attributable to the increased ionic conductivity (by about two orders of magnitude) and the effectively reduced recombination rate at the interface between the TiO₂ and SPE. However, the effects of the conduction band shift upon contact with the SPE have yet to be considered [14]. In other words, quantitative analyses to understand the effects of PEO-based SPEs on the photovoltaic performance (including the conduction band shift (CB) and

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electron recombination, which may have a large impact on the V_{oc} due to the physico-chemical properties of the solid polymer electrolyte) have not been seriously attempted.

In this context, we quantitatively investigated the physico-chemical origins of the conduction band (CB) shift and the electron recombination in a dye-sensitized photoelectrode with an SPE based on PEO/poly(ethylene glycol) dimethyl ether (PEGDME), both of which contain EO units. To obtain a more accurate comparison, two representative metallic and organic cations, i.e., lithium (Li^+) and 1-methyl-3-propylimidazolium (MPI^+), are used in both an SPE and a liquid electrolyte (LE). Notably, for the first time, the change in the Fermi voltage V_F was quantitatively evaluated as a function of the salt concentration in the electrolyte. The CB shift of the TiO_2 upon contact with the SPE was characterized by looking at changes in the chemical capacitance, the binding energy, and the work function of the Ti atoms. The chemical capacitance and the recombination resistance were obtained by fitting the experimental data with a diffusion-recombination model [15]. Finally, it was concluded that the advantages of the PEO-based polymer electrolyte were caused by the unique functions of the EO units in both PEO and PEGDME. Such advantageous properties can be applied to further improve the performance of SPE-based solar cells.

2. Experimental

2.1. Electrolyte preparation

The polymer electrolyte was obtained by dissolving XI/I_2 (X is either Li^+ or 1-methyl-3-propylimidazolium, MPI^+) in a blend matrix of high molecular-weight poly(ethylene oxide) (PEO $\bar{M}_w = 10^6$ g/mol) and low-molecular-weight poly(ethylene glycol) dimethyl ether (PEGDME $\bar{M}_w = 500$ g/mol) at a mole ratio of $[-\text{O}-]:[\text{XI}] = 10:1$ and $[\text{XI}]:[\text{I}_2] = 10:1$. The blend ratio of PEO to PEGDME was fixed at 4:6 (w/w). The preparation method followed the procedure described in a previous work [16]. Acetonitrile (AN) was employed as a solvent; this was subsequently dried out completely for more than one day to form the solid polymer electrolyte. In the case of the liquid electrolyte, in order to obtain a more accurate analysis, its composition was maintained to be the same as the SPE. The concentration of the LE is $[\text{XI}]:[\text{I}_2] = 10:1$ (X is Li^+ or MPI^+) and $[\text{XI}] = 2.3$ M in AN. All chemicals were purchased from Sigma Aldrich and used without further treatment.

2.2. DSC fabrication

FTO (fluorine-doped SnO_2)-coated conductive glass (TEC-8, $8 \Omega/\square$, Pilkington) was used as a transparent electrode substrate. The counter electrode was prepared with 0.01 M H_2PtCl_6 in an isopropanol solution and deposited onto the FTO substrate by spin coating. This was sintered at 450°C for 30 min. In the case of the liquid electrolyte, the counter electrode was drilled in order to make small holes for electrolyte injection. The holes were sealed using a small piece of Surlyn and a microscope coverslip. To form the blocking layer on the FTO glass, the substrate was dipped into a diluted TiCl_4 aqueous solution (50 mM) at 70°C for 20 min, rinsed with deionized water and ethanol, and sintered at 450°C for 30 min. After the pre- TiCl_4 treatment, the TiO_2 film was doctor-bladed using TiO_2 paste (CC&C, 18–20 nm) and then heated at 450°C for 30 min. The thickness of the TiO_2 layer was $4 \mu\text{m}$ and the active area was 0.25 cm^2 . The TiO_2 substrate was treated again with the TiCl_4 aqueous solution (50 mM) at 70°C for 20 min and sintered at 450°C for 30 min. The TiO_2 electrodes were subsequently dipped into 0.3 mM N719 dye (cis-bis(isothiocyanato)-bis-(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)-bis-

