

## Energy-storable dye-sensitized solar cell with a polypyrrole electrode†

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A three-electrode-type solar-rechargeable battery, energy-storable dye-sensitized solar cell (ES-DSSC), has been constructed by the hybridization of a typical Grätzel cell and a conducting polymer charge-storage electrode; efficient photo-charging can be accomplished by visible-light irradiation.

Dye-sensitized solar cells (DSSCs)<sup>1–5</sup> have attracted much attention over the past decade because of their low production cost and their relatively high performance.<sup>6</sup> Since DSSCs provide colorful and/or flexible solar cells,<sup>4,7–9</sup> they are expected to open a new use of solar cells. Among DSSCs, the Grätzel cell is recognized as an epoch-making system as a result of its record cell efficiency;<sup>4</sup> however, there is still scope for improvement not only in the durability but also in the power stability. To achieve the power stability under fluctuating ambient solar irradiation, we focused on the chemical process of the DSSC as a typical photoelectrochemical cell (PEC).<sup>10</sup> In a PEC, incident light-energy is first converted into chemical energy, and it then produces electricity. The chemical energy-storage process, which is very different from that of conventional silicon-based solar cells, offers a great advantage when making a storage cell. With this in mind, we developed a novel type of solar-rechargeable battery, an 'energy-storable dye-sensitized solar cell (ES-DSSC)', by hybridizing a typical Grätzel cell and a conducting polymer storage cell. The ES-DSSC can store energy by photo-charging under visible-light irradiation and output the electrical power even in the dark.

The configuration of the ES-DSSC is a bridging three-electrode system<sup>11,12</sup> with a charge-storage electrode (Fig. 1). Compartment A is a part of the DSSC, and compartment B is a part of the charge-storage electrode. Each element of compartment A was selected

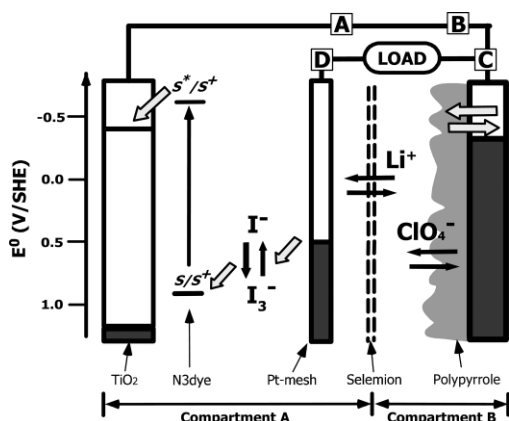


Fig. 1 Outline of the mechanism of the ES-DSSC. White arrows represent the electron transfer at the interfaces. Each set of black arrows represents the diffusion of ionic species.

from a typical Grätzel cell. As a photoelectrode, a Ru-complex dye [N3dye: *cis*-Ru<sup>II</sup>(LH<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>, LH<sub>2</sub> = 2,2'-bipyridyl-4,4'-dicarboxylic acid] adsorbed meso-porous TiO<sub>2</sub> (layer thickness: *ca.* 10.8 nm, particle size: *ca.* 30 nm in diameter, see SEM picture in ESI†) on an FTO electrode (Nisinoda Electronics Co.) was used. The counter electrode was a Pt-mesh electrode (1 cm × 1 cm, 100 mesh). The electrolyte solution of compartment A was 0.5 M lithium iodide (LiI) and 0.05 M iodine (I<sub>2</sub>) dissolved in propylene carbonate (PC). In compartment B, polypyrrole (PPy) on ITO (Evers Co.) was used as a charge-storage material. PPy is a useful material for a polymer storage battery.<sup>13–17</sup> The PPy-coated ITO electrode (apparent surface area: 1 cm<sup>2</sup>) was prepared under galvanostatic conditions at 50 μA cm<sup>-2</sup> from a 0.1 M pyrrole and 0.1 M LiClO<sub>4</sub> PC solution. The polymerization volume of pyrrole was regulated by electropolymerization charges of 50, 100 and 200 mC cm<sup>-2</sup>. The PPy film showed a reversible voltammogram with sharp peaks at about -0.35 V *vs.* SCE (Fig. 2), indicating a reversible doping/undoping reaction,<sup>16</sup> which is the suitable electrochemical behavior for the charge-storage. The electrolyte solution of compartment B was a 0.5 M LiClO<sub>4</sub> PC solution without monomeric pyrrole. Compartment A and B were separated by a low-resistance cation-exchange membrane, Selemion (Asahi glass Co., Ltd.). The cell was sealed using 2 mm-thick silicon rubber to separate each electrode.

