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Communications

Doubly Extended Catalytic Surface Formed by Electrodeposition in Solid State Dye-Sensitized Solar Cells Employing Polymer Electrolyte

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Introduction

Inspired by the great promise of dye-sensitized solar cells (DSCs) as low cost and highly efficient devices, researchers in both academia and industry have given these devices considerable attention.[1] A DSC typically comprises a photoelectrode sensitized by dyes attached to a mesoporous TiO_2 layer, a counter electrode (CE) commonly composed of a platinum (Pt) catalyst, and a redox electrolyte that mediates ion transfer between the two electrodes.[2] The most recent efficiency record of ~13% for porphyrin DSCs was by a device that used liquid redox electrolytes.[3] For practical device operation under light, thermal, or bending stress, however, the inherent volatility and fluidity of liquid electrolytes requires completely hermetic sealing technology. Instead, a great deal of research has been conducted on non-fluidic electrolytes, including gel electrolytes[4-6] and solid polymer electrolytes,[7-9] as well as solid-state hole transport materials.[10-12] However, solid-state DSCs have poor energy conversion efficiency compared to liquid-state ones, mostly because of the much lower ionic conductivity of the solid polymer electrolytes.[13] In addition, when a solid polymer electrolyte is utilized, it tends to have poor contact with the CE simply because both are solid; this results in high charge transfer resistance at the CE, where the charge transfer reaction $I_3^- + 2e^- \rightarrow 3I^-$ occurs, and consequently deteriorates the energy conversion efficiency further. When a solid polymer electrolyte is used, a good avenue for overcoming the large charge transfer resistance at the CE is to increase the surface area of the catalysts, such as by forming porous CEs.[14,15]

The goal of the present work was to develop a facile and simple method to increase the effective Pt surface area of the CEs for use in solid-state DSCs incorporating polymer electrolytes, without forming porous structures, by means of pulse current electrodeposition (PCED).[16,17] Compared to direct current electrodeposition, PCED deposits layers with greater physical and chemical stability, and also allows facile size tuning. Additionally, compared to conventional thermal decomposition, PCED provides the Pt NPs with high catalytic area, and is applicable to flexible devices because it does not require high-temperature (~400 °C) processing. So far, however, the Pt-electrodeposited substrates mostly serve as CE for liquid-state DSCs based on fluidic medium such as acetonitrile, methoxypropionitrile.[16-18] Thus, discovering suitable condition of electrodeposition methods for solid polymer electrolyte DSCs can be a challenging task.

Experimental

Preparation of Counter Electrodes. Electrodeposited Pt CEs and reference Pt CEs were prepared on transparent SnO_2:F-layered conductive glass (FTO, 8 Ω/cm^2), purchased from Pilkington. Pt electrodeposition was carried out at room temperature by an Autolab PGSTAT30 Potentiostat/Galvanostat, using an aqueous precursor solution of 10 mM $H_2PtCl_6 \cdot 6H_2O$ and 10 mM KCl. The FTO glass substrate, Pt wire, and an Ag/AgCl electrode were respectively used as the working electrode, the CE, and the reference electrode. The pulse current density was varied from 15 to 90 mA/cm^2, and the on-off cycle of 0.1 s on followed by 0.3 s off was used for all samples. The total charge density was fixed at 3 C/cm^2. For comparison, a reference Pt CE was prepared by a thermal decomposition method: a 0.05 M solution of H_2PtCl_6 in isopropanol was spin coated onto FTO glass followed by sintering at 400 °C for 30 min.

Fabrication of Solar Cells. All chemicals were used without further purification. Photoanodes were fabricated by spin coating Ti(IV) bis(ethyl acetoacetato)diisopropoxide solution (2 wt% in 1-butanol, Aldrich) onto FTO glass substrates and sintering them at 450 °C for 30 min. Commercial TiO_2 paste (Ti-Nanoxide T, Solaronix) was deposited onto the FTO glasses followed by a sintering process at 450 °C for 30 min. The resulting 12-μm-thick mesoporous TiO_2 films were immersed overnight in distilled ethanolic solution carrying 0.15 mM N719 dye $(Ru(dcbpy)_2(NCS)_2$ 535-bisTBA, Solaronix).