tetrabutylammonium, Solaronix) in a mixed solvent (1:1 by volume) of acetonitrile (Sigma-Aldrich) and tert-butanol (Sigma Aldrich) for 18 h at 30°C . The samples were then rinsed with acetonitrile and dried under a nitrogen gas flow. Surlyn ($25 \mu\text{m}$, Dupont) was placed onto the working electrode as a spacer material. The prepared photoanode and counter electrodes were sealed together in a sandwich configuration. For the SPE-based DSCs, Surlyn was first placed onto the working electrode as a spacer and then an SPE solution was cast onto the working electrode and dried. Finally, both the working electrode and the counter electrode were clipped tightly together. The cells were stored at room temperature for one day to ensure that the SPE was able to penetrate into the TiO_2 nanopores before measurement.

2.3. Characterization

The current–voltage characteristics of DSCs were measured by a Keithley Model 2400 source meter and a solar simulator with a 300 W xenon arc-lamp (Newport) under 1 sun illumination (AM 1.5, $100 \text{ mW}/\text{cm}^2$). The light intensity was calibrated by a silicon solar cell (PV Measurements, Inc.). A light-shading mask was placed on the residual area of the front side of the FTO substrate, but did not cover the 0.25-cm^2 TiO_2 active area. In addition, the quantum efficiencies of DSCs were analyzed by investigating the incident photon-to-current efficiency (IPCE) (PV Measurements, Inc.). IPCE spectra were measured in the spectral range of 300–800 nm with a resolution of 10 nm. The chemical capacitance and recombination resistance at the TiO_2 interface was characterized by impedance spectroscopy (IS) using Autolab (Metrohm) under illumination conditions. The applied bias potential ranged from 0 to 1 V and the frequency range varied from 1 MHz to 10 mHz with a fixed amplitude of 10 mV. To analyze the PEGDME adsorption on TiO_2 , TiO_2 electrodes (with and without being dipped into PEGDME ($\bar{M}_w = 250$ and 500)) were evaluated by X-ray photoelectron spectroscopy (XPS) and UV-photoelectron spectroscopy (UPS). The XPS data were obtained from a PHI 5400 X-ray photoelectron spectrometer (Perkin-Elmer Physical Electronics) and the UPS data were obtained from an AC-2 instrument (RKI Instruments) at the high resolution (0.01 eV). The repeatability precision of the work function from UPS was 0.015 eV (standard deviation) and the UV intensity energy range was 3.4–6.2 eV. To avoid the error from UV damages, we used the most adjacent as the average value from the five time measurements. To estimate the diffusion length, intensity-modulated photocurrent spectroscopy (IMPS) under short-circuit conditions and intensity-modulated photovoltage spectroscopy (IMVS) under open-circuit conditions were used with an IM6 instrument (Zahner, Germany). A white light-emitting diode (LED, $\lambda_{\text{emiss}} = 603 \text{ nm}$, $\Delta\lambda = 105 \text{ nm}$) was used as the modulated light source to ensure homogeneous illumination of the TiO_2 photoanodes. The applied light intensities ranged from 250 to $7 \text{ W}/\text{m}^2$. To interpret cation capturing, EIS was used (using the same conditions as before) to compare the differences of the conduction band shift. FT-IR spectra were collected by an Avatar-370DTGS FT-IR spectrometer (Thermo Nicolet, USA) in transmission mode with a resolution of $1/\text{cm}$.

