Electrochemical Investigation of PEDOT Counter Electrode for Dye-Sensitized Solar Cells

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ABSTRACT

Conversion efficiency of a dye-sensitized solar cell (DSC) using poly(3,4-ethylenedioxythiophene) (PEDOT)-coated transparent conducting substrate as counter electrode was shown to be 7.88%, which is slightly higher compared to a DSC using classical platinum sputtered counter electrode (7.65%). From electrochemical impedance analysis, the PEDOT based cell was found to show lower charge-transfer resistance assigned to the I^-/I_3^- redox reaction as a mediator on the counter electrode compared to the platinum based cell. More quantitatively, electron transfer rate constant (k^0) for the I^-/I_3^- redox reaction on the counter electrode was remarkably estimated by voltammetric kinetic analysis. The k^0 obtained for the PEDOT electrode ($3.47 \times 10^{-3} \text{ cm s}^{-1}$) was larger than that for the platinum electrode ($2.76 \times 10^{-3} \text{ cm s}^{-1}$) by comparing the approximately same electrode thickness and surface roughness. This research revealed the higher conversion efficiency of the PEDOT based cell is attributed to essentially faster the mediator reaction (reduction of I_3^-) on the counter electrode in its cell.

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Keywords : PEDOT, Dye-sensitized Solar Cell, Counter Electrode, Catalytic Activity

1. Introduction

Dye-sensitized solar cells (DSCs) have been attracted to be a potential candidate of the next-generation solar cell having unique features.^{1–10} A general DSC consists of a sandwich structure with a dye-adsorbed nanoporous TiO_2 photoanode, an organic electrolyte containing iodide/triiodide (I^-/I_3^-) as redox mediator, and a counter electrode (also known as cathode).^{1,2} The counter electrode is a platinum film coated on a conducting substrate due to its high electrocatalytic activity for reduction of I_3^- and high corrosion stability for I^-/I_3^- electrolyte. However, platinum is an expensive and less amount of deposit in the earth. Cost-effective counter electrode with high electrocatalytic activity has been strongly required for the commercialization of DSC.

Several carbonaceous materials such as carbon black,¹¹ amorphous carbon,¹² carbon nanotube,^{13,14} and graphene¹⁵ have been investigated as electrocatalytic film for counter electrode substituting platinum. For example, high conversion efficiency ($\sim 9\%$) obtained for a carbon black counter electrode was reported.¹¹ To obtain the higher conversion efficiency, thick film (10–15 μm) and annealing before use should be required.

Meanwhile, conducting polymer especially PEDOT (poly(3,4-ethylenedioxythiophene)) has been investigated as the counter electrode, due to high conductivity, stability, and low cost.^{16–24} Yohannes and Inganas firstly demonstrated that electrochemically prepared PEDOT (ClO_4^- dopant) on the transparent conducting oxide (TCO) glass substrate has electrocatalytic activity for the redox reaction of I^-/I_3^- .¹⁶ Yanagida et al.¹⁸ reported that conversion efficiency of the DSC with chemically polymerized PEDOT (*p*-toluenesulfonate dopant, 700–2000 nm in film thickness) on the TCO glass as the counter electrode was around 3.6%, which was slightly higher to the cell with sputtered platinum (no information about film thickness) counter electrode ($\sim 3.4\%$). In 2010, Pringle et al.²⁰ used electrochemically prepared PEDOT with porous

structure (trifluoromethanesulfonyl imide dopant) on the plastic TCO substrate as the counter electrode and obtained a conversion efficiency of 8.0%, even though a platinum cell was 7.9%. Their earlier reports suggest that PEDOT showed high performance as the counter electrode, regardless of polymerization methods or dopant species. The PEDOT counter electrode become one of the important candidates for the low cost DSC. However, detailed electrochemical behavior or quantitative evaluation for electrocatalytic activity of the PEDOT counter electrode have not been investigated. Comparing the cell performance or electrocatalytic activity of PEDOT and platinum with approximately same thickness and surface roughness has not been reported so far.

