

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

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Application of a conducting polymer, Poly(3,4-ethylenedioxythiophene)(PEDOT) to a hole transport material and counter electrode material in dye-sensitized solar cells (DSCs) were studied. An all-solid state DSC was fabricated using *in situ*-electrochemically polymerized PEDOT as hole-transport material that showed the higher conversion efficiency under simulated sunlight than the solid DSCs using polypyrrole. This result was associated with high transparency in visible light range and high conductivity of PEDOT. We also applied the chemically polymerized TsO⁻ doped PEDOT to the counter electrode in DSCs, because it showed the highest conductivity of PEDOT films. CV measurements showed that the TsO⁻ doped PEDOT electrode have almost the same catalytic activity as a counter electrode with Pt. The liquid DSCs with this PEDOT counter electrode showed the almost same I-V characteristics and stability as the cell with Pt.

Key words: dye sensitization, solar cells, conducting polymer; poly(3,4-ethylenedioxythiophene), electrochemical polymerization, counter electrode

1. INTRODUCTION

Dye sensitized solar cells (DSCs) have been attracting considerable attention because of their high efficiency, simple fabrication process and low production cost. The highest conversion efficiency reported for this device is around 10% under AM 1.5 (100 mW·cm⁻²) irradiation when used in conjunction with liquid electrolytes containing I⁻/I₃⁻ redox couples [1,2]. The use of liquid electrolyte causes several problems like sublimation of the iodine or leaks of the electrolyte that result in difficulty of hermetic sealing. Replacing the liquid electrolyte by solid-state hole transport material is an essential research subject for long-time stability of DSCs. Several attempts have been made to replace the liquid electrolyte by p-type semiconductors [3,4] or organic hole transport materials (HTMs) [5-8]. However, the conversion efficiency of these devices was relatively low particularly under high light irradiance. It is due to high frequencies of charge recombination from TiO₂ to HTMs or poor electronic contact between dye molecules and the HTMs caused by incomplete penetration of solid HTMs in the void of the mesoporous TiO₂ electrodes.

To solve these problems, we previously proposed *in situ* photo-electrochemical polymerization of pyrrole as a hole transport phase in the void of the dye-adsorbed mesoporous TiO₂ films [9-11]. However, polypyrrole (PPy) absorbs visible light, which leads to decrease in light harvesting efficiency of the cell. Here we report the fabrication of solid state DSCs (sDSCs) using *in situ* photo-electrochemically polymerized poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole transport phase. PEDOT has high transparency in visible light range, high conductivity and remarkable stability at room temperature [12]. Therefore, PEDOT seems to be more suitable for HTM than PPy. We previously

reported that chemically polymerized PEDOT could work as a stable hole transport material [13]. Influence of polymerization method was also studied.

In addition, some researchers reported that electrochemically polymerized PEDOT also have high catalytic activity for I₃⁻ reduction [14,15]. Counter electrodes (CEs) of DSC are usually made of platinum that is vacuum deposited on conducting glasses to reduce overpotential for reduction of I₃⁻ to I⁻ in redox electrolyte. Although Pt has high catalytic activity for I₃⁻ reduction, high conductivity and stability, it is one of the expensive component materials in DSCs [16]. 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 [17-20], the conversion efficiency of cells based on carbon CE was relatively low due to the poor catalytic activity for I₃⁻ reduction per unit area and lower conductivity. We studied about the application of chemically polymerized PEDOT to a counter electrode on liquid DSCs. The material cost and fabrication cost of the PEDOT CE is apparently lower than that of Pt CE, because production cost of 3,4-ethylenedioxythiophene 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.

