Surface treatment of dye-sensitized solar cell using dielectric barrier discharge

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Abstract— **Dye-sensitized solar cell (DSSC) is receiving increasing attention as low-cost photovoltaic device. The DSSC has a nanoporous TiO_2 electrode made by sintering a TiO_2 paste applied on a conductive glass plate at 450-550 °C. To improve the performance of the TiO_2 electrode, we have developed surface treatment of the TiO_2 electrode using dielectric barrier discharge (DBD). The DBD treatment improves the energy conversion efficiency, η, of DSSC by a factor of 1.1. In addition, the DBD treatment has an effect of lowering the sintering temperature, T_s, of TiO_2 paste. Without the DBD treatment, η decreases with T_s and becomes 0% for $T_s \leq 300$ °C. On the other hand, with the DBD treatment, $\eta = 0.8\eta_0$ for $T_s = 300$ °C and $\eta = 0.3\eta_0$ for $T_s = 150$ °C, where η_0 is the energy conversion efficiency for DSSC sintered at 450 °C without the DBD treatment. The DBD treatment is also applied to plastic substrate DSSC in addition to the glass substrate DSSC. However, the DBD treatment causes damage to the TiO_2 electrode and cannot be applied to the plastic substrate DSSC. More moderate DBD treatment is required for the plastic substrate DSSC to avoid the damage on the TiO_2 electrode.**

INTRODUCTION

Dye-sensitized solar cell (DSSC) is one of next-generation solar cells. In Japan's PV roadmap towards 2030 (PV2030+) by New Energy and Industrial Technology Development Organization (NEDO), its cell conversion efficiency is targeted at 18% by 2025. To achieve this target, much effort is required because the present highest conversion efficiency is only 11.4% [1]. To improve the energy conversion efficiency, we have developed surface treatment of DSSC photoelectrode using corona discharge and dielectric barrier discharge (DBD) [2-4]. The DSSC photoelectrode consists of nanoporous dye-sensitized TiO_2 film produced as follows.

(i) TiO_2 paste containing TiO_2 nanoparticles, organic binder, and solvent is applied on a transparent conductive glass or plastic substrate.

(ii) The applied TiO_2 paste is sintered for evaporation of the organic binder and the solvent and for necking of TiO_2 nanoparticles. The sintering temperature is 450 °C for the glass substrate and 150 °C for the plastic substrate (plastic is not heat-resistant).

(iii) The resulting nanoporous TiO_2 film is dipped into dye solution to be colored.

The DBD treatment is applied between (ii) and (iii) processes. It results in decrease of oxygen vacancies on the TiO_2 surface, acceleration of the necking of TiO_2 nanoparticles, and increase in specific surface area and hydrophilicity on the TiO_2 surface leading to increase in dye adsorption on the TiO_2 surface [3, 4]. All these effects improve energy conversion efficiency.

Since the sintering temperature of plastic substrate (150 °C) is not sufficient for the evaporation of the organic binder, a binder-free TiO_2 paste is often used for the plastic substrate. The energy conversion efficiency of the plastic substrate DSSC is much lower than the glass substrate DSSC due to the low sintering temperature and the lack of organic binder. Although the plastic substrate DSSC has many advantages (low-cost, lightweight, and flexible), it is not widely used due to its low energy conversion efficiency. The DBD treatment can be applied to the plastic substrate DSSC as well as the glass substrate DSSC because it is a low-temperature process. In this paper, our recent development of the DBD treatment on the glass and plastic substrate DSSCs is presented.

EXPERIMENT

A. Glass substrate DSSC

The glass substrate DSSC is prepared as follows. TiO_2 paste (JGC Catalysts and Chemicals PST-18NR) is applied on a transparent conductive glass substrate (AGC Fabritech, fluorine doped tin oxide: FTO, 20 Ω/sq.). The area of the TiO_2 film is 5×5 mm^2. It is then sintered at a constant temperature between 150 and 500 °C. The sintering temperature is usually around 450 °C, but in the present experiment various sintering temperatures are examined. The sintering time is 72, 24, 10, 5, and 1 h for sintering temperature of 150, 200, 250, 300, and above 400 °C, respectively. The resulting TiO_2 film is treated using DBD. See section II-C for details of the DBD treatment. The thickness of the resulting TiO_2 film is about 4 μm. After the DBD treatment, the sample is immersed in a dye solution (Solaronix N-719, 1.9 mM/L in ethanol) for 24 h at 25 °C. Finally, the substrate is glued to a platinized counter electrode with a spacer sheet, and electrolyte (Solaronix Iodolyte AN 50) is injected between the substrate and the counter electrode.

B. Plastic substrate DSSC

For the plastic substrate DSSC, binder-free TiO_2 paste (Peccell Technologies PECC-01-06) is applied on a transparent conductive polyethylene naphthalate (PEN) substrate (Peccell Technologies PECF-IP, indium-tin-oxide: ITO, 13 Ω/sq.). The area of the TiO_2 film is 5×5 mm^2. It is then sintered at 150 °C for 1 h and treated using DBD.