In this paper, DSC test piece using PEDOT formed on transparent conducting substrate electrochemically as counter electrode is fabricated and evaluated to compare platinum counter electrode. The PEDOT and platinum films are prepared as approximately same film thickness and surface roughness. The film thickness is reduced to nanometer size (35 nm), in order to eliminate the difference of surface area as much as possible. Then, detailed electrochemical behavior of the PEDOT counter electrode is investigated to reveal its higher conversion efficiency of the PEDOT based DSC, comparing the platinum counter electrode. The electron transfer rate constant (k^0) for the I^-/I_3^- redox reaction on the counter electrodes by a voltammetric kinetic analysis is investigated for the quantitative discussion.

2. Experimental

2.1 Materials

The F-doped SnO_2 -coated (FTO) glass, used as the transparent conducting substrates for the photoanode and counter electrode, was purchased from AGC Inc., ($< 10 \text{ Ohm/sq}$). The organometallic dye of N719 [$\text{RuL}_2(\text{NCS})_2$, $\text{L} = 4,4'$ -dicarboxylate-2,2'-bipyridine] (Ardrich) was dissolved in acetonitrile (Wako Chemicals, 99.8%) and tert-butanol (Aldrich, 99.0%). TiO_2 paste was purchased from JCG C&C (PST-18NR). For the counter electrode, 3,4-ethyl-

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enedioxythiophene monomer was used (Aldrich, 97%) without distillation. The electrolyte for DSC measurement or electrochemical analysis, LiI (Wako Chemicals, 97%), I₂ (Wako Chemicals, 99.0%), 1,2-dimethyl-3-propylimidazolium iodide (Tokyo Chemical Industry, 98.0%), 4-tert-butylpyridine (Aldrich, 96%) were used as received. 1 M LiBF₄/acetonitrile ready-made electrolyte was used (Tomiya Pure Chemical Industries Ltd.) as prepared.

2.2 Fabrication and measurement of DSC

The TiO₂ layers were formed on the FTO glass by a screen printing process with 5 mm × 5 mm square area. After the printing, pre-drying at 120 °C for 20 min and annealing at 450 °C for 15 min were carried out to obtain the crystallized TiO₂ layer. The thickness of the TiO₂ layer was 12 ± 1 μm. Then, the TiO₂ layer was immersed in the dye solution (0.5 mM of N719 in acetonitrile/tert-butanol in 1 : 1 volume ratio) for 20 h for adsorption of the dye molecules to the surface of the TiO₂ completely. After rinse with ethanol, the obtained photoanode and counter electrode were sandwiched by the insertion of a 50 μm thick of thermo-melting film (Surlin, DupontTM), and then, heat treatment (120 °C, 30 s) was carried out for sealing. Next, the electrolyte composed 0.1 M of LiI, 0.05 M of I₂, 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide and 0.5 M of 4-tert-butylpyridine in acetonitrile was injected from a hole placed in the counter electrode substrate. To seal the hole with the Surlin and cover glass, the DSC test piece was obtained. The PEDOT counter electrode was prepared by an electrochemical polymerization on the FTO glass with a normal galvanostatic mode. Obtained thickness of the PEDOT film on FTO glass were estimated for ca. 35 nm to control charge density during the electrochemical polymerization. The platinum counter electrode was prepared by a magnetron sputtering on the FTO glass resulting thickness ca. 35 nm to control sputtering time. Obtained PEDOT and platinum films were characterized for surface roughness by AFM (VN-8000, KEYENCE). Arithmetic mean roughness (Ra) of the PEDOT and platinum films were estimated by measuring average values of 5 times.

The DSC performance was evaluated for the photocurrent-voltage (I-V) curve under AM 1.5 (100 mW cm⁻²) using a solar simulator (XES-40S1, SAN-EI ELECTRIC). The photocurrent was monitored during voltage step of 0.05 V/sec to obtain the I-V curve by use of a source meter (Keithley2401). The measurement temperature was controlled at 20 °C with a Peltier thermo-cooler. The solar simulator was calibrated with an illuminance meter (Konica Minolta, T10-A) before I-V measurement, to obtain the good reproducibility.