3. Results and discussion

Fig. 1a shows the photocurrent density–voltage characteristics of dye-sensitized solar cells (DSCs) employing a solid polymer electrolyte (SPE) as compared to DSCs using a liquid electrolyte (LE). These measurements were taken at 1 sun conditions (AM 1.5 and $100 \text{ mW}/\text{cm}^2$). To minimize variations arising from different TiO_2 thicknesses, the film thickness was fixed at $4 \mu\text{m}$ in this study (for both solid- and liquid-state DSCs). Interestingly, the

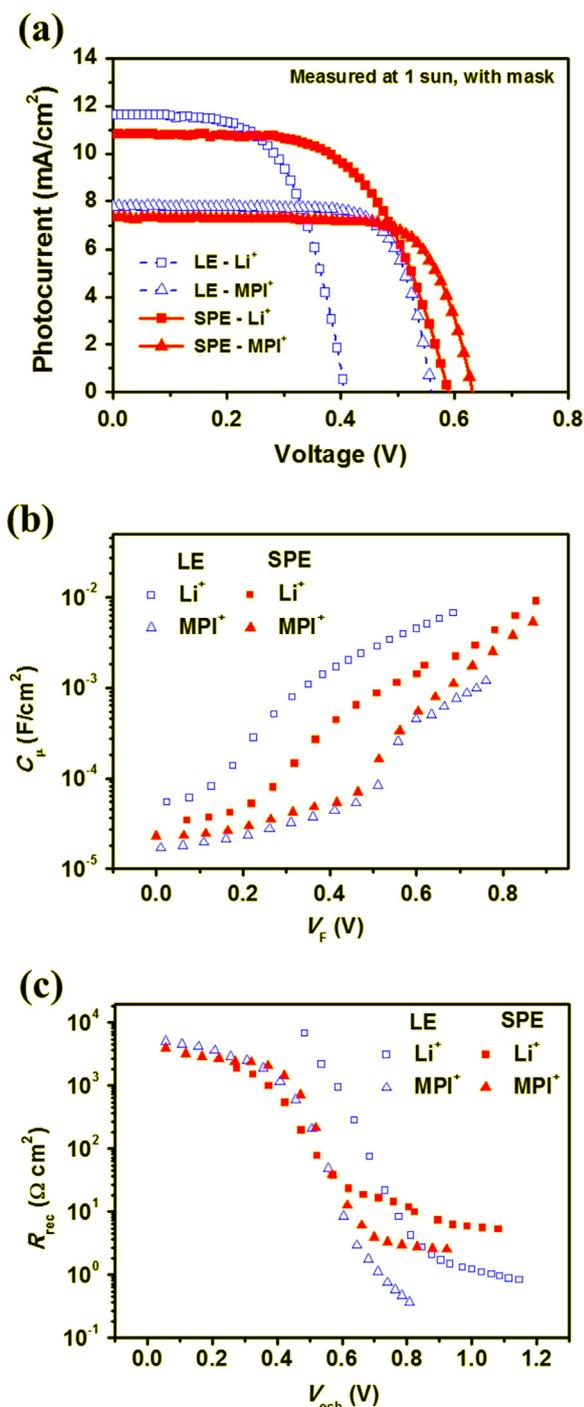


Fig. 1. Photoelectrochemical properties of DSCs with various electrolytes: (a) J - V curves, (b) chemical capacitance (C_{μ}) with respect to the Fermi level voltage (V_F , removing the effects of the series resistance and counter electrode), (c) recombination resistance (R_{rec}) replotted against the equivalent common CB voltage (V_{ecb}). All results are measured at 1 sun conditions (AM 1.5, 100 mW/cm²). The thickness of the photoanode was fixed at 4 μ m.

solid state DSC employing a polymer electrolyte shows a higher power conversion efficiency (PCE) than the device with the LE, regardless of the cation that was used (both metallic Li⁺ and organic 2-methyl-5-propyl imidazolium MPI⁺). The major photo-voltaic parameters are listed in Table S1 (Supporting Information). The higher PCEs obtained with SPEs are mostly attributable to the increase in the open-circuit voltage (V_{oc}) in combination with the nearly unchanged fill factor (FF) and the small decrease in the short-circuit photocurrent density (J_{sc}). It is also noteworthy that

the difference in the V_{oc} between SPEs using Li⁺ and MPI⁺ (0.05 V) is much smaller than the difference obtained with the LE (0.14 V).