2. EXPERIMENTAL

2.1 Fabrication of sDSCs with PEDOT as a HTM

A compact TiO₂ layer was deposited on an optically transparent conducting glass (FTO, coated F-doped SnO₂, 10 Ω/square, Nippon Sheet Glass) as reported procedure [13] to avoid a direct contact between the hole transport phase and the FTO that causes short circuit of the cell. A commercial mesoporous TiO₂ paste (nanoxide-T, Solaronix) was deposited using doctor blade technique onto this compact TiO₂ layer and heated at 450°C for 30min. Thickness of the TiO₂ was around 5 μm. The TiO₂ electrode was immersed in a 3.0×10⁻⁴ M Ru dye {(Bu₄N)₂[Ru(dcbpyH)₂(NCS)₂] (Solaronix) in a mixture of acetonitrile and *tert*-butanol (50/50, v/v)} solution at room temperature for 24h in the dark. The electrode was then rinsed with acetonitrile and dried.

PEDOT was introduced into the void of the dye-adsorbed TiO₂ films by photoelectrochemical polymerization under potentiostatic conditions as reported [9-11]. A three-electrode one-compartment cell with a dye-adsorbed TiO₂ on FTO working electrode, Pt wire counter electrode and an Ag/AgCl reference electrode dipped in an acetonitrile solution of 0.01M *bis*(3,4-ethylenedioxythiophene) (*bis*-EDOT) and 0.1M LiClO₄ was used on the polymerization. The polymerization was achieved by applying the constant potential (+0.15V vs. Ag/AgCl) on the dyed films followed by light irradiation of a 500 W Xe lamp (18 mW·cm⁻² > 520 nm) for 5 min. Total charge of anodic photopolymerization was about 20 mC·cm⁻². After polymerization, an ionic liquid, 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfone)imide (EMITFSI) solution of 0.2M lithium bis-(trifluoromethanesulfone)imide (LiTFSI) and 0.2M 4-*tert*-butylpyridine (*t*BP) was casted on the electrode, being left standing for 24h, and then the ionic liquid solution on the electrode surface was wiped off. We previously reported that this treatment significantly improved the photovoltaic performance without decrease of long-term stability of the sDSCs with chemically polymerized PEDOT [13]. The resulting electrode was clipped with a gold-sputtered conducting glass to make a sandwich type cell. Difference on absorption spectra of the dyed TiO₂ electrode before/after polymerization of PEDOT or PPy were measured using a UV-visible light spectrometer (Hitachi, U-3000).

The photoelectrochemical properties of the solid cells were studied by recording the current-voltage characteristics under dark or illumination of AM 1.5 (1 Sun, 100 mW·cm⁻²) using a solar simulator (Yamashita Denso, YSS-80). Incident photo-to-current conversion efficiency (IPCE) was also evaluated using a commercial setup for IPCE measurement (PV-25DYE, JASCO) under 5 mW·cm⁻² monochromatic light illuminations.

2.2 Application of PEDOT CE in liquid DSCs

Procedures of chemical polymerization of PEDOT-TsO were followed by the method of Leeuw et al [21]. 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 spincoated (1000 rpm for 1 min) or casted on a FTO glass and then the glass was heated at 110 °C for 5 min for thermal polymerization. After

polymerization, the electrodes were rinsed in methanol and dried. Thickness of the PEDOT-TsO film was varied by the repetitive spincoat or the amount of casting solution. The film thickness was measured by a profilometer (Veeco, dektak3). 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 I₂ and 0.1 M LiClO₄. CV performed using a BAS 100B/W electrochemical measurement system (scan rate : 0.1V·s⁻¹).

Interfacial charge transfer resistances (R_{CT}) were evaluated by impedance measurements. Procedure of the impedance measurement was followed by previous literatures [18,22]. The cells consisted of two identical Pt sputtered or PEDOT deposited FTO electrode sealed with a HIMALAN 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 I₂ and 0.5 M of 4-*tert*-butylpyridine (*t*BP) in methoxyacetonitrile. (organic liquid electrolyte, OLE) or 0.5 M of I₂ in 1-methyl-3-hexylimidazoliumiodide (ionic liquid electrolyte, ILE). These concentrations and additives are usual for DSCs [23,24]. Impedance spectra were recorded over frequency ranges of 0.01Hz to 100kHz using a voltaLab 40 PGZ301 (Radiometer Analytical, S. A.).

