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Energy-storable Dye-sensitized Solar Cells with Interdigitated Nafion/Polypyrrole–Pt Comb-like Electrodes

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A single plate storage battery composed of Nafion-coated polypyrrole and I_3^-,I^-|Pt electrodes in an interdigitated comb-like structure was set in an energy-storable dye-sensitized solar cell (ES-DSSC). The new ES-DSSC has a simple electrochemical cell structure having a single electrolyte with a typical photoanode and a dual functional electrode assembly.

One issue in common solar cells is that the generated electric power varies with the photoirradiation strength depending on changeable weather and the incident angle of the sun. Recently, practical solar cells with a self-stabilizing function[1–4] have been constructed by the adaptation of dye-sensitized solar cells (DSSCs)[5,6] to an energy-storable dye-sensitized solar cell (ES-DSSC). A typical DSSC, which is composed of a photoanode and a counter electrode, is operated by an electrochemical reaction of I_3^-/I^-. The redox reaction is useful for combination with an electrochemical storage battery. In our first model of ES-DSSC,[2] I_3^-/I^- redox reaction is coupled with a polypyrrole (PPy) redox reaction using a cationic exchange membrane to construct a storage battery. Although the three-electrode system successfully generated and stored electricity under photoirradiation, one of the issues in the ES-DSSC was that two different electrolytes should be used in the opposite sides of the cationic exchange membrane.[2] Consequently, the durability of the cell was limited by the leakage of the two electrolytes through cationic exchange membrane. In order to overcome this issue, a novel type of ES-DSSC, which uses only a single electrolyte and a dual functional electrode assembly playing the roles of charge-storage and counter electrodes, has been designed. This storage battery component is composed of Nafion®-coated PPy and I_3^-,I^-|Pt electrodes in an interdigitated comb-like structure.

The cell configuration of the newly designed ES-DSSC is shown in Figure 1. The photoanode was composed of an N719-dye-adsorbed TiO_2-nanoparticle layer (ca. 6 µm, 10 mm × 10 mm) formed on a fluorine-doped tin oxide (FTO) glass substrate ($10\,\Omega\,sq^{-1}$, Nippon Sheet Glass). The counter Pt electrode and charge-storage PPy electrode were formed in two interdigitated comb-like electrodes, individually. At first, two interdigitated comb-like electrode patterns were formed on an FTO substrate with a mask by chemical etching with an aqueous HCl solution and Zn powder. The width of each electrode finger was 0.875 mm, and the distance between two adjacent fingers in a comb was 1.225 mm. The Pt layer was sputtered on one of the combs. Then, the PPy layer was electrochemically deposited on the other comb. The electropolymerization was carried out in a propylene carbonate solution containing 0.1 M pyrrole and 0.1 M $LiClO_4$ under a constant current flow of $0.5\,mA\,cm^{-2}$ using a three-electrode cell. The Nafion® layer, which is an anionic polymer, was deposited on the PPy layer by electrophoresis. The $1\text{-}cm^2$ electrophoresis cell, which contained a 5 wt % Nafion® perfluorinated resin solution (274704, Aldrich) in the gap of 1 mm between the PPy working electrode and a counter electrode, was biased with +30 V for 1 min. After the deposition, the electrode was thermally annealed at 120 °C for 5 min. Finally, the electrode was pretreated with a 0.5 M $LiClO_4$ solution in acetonitrile to exchange H^+ with Li^+. Himilan® (DuPont–Mitsui polychemical Co., Ltd.) films with a total thickness of 0.6 mm were used as the sealant. The electrolyte solution of the ES-DSSC was a 0.5 M LiI and 0.05 M I_2 solution in acetonitrile.

Although the Pt area decreased by more than half of the total substrate area, the diffusion distance of the ionic species was not so elongated by the use of the interdigitated pattern electrode. The photocharge–discharge scheme is shown in Figure 2. A part of the generated electrons in the photoanode under illumination were stored in the PPy electrode, whereas PPy simultaneously

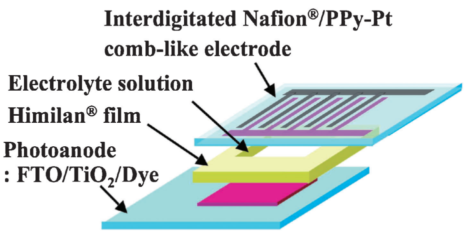

Figure 1. Cell configuration of the ES-DSSC with the interdigitated Nafion®/PPy–Pt comb-like electrode.

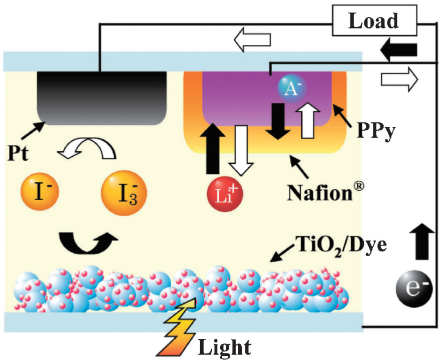

Figure 2. Operation scheme in the ES-DSSC with the interdigitated Nafion®/PPy–Pt comb-like electrode; photocharge (black arrows) and discharge (white arrows).