The change in the V_{oc} is mostly dependent on the change in the Fermi level of the TiO₂ layer because the Fermi energy of an electrolyte that contains redox couples is nearly fixed, even during light illumination. The pseudo-Fermi level of the TiO₂ layer is, in turn, determined mostly by the TiO₂ conduction band (CB) shift upon its contact with an electrolyte, the photocurrent generation rate, and the interfacial electron recombination kinetics [17,18]. A high V_{oc} will be interpreted in terms of the TiO₂ CB shift (upon its contact with an electrolyte), and the interfacial electron recombination kinetics will be determined via impedance spectroscopy (IS) [15,19,20]. Data analysis with an equivalent diffusion-recombination circuit model gives the chemical capacitance (C_{μ}) and the recombination resistance (R_{rec}) [15].

Fig. 1b shows the chemical capacitance C_{μ} depending on the corrected Fermi voltage (V_F), where $V_F = V_{app} - V_s - V_{ce}$. Here, V_{app} is the applied potential for IS and V_s and V_{ce} are the potential drops due to the series resistance and the counter electrode, respectively [21]. In the case of Li⁺, V_F increased significantly for the SPE (as compared to the LE), whereas it was slightly decreased or nearly unchanged in the case of MPI⁺. This suggests that the conduction band shift in the SPE influences the increase in the V_{oc} to a large extent in the case of Li⁺, but has only a marginal effect with MPI⁺. Fig. 1c depicts the change in R_{rec} as a function of the equivalent conduction band potential V_{ecb} ($V_{ecb} = V_F - \Delta E_c/q$, where ΔE_c is the shift in the conduction band with respect to the reference $E_{c,ref}$; $\Delta E_c = E_c - E_{c,ref}$) [21]. In the relevant large-voltage domain, the recombination resistance R_{rec} is much larger in the SPE than it is in the LE at large V_{ecb} values (near the V_{oc}), regardless of the cation that is used. This result matches well with the electron lifetime results, which showed that the lifetime was more than twice as long with the PEGDME-adsorbed photoanode, as compared to the bare TiO₂ photoanode (Fig. S1a in the Supporting Information). Consequently, the electron diffusion length was also longer with the SPE (Fig. S1b in the Supporting Information). Therefore, we suggest that the large increase in the V_{oc} (~ 0.17 V) for the SPE with Li⁺ is caused by both the conduction band shift and the large R_{rec} , whereas the small increase (~ 0.07 V) with MPI⁺ is mostly attributable to the increase in R_{rec} .

3.1. Quantitative analyses of the CB shift

The effects of the cation concentration on the CB shift are quantitatively analyzed in greater detail by measuring the V_F changes (ΔV_F) in the TiO₂ layer as a function of the salt concentration for DSCs employing a polymer electrolyte. V_F can be directly evaluated from its relationship with C_{μ} , which can provide quantitative information about the position of the CB [21–23]:

$$C_{\mu} = C_a \exp[\alpha(E_c - E_{F,redox})/k_B T] \exp(-\alpha q V_F / k_B T) \quad (1)$$

Here, $C_a = L(1-p)q^2 N_t / k_B T$ with L , p , and N_t , being the thickness, the porosity, and the number of trap states of the TiO₂, respectively. q is the elementary charge, k_B is the Boltzmann constant, and T is the absolute temperature. α is a parameter related to the electron trap distribution below the CB. E_c and $E_{F,redox}$ are referred to as the CB level of TiO₂ and the electrolyte Fermi level, respectively. If $E_{F,redox}$ of the electrolyte remains unchanged at the same chemical capacitance C_{μ} in TiO₂, then Eq. (1) can be reduced to:

$$\Delta E_c = q \Delta V_F \quad (2)$$

Eq. (2) suggests that the effects of the salt concentration in the bulk, in terms of the extent of the CB shift ΔE_c of TiO₂, can be deduced by measuring ΔV_F .