Dye adsorbed TiO₂ films on FTO glasses were fabricated using the commercial TiO₂ 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 solutions was introduced into the mesoporous dyed-TiO₂ 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. Cell performance was described as the averaged result of at least 4 samples. The area of the dye-coated TiO₂ electrode was 0.3 cm².

3. RESULTS AND DISCUSSIONS

3.1 Photovoltaic properties of sDSCs with PEDOT

Table 1 and Fig. 1 shows the photovoltaic characteristics of the sDSCs using *in situ* photoelectrochemically polymerized PEDOT (PEP-PEDOT), PEP-PPy [11] and chemically polymerized PEDOT(CP-PEDOT) [13]. The short circuit photocurrent density (J_{SC}) of sDSCs with PEP-PEDOT was about 20 times higher than that of CP-PEDOT, which suggested that the PEP method could make better electronic contact between dye and HTM than the CP method. J_{SC} of the sDSCs with PEP-PEDOT was about 7 times higher than the sDSCs with PEP-PPy. The sDSCs using PEP-PEDOT as a HTM showed J_{SC} of 2.3 mA·cm⁻² and η of 0.53%. These values are the highest among those of the sDSCs fabricated with organic polymer HTMs. These results could be attributed to the high transparency and better charge transport property of the PEDOT.

Table 1. Cell performances of the solid-state DSCs.

HTM	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF	η [%]
PEP-PEDOT	0.47	2.3	0.50	0.53
CP-PEDOT[13]	0.40	0.075	0.37	0.012
PEP-PPy[11]	0.72	0.32	0.78	0.34

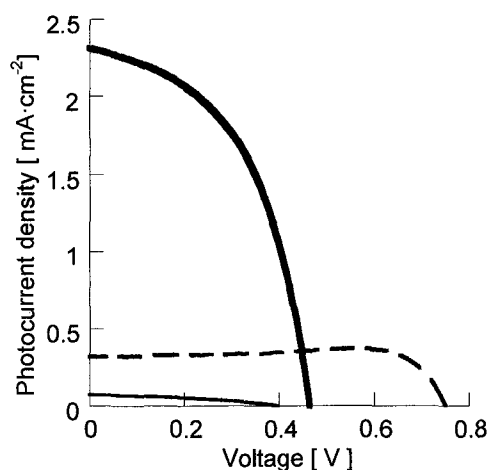


Fig. 1. I-V curves of the fabricated sDSCs using CP-PEDOT[13] (solid line), PEP-PEDOT (bold line), and PEP-PPy[11] (dashed line) under an illumination of AM 1.5 condition.

At the same amount of charge for the polymerization (10mC·cm⁻²), the increase of absorbance on the dyed electrode after polymerization of PEP-PEDOT was much lower than that of PEP-PPy (Fig. 2), which corresponds to increase of the light harvesting efficiency of the sDSC based on PEDOT. Fig. 3 shows the shape of IPCE spectra of PEP-PEDOT sDSC, PEP-PPy sDSC and typical liquid DSC where the intensities were normalized at the peaks for PEDOT and liquid, and at the shoulder for PPy. IPCE of PEP-PEDOT sDSCs was higher than that of PEP-PPy in visible range and the shape of the spectrum was close to the shape of the liquid DSCs. These results confirm that PEP-PEDOT was more suitable than PEP-PPy for HTM of sDSC. The open circuit voltage (V_{OC}) and fill factor (FF) of the sDSC with PEP-PEDOT were lower than that of the sDSC with PEP-PPy, which would be explained as due to the unfavorable contact at TiO₂/Dye surface of PEDOT that is more conductive than PPy. The electron leakage at FTO / PEDOT interface is also conceivable as decrease of shunt resistance of the cell.