Under AM1.5 irradiation (Solar Simulator CEP-2000, Bunkohkeiki Co., Ltd.), the photocurrent-voltage curve (see ESI†) and cell performance (energy conversion yield: *ca.* 0.5–1%) of the ES-DSSC were nearly identical to that of the DSSC without a charge-storage electrode. The open circuit voltage (*V*<sub>oc</sub>) of the ES-DSSC was *ca.* 700–800 mV by the use of PC solution, although it depended upon the solvent conditions. When the redox potential (*E*<sub>redox</sub>) of the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> under photoirradiation was kept at about +0.30 V *vs.* SCE, the electron from the conduction band of TiO<sub>2</sub> was considered to have a negative potential of *ca.* -0.50 to -0.40 V *vs.* SCE. Since the redox potential of the PPy estimated from cyclic voltammetry (CV) was about -0.35 V *vs.* SCE, the dye-

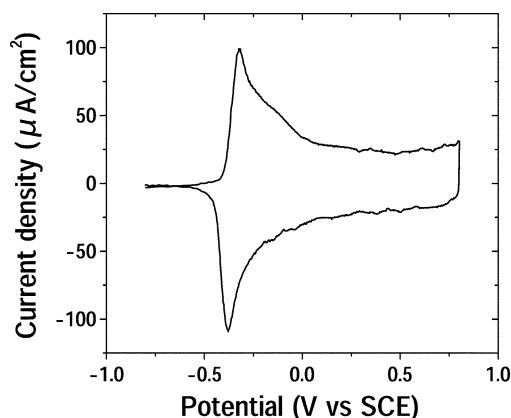


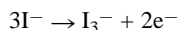
Fig. 2 Cyclic voltammogram of PPy film on an ITO electrode in 0.5 M LiClO<sub>4</sub>/PC. The scan rate is 5 mV s<sup>-1</sup>.

sensitized TiO<sub>2</sub> has sufficient potential to inject the electron to the doped PPy film.

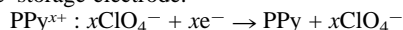
Under photoirradiation without an external load (the open circuit between C and D in Fig. 1), the photoexcited N3dye injected the electron to TiO<sub>2</sub>, and the electron was transferred and stored by the PPy in compartment B. On the other side, the oxidized N3dye received the electron from I<sup>-</sup> in compartment A, and then I<sup>-</sup> was oxidized to I<sub>3</sub><sup>-</sup>. After sufficient photoirradiation, the PPy film was completely de-doped and the charge was balanced to the oxidation of I<sup>-</sup>. The absorption spectrum of the PPy film after illumination for 30 min under the AM1.5 irradiation (Fig. 3) indicated an almost neutral state.<sup>17</sup> This result confirmed that the energy storage was accomplished by the undoping of the PPy film. In a sufficiently 'photo-charged' cell, the output current was obtained between the counter electrode and the charge-storage electrode even in the dark. The output current was due to the electrochemical doping process of undoped PPy film by I<sub>3</sub><sup>-</sup>. When A-B was open in the charged cell, the output was also obtained. In these processes, photo-charging and discharging is accomplished as the following reactions.

