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Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 153–157

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

I^-/I_3^- redox reaction behavior on poly(3,4-ethylenedioxythiophene) counter electrode in dye-sensitized solar cells

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Received 9 September 2003; received in revised form 4 November 2003; accepted 16 November 2003

Abstract

I^-/I_3^- redox reaction behaviors on chemically polymerized *p*-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO) and sputtered-Pt electrode were characterized to compare its performance as the counter electrode in dye sensitized solar cells (DSCs). Adsorption of iodide species at the PEDOT surface, as well as Pt surface was little affected the redox reaction at the low concentration of redox couple. The PEDOT-TsO film had porous structure and charge transfer resistance of the PEDOT-TsO electrode decreased with the thickness. Photovoltaic performance of DSCs with PEDOT-TsO counter electrode (CE) also improved with the thickness of PEDOT-TsO when ionic liquid was used for the electrolyte. The use of porous PEDOT-TsO counter electrode that has low cost, simplified fabrication process and sufficient catalytic activity could enhance the potential of the DSCs for practical use.

Keywords: Dye sensitization; Solar cell; PEDOT; Counter electrode; Conjugated polymer

1. Introduction

Dye sensitized solar cells (DSCs) have been attracting considerable attention because of high efficiency, simple fabrication process and low fabrication cost [1,2]. Counter electrodes (CEs) of DSC are usually made of platinum that is vacuum deposited on conducting glasses to reduce over-potential for reduction of I_3^- to I^- in redox electrolyte. Although, Pt has high catalytic activity for I_3^- reduction, high conductivity and stability, it is one of the expensive component materials in DSCs [3]. Hence, development of the CE with alternative materials is expected to reduce production cost of the cells. While some porous carbon materials were attempted to replace the Pt electrode [4–7], the conversion efficiency of cells based on carbon CE was relatively low due to the poor catalytic activity for I_3^- reduction per unit area and lower conductivity.

In 1988, Johas et al. developed an electronically conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) that has many attractive properties such as high conductivity, transparency, remarkable stabilities [8–11] and catalytic activity for I_3^- reduction [12]. The material cost and fabrication cost of the PEDOT CE is apparently lower than that of Pt CE, because production cost of 3,4-ethylendioxythiophene monomer could be reduced by mass production and the chemical polymerization is more simple and low temperature process than the other energy-consuming methods such as vacuum deposition, thermal deposition and electrochemical deposition. Furthermore, this chemical method is also applicable to produce a large size CE. Therefore, chemically polymerized PEDOT seems to be more suitable candidate for CE instead of Pt. We previously reported that DSCs fabricated using chemically polymerized *p*-toluenesulfonate doped PEDOT (PEDOT-TsO, Fig. 1) on a conductive glass as a CE showed comparable conversion efficiency and durability with the cell using Pt sputtered CE [13,14]. However, it was rarely reported about this redox reaction mechanism on the PEDOT-TsO films in detail [12,15].In addition, Hayase et al. [16,17] recently reported that the performance of the PEDOT CE was altered by type of electrolyte, e.g. organic liquid, ionic liquid, and ionic gel electrolytes. Room-temperature ionic liquids have attractive features in chemical stability, non-volatility, non-flammability, and wide electrochemical window. Several studies about DSCs using ionic liquid electrolytes have been reported to improve the long-term stability of the cell [14,18–24]. However, because ionic liquid electrolytes have high viscosity (10^3–10^4 mPa s) and lower conductivity ($\sim10^{-3}$ S cm^{-1}) than organic liquid electrolytes ($\sim10^{-2}$ S cm^{-1}), high I_2 concentration conditions (0.3–0.5 M) are required to provide the appropriate current density in DSCs [21]. Hence

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doi:10.1016/j.jphotochem.2003.11.017

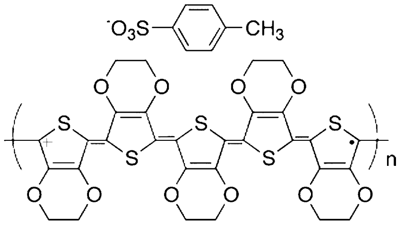

Fig. 1. Chemical structures of *p*-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO).

the counter electrode for DSCs based on ionic liquid should have better performance than that for the typical fluid organic liquid electrolytes.

In this paper, the I^-/I_3^- redox reaction behavior on the PEDOT-TsO and Pt electrodes was characterized in terms of the relationship between PEDOT-TsO thickness and the redox behavior on the electrode, and the charge transfer resistance between these CEs and the I^-/I_3^- redox couple. The performances of these CEs were also evaluated by photovoltaic characteristics of the DSCs.