3.2 Performance of PEDOT counter electrode in DSCs

Fig. 4 shows the cyclic voltammograms of Γ^-/I_3^- redox electrolyte on PEDOT films. The oxidation/reduction peaks of Γ^-/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

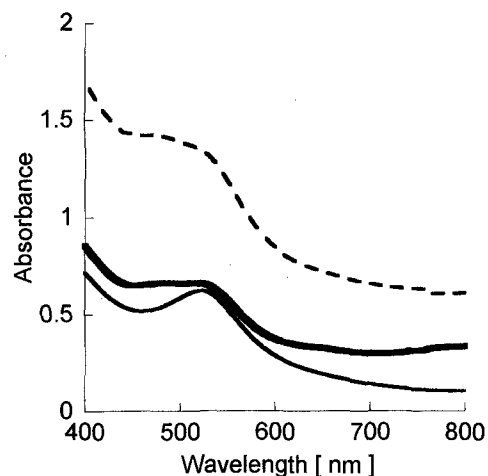


Fig. 2. Absorbance spectra of the FTO / TiO₂ / dye electrode (solid line), FTO / TiO₂ / dye / PEP-PEDOT (bold line) and FTO / TiO₂ / dye / PEP-PPy (dashed line) (polymerized charge :10 mC·m⁻²).

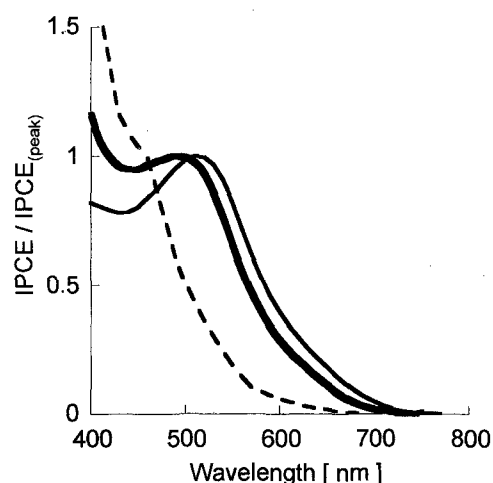


Fig. 3. Normalized IPCE spectra of the typical liquid DSCs (solid line), sDSCs with PEP-PEDOT (bold line), and sDSCs with PEP-PPy (dashed line).

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 Γ^- or I_3^- to the active site of the PEDOT chain resulting increase the overpotential.

Table 2 shows the photovoltaic characteristics of the cells with PEDOT-TsO, PEDOT-PSS, and Pt counter electrode under AM 1.5 irradiation. The cell with PEDOT-TsO showed the almost same properties as the cell with Pt. The comparable V_{OC} 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 lowering of FF .

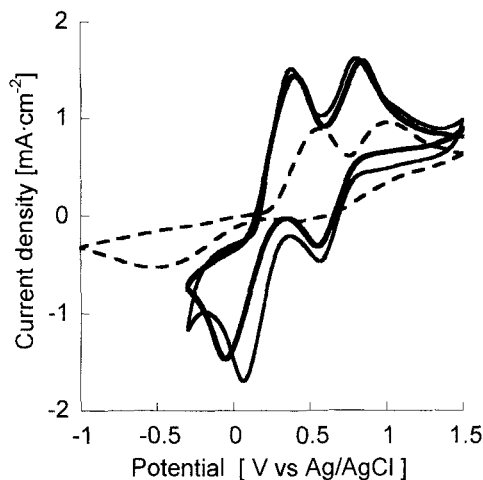


Fig. 4. Cyclic voltammograms of iodide species on Pt (thickness~70nm, solid line), PEDOT-TsO (thickness~50nm bold line) and PEDOT-PSS (thickness~50nm dashed line) in acetonitrile solution of 10mM Li, 1mM I₂ and 0.1M LiClO₄.

Table 2. Cell performances of the dye-sensitized solar cells with various CE using organic liquid electrolyte.

CE	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	η [%]
PEDOT-TsO ^a	0.67	11.2	0.61	4.60
PEDOT-PSS ^a	0.68	11.0	0.28	2.10
Pt ^b	0.68	11.1	0.62	4.67

^athickness~50nm, ^bthickness~70nm.

Fig. 5 shows an influence of the PEDOT thickness on the Γ/I_3^- redox reaction in acetonitrile. The cathodic and anodic peak currents increased with the PEDOT thickness. CV measurement without Γ/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.* theoretically and experimentally reported that a porous carbon CE reduces the interfacial charge transfer resistance between electrolyte and CE [19]. Hence, the increase of thickness on PEDOT-TsO film could expect to improve the performances as CE in DSCs.