Fig. 2 shows ΔV_F , which represents the extent of the downward shift of the CB of the TiO_2 layer with respect to the reference concentration (1.1 M), as a function of the molar concentration of the salt (LiI and MPII) in the electrolyte. The original C_μ vs V_F data, which were obtained by varying the salt concentration, are shown in Fig. S2 and Table S2 (Supporting Information). Fig. 2 demonstrates that the SPE shows a smaller ΔV_F and a smaller downward shift in the TiO_2 CB than the LE, regardless of the cation that is used or its concentration; this results in a larger V_{oc} . Interestingly, the extent of the absolute value of $\langle \Delta V_F \rangle$ increases nearly linearly with the salt concentration, with the exception of SPE-Li⁺. The linear increase in $\langle \Delta V_F \rangle$ with the salt concentration indicates that the concentration of the cation adsorbed on the TiO_2 layer may also increase with increasing salt concentration in the bulk. In the case of SPE-Li⁺, however, the increasing slope becomes steeper between 2.2 M and 3.3 M, which presumably results in the larger downward shift of the CB. These results can be explained by the saturation of the cation-capturing ability of the

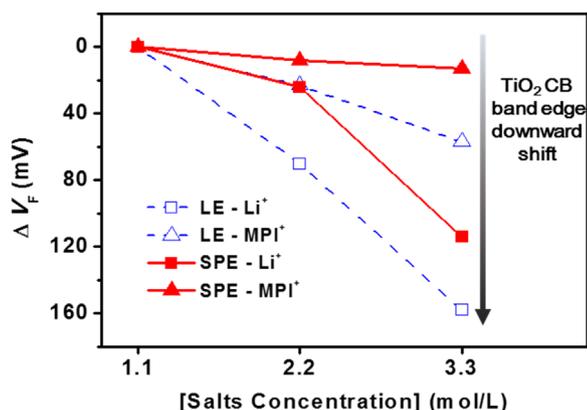


Fig. 2. V_F changes (ΔV_F) of DSCs as a function of the salt concentration in the electrolyte. ΔV_F is calculated from the C_μ versus V_F curve at the same C_μ .

EO units in PEO and PEGDME at 2.2 M.

The effects of the type of cation on the E_c shift can also be deduced from Fig. 2. The steeper change in the downward shift of E_c with Li⁺, as compared to the shift with MPI⁺, in both the LE and SPE seems to be attributable to the fact that 1) Li⁺ is more effective at adsorbing on the TiO_2 layer than MPI⁺ (due to cation effects) [24] and 2) the interactions of Li⁺ with the solvent (LE or SPE) are stronger than those with MPI⁺; this will be described in the next section.

Following the above results, it is confirmed that the SPE shifts the TiO_2 CB downward less significantly (i.e., a smaller ΔV_F), which reduces the recombination rate relative to the LE. These characteristics may arise from the ethylene oxide (EO) groups in PEO and PEGDME; in particular, they have the special ability to coordinate with both of the cations (Li⁺ and MPI⁺) in the electrolyte as well as with metallic Ti atoms at the TiO_2 surface.

3.2. Cation capturing

It is known that the TiO_2 CB shift is strongly influenced by the types of solvent, ion, and dye that are used [28]. In particular, the type and amount of the cation that is adsorbed on the TiO_2 layer play an important role in determining the TiO_2 CB shift, which is dictated by the free ion concentration in both the bulk electrolyte and in the nanopores of the TiO_2 layer. When the SPE contains EO units, the EO units may coordinately interact with cations in the SPE (such as Li⁺ and MPI⁺) and capture them to reduce the effective cationic concentration. In other words, the effective concentration in both the bulk and nanopore phases may be reduced when EO groups capture cations. This, in turn, lowers the cationic concentration that is adsorbed on the TiO_2 layer, which influences the degree of the CB shift ΔE_c in comparison with the LE (Fig. 2). The effects of cation capturing on ΔE_c in both the LE and SPE are comparatively and schematically illustrated in Fig. 3. The cations in the LE are readily adsorbed on the TiO_2 layer without a large hindrance, resulting in a large downward shift of E_c , as shown in