2.3 Electrochemical analysis for the counter electrodes

Electrochemical impedance spectroscopy (Solatron, 1252A Frequency Analyzer/SI1287 Electrochemical Interface) was carried out for the DSCs on open circuit condition under 100 mW cm⁻² illumination (AM 1.5) to investigate charge transfer resistance on the counter electrode in its cell. Amplitude and frequency range were 10 mV and 100 kHz–0.1 Hz. A software for fitting of impedance parameters was used as ZPlot (Ametec Scientific Instruments).

Cyclic voltammogram (CV) of the counter electrodes was measured using three-electrode system to evaluate their electrochemical behavior in the I⁻/I₃⁻ redox system. A counter electrode and a reference electrode were used as Pt mesh and Ag/Ag⁺ (consisting of Ag wire in a solution of 10 mM AgNO₃ in acetonitrile). The CV measurement was performed at potential ranged from -0.55 to +0.25 V in a 1 M LiBF₄/acetonitrile electrolyte containing 10 mM LiI, and 1 mM I₂. The potential scan rate was widely and finely changed from 5 to 500 mV s⁻¹ to estimate kinetic parameters.

Figure 1. Surface roughness of the (a) base FTO substrate, (b) sputtered platinum on FTO, and (c) PEDOT on FTO by measuring AFM.

Figure 2. Photocurrent-voltage curves for DSCs with PEDOT counter electrode (○) and with Pt counter electrode (●) in acetonitrile based electrolyte under illumination of AM 1.5–100 mW/cm².

3. Results and Discussion

3.1 Photovoltaic behavior for the DSCs

Figure 1 shows surface roughness of the PEDOT and platinum counter electrodes by using AFM. Ra of the PEDOT (10.5 nm) and platinum (12.5 nm) are approximately close. Both films were uniformly formed on the FTO substrate.

The photocurrent-voltage curve for DSCs with the PEDOT counter electrode (PEDOT-DSC) and with the Pt counter electrode (Pt-DSC) under 100 mW cm⁻² illumination (AM 1.5G) is depicted in Fig. 2. The film thickness of PEDOT and Pt is the same (35 nm). The PEDOT-DSC exhibits reasonable I-V curves as well as the Pt-DSC. In particular, the photocurrent drop (0.45 V~) for the PEDOT-DSC slightly gentler than that for the Pt-DSC, indicating lower cell

Table 1. Photovoltaic properties of DSCs with PEDOT or Pt counter electrode from photocurrent-voltage measurement.

Counter electrode	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta/\%$
PEDOT	17.8	0.662	0.668	7.88
Pt	17.7	0.662	0.653	7.65

Table 2. Impedance parameters of the DSC with PEDOT or Pt counter electrode by fitting with equivalent circuit based on impedance spectra.

Counter electrode	R_s/Ω	R_{CT-C}/Ω	R_{CT-P}/Ω	CPE		C/F	W/Ω
				$CPE-T$	$CPE-P$		
PEDOT	7.65	3.28	23.3	2.88×10^{-4}	0.805	0.046	2.14
Pt	6.87	7.05	22.0	4.97×10^{-4}	0.764	0.038	5.96

parameters obtained by fitting with the equivalent circuit are listed in Table 2. The R_{CT-C} obtained for the PEDOT-DSC is smaller than that for the Pt-DSC, indicating lower charge transfer resistance on counter electrode. The reduction reaction of I_3^- on the PEDOT counter electrode can be occurred faster than that on the Pt counter electrode in the cell. Also, W obtained for the PEDOT-DSC is smaller than that for the Pt-DSC. This is probably caused by concentration gradient of iodide species between counter electrode and photoanode. Fast reduction reaction of I_3^- on counter electrode make the concentration gradient of iodide species in the PEDOT-DSC. In addition, the CPE parameters obtained for the PEDOT-DSC is close to that for the Pt-DSC. This result probably provides that electrode porosity of the PEDOT-DSC and the Pt-DSC is similar in this study.

