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2009 Chinese Phys. Lett. 26 128201

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Effect of Poly(Ether Urethane) Introduction on the Performance of Polymer Electrolyte for All-Solid-State Dye-Sensitized Solar Cells *

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(Received 21 May 2009)

The introduction of poly(ether urethane) (PEUR) into polymer electrolyte based on poly(ethylene oxide), LiI and I₂, has significantly increased the ionic conductivity by nearly two orders of magnitudes. An increment of I₃⁻ diffusion coefficient is also observed. All-solid-state dye-sensitized solar cells are constructed using the polymer electrolytes. It was found that PEUR incorporation has a beneficial effect on the enhancement of open circuit voltage V_{OC} by shifting the band edge of TiO₂ to a negative value. Scanning electron microscope images indicate the perfect interfacial contact between the TiO₂ electrode and the blend electrolyte.

PACS: 82.80.Fk, 84.60.Dn, 83.80.Es

Since the pioneering work reported by Gratzel, dye-sensitized solar cell (DSSC) has attracted much attention for its high efficiency and low cost.^[1] Up to date, the conversion efficiency of DSSC has reached 10–11%.^[2] However, these liquid electrolyte-based devices require perfect sealing which retards the commercial application. To solve this problem, solid polymer electrolyte, with many desirable properties, such as easy fabrication in a wide variety of shapes and great safety, has been widely exploited in the development of all-solid-state DSSC. However, DSSC assembled with polymer electrolytes exist much lower conversion efficiencies than those of liquid electrolytes. Several attempts, such as the introduction of inorganic nanofiller,^[3–7] plasticizer,^[8,9] blend polymer^[5,10–11] etc., were performed to improve the ionic conductivity and diffusion of free charge carriers in polymer electrolytes. Among them, polymer blend is an effective approach to obtain electrolyte with high performance by adjusting polymer composition.

In the present work, a sort of poly (ether urethane) (PEUR) prepolymer was introduced into poly (ethylene oxide) (PEO) polymer electrolytes, considering its functions of inhibiting PEO crystallization and promoting electrolyte penetration. In particular, the urethane bond (containing nitrogen atom), which is abundantly present in PEUR, could adsorbed on the surface of TiO₂ electrode, thus could be expected to improve the photovoltage of DSSC. In our previous work, cells assembled with PEUR/PEO blend electrolyte have achieved good performance.^[12] Here we detailedly investigate the effect of PEUR addition on the ionic conductivity; ionic diffusion and crystalline properties of PEO based polymer electrolytes. The

role of PEUR on DSSC performance is also studied.

PEO with a molecular weight (MW) of 4×10^6 g·mol⁻¹ from Aldrich was used. PEUR prepolymer was obtained as follows: firstly, polyethylene glycol (MW = 400) reacted with an excess 2,4-Diisocyanatotoluene for several hours, then the mixture was poured into excess ethanol and kept stirring overnight. After removing the excess ethanol, the mixture was dried under vacuum to obtain the PEUR. In the present investigation, the reaction time was set as 1 h and 2 h to obtain PEUR with different molecular weights of 7100 and 3000, which are donated as PEUR-A and PEUR-B, respectively. Polymers and salts were dissolved in acetonitrile and then the solvent was removed to obtain solid-state electrolytes. The content of lithium iodide (LiI) and iodine (I₂) are kept at 30 wt% and the weight ratio of PEUR and PEO is 5 : 5 for blend electrolyte. Preparation of TiO₂ electrode and measurements were carried out according to our previous report.^[13] Mott-Schottky measurement was performed on solartron 1287 electrochemical interface and solartron 1255B frequency response analyzer, using the three electrodes system, the TiO₂ electrode as working electrode, Pt coil as counter electrode and saturated calomel electrode (SCE) as reference electrode. X-ray diffraction (XRD) patterns of the electrolyte samples were recorded at 40 kV on a Rigaku D/max 2500 using Cu K α irradiation.

Figure 1 represents the cross-sectional field emission scanning electron microscope (FE-SEM) images of various TiO₂ electrodes: blank (a,b), deposited with PEO electrolyte (c,d) and PEUR/PEO blend electrolyte (e,f). Herein, TiO₂ nanocrystalline films with inverse opal structures are employed for easy

*Supported by the High-Tech Research and Development Program of China under Grant No 2007AA05Z439, the National Basic Research Program of China under Grant No 2006CB202605, and the National Natural Science Foundation of China under Grant No 20873162.

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penetration and light scattering. Before introducing polymer electrolyte, TiO₂ nanoparticles and pores are distinguishable (Figs. 1(a) and 1(b)). These pores still exist in the PEO electrolyte deposited sample (Figs. 1(c) and 1(d)), indicating the incomplete filling of PEO electrolyte into TiO₂ electrode. However, TiO₂ nanoparticles are indistinct and pores completely disappeared after the introduction of PEUR/PEO electrolyte (Figs. 1(e) and 1(f)), which illustrate the good penetrating of PEUR/PEO blend electrolyte into TiO₂ electrode. This is a precondition of good interfacial contact, corroborating the high performance of all-solid-state dye-sensitized solar cells.