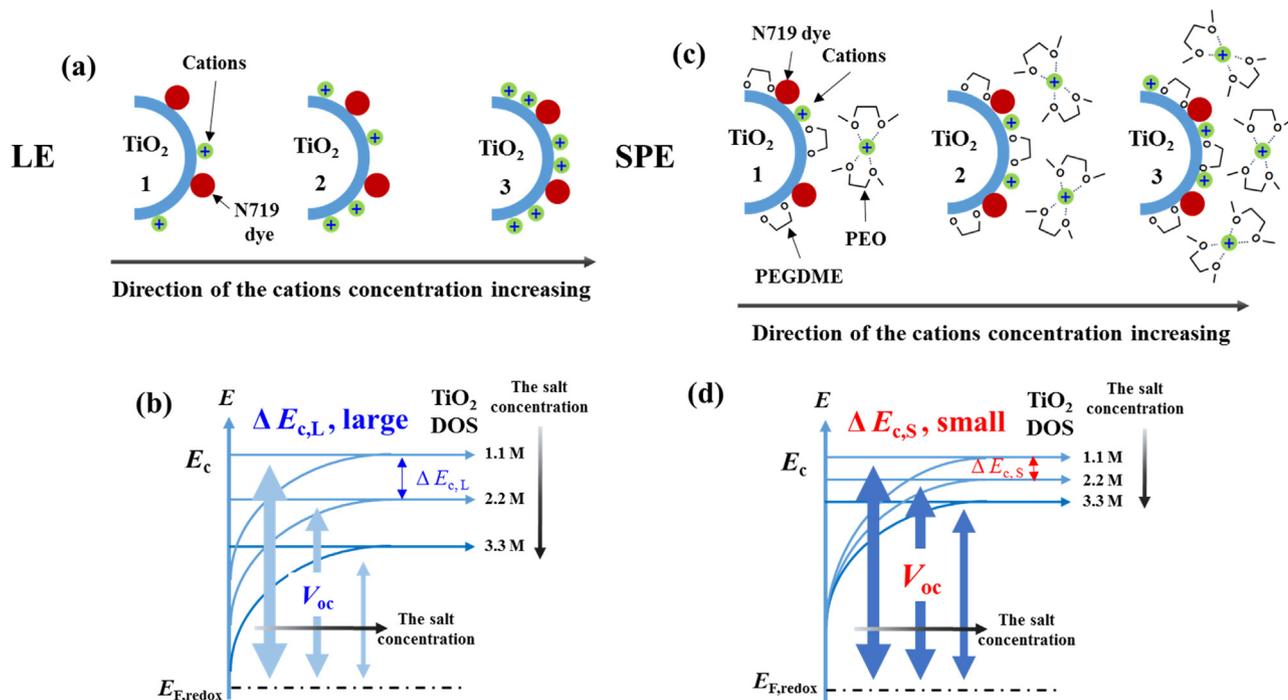


Fig. 3. Schematic illustrations of the TiO_2 /electrolyte interface. (a) Cations can be readily adsorbed on the TiO_2 layer in the LE. The number of adsorbed cations on TiO_2 is proportional to the cation concentration in the bulk, up until saturation. (c) Only a portion of the cations may be adsorbed in the SPE. Some cations in the bulk electrolyte may be captured by the EO units of PEO. The comprehensive energetic schemes of the density of states (DOS) in TiO_2 for different molar concentrations of salt in the (b) LE and (d) SPE.

