The enhancement of dye adsorption in dye-sensitized solar module by an electrical adsorption method

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ABSTRACT

Dye-sensitized solar cell (DSC) has been considered as a strong alternative to conventional photovoltaic devices. The highest efficiency reached over 12%. Therefore, recent DSC researches extended the scope of the investigation such as the scaling-up and commercialization. In this work, the electrical dye-adsorption method was proposed for the faster dye-adsorption. Fast dye-adsorption is considerably effective to enhance the productivity of DSC because adsorption process takes the longest time in the whole process. This work focused on the analysis of electrical adsorption process and its application to a large DSC module as a real power source. The effect of electrical adsorption was confirmed by the change of photocurrent and absorbance of dye-dissolved solution. The proposed process was applied to large DSC modules and performance dependence was investigated according to the adsorption time. After the dye-adsorption for 6 h, an efficiency of a DSC module electrically dye-adsorbed was 51.5% higher than that of a DSC module conventionally dye-adsorbed. As a result, the adsorption time of DSC module was much shortened from 18 to 6 h by the proposed method.

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1. Introduction

Since Grätzel developed a dye-sensitized solar cell (DSC) in 1991 [1], it has been considered as a possible alternative to conventional photovoltaic devices based on silicon or compound semiconductors [1–5]. Due to its advantages of high efficiency, simple fabrication process, low production cost and a short energy-payback time, DSC has been intensively studied in a couple of decades at various research fields such as physics, chemistry, materials, electronics, and so on [6–12]. Continuous researches have led to the enhancement of performance and the highest efficiency exceeded 12% recently [13]. As the performance of a small cell became higher, DSC researches extended the investigation scope, i.e. scaling-up and commercialization [14–19]. The development of cheaper materials, the simplification of manufacture process, and the improvement of long-term stability were investigated with this tendency [20–22]. We also tried to reduce the dye-adsorption time using an electric field [23]. Some researches reported fast dye-adsorption methods. They accelerated dye-adsorption speed using pressurized CO_2, controlled dye concentration and adsorption temperature [24–28]. High concentration of dye deserves to have fast dye adsorption but it is not helpful for DSC to commercialize because the concentration is not economical. High adsorption temperature also had fast adsorption with active molecular motion. However, Sauvage et al. reported that lower adsorption temperature had better performance with decreased charge recombination and low desorption rate [29]. Pressurized CO_2 method had relatively complicated process despite its fast adsorption. In this work, for the faster dye-adsorption, high voltage was applied to plate electrodes. Then, external electric field vertically formed into the dye solution and the density of ionized dye molecules was raised around TiO_2 layer and the dye-adsorption process became faster. This method is more effective with low dye concentration and applicable at low adsorption temperature. It is much simpler than above methods. This method is also applicable to not only Ru dye but also other ionized dye solution. Here, the effect of electrical adsorption was demonstrated in cases of large modules as well as small cells. The enhancement on the dye-adsorption of large modules plays an important role in the practical manufacture of DSC because modules of wide area have much longer adsorption time and the enhancement of modules is directly linked with the commercialization. The characterization of electrical adsorption and the application of large DSC modules were conducted as a research for the commercialization. For the exact comparison of dye-adsorbed amount, desorbed dye molecules were analyzed. It could confirm the influence of proposed dye-adsorption method because possible experimental errors from counter electrode and electrolyte were excluded. After that, the electrical adsorption was examined with large DSC modules (12 cm²) having grid electrodes and its influence was investigated. To verify the improvement of proposed dye-adsorption method, the photovoltaic performance and the absorbance spectra were examined.

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2. Experimental details

DSC modules were fabricated as follows. Fluorine-doped tin oxide (FTO) substrates (13 Ω per sq., Hartford Glass Co. Inc.) were used as the transparent conductive oxide to make the photo and counter electrodes. They were cleaned by sonicating in ethanol and dried using a stream of nitrogen. For grid electrodes, silver paste (590-G, Electro-Science Laboratories, Inc.) was printed on the FTO substrate and dried at 125 °C for 10 min and sintered at 450 °C for 30 min consecutively. For the photo electrode, a uniform and nano-porous TiO_2 (Ti-Nanoxide T/SP, Solaronix) layer with a thickness of approximately 50 μm was pasted onto the FTO substrate by the doctor blade method. The prepared film was sintered at 450 °C for 30 min, and then its thickness was lowered to 8 μm. The FTO/TiO_2 electrodes were soaked in a 0.2 mM N719 dye (cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-discarboxylato)-ruthenium(II)-bis-tertabutylammonium, $RuC_{58}H_{86}N_8O_8S_2$) solution with and without an electric field. Adsorption time was varied from 1 to 24 h. Fig. 1 shows the schematic of electrical adsorption for illuminating. High voltage was applied to plate electrodes for the formation of an electric field. Electric field (E) is changed by the distance (d) between plate electrodes as well as applied voltage (V) according to 'E = V/d'. Here, the distance was therefore fixed at 15 mm and electric field was controlled by adjusting applied voltage from 0 to 10 kV. For the avoidance of dye-adsorption on grid electrodes, they were covered with mask during the adsorption. Excess dye molecules were removed by rinsing with ethanol after dye-adsorption. For the desorption test, dye-adsorbed TiO_2 films were soaked in 0.1 M aqueous NaOH solution and all of the adsorbed dye molecules were dissolved in the solution. Absorbance of dye-dissolved solution was measured for the comparison of the adsorbed dye amount. Absorbance spectra were optically measured from 400 to 900 nm by an ultraviolet-visible (UV-VIS) spectrophotometer (U2000, Hitachi). For the counter electrode, a 0.1 μm thick platinum layer was sputtered on FTO substrate. RF sputter deposition was operated at a working pressure of 0.37 Pa of Ar, with a power of 150 W. After that, the photo and counter electrodes were sealed using a thermoplastic hot-melt sealant (SX 1170-60, Solaronix) with a thickness of 60 μm. The sealed module was completed by injecting a redox electrolyte through a pre-drilled hole into the counter electrode. The redox electrolyte consisted of 0.5 M LiI, 0.05 M I_2 and 0.5 M 4-tertbutylpyridine in acetonitrile. Another DSC module was fabricated as a reference under identical process except for the dye-adsorption process.