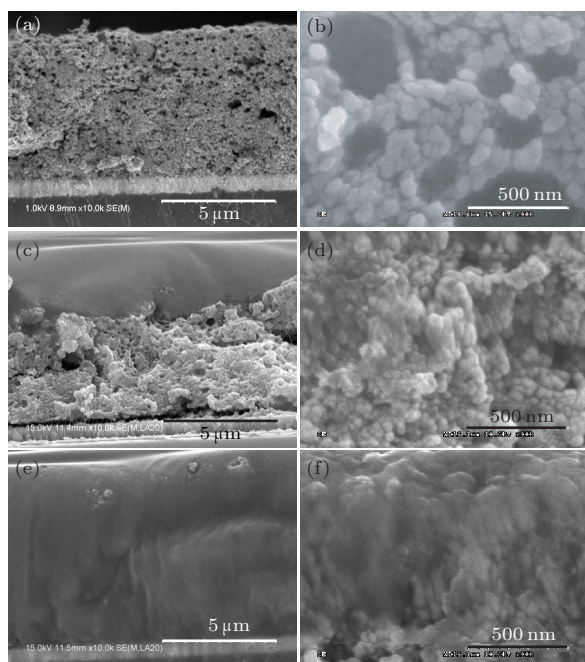


Fig. 1. Cross-sectional FE-SEM images of various TiO₂ electrodes: blank (a,b), deposited with PEO electrolyte (c,d) and PEUR/PEO blend electrolyte (e,f).

XRD analysis was carried out to confirm the effect of PEUR on PEO crystallization. Figure 2 demonstrates the XRD patterns of different electrolyte compositions: LiI (a), PEO (b), PEO/PEUR ($w : w = 5 : 5$, without LiI/I₂) (c) and PEO/PEUR blend electrolyte (d). The XRD pattern of LiI shows intense diffraction peaks at $= 21.1^\circ, 25.5^\circ, 29.6^\circ, 41.9^\circ, 50.2^\circ, 53.5^\circ, 67.7^\circ$ and 69.7° , indicating the crystallization of lithium iodide. The characteristic diffraction peaks of crystalline PEO are apparent in the range $2\theta = 15^\circ - 30^\circ$. The intensities of these diffraction peaks are markedly decreased in the diffraction pattern of PEO-PEUR sample, which indicates

that the crystallization of PEO has been disturbed by the incorporation of PEUR prepolymer. After adding LiI and I₂ into PEO-PUER matrix, nearly all diffraction peaks ascribed to PEO and LiI have disappeared in sample *d*, illustrating the complete dissolution of lithium salts in polymer matrix and the amorphous nature of such prepared blend electrolyte.

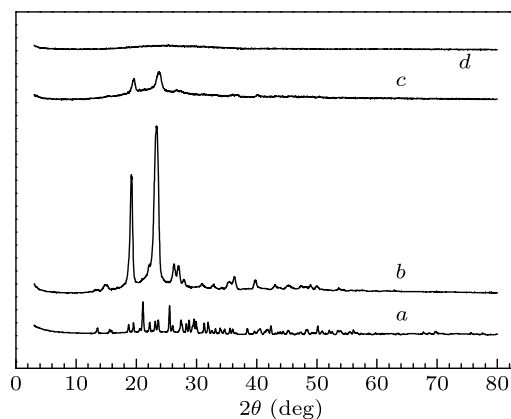


Fig. 2. XRD patterns of different electrolyte compositions: LiI (a), PEO (b), PEO-PEUR ($w : w = 5 : 5$, without LiI/I₂) (c) and PEO/PEUR blend electrolyte (d).

Table 1 summarizes the electrical and photoelectrochemical characteristics of pure PEO polymer electrolyte and PEUR-A/PEO blend electrolyte. As can be seen from this table, after PEUR incorporation, apparent enhancement in open circuit voltage V_{OC} was observed. We consider that the improved V_{OC} might be due to the negative movement of TiO₂ flatband potential. The urethane bond in the PEUR may prone to be adsorbed on the surface of TiO₂ electrode, thus can significantly affect the TiO₂ flatband potential, which will induce the enhancement of photovoltage. In addition, the short circuit current density J_{SC} and fill factors (FF) also yield considerable improvements after adding PEUR. These increases can be explained by the improvements of ionic conductivity σ and I_3^- diffusion coefficient ($D_{app}(I_3^-)$) of the polymer electrolytes. The ionic conductivity of PEUR/PEO blend electrolyte is $1.04 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is nearly two magnitudes higher than that of pure PEO based electrolyte with $8.64 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$. Also, the increase of I_3^- diffusion coefficient is apparent which favors the regeneration of excited dye, corroborating the increase of J_{SC} value. We consider the inhibition of PEO crystallization by PEUR (which was confirmed in Fig. 2) is the reason for the improved ionic conductivity and ionic diffusion.

Table 1. Electrical and photoelectrochemical characteristics of pure PEO polymer electrolyte and PEUR-A/PEO blend electrolyte.