2. Experimental

Procedures of chemical polymerization of PEDOT-TsO were followed by the method of Leeuw et al [25]. The monomer 3,4-ethylenedioxythiophene (Bayer) was added in a solution of Fe(III) tris-*p*-toluenesulfonate and imidazole dissolved in *n*-butanol. This monomer solution was spin-coated (1000 rpm for 1 min) or casted on a fluorine-doped thin oxide (FTO) glass (8 Ω per square, Asahi Glass) and then the glass was placed at a temperature of 110 °C for 5 min for thermal polymerization. After polymerization, the samples were rinsed in methanol to remove the Fe(II) bis-*p*-toluenesulfonate from the film and dried. Thickness of the PEDOT-TsO film was varied by the repetitive spin-coat or the amount of casting solution. The film thickness was measured by a profilometer (Vecco, dektack3). The platinum electrodes were prepared by a DC magnetron sputtering (JEOL JFC-1600, deposition rate: 14 nm/min) on the FTO glass.

Cyclic voltammetry (CV) was carried out in a three-electrode one compartment cell with a PEDOT on FTO working electrode, Pt foil counter electrode and an Ag/AgCl reference electrode dipped in an acetonitrile solution of 10 mM LiI, 1 mM I_2 and 0.1 M $LiClO_4$. CV performed using a BAS 100B/W electrochemical measurement system (scan condition: 20–200 mV s^{-1}).

Interfacial charge transfer resistances (R_{CT}) were evaluated by impedance measurements. Procedure of the impedance measurement was followed by previous works [5,26]. The cells consisted of two identical Pt sputtered or PEDOT deposited FTO electrode sealed with a HIMILAN film (thickness: 50 μm, Mitsui DuPont Polychemical), which serves as a spacer. The cells were filled with the electrolyte: 0.1 M of LiI, 0.3 M of 1,2-dimethyl-3-propylimidazolium iodide (DMPImI), 0.05 M of I_2 and 0.5 M of *t*-butylpyridine (*t*BP) in methoxyacetonitrile. (organic liquid electrolyte (OLE)) or 0.5 M of I_2 in 1-methyl-3-hexylimidazoliumiodide (ionic liquid electrolyte (ILE)). These concentrations and additives are usual for DSCs [20,21]. Impedance spectra were recorded over frequency ranges of 0.1–100 kHz using a voltaLab 40 PGZ301 (Radiometer Analytical S.A.).

Dye adsorbed TiO_2 films on conducting glasses (F-doped SnO_2, 10 Ω per square, Nippon Sheet Glass) were fabricated using the commercial TiO_2 paste (nanoxide-T, Solaronix) and Ru dye (Ruthenium TBA 535(N719), Solaronix) as reported [2]. The resulting film was clipped with the CE and then one of the above-mentioned electrolyte solution was introduced into the mesoporous dyed-TiO_2 electrode through a capillary action. In I–V measurement, the OLE and ILE were also used for the electrolyte. Photon to energy conversion efficiency was measured under AM 1.5 irradiation (100 mW cm^{-2}, from a solar simulator, YSS-80 Yamashita Denso). Cell performance was described as the averaged result of at least four samples. The area of the dye-coated TiO_2 electrode was 0.3 cm^2.

3. Results and discussion

3.1. Influence of the I_2 adsorption on the PEDOT electrodes

Fig. 2 shows cyclic voltammograms of the I^-/I_3^- redox couple on the PEDOT-TsO coated electrodes with various scan rate in acetonitrile, and Fig. 3 illustrates a relationship between the cathodic and anodic peaks and the square root of the scan rate. The linear relationship in Fig. 3 indicates the diffusion limitation of the redox reaction on PEDOT-TsO [15]. This phenomenon shows the adsorption of iodide

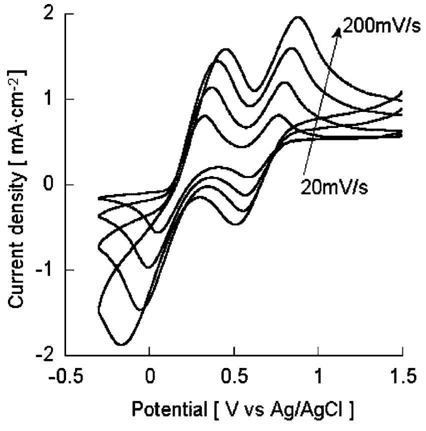

Fig. 2. Cyclic voltammograms of iodide species on PEDOT-TsO (thickness:∼0.1 μm) with various scan rate in acetonitrile solution of 10 mM Li, 1 mM I_2, and 0.1 M $LiClO_4$.

