Application of Poly(3,4-ethylenedioxythiophene) to Counter Electrode in Dye-Sensitized Solar Cells

Yasuteru Saito, Takayuki Kitamura, Yuji Wada, and Shozo Yanagida*
Material and Life Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871

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Dye-sensitized solar cells fabricated using chemically polymerized poly(3,4-ethylenedioxythiophene) on a conductive glass as a counter electrode showed comparable conversion efficiency with a cell using platinum sputtered counter electrode.

Dye sensitized solar cells (DSCs) have been attracting considerable attention because of high efficiency, simple fabrication process and low fabrication costs.[1] Counter electrodes of the cells are usually made of Pt which is vacuum deposited on conducting glasses to catalyze reduction of I_3^- to I^- in redox electrolyte. Since Pt is one of the expensive materials in DSCs,[2] development of the electrodes with the other materials expected to reduce production cost of the cells. Some porous carbon materials were attempted to replace the Pt electrode.[3] However, the conversion efficiency of these cells was relatively low owing to the poor catalytic activity for I_3^- reduction.

Recently, Johas et al. developed an electronically conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), and showed that PEDOT have high room temperature conductivity and remarkable stabilities.[4] In addition, Yohannes et al. reported that electrochemically polymerized doped PEDOT can catalyze the reaction of I_3^-/I^- redox couple in an organic solar cell.[5]

Here, we report the application of chemically polymerized PEDOT to a counter electrode on dye-sensitized solar cells. Production cost of 3,4-ethylendioxythiophene monomers could be reduced by mass production. Since the chemically polymerization method needs no instrument except for a heating apparatus, it is more simple process than the electrochemical method. This method is also easy to make a large size electrode and can provide the polymer film with high conductivity (550 S/cm) and high stability.[6] Therefore, chemically polymerized PEDOT seems to be more suitable for the counter electrode material than Pt. Influence of dopant anion on the catalytic activity was also examined.

Procedures of chemical polymerization of TsO^- doped PEDOT (PEDOT-TsO, Figure 1(a)) were followed by the method of Leeuw et al.[6] The monomer 3,4-ethylenedioxythiophene (Bayer) was added in a solution of Fe(III) tris-*p*-toluenesulfonate and imidazole dissolved in 1-butanol. This monomer solution was spincoated on an ITO glass (7 ohm/square, Kuramoto Glass) at 500 rpm for 1 min and then the glass placed at a temperature of 110 °C for 5 min. After polymerization, the sample was rinsed in methanol to remove the Fe(II) bis-*p*-toluenesulfonate from the film and dried. Polystyleneslufonate doped PEDOT (PEDOT-PSS, Figure 1(b)) electrode was prepared as follows. PEDOT-PSS dispersed in water (Aldrich) was filtrated and spincoated on an ITO glass at 500 rpm for 1 min. The resulting film was heated at 110 °C for 5 min to dryness. Thickness of the PEDOT-TsO and PEDOT-PSS are each 30–50 nm. Conductivities of these PEDOT-TsO and PEDOT-PSS films were 550 S/cm and 10 S/cm, respectively.

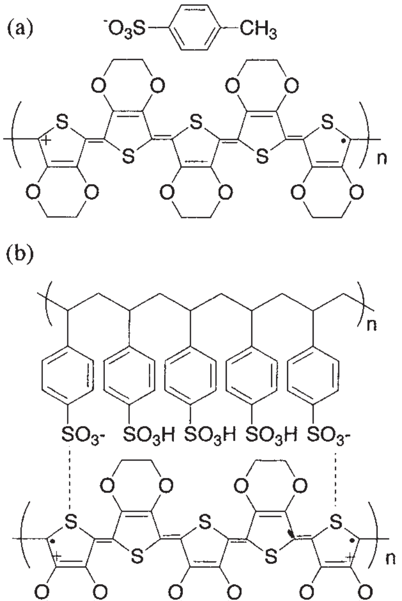

Figure 1. Chemical structures of (a) PEDOT-TsO and (b) PEDOT-PSS.

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

Dye adsorbed TiO_2 films on conducting glasses (F doped SnO_2, 10 ohm/square, NSG) were fabricated using commercial TiO_2 powder (P25, Nippon Aerosil) and Ru dye $((Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$, Ruthenium TBA 535, Solaronix) as reported procedure.[1] The resulting film was clipped with the counter electrode and then an electrolyte solution was introduced into the mesoporous TiO_2 film through capillary action. The electrolyte solution was composed of 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 *tert*-butylpyridine (*t*BP) in methoxyacetonitrile. 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 average values of at least 3 samples. The area of the dye-adsorbed TiO_2 electrode was 0.35 cm^2.

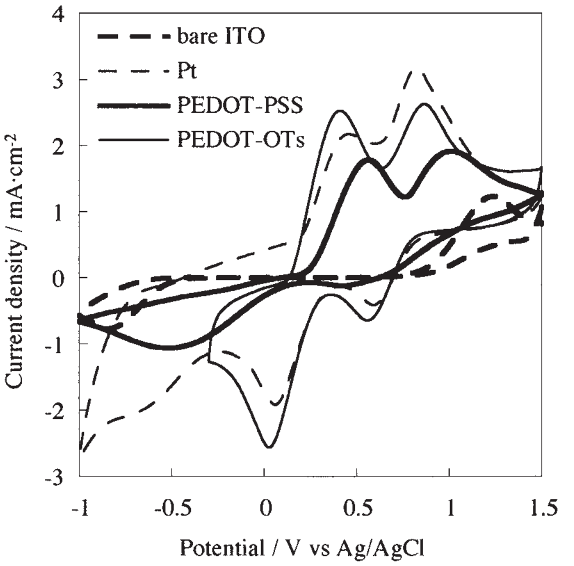

Figure 2. Cyclic voltammograms of iodide species on ITO, PEDOT-TsO, PEDOT-PSS, and Pt in acetonitrile solution of 10 mM LiI, 1 mM I_2 and 0.1 M $LiClO_4$.