Before their characterization, the modules were stored in the dark under open-circuit conditions for 24 h to allow the electrolyte to penetrate into the TiO_2 pores. The photovoltaic performance was measured under 1 sun (air mass 1.5, 100 mW/cm^2) by a source meter (Model 2400, Keithley Instrument, Inc.). During their irradiance and characterization, the cells were covered with a black mask fitting the active area of the cell. The active area was 5 rectangles of 2.4 cm^2 (4.0 cm × 0.6 cm) and total irradiated cell area was 12.0 cm^2. Current–voltage (I–V) characteristic curves and Eq. (1) were used to calculate the short-circuit current (I_{SC}) and density (J_{SC}), open-circuit voltage (V_{OC}), fill factor (FF) and an overall efficiency (η).

$$\eta = \frac{P\max}{Pin} \times 100 = \frac{FF \cdot Voc \cdot Jsc}{Pin} \times 100 (\%) \qquad (1)$$

3. Results and discussion

Fig. 2 shows the change in efficiencies of electrically dye-adsorbed DSCs according to the applied voltage [20]. Dye-adsorption time was 4 h. As can be seen, the performance was enhanced with an electric field. DSCs were not deteriorated by high voltage below 2 kV. However, device was broken down from 5 kV and DSCs were also deteriorated. Accordingly, DSC with 2 kV had the best performance without any deterioration and all applied voltage was fixed at 2 kV in subsequent experiment. In this process, the change of adsorption temperature by electric field was also considered because the temperature was one of important factors which affected the dye-adsorption speed as mentioned above. However, the change of adsorption temperature was less than 5 °C with 2 kV of applied voltage. That is, it was confirmed that the temperature did not affect the dye-adsorption in this electrical adsorption process.

Performance dependence on the adsorption time with conventional and proposed methods was investigated. Figs. 3 and 4 show the change in J_{SC} of DSCs and UV-VIS spectra of dye-dissolved NaOH solution from FTO/TiO_2/dye electrodes with conventional and electrical dye-adsorption methods under various adsorption times [22]. Irradiated area was 0.25 cm^2. Here, 'C' and 'E' means conventional and electrical adsorption methods, and the number means adsorption time (h). The dye-adsorption time of small cells was much decreased from 12 to 5 h. However, other factors such as the carrier transport in the electrolyte and the electrochemical catalytic activity were not excluded perfectly in this comparison. Therefore, the analysis of desorbed dye amounts was so effective for the exact comparison because only dye-adsorbed electrodes were used. The peak values were overall low because the concentration of dye molecules was lowered by watery NaOH solution. However, the difference of absorbance according to the adsorption method and time was clear. Inset shows the peak value at 500 nm for illuminating. Dye adsorption of proposed method was much faster than that of conventional method. In detail, dye amount electrically adsorbed for 1 h (E1) was more than that conventionally adsorbed for 2 h (C2) and dye amount electrically adsorbed for 4 h (E4) was almost equal to that conventionally adsorbed for 12 h (C12). These results support the comparison of photocurrent in Fig. 3 because the photocurrents of DSCs with conventional and electrical adsorption were also saturated at that time. Therefore,
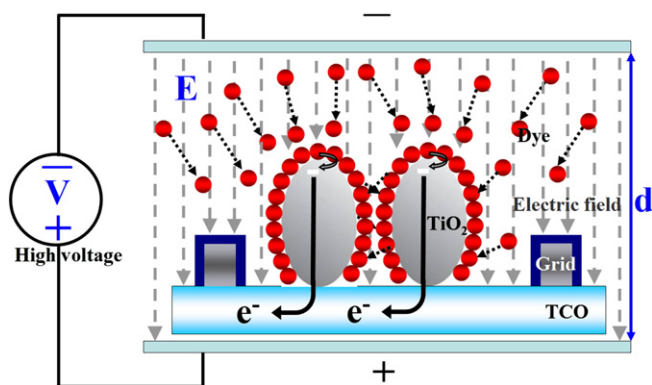

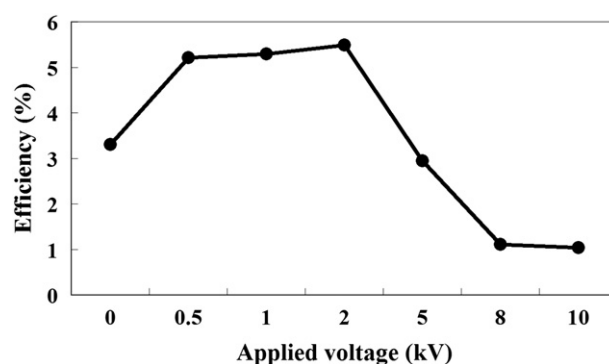**Fig. 1.** The schematic of electrical dye-adsorption process with DSC module.

Fig. 2. The change in efficiencies of electrically dye-adsorbed DSCs with various applied voltages.