#### Photo-charging process

Photo electrode:

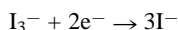


Charge-storage electrode:



#### Discharging process

Counter electrode:



Charge-storage electrode:



After the photo-charging of the ES-DSSC,  $V_{oc}$  was kept at more than a few hundred mV in the dark. Although the  $V_{oc}$  of the discharged cell was very low, it gradually increased under ongoing illumination. According to the photo-charging time,  $V_{oc}$  was kept at a higher voltage and the keeping period of  $V_{oc}$  was elongated, indicating the accumulation of the electrons. After 30 min of photo-charging, the  $V_{oc}$  was kept over about 600 mV for more than 10 min, which corresponds to the maximum difference of the  $E_{redox}$  between the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple and the PPy doping/undoping redox potential. Fig. 4 shows the charged electricity estimated from the discharge current in the dark as a function of the photo-charging times for various polymerization amounts of PPy. The stored charge of the ES-DSSC increased with the increase in the photo-charging time. Additionally, the charged electricity of the ES-DSSC increased with the increase in the polymerization amount of PPy. For the PPy of the 50 mC cm<sup>-2</sup> polymerization, the maximum charged value was 1.91 mC cm<sup>-2</sup> at 30 min photo-charging. Since the ideal charge capacity of the PPy film estimated from the CV

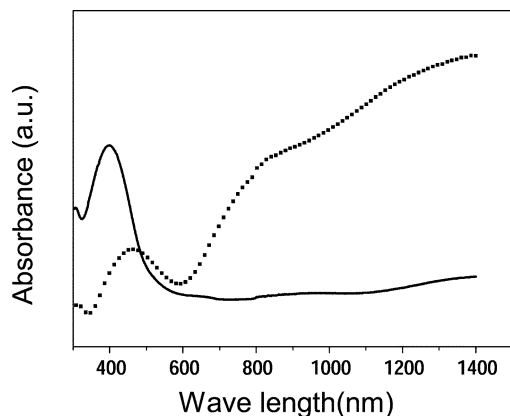


Fig. 3 Absorption spectra of PPy film before (···) and after (—) illumination for 30 min.

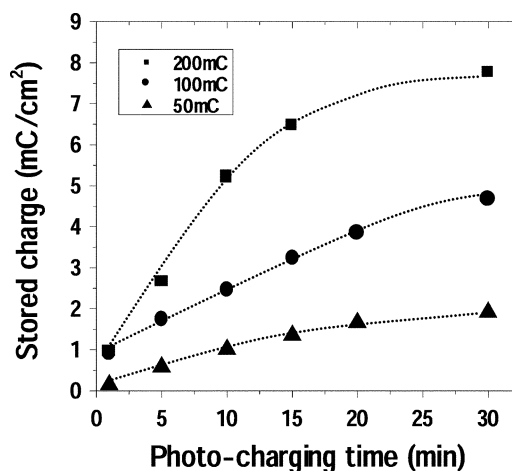


Fig. 4 Stored charge vs. various periods of photo-charging on PPy films. The charge depends on the polymerization electricity (▲: 50 mC, ●: 100 mC, and ■: 200 mC).

data in Fig. 2 was about 8.5 mC cm<sup>-2</sup>, the charge-storage efficiency of the ES-DSSC was up to 22%. The storage efficiency was kept during more than ten charging/discharging cycles (ESI<sup>†</sup>). However, the storage efficiencies decreased with the increase in the polymerization amount of the PPy. This result means that the growth of the PPy film thickness prevented the PPy from an overall doping/undoping process. The storage efficiencies could be improved by the structural control of the PPy film and the enhancement of the ionic mobility in the cation-exchange membrane. Although the many photoelectrochemical storage cells (PESCs) reported to date include the photocorrosion reaction of the semiconductor photoelectrodes, our system did not include such a corrosion process. Further improvements in efficiency and capacity are in progress.

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