Electrolyte	J_{SC} ($\text{mA}\cdot\text{cm}^{-2}$)	V_{OC} (mV)	FF	η (%)	$D_{app}(I_3^-)$ ($10^{-7} \text{ cm}^2\cdot\text{s}^{-1}$)	σ ($\text{S}\cdot\text{cm}^{-1}$)
Pure PEO	4.01	601	0.53	1.27	0.337	8.64×10^{-6}
PUER-A/PEO	6.53	686	0.64	2.88	1.41	1.04×10^{-4}

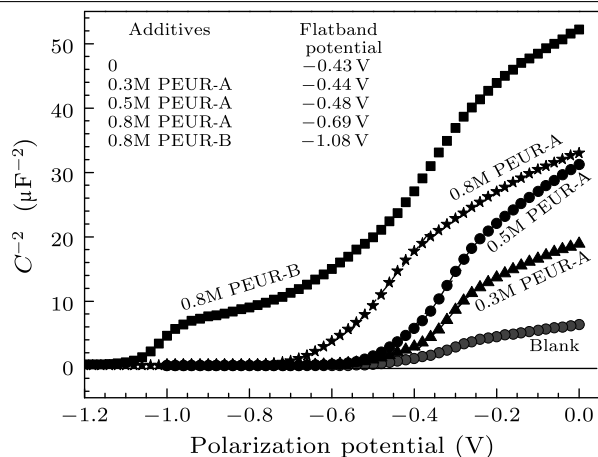


Fig. 3. Mott-Schottky plots of TiO_2 electrodes in various electrolytes containing PEUR with different MW and concentrations.

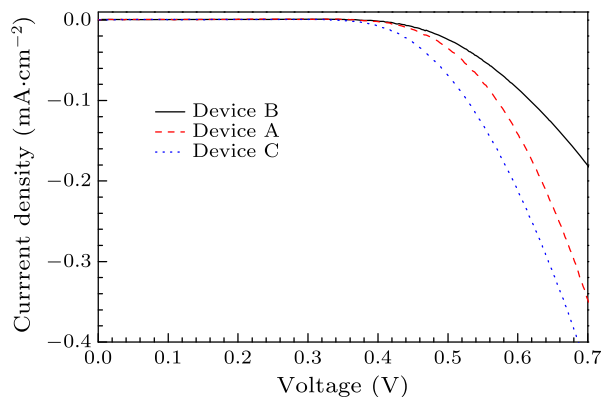


Fig. 4. Dark current characteristics of devices employing PEUR-A/PEO (device A), PEUR-B/PEO (device B) and pure PEO (device C) polymer electrolytes.

To confirm the negative movement of band-edge potential after PEUR incorporation, the Mott-Schottky measurement is employed.^[14] The supporting electrolyte is 0.5 M KI/0.05 M I_2 dissolved in ethylene carbonate/propylene carbonate (EC/PC) ($v : v = 4 : 1$) (pH = 7) with PEUR of various concentrations. For comparison, PEUR-B is also used. Figure 3 demonstrates the Mott-Schottky plots of TiO_2 electrodes in various electrolytes containing PEUR with different MW and concentrations. Flatband potential V_{fb} , essentially the conduction band edge E_{cb} , are summarized. The V_{fb} values of the TiO_2 electrodes largely depend on the concentration of PEUR. At low PEUR-A concentration, TiO_2 electrode reveals little change on its Fermi level. However, as the concentration increases, obvious shifts can be observed. After adding 0.8 M PEUR-A in the electrolyte solution, the V_{fb} value shifts from -0.43 V to -0.69 V versus SCE. PEUR molecular weight also has crucial in-

fluence on V_{fb} of the electrode. As the MW of PEUR decreases from 7100 to 3000, V_{fb} of the TiO_2 electrode reveals a corresponding movement from -0.69 V to -1.08 V versus SCE. This result can be ascribed to the smaller coil size of PEUR-B, which can be adsorbed on the surface of TiO_2 more easily.

Dark current measurements are performed to study the charge recombination of devices employing PEUR-A/PEO (device A), PEUR-B/PEO (device B) and pure PEO (device C) polymer electrolytes (Fig. 4). Obviously, the onset of the dark current of device C was shifted to a negative value after the addition of PEUR, implying the constraint of charge recombination by the adsorption of PEUR on the surface of TiO_2 electrode. Moreover, corresponding to the Mott-Schottky results aforementioned in Fig. 3, device B also reveals a small charge recombination with a smaller dark current than device A.

In conclusion, a high-performance DSSC has been prepared by using PEUR/PEO polymer blend electrolyte, yielding a considerable conversion efficiency $\eta = 2.88\%$ under $100 \text{ mW}\cdot\text{cm}^{-2}$ illumination. The beneficial effect of PEUR on V_{OC} is observed, induced by the negative shift of the band edge of the TiO_2 electrode. The introduction of PEUR has also significantly increased the ionic conductivity and I_3^- diffusion of PEO based polymer electrolyte, leading to considerable increases in J_{SC} and FF values of all-solid-state DSSCs.

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