Figure 2 shows the cyclic voltammograms of I^-/I_3^- redox electrolyte on PEDOT films. Because dedoping of TsO^- occurred at −0.6 V vs Ag/AgCl for PEDOT-TsO electrode, CV was measured at the range of −0.3 ~ 1.5 V on PEDOT-TsO. In the case of the PEDOT-PSS electrode, dedoping did not occur until −1.0 V vs Ag/AgCl. The oxidation/reduction peaks of I^-/I_3^- observed on the PEDOT-TsO electrode were similar to the behavior on the Pt electrode. With the bare ITO glass electrode the oxidation/reduction peaks were absent. In the case of the PEDOT-PSS electrode, the oxidation current was significantly decreased and the reduction peaks were separated. The significant decrease of the oxidation current could be explained by the reduction of the redox active site of the PEDOT-PSS film due to the exposure of PSS^-, which prevent the approach of I^- or I_3^- to the active site of the PEDOT chain resulting in the increase of the overpotential. Another explanation is that partial exchange of TsO^- anion with I^- and I_3^- in PEDOT-TsO[7] promotes the smooth redox reaction, but exchange of polymer PSS^- could not be expected in PEDOT-PSS.

Figure 3 shows photocurrent-voltage curves of the cells with PEDOT-TsO, PEDOT-PSS, and Pt counter electrode under AM 1.5 irradiation. V_{OC}, J_{SC}, fill factor (FF) and efficiency (η) of the cells were listed in Table 1. The cell with PEDOT-TsO showed the almost same properties as the cell with Pt. The comparable V_{OC} and J_{SC} but lowering of FF were observed in the cell with the PEDOT-PSS. This result agreed with the lower catalytic activity of I_3^- reduction of PEDOT-PSS on CV. As compared to PEDOT-TsO, the conductivity of PEDOT-PSS is relatively low, which could lead to the lowing of FF.

A quasi-solid-state dye sensitized solar cell with TsO^- doped PEDOT counter electrode shows excellent durability as well as the cell using a Pt counter electrode without any sealings (at least 80 days).[8] This durability was caused by the excellent stability under ambient conditions of the PEDOT film.[4]

In conclusion, chemically polymerized *p*-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) film can be used as a counter electrode of dye-sensitized solar cells.

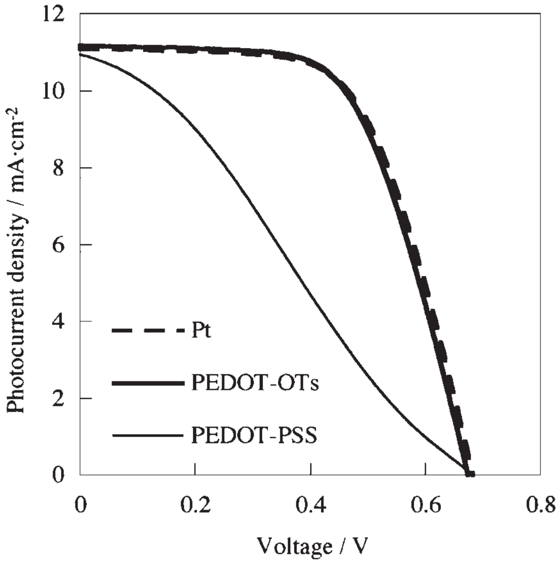

Figure 3. Photocurrent-voltage curves of the cells with PEDOT-TsO, PEDOT-PSS and Pt as counter electrodes under AM 1.5 (100 mW cm^{-2}) irradiation.

Table 1. Cell performances of the dye-sensitized solar cells

CE	V_{OC}/V	J_{SC}/mA cm^{-2}	FF	η/%
PEDOT-TsO	0.67	11.2	0.61	4.60
PEDOT-PSS	0.68	11.0	0.28	2.10
Pt	0.68	11.1	0.62	4.67

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References

1 a) B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991). b) Md. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993).
2 G. Smestad, C. Bignozzi, and R. Argazzi, *Sol. Energy Mater. Sol. Cells*, **32**, 259 (1994).
3 a) A. Kay and M. Grätzel, *Sol. Energy Mater. Sol. Cells*, **44**, 99 (1996). b) N. Papageorgiou, P. Liska, A. Kay, and M. Grätzel, *J. Electrochem. Soc.*, **146**, 898 (1996).
4 a) A. G. Bayer, Eur. Patent 339340 (1988). b) F. Jonas and L. Schrader, *Synth. Met.*, **41–43**, 831 (1991). c) M. Dietrich, J. Heinze, G. Heywang, and F. Jonas, *J. Electroanal. Chem.*, **87**, 369 (1994). d) L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.*, **12**, 481 (2000).
5 T. Yohannes and O. Inganäs, *Sol. Energy Mater. Sol. Cells*, **51**, 193 (1998).
6 D. M. de Leeuw, P. A. Kraakman, P. F. G. Bongaerts, C. M. J. Mutsaers, and D. B. M. Klaassen, *Synth. Met.*, **66**, 263 (1994).
7 S. Biallozor and A. Kupniewska, *Electrochem. Commun.*, **2**, 480 (2000).
8 a) W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada, and S. Yanagida, *J. Phys. Chem. B*, **105**, 12809 (2001). b) W. Kubo, Y. Makimoto, T. Kitamura, Y. Wada, and S. Yanagida, *Chem. Lett.*, Submitted.