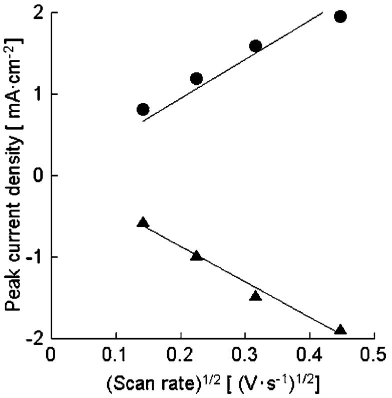

Fig. 3. Relation of cathodic(around 0.8 V vs. Ag/AgCl,(●)) and anodic peaks (around 0 V vs. Ag/AgCl, (▲)) vs. (scan rate)$^{1/2}$ in Fig. 2.

species is little affected the redox reaction at the PEDOT-TsO surface as well as Pt surface under these conditions [26], and this also suggest that no specific interaction between I^-/I_3^- redox couple and PEDOT-TsO electrode as is the case of Pt electrode.

3.2. Influence of thickness on the PEDOT electrodes

Fig. 4 shows an influence of the PEDOT thickness on the I^-/I_3^- redox reaction in acetonitrile. The cathodic and anodic peak currents increased with the PEDOT thickness. CV measurement without I^-/I_3^- redox couple showed that charge-discharge currents of electrical double layer increased with the PEDOT thickness. These behaviors confirmed the porous structure of the PEDOT-TsO electrode. Papageorgiou et al. [6] theoretically and experimentally reported that a porous carbon CE reduces the interfacial charge transfer resistance between electrolyte and CE. Hence, the increase of thickness on PEDOT-TsO film could expect to improve the performances as CE in DSCs.

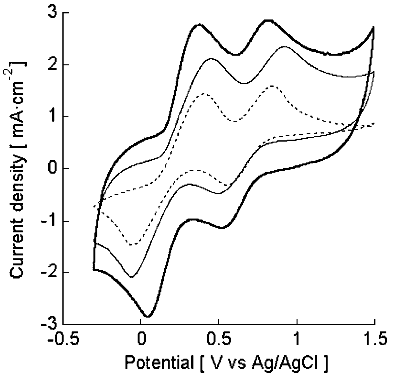

Fig. 4. Cyclic voltammograms of iodide species on PEDOT-TsO with thickness of $\sim$100 nm (- - -), $\sim$400 nm (—) and $\sim$4 μm (—) in acetonitrile solution of 10 mM Li, 1 mM I_2 and 0.1 M $LiClO_4$.

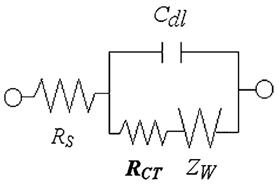

Fig. 5. Cole–Cole plots on the impedance measurements of the cell with ILE.

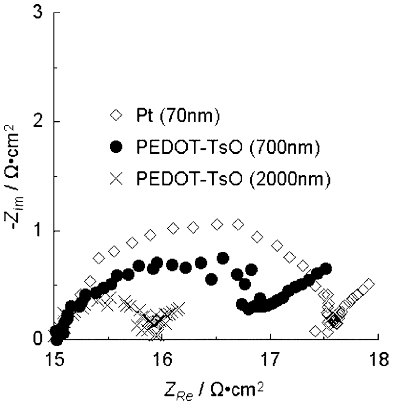

Fig. 6. Equivalent circuit of impedance spectrum in this measurement cells. R_{CT}: charge transfer resistance, C_{dl}: double layer capacity, R_S: serial resistance, Z_W: Warburg impedance (diffusion impedance).

3.3. Charge transfer resistance (R_{CT}) at the PEDOT electrode

Fig. 5 shows the typical impedance spectra measured with the sandwich type cells consisted of two identical electrodes. When this type of the cell was used, the equivalent circuit for this impedance measurement could be described as Fig. 6 [5,26]. The ohmic serial resistance (R_S) can be determined to the impedance where the phase is zero, which is around 100 kHz of frequencies. In the frequency range of 10–100 kHz, the impedance was dominated by the RC network of the electrolyte/electrode interface, consisting of the charge transfer resistance (R_{CT}) and capacitance of electrical double layer (C_{dl}). The impedance in the range of 0.1–10 Hz could be attributed to the diffusion impedance (Warburg impedance, Z_W).

Table 1 summarized the R_{CT} of the Pt and PEDOT electrode with various thickness evaluated from the impedance

Table 1
Charge transfer resistance (R_{CT}) of cell with various counter electrodes

Material	Thickness (nm)	R_{CT} (Ω cm^2)	
		OLE	ILE
Pt	4	6–7	10–11
	15	2–2.5	4–4.5
	70	1–1.5	2–2.5
	50	10–11	8–9
PEDOT-TsO	700		1.2–1.6
	1500	0.4–0.5	0.8–0.9

measurements using the equivalent circuit. In the both OLE and ILE, The R_{CT} between electrolyte and PEDOT-TsO decreased with increase of the thickness of PEDOT-TsO. The reduction of R_{CT} is attributed to the increase of surface area with the thickness. R_{CT} of Pt electrode also decreased with the thickness because of its porous structure [5,6,26].