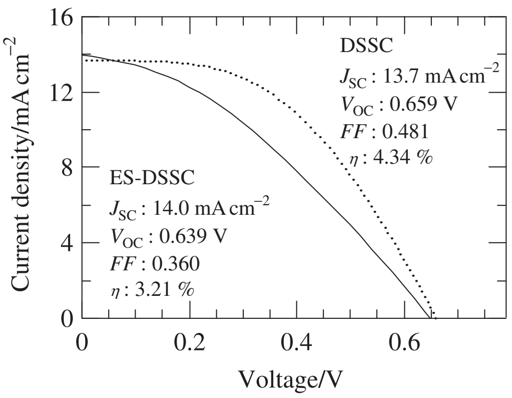

Figure 3. *I–V* characteristics of the ES-DSSC (bold line) and a conventional DSSC (dotted line) with the same cell gap.

released the anion dopant (A^-: ClO_4^-). At the same time, I_3^- was stored in the electrolyte, and Li^+ moved toward the PPy layer through the Nafion® film to remain neutral. The discharge reaction took place by the process opposite to the photocharge reaction.

Photovoltaic performance was evaluated by measuring the *I–V* curve between the photoanode and Pt electrode of the ES-DSSC under the illumination of 100 mW cm^{-2} (AM 1.5). Figure 3 shows the *I–V* characteristics of the ES-DSSC and a normal DSSC, wherein the area of the Pt counter electrode is the same as that of the photoanode. Both cells were found to yield almost the same short-circuit photocurrent densitiy (J_{SC}) values. In a separate experiment wherein the area of the Pt layer in the counter electrode of the DSSC was halved (10 mm × 5 mm), the resulting J_{SC} value was only half that of the original DSSC setup. Thus, the interdigitated electrode structure can effectively reduce the I_3^- diffusion distance.[7] The open-circuit voltage (V_{OC}) in the ES-DSSC is slightly lower than that in the DSSC. Fill factor (*FF*) values in the ES-DSSC significantly decreased compared with that in the DSSC. The lower *FF* in the ES-DSSC probably originate from the charge-transfer resistance of the Pt electrode due to the smaller Pt area. The total photoelectric conversion efficiencies (η) of 3.21 and 4.34% were obtained in the ES-DSSC and DSSC, respectively. In order to achieve the comparable performance with the DSSC, the specific Pt area must be enlarged to reduce the charge-transfer resistance. Furthermore, the decrease of the cell gap together with finger width and the finger interval in the interdigitated electrode is necessary to enhance J_{SC}.

Figure 4 gives the discharge voltage curve of the ES-DSSC using the 1 C cm^{-2} electropolymerized PPy electrode. After 30 min of photocharge without load, the cell was discharged by a constant current of 30 µA cm^{-2} flowing between the Pt and PPy electrodes. The maximum discharge capacity of 37.8 mC cm^{-2} was obtained in the cell. This value was half that of the ES-DSSC with the mesh-type charge-storage electrode. This is because the PPy characteristics significantly depend on the substrate properties used for electropolymerization. The coulomb efficiencies of about 20–30% were obtained in the photocharge/discharge processes because of the self-discharge reaction with I_3^- leaked through the Nafion® layer. The ES-DSSC with the interdigitated electrode cannot store a large amount of charge due to the smaller active area, but it is useful for low-power consumption applications. In the sealed ES-DSSC, the stable photocharge/discharge cycles were repeated 70 times.

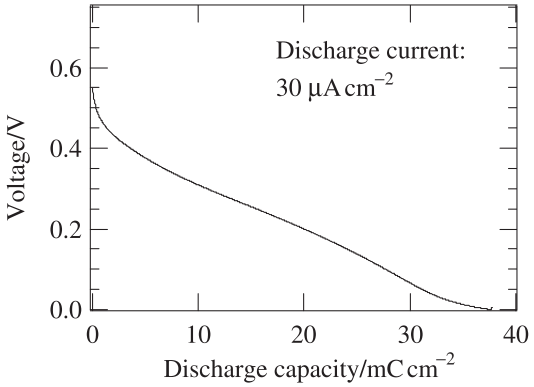

Figure 4. Discharge voltage curve of the ES-DSSC with the 1 C cm^{-2} electropolymerized PPy electrode.

In conclusion, the ES-DSSC with Nafion®-coated polypyrrole and Pt electrodes in the interdigitated comb-like structure gave a short-circuit photocurrent density as high as that of a conventional DSSC. This type of ES-DSSC can be used for small-scale electric storage applications and also for temporal output power stabilization of solar cells. Since the ES-DSSC has the same geometry and electrolyte as conventional DSSC, it can be applied to the various existing DSSC systems.

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References

1 T. Murakami, N. Kawashima, T. Miyasaka, *Chem. Commun.* **2005**, 3346.
2 H. Nagai, H. Segawa, *Chem. Commun.* **2004**, 974.
3 Y. Saito, S. Uchida, T. Kubo, H. Segawa, *ECS Trans.* **2008**, *16*, 27.
4 Y. Saito, S. Uchida, T. Kubo, H. Segawa, *Thin Solid Films* **2010**, *518*, 3033.
5 B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
6 J. M. Kroon, N. J. Bakker, H. J. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Würfel, R. Sastrawan, J. R. Durrant, E. Palomares, H. Pettersson, T. Gruszecki, J. Walter, K. Skupien, G. E. Tulloch, *Prog. Photovoltaics Res. Appl.* **2007**, *15*, 1.
7 N. Papageorgiou, C. Barbé, M. Grätzel, *J. Phys. Chem.* **1998**, *102*, 4156.