3.3 Estimation of electron transfer rate constant (k^0)

Figure 4 shows cyclic voltammograms obtained for the PEDOT (Fig. 4(a)) and the Pt (Fig. 4(b)) counter electrodes in the acetonitrile electrolyte containing I^-/I_3^- redox species. A redox couple is clearly observed for the both electrodes at all scan rate from

resistance of PEDOT-DSC. The DSC performances, short-circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and conversion efficiency (η) of the cells are listed in Table 1. The PEDOT-DSC shows almost same J_{sc} and V_{oc} , but slightly higher FF and η compared with the Pt-DSC. Accurately, this comparison with same film thickness of the counter electrode provides that the PEDOT-DSC found to be show essentially higher FF compared to the Pt-DSC in this study. Higher FF of PEDOT based DSCs compared to Pt based DSCs were previously reported.^{17–19,21} However, film thickness of PEDOT and Pt were not controlled in the previous reports.

3.2 Electrochemical impedance analysis for the DSCs

Electrochemical impedance spectroscopy (EIS) is performed to investigate resistance distribution of the DSC with different counter electrode. Figure 3(a) shows impedance spectra (Nyquist plots) of the PEDOT-DSC and the Pt-DSC at open circuit condition under 100 mW cm⁻² illumination (AM 1.5G). Three distinct semicircles are observed for both DSCs.^{7,11} The impedance spectra were fitted using an equivalent circuit diagram (Fig. 3(b)) to extract the impedance parameters related with reaction processes in the cells.^{11,22,25} In this circuit, R_s is the series resistance of the cell, R_{CT-C} is the charge transfer resistances on the counter electrode, R_{CT-P} is the charge transfer resistance at photoanode interface, W is the Warburg impedance attributing the diffusion of iodide species in electrolyte. C is the double layer capacitance at the electrode-electrolyte interface. CPE is the constant phase element, which is relate to interfacial capacitance reflecting the roughness of the electrodes. The impedance of CPE is described as $Z_{CPE} = 1/T(j\omega)^P$, T and P are frequency-independent parameters. The impedance

Figure 3. (a) Nyquist plots obtained for DSCs with PEDOT counter electrode (○) and with Pt counter electrode (●) at open circuit condition under illumination of AM 1.5–100 mW cm⁻². (b) Equivalent circuit diagram for fitting impedance parameters related with reaction processes in the DSC from impedance spectroscopy.

Figure 4. Cyclic voltammogram obtained for PEDOT (a) and Pt (b) counter electrodes in 1 M LiBF₄/acetonitrile electrolyte containing 10 mM LiI, and 1 mM I₂ at scan rate of 5, 10, 20, 50, 100 mV s⁻¹ (scan rates are shown in figure).

Figure 5. Redox peak separation potential (ΔE_p) as a function of square root of scan rate at cyclic voltammograms obtained for PEDOT (○) and Pt (●) counter electrodes.

5 mV s^{-1} to 100 mV s^{-1} . This redox couple is assigned to Eqs. (1) and (2).

At the high scan rate over 50 mV s^{-1} , sharp reduction peak is observed for the PEDOT electrode compared with the Pt counter electrode. This indicates that the PEDOT electrode shows higher electrocatalytic activity than the Pt electrode. In order to investigate more quantitatively, electron transfer rate constant (k^0) for the redox reaction of I_3^-/I^- on the PEDOT and Pt electrodes is estimated. Figure 5 depicts peak separation potential (ΔE_p) as a function of square root of scan rate ($v^{1/2}$) in the cyclic voltammogram at scan rate from 20 mV s^{-1} to 500 mV s^{-1} . The linear relationship is obtained for the ΔE_p vs. $v^{1/2}$ in both PEDOT ($R^2 = 0.9906$) and Pt ($R^2 = 0.9950$) electrodes. According to this result, the redox reaction of I_3^-/I^- on the PEDOT and Pt electrodes is considered to be quasi-reversible reaction.²⁶ In case of the quasi-reversible reaction, k^0 can be experimentally estimated by Nicholson plot.^{27,28}