3.4. Relationship between R_{CT} at the PEDOT CE and cell performance

In the case of DSCs based on organic liquid electrolyte with low viscosity, the diffusion rate of iodide species is sufficient to meet the demand of a current density on typical DSCs (~20 mA cm^{-2}) even at low concentration of I_2 (0.05 M). Hauch et al. reported that 2 nm of sputtered Pt (R_{CT} ~2 Ω cm^2) is sufficient for a DSC with acetonitrile as the solvent [26]. We also reported the comparable performances of DSCs with Pt and PEDOT-TsO when OLE was used [13]. In addition, thickness of the PEDOT-TsO (50–2000 nm) or Pt (5–70 nm) was rarely affected the conversion efficiency of the OLE-DSCs (data not shown). Thus, no obvious difference between PEDOT and Pt was observed in the case of the OLE-DSCs.

On the other hand, ILE-DSCs requires the high I_2 concentration conditions (0.3–0.5 M) to provide the sufficient current density in ILE-DSCs as mentioned above. Therefore, R_{CT} at CEs could affect the solar cell performances in the case of ILE-DSCs. PEDOT-TsO electrode (thickness >700 nm) has lower R_{CT} than Pt electrode (thickness ~70 nm) (Table 1). This means that the PEDOT-TsO electrode with high surface area could show higher performance than the Pt electrode as CE in DSCs. Fig. 7 shows short circuit photocurrent density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and total conversion efficiency (η) of the ILE-DSCs using Pt and two kinds of PEDOT-TsO CEs with different thickness. The cell with the thicker PEDOT-TsO CE (thickness ~2 μm) showed higher V_{OC}, FF, and total conversion efficiency than the cell with PEDOT-TsO CE (thickness ~50 nm) and Pt CE (thickness ~70 nm) when ionic liquid was used for the electrolyte. This improvement could be attributed to the decrease of R_{CT} at the interface of electrolyte and the CE. These results also confirmed that the performance of CE improved with the increase of surface area of the CE [5,6]. This improvement of CE affected the photovoltaic performance of the DSCs, especially in the use of electrolyte with low transport rate of redox couple, e.g. ionic liquid electrolyte, polymer electrolyte and gel electrolyte. Further optimization on the PEDOT structure, such as porosity, thickness, and dopant ion, etc. for each cell composition could enhance the photovoltaic performance, reducing the fabrication cost of the DSCs.

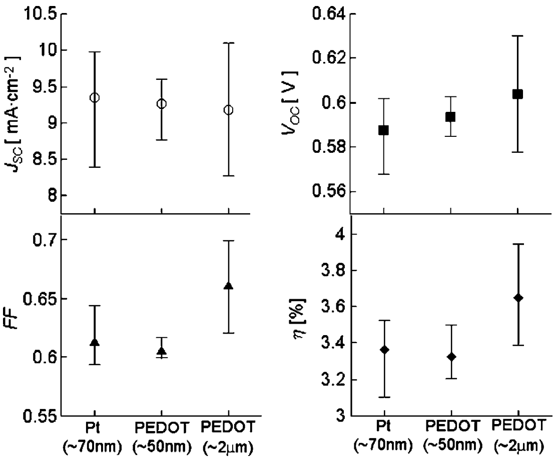

Fig. 7. Comparison of photovoltaic characteristics on the ILE-DSCs using Pt CE (thickness: ~70 nm) and PEDOT-TsO CE (thickness: ~50 nm and ~2 μm).

4. Conclusion

The CV and impedance measurement reveal that the I^-/I_3^- redox reaction on chemically polymerized *p*-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO) shows no specific behavior compare to the behavior on the sputtered-Pt electrode. The surface area of PEDOT-TsO electrode increased with the thickness because of its porous structure, and this increase of active area in the PEDOT-TsO CE improved the photovoltaic performance of the DSCs when ionic liquid was used for the electrolyte. This improvement corresponds to the decrease of charge transfer resistance at the interface of the electrolyte and the PEDOT CE. These results suggested that the increase of surface area of CE was effective to enhance photovoltaic performance in the DSCs. The porous PEDOT-TsO CE would be superior to Pt and carbon CEs in terms of fabrication process, fabrication cost and performance.

Acknowledgements

The authors wish to acknowledge H.C. Stalk V TECH for kindly supplying the 3,4-ethylenedioxythiophene. This work was partially supported by Open Competition for the Development of Innovative Technology (No. 12310) in Grant-in-Aid for the Creation of Innovations through Business–Academic–Public Sector Cooperation from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the Strategic Research Base, Frontier Research Center, (Graduate School of Engineering,) Osaka University, supported by the Japanese Government's Special Coordination Fund for Promoting Science and Technology.

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