C. DBD treatment

The DBD occurs between a HV plane electrode covered with 2-mm-thick glass plate and a ground plane electrode in a closed chamber. The distance between the glass surface and the ground electrode is 2.2 mm. An ac high voltage is applied to the electrodes. Two types of DBD treatment are used: “direct” and “indirect” DBD treatments. In the direct treatment, the sample is placed on the ground electrode so that the TiO_2 film is subjected to the DBD. The area other than the TiO_2 film (5×5 mm^2) is masked with insulating rubber to avoid the DBD generation. The chamber is filled with air or air-like mixture (dry or humid O_2/N_2 mixture). The substrate temperature immediately after the DBD treatment is below 50 °C measured using an infrared camera. This indicates that the DBD treatment is a low-temperature process.

In the indirect treatment, the sample and the DBD electrodes are separated by 30 mm in the closed chamber filled with O_2. The TiO_2 film is not subjected to the DBD, but to O_3 produced by the DBD ($V_{\text{p-p}}$ = 36 kV, 200 Hz). The treatment time is 3 h. The indirect treatment is also possible using air DBD. However, O_2 DBD is used because it is more efficient than air DBD.

RESULTS AND DISCUSSION

D. Glass substrate DSSC

TiO_2 paste applied on a glass substrate is sintered at 450 °C and treated with direct DBD in dry or humid O_2/N_2 mixture. Figure 1 shows the effect of humidity and O_2 concentration on the DBD treatment, where η_0 and η on the vertical axis represent energy conversion efficiencies before and after the DBD treatment, respectively. Each plot is average of 6 to 10 samples. η is measured using a 100 mW/cm^2 irradiation of calibrated xenon lamp (Hamamatsu L2274). Figure 1 shows that the effect of DBD treatment is maximized at O_2 = 10~15%, and the humid gas (relative humidity > 90%) is preferable to the dry gas for the DBD treatment. It is deduced from Fig. 1 that radicals such as OH, O, and/or O_3 produced from H_2O and O_2 molecules improve the performance of the TiO_2 film.

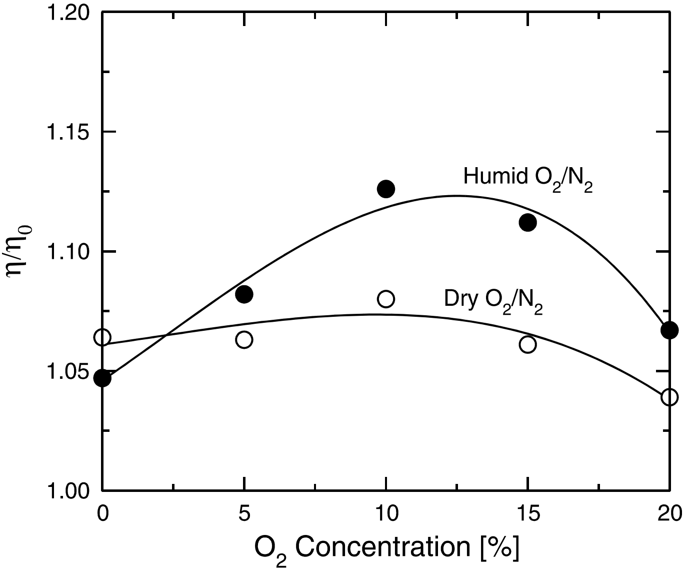

Fig. 1. Improvement of energy conversion efficiency by direct DBD treatment ($V_{\text{p-p}}$ = 36 kV, 200 Hz) in dry and humid O_2/N_2 mixture. Glass substrate DSSC sintered at 450 °C is treated for 5 min.

The DBD treatment can lower the sintering temperature [4]. Figure 2 shows the result. In this experiment, the TiO_2 film is sintered at constant temperature between 150 and 500 °C, then treated by indirect DBD for evaporation of the organic binder and the solvent by O_3 oxidization. Then, the TiO_2 film is treated by direct DBD in humid air (relative humidity > 90%) for necking of TiO_2 nanoparticles and for further evaporation of the binder and the solvent. When the sintering temperature is lower than 400 °C, the DBD treatment time should be long because the evaporation of the binder and the solvent takes long time. However, when the treatment time is long, the direct DBD causes damage on the TiO_2 film, while the indirect DBD does not cause any damage. This is the reason for using the indirect DBD treatment in addition to the direct DBD treatment.

In Fig. 2, without the DBD treatment, η decreases with the sintering temperature, T_s, and becomes 0% for $T_s \leq 300$ °C. However, with the DBD treatment, η keeps high value for $T_s \leq 300$ °C and $\eta = 1.5\%$ even for $T_s = 150$ °C. It indicates that the sintering temperature can be lowered using the DBD treatment. The low sintering temperature enables us to use materials which are not heat-resistant. If $T_s \leq 300$ °C is achieved, low electric resistance ITO can be used instead of generally used FTO with high electric resistance. If $T_s \leq 150$ °C is achieved, the plastic substrate DSSC can be produced using the TiO_2 paste containing organic binder. It may result in higher η than the plastic substrate DSSC produced using binder-free TiO_2 paste. There are previous researches on plasma treatment of TiO_2 electrode of DSSC [5-10]. But they treated DSSC sintered at high temperature, and they did not intend to lower the sintering temperature. Our DBD treatment offers a new avenue for the use of highly efficient materials which are not heat-resistant.