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The electrolyte was prepared by blending PEO (M_W= 1,000,000 g/mol) with PEGDME (M_W=500 g/mol) in which the weight ratio of PEO to PEGDME was fixed at 4:6. And the molar ratio between polymers and salts, *i.e.* [-O-]:[KI]:[I_2] was fixed at 10:1:0.05. All constituents were vigorously stirred in acetonitrile which is removed after fully dissolving salts in polymers. For the fabrication of DSCs, this polymer electrolyte was first cast onto dye-adsorbed TiO_2 photoelectrodes. Then, the Pt-deposited FTO electrodes were placed onto the electrolyte film under mild pressure and both electrodes were clipped to fix them together, and were dried under vacuum conditions to fully remove the residual solvent.

Characterization Methods. FE-SEM analysis was carried out by using a scanning electron microscope (JSM 6400, JEOL, Japan). Photovoltaic performance of the DSCs was evaluated by using a Keithley Model 2400 source meter, under 1 sun illumination (AM 1.5, 100 mW/cm) provided by a solar simulator equipped with a 300 W xenon arc lamp (Newport). Light intensity was calibrated by using a reference silicon solar cell (PV Measurements Inc.). Spectra of light reflected by the CE were acquired by using a UV-vis spectrophotometer (JASCO/V-670). Impedance spectra of symmetrical Pt-Pt cells were obtained by using an IM6 (Zahner) operated over the frequency range of 1 MHz to 500 mHz at zero bias voltage in the dark. Impedance spectra were fitted by using ZView software to provide numerical values.

Results and Discussion

The PCED method has great merit in size tunability and film deposition because Pt ions can be sufficiently supplied to the substrate during the pulse current off time.[16] For the preparation of a CE deposited with Pt NPs, PCED was carried out using an on-off cycle of 0.1 s on (pulse current) and 0.3 s off (off current) applied to a fluorine-doped tin oxide (FTO) glass substrate used as a working electrode (Figure 1). The off current was fixed at 10 mA/cm^2 and the pulse current was varied from 15 to 90 mA/cm^2. The total charge density was fixed at 3 C/cm^2. For comparison, a reference Pt electrode was prepared by conventional thermal decomposition method.

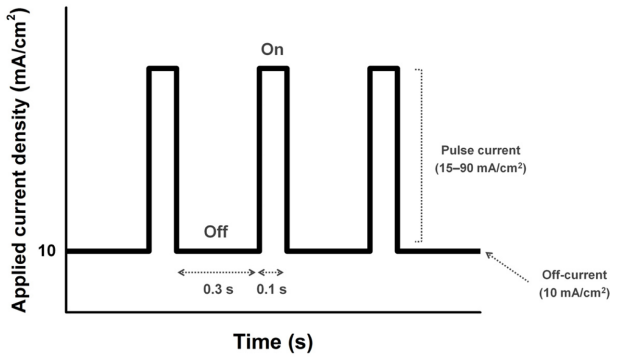

Figure 1. Concept of PCED method.

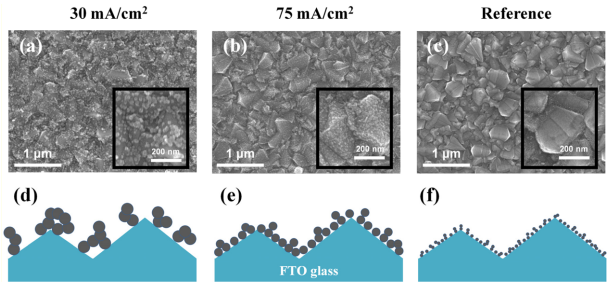

Figure 2. (a-c) SEM images and (d-f) corresponding schematic drawings of Pt NPs deposited onto FTO glass substrates by PCED and the reference thermal decomposition methods.

Deposition by means of both the PCED and reference methods formed fine films composed of small Pt NPs on the FTO glass substrate (Figure 2). SEM images revealed that both the size of the Pt NPs and the apparent surface roughness were dependent on the pulse current applied during the PCED process (Figures 2(a)-(c)). The Pt NP size was estimated to be approximately 20 and 10 nm for the PCED samples formed under pulse currents of 30 and 75 mA/cm^2, respectively, and <5 nm for the reference sample. More specifically, the Pt NPs were apparently partly aggregated under the pulse current of 30 mA/cm^2, and were not uniformly deposited over the FTO substrate. Note that dendritic growth and consequent inhomogeneous surface morphology of Pt was previously observed for PCED carried out under nonoptimal conditions.[16] However, use of the pulse current of 75 mA/cm^2 clearly mitigated the surface inhomogeneity of the deposited Pt layer; this condition produced smaller and more homogenously distributed Pt NPs, as schematically described in Figures 2(d)-(f).