Nicholson devised a method for determination of the k^0 by relating ΔE_p in the cyclic voltammogram. He numerically calculated the change in the ΔE_p as a function of a kinetic parameter ψ (unitless parameter), that is directly proportional to the reciprocal of the k^0 ,

$$\psi = k^0(D_O/D_R)^\alpha(RT/\pi nFD_O)^{1/2}v^{-1/2} \quad (3)$$

Here, D_O and D_R are the diffusion constant of the oxidized and reduced species, n is the number of electrons transferred per species, α is the transfer coefficient. v is the scan rate in the cyclic voltammogram. In the Nicholson's classic paper,²⁷ estimated ψ values are listed with corresponded ΔE_p values. By using the ΔE_p in cyclic voltammogram and ψ , k^0 can be estimated for redox reaction of I_3^-/I^- on the PEDOT and Pt electrodes. In this study, the D_O and D_R were estimated from Eqs. (4) and (5).

$$I_{OP} = (2.69 \times 10^5)n^{2/3}AC_O^*D_O^{1/2}v^{1/2} \quad (4)$$

$$I_{RP} = (2.69 \times 10^5)n^{2/3}AC_R^*D_R^{1/2}v^{1/2} \quad (5)$$

I_{OP} and I_{RP} are the oxidation and reduction peak currents in the cyclic voltammogram, C_O^* and C_R^* are the concentration of oxidized and reduced species in the bulk solution, A is the surface area of electrode. The α is used as 0.5 in this work.

Table 3 shows estimated k^0 values for redox reaction of I_3^-/I^- on the PEDOT and Pt electrodes by Nicholson plot, which is the plots in linear relationship of ψ vs. $v^{-1/2}$ obtained from the cyclic voltammograms (Fig. 6). From past reports,^{29,30} the k^0 for redox reaction of I_3^-/I^- was estimated ranged from 10^{-3} to $10^{-4} \text{ cm s}^{-1}$.

Table 3. Estimated k^0 values for redox reaction of I_3^-/I^- on the PEDOT and Pt electrodes by Nicholson plot (ψ vs. $v^{-1/2}$) obtained from the cyclic voltammograms.

Counter electrode	$k^0/\text{cm s}^{-1}$
PEDOT	3.47×10^{-3}
Pt	2.76×10^{-3}

Figure 6. Nicholson's kinetic parameter (ψ) vs. reciprocal of the square root of scan rate at cyclic voltammograms obtained for PEDOT (○) and Pt (●) counter electrodes.

This indicates the k^0 estimation in this study is considered to be reasonable. The k^0 on the PEDOT electrode ($3.47 \times 10^{-3} \text{ cm s}^{-1}$) was higher than that on the Pt electrode ($2.76 \times 10^{-3} \text{ cm s}^{-1}$). This result interprets that PEDOT electrode shows essentially higher electrocatalytic activity for redox reaction of I_3^-/I^- compared with Pt electrode, because it was the compared with the same film thickness. Higher cell performance of the PEDOT-DSC is attributed to the essentially higher electrocatalytic activity of the PEDOT counter electrode compared to the Pt counter electrode. It is assumed that the high electrocatalytic activity of the PEDOT counter electrode is due to the high affinity between PEDOT and iodide species. Since iodide species can be adsorbed into PEDOT surface,¹⁸ reduced activation energy for the mediator reaction is supposed.

4. Conclusions

A DSC using PEDOT counter electrode showed higher conversion efficiency, compared to a DSC using classical platinum sputtered counter electrode. From electrochemical impedance analysis, the PEDOT based cell showed lower charge-transfer resistance assigned to the I^-/I_3^- redox reduction on the counter electrode compared to the platinum based cell. More quantitatively, electron transfer rate constant (k^0) on the PEDOT electrode was remarkably estimated for the I^-/I_3^- redox reaction by Nicholson theory. The k^0 on the PEDOT electrode ($3.47 \times 10^{-3} \text{ cm s}^{-1}$) was larger than that on the platinum electrode ($2.76 \times 10^{-3} \text{ cm s}^{-1}$) at approximately same film thickness and surface roughness, indicating the PEDOT electrode shows essentially higher electrocatalytic activity.

CRediT Authorship Contribution Statement

Kenji Machida: Conceptualization (Lead)
 Kazuya Koseki: Conceptualization (Supporting)
 Shingo Takeuchi: Conceptualization (Supporting)

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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