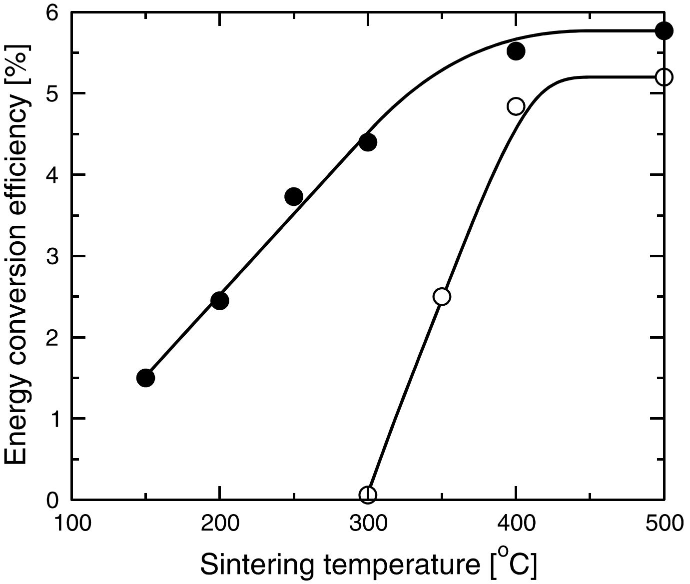

Fig. 2. Energy conversion efficiency of glass substrate DSSCs produced using sintering temperatures of 150 to 500 °C with DBD treatment ($V_{p\text{-}p} = 33$ kV and 2 kHz, filled circle) and without DBD treatment (open circle).

E. Plastic substrate DSSC

The direct DBD treatment is applied to TiO_2 film of the plastic substrate. However, since the adhesion between the TiO_2 film and the plastic substrate is weak, the direct DBD treatment causes severe damage on the TiO_2 film and causes peeling of the TiO_2 film from the plastic substrate. To avoid the peeling, the DBD voltage needs to be very low. Figure 3 shows an example. For $V_{\mathrm{p\text{-}p}} \geq 21$ kV, the peeling occurs and η substantially decreases. For $V_{\mathrm{p\text{-}p}} \leq 18$ kV, the peeling does not occur, but the improvement of η is negligible because the DBD is too weak. To avoid the film damage, we are now trying to use indirect DBD treatment, mesh electrode for cutoff the direct exposure of the TiO_2 film surface to the DBD streamer, etc.

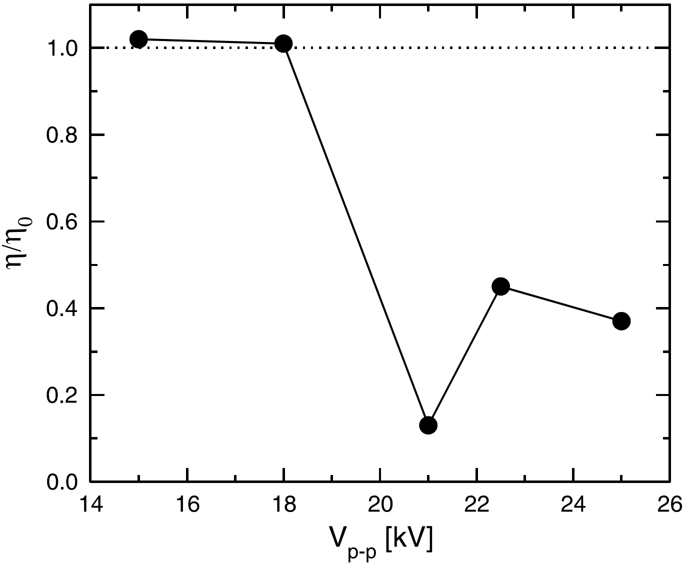

Fig. 3. Energy conversion efficiency of plastic substrate DSSCs treated with direct DBD in humid air.

CONCLUSION

The DBD treatment improved the energy conversion efficiency of glass substrate DSSC. The improvement of DSSC sintered at 450 °C was about a factor of 1.1. It was shown that the DBD treatment can lower the sintering temperature. It enables us to use highly efficient materials which are not heat-resistant. For the plastic substrate DSSC, the DBD treatment was not effective because it caused peeling of the TiO_2 film from the substrate. We are now trying to avoid the peeling to apply the DBD treatment to the plastic substrate DSSC. The DBD treatment is influenced by many parameters (DBD voltage and frequency, treatment time, ambient gas composition, electrode geometry, etc.). The effect of DBD treatment can be further improved by further optimization of these parameters.

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