To characterize the performance of the Pt-coated FTO glass samples as CEs, solid-state DSCs employing polymer electrolyte were fabricated using N719 as the dye. The electrolyte was prepared by blending poly(ethylene oxide) (PEO) with poly(ethylene glycol dimethyl ether) (PEGDME), and potassium iodide (KI), iodine (I_2).[19] The *J-V* characteristics of the DSCs were evaluated at 1 sun illumination; the results are depicted in Figure 3(a) and summarized in Table I. In the pulse current range between 15 and 90 mA/cm^2, the energy conversion efficiency (η) increased almost linearly with pulse current up to 60 mA/cm^2, and then plateaued thereafter. The same trend was observed in the short-circuit current density (J_{SC}), whereas the charge transfer resistance (R_{ct}) of the Pt-Pt symmetric cell[19,20] decreased sharply (Figure 3(b)); representative impedance spectra for the DSCs are suggested by the Nyquist plots in Figure 3(c). The representative spectra of 30 and 75 mA/cm^2 samples in Figure 3(c) were chosen before/after 60 mA/cm^2 pulse current density, *i.e.* starting point of plateau. In principle, high R_{ct} values indicate that charge transfer at the CE could become seriously suppressed, thereby reducing the photocurrent. Consistent with this, R_{ct} and J_{SC}

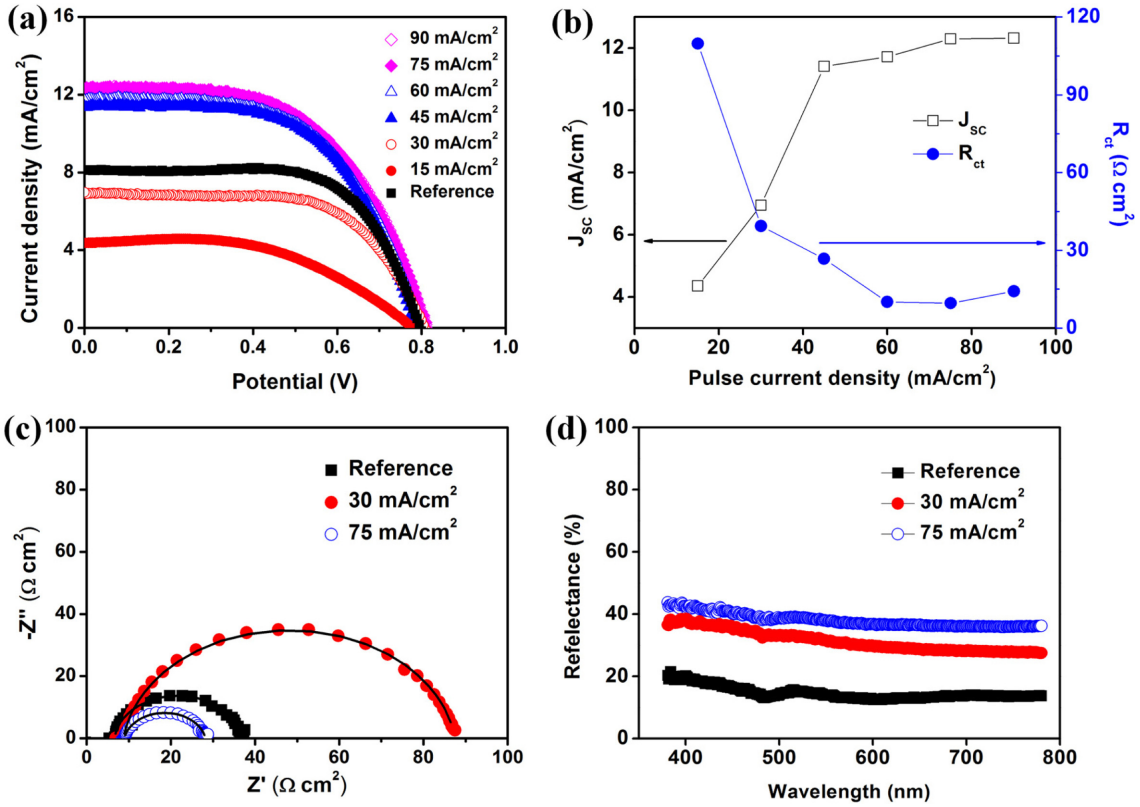

Figure 3. (a) Photovoltaic characteristics of DSCs evaluated under 1 sun illumination conditions. (b) J_{SC} and R_{ct} versus the pulse current used during CE deposition. (c) Representative Nyquist plots; fitting curves are shown as black lines. (d) Light reflectance by Pt-coated FTO substrates.