Fig. 3a. Alternatively, in the case of the SPE (Fig. 3c), all of the cations may not freely adsorb onto the TiO₂ layer because some cations in the bulk polymer electrolyte are captured by the EO units of the PEO or PEGDME chains. Therefore, the absolute quantities of the cations that are adsorbed on the TiO₂ layer with the SPE are smaller compared to the LE. This results in the smaller downward shift of the CB and the increase in the V_{oc} .

The strength of the cation capturing by the EO units between two cations (i.e., Li⁺ and MPI⁺) has been demonstrated by FT-IR (Fig. S3 in the Supporting Information). The band corresponding to the C–O–C stretching vibration near 1098/cm shifts depending on the degree of the interaction between the oxygen atoms and the cation. As expected, the extent of this band shift is larger for Li⁺ (1098–1086/cm) than it is for MPI⁺ (1098–1089/cm), indicating the stronger interactions with Li⁺ (a smaller ion with a higher charge density). In other words, the stronger interactions of Li⁺ with the EO units in the SPE cause smaller concentrations of Li⁺ to be adsorbed on the TiO₂ surface. Alternatively, the weaker interaction of MPI⁺ has a much smaller effect on the adsorbed concentration change between the LE and SPE. Conclusively, the cation-capturing abilities of the EO units of the SPE induce a decrease in the cationic concentration that is adsorbed on the TiO₂ layer, resulting in smaller ΔE_c and ΔV_F (Fig. 2).

3.3. Surface adsorption

Both PEO and PEGDME contain ethylene oxide (EO) units that may be adsorbed on the TiO₂ surface via their specific interactions with Ti atoms. The adsorption of PEO on various oxide surfaces has already been demonstrated and can be explained by an acid-base reaction between the EO group (a Lewis base) and strong Brønsted acid sites on the oxide surface [25].

The adsorption of PEO and PEGDME on the TiO₂ mesoporous layer was examined by XPS and UPS. Fig. 4a shows the comparison between the Ti2p XPS spectra for an untreated TiO₂ film (as a reference) and PEGDME-treated films with various average molecular weights of PEGDMEs ($M_w=250$ and 500; PEGDME 250 and PEGDME 500). The binding energy of Ti2p for the PEGDME-treated electrode (457.9 eV) was smaller than it was for the untreated surface film (458.5 eV), suggesting that electron-donating interactions from the unpaired electrons of oxygens in the EO units to electron deficient sites on the TiO₂ surface may occur upon the adsorption of PEGDME [26].

In order to investigate the effects of the electron-donative

adsorption of PEGDME or PEO on the TiO₂ CB band energy shift in greater detail, the work functions were measured with UPS. These results are depicted in Fig. 4b. The change in the work function of a semiconductor, defined as the minimum energy needed to move an electron from its Fermi energy level (E_F) into the vacuum energy level (E_{vac}), represents the CB shift of the semiconductor [27]. Fig. 4b shows the energy levels of two different electrodes: N719 dye-attached TiO₂ electrodes on FTO untreated (neat) and the same electrode configuration treated with PEGDME (PEGDME 500). The work function values for the neat and PEGDME 500 electrodes are -5.28 and -5.18 eV vs E_{vac} , respectively. The smaller work function of PEGDME 500 indicates that oxygen atoms in PEGDME, which possess Lewis base properties, donate electrons to the TiO₂ surface by the surface adsorption of PEGDME. It also demonstrates the negative CB shift of the TiO₂ layer upon the surface adsorption of PEGDME.

In addition, the interactions of the EO units in PEO and/or PEGDME with Ti atoms in the TiO₂ layer help the PEO and PEGDME cover and/or passivate the TiO₂ surface. The surface passivation layer formed on the TiO₂ surface can also reduce the cationic concentration that is adsorbed. These comprehensive energetic schemes, as a function of the molar concentration of the cation in the LE and SPE, are shown in Fig. 3b and d, respectively. These schemes indicate that the degree of the downward shift of the TiO₂ CB in SPEs ($\Delta E_{c,S}$) may be smaller than the shift in LEs ($\Delta E_{c,L}$) as the cation concentration increases. This also contributes to the increase in the V_{oc} for solid state DSCs that employ an SPE.

