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

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Dye-sensitized solar cells (DSSCs) have attracted much attention because of the low production cost, the relatively high performance, and the application to the colorful and/or flexible solar cells. In this study, 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 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. As a photoelectrode, N3dye adsorbed meso-porous TiO<sub>2</sub> prepared on an FTO-glass electrode was used. The counter electrode was a Pt-mesh electrode (1cm×1cm, 100mesh). The electrolyte solution of compartment A was 0.5M LiI and 0.05M I2 dissolved in propylene carbonate (PC). In compartment B, polypyrrole (PPy) on ITO prepared under galvanostatical conditions at  $50\mu$ A/cm<sup>2</sup> from a 0.1M pyrrole and 0.1M LiClO<sub>4</sub> PC solution was used as a charge-storage material in 0.5M lithium perchlorate (LiClO<sub>4</sub>) PC solution. The polymerization volume of pyrrole was regulated by electropolymerization charges of 50, 100 and 200 The PPy film showed a reversible  $mC/cm^2$ . voltammogram (Fig.2) with sharp peaks at about -0.35V vs. SCE, indicating a reversible doping/undoping reaction, which is the suitable electrochemical behavior for the charge strage from the conduction band of the TiO<sub>2</sub>. Compartment A and B were separated by a lowresistance cation-exchange membrane, Selemion (Asahi glass Co., Ltd.).

Under AM1.5 irradiation, the photocurrentvoltage curve of the ES-DSSC was nearly identical to that of the DSSC without a charge-strage electode. The open circuit voltage (Voc) of the ES-DSSC was 700-800mV. It was confirmed that the ES-DSSC had comparable performance to the conventional DSSC. Under photoirradiation without an external load, the photoexcited N3 dye injected the electron to the conduction band of  $TiO_2$ , and the photogenerated electron was transfered and stored by the PPy in compartment B. On the other side, the oxidized N3 dye received the electron from  $I^-$  in compartment A, and then  $I^-$  was oxidized to  $I_3^-$ . After the sufficient photoirradiation, the PPy film was completely de-doped and the charge was balanced to the oxidation of  $I^-$  to  $I_3^-$ . 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, which can electrochemically be oxidized by  $I_3^-$ . When A-B was open, the output was also obtained. After the photo-charging of the ES-DSSC, Voc was kept at more than a few handred mV in the dark. According to the photo-charging time, Voc was kept at higher voltage and

the keeping period of Voc was elongated, indicating the accumulation of the electron. Figure 3 shows the charged electricity estimated from the discharge current in the dark as a function of the photo-charging times for various polymerization volumes 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 volume of PPy.

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## Reference

1) H. Nagai. and H. Segawa, *Chem. Commun.* 974-975, **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.





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



**Fig.3** Stored charge by various periods of photo-charging on PPy films. The charge depends on the polymerization electricity (  $\blacktriangle$ : 50mC,  $\bigoplus$ : 100mC, and  $\blacksquare$ : 200mC).