Table 3 summarized the results of impedance measurement. In this measurement, charge transfer resistance (R_{CT}) per projected area was calculated. In the both OLE and ILE, 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 [18,19,22].

In the case of DSCs based on organic electrolyte with low viscosity, the diffusion rate of iodide species is sufficient to meet the demand of a current density on typical DSCs (~20mA·cm⁻²). Hauch *et al.* reported that 2 nm of sputtered Pt (R_{CT} ~2 Ω ·cm²) is sufficient for a DSC with acetonitrile as the solvent [22]. Table. 2 also showed the comparable performances of DSCs with Pt

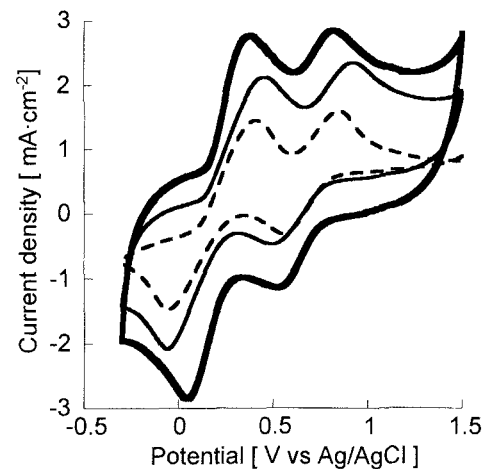


Fig. 5. Cyclic voltammograms of iodide species on PEDOT-TsO with thickness of ~50nm (dashed line), ~400nm (solid line) and ~4 μ m (bold line) in acetonitrile solution of 10mM Li, 1mM I₂ and 0.1M LiClO₄.

and PEDOT-TsO when organic liquid electrolyte was used. Thus, no obvious difference is observed in the case **Table 3.** Charge transfer resistance (R_{CT}) per unit area of the cell using 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
PEDOT-TsO	50	10~11	8~9
	700		1.2~1.6
PEDOT-PSS	1500	0.4~0.5	0.8~0.9
	3000	60	5~6

of organic liquid electrolyte DSC.

On the other hand, in the case of DSCs with ILE, R_{CT} could affect the solar cell performances. PEDOT-TsO electrode (thickness > 700 nm) has lower R_{CT} than Pt electrode (thickness ~70 nm). This means that the PEDOT-TsO electrode with high surface area could show higher performance than the Pt electrode as CE in DSCs.

Table 4. Photovoltaic performances of the dye-sensitized solar cells with Pt and PEDOT-TsO CE using ionic liquid electrolyte.

CE	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF	η [%]
Pt(~70nm)	0.59	9.59	0.61	3.49
PEDOT(~50nm)	0.60	9.57	0.61	3.50
PEDOT(~2 μ m)	0.62	9.26	0.68	3.94

Table 4 shows the photovoltaic characteristics 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 $\sim 2\mu\text{m}$) showed higher V_{OC} , FF and total conversion efficiency than the cell with PEDOT-TsO CE (thickness $\sim 50\text{ nm}$) and Pt CE (thickness $\sim 70\text{ nm}$) 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 [18,19]. 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.

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) [25]. This durability was caused by the excellent stability under ambient conditions of the PEDOT film [26].

4. CONCLUSION

Solid-state DSC using photo-electrochemically polymerized PEDOT as HTM and liquid DSCs with chemically polymerized PEDOT as counter electrodes were successfully fabricated. These results suggested that the PEDOT could apply to the dye-sensitized solar cells as the alternative materials. Further optimization of the DSCs using the PEDOT could resolve the problem for practical use of the cells such as long-term stability, conversion efficiency and fabrication cost.

ACKNOWLEDGEMENTS

The authors wish to acknowledge H.C. Stalk V TECH Ltd. for kindly supply of 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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(Received October 13, 2003; Accepted March 16, 2004)