Table I. Photovoltaic Parameters of Solid-State DSCs Employing Polymer Electrolyte and CEs Deposited under Various Conditions

Sample	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
15 mA/cm^2	0.85	4.4	0.51	1.9
30 mA/cm^2	0.84	7.0	0.61	3.6
45 mA/cm^2	0.81	11.4	0.58	5.3
60 mA/cm^2	0.83	11.7	0.55	5.4
75 mA/cm^2	0.84	12.3	0.54	5.6
90 mA/cm^2	0.84	12.3	0.54	5.6
Thermal	0.79	8.1	0.67	4.3

apparently had dependencies upon pulse current that were the inverse of each other. Meanwhile, the open circuit voltage (V_{oc}) remained nearly constant and the fill factor (FF) was rather fluctuated. In particular, FF values displayed slightly lower than reference, probably attributed to a rise in ion diffusion resistance under high light illumination condition. Note that η of 5.6% was achieved at the pulse current of 75 mA/cm^2, with V_{OC} of 0.84 V and FF of 0.54; this represented an improvement of as much as 30% in terms of η relative to the reference device. This improved performance was attributed primarily to the great enhancement observed in photocurrent (from 8.1 to 12.3 mA/cm^2).

Light reflection by the CE was also measured to investigate its effects on photocurrent. The CE deposited at 75 mA/cm^2 showed light reflection of ~40% throughout the 300-800 nm spectral range, whereas the reference CE showed ~20% reflection (Figure 3(d)). This increased light reflection in CEs made by PCED may have contributed to the improvement in photocurrent to some extent. However, the reduction in R_{ct} at the surface of the CE would be much more important in enhancing the photocurrent density.

The electrical double layer capacitance (C_{dl}), which represents the catalytic surface area,[20] was readily attainable from the impedance spectra seen in Figure 3(c). It is worth noting that R_{ct} has a reciprocal relationship with C_{dl} for a given catalyst material; that is to say, high C_{dl} corresponds to low R_{ct}, which in turn corresponds to enhanced J_{SC}. When two CEs prepared at the pulse current of 75 and 30 mA/cm^2 were compared, representing the highest and lowest J_{sc}, respectively, the former showed C_{dl} of 20.0 μF/cm^2 and the latter 12.9 μF/cm^2. These results imply that the effective surface area of the Pt NPs prepared using the pulse current of 75 mA/cm^2 was almost twice that prepared by using the

30 mA/cm^2 condition, and therefore the J_{SC} for the former (12.3 mA/cm^2) is much higher than that for the latter (7.0 mA/cm^2). However, relative to the CE prepared by PCED under 30 mA/cm^2 pulse current, the reference CE exhibited higher J_{SC} (8.1 mA/cm^2) despite its lower C_{dl} of 9.3 μF/cm^2. It is thus reasonable to remark that the coarse deposition of the rather larger Pt NPs (~20 nm) formed at the 30 mA/cm^2 pulse current had the detrimental effect of reducing the effective area for charge transfer to the electrolyte.

In conclusion, to prepare CEs suitable for use in solid-state DSCs employing solid polymer electrolyte, catalytic Pt NPs were deposited on FTO glass by a PCED method, without the formation of nano- or mesoporous films. The CE fabricated under the optimized condition of 75 mA/cm^2 pulse current yielded overall energy conversion efficiency of up to 5.6% under 1 sun condition in a DSSC that used a PEO-based polymer electrolyte; this was nearly 30% higher than the 4.3% efficiency achieved by using a CE fabricated by conventional thermal decomposition. This efficiency improvement was attributed by increased short circuit current density, which in turn was caused primarily by an increase in effective surface area and partly by an increase in light reflection. Therefore, it is concluded that the use of PCED is very powerful in improving the effective surface area of the Pt NP layers of CEs used in solid-state DSCs employing polymer electrolyte, and that this PCED method can offer new possibilities in the design of flexible electrodes for polymer electrolyte-based electrochemical cells.

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