4. Conclusions

The smaller downward shift of the TiO₂ conduction band (CB) energy upon contact with a solid polymer electrolyte (SPE) in DSCs, as well as the reduced electron recombination, which results in a higher V_{oc} (as compared with a liquid electrolyte (LE)), are mostly attributable to the abilities of cation capturing and to the TiO₂ surface adsorption of ethylene oxide (EO) groups in PEO-based SPEs; this occurs via coordinative interactions with metallic Li⁺ cations and Ti atoms. Notably, the CB shift was quantitatively evaluated by measuring ΔV_F with various concentrations of salt; to the best of our knowledge, this is the first time that this has been done. PEO chains containing EO units can capture cations in the electrolyte, such as Li⁺ or MPI⁺, to reduce their effective concentration, resulting in a lower concentration of cations

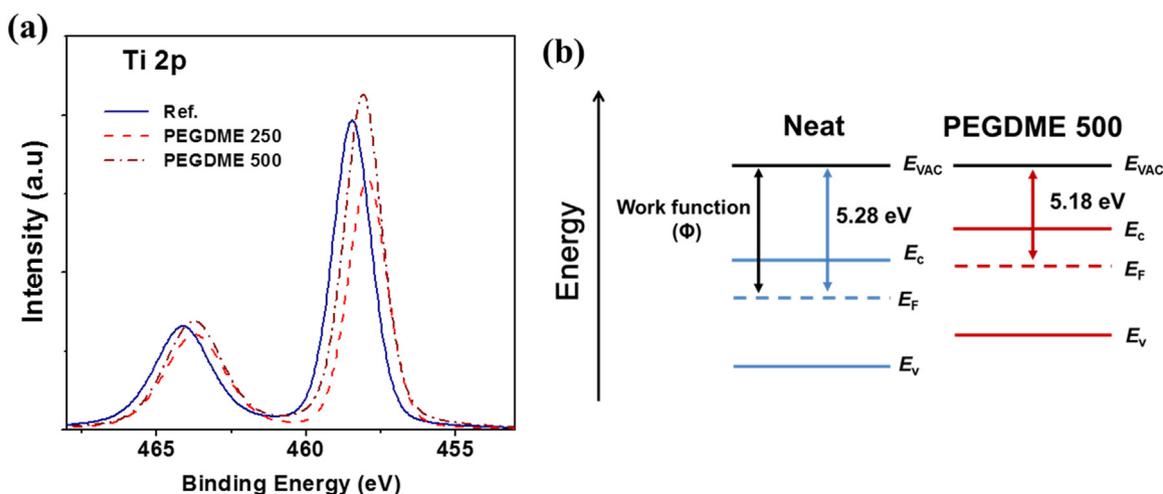


Fig. 4. (a) XPS for Ti 2p binding energy of the untreated TiO₂ film (Ref.) and the spin-coated films with two PEGDME polymers with different average molecular weights (250 and 500). (b) Work functions of Ti atoms in the TiO₂ layer with N719 dyes attached (neat) and with the additional PEGDME 500 treatment; measured by UPS (E_{VAC} : vacuum energy, E_C : conduction band, E_F : Fermi energy, E_V : valence band, and Φ : work function).

adsorbed on the TiO₂ layer and reduced electron recombination. In addition, EO groups that are coordinatively adsorbed on the surface of the TiO₂ layer induce a smaller downward shift in the CB and act as a barrier to reduce the electron recombination rate. These advantages of SPEs can be successfully utilized to further improve the performance of solid state electrochemical devices that have fast recombination and/or low V_{oc} (e.g., quantum dot-sensitized solar cells).

Notes

The authors have no competing financial interests to declare.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2016.09.006>.

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