19pF-4

Development of Low-Temperature annealing Technique for Plastic Dye-Sensitized Solar Cells

プラスチック基板型色素増感太陽電池の低温焼成技術の開発

Shungo Zen, Yuki Inoue, Ryo Ono and Tetuji Oda
全俊豪, 井上湧貴, 小野亮, 小田哲治

The University of Tokyo Department of Advanced Energy
2-11-16 Engineering department 10-200, Yayoi, Bunkyo-ku, Tokyo, 113-0032,Japan
東京大学 〒113-0032　東京都文京区弥生2-11-16工学部10号館200号室

Dye-sensitized solar cells (DSSCs) requires annealing of a TiO_2 photoelectrode at 450-550◦C to be manufactured. However, the high-temperature annealing is disadvantageous because it limits the use of materials that cannot withstand high temperatures. In our previous work, we propose a technique for annealing the TiO_2 electrode in 150◦C by using both atmospheric-pressure non-thermal plasma and ultraviolet (UV) light. We are also succeeded in manufacturing plastic DSSCs annealed at 150◦C by using the technique. In this paper, we analyzed the mechanism of 150◦C-annealed DSSCs by using a frequency response analyzer (FRA), and discussed the impedance of TiO_2 photoelectrode. It was founded that our low-temperature annealing technique is due to reactive oxygen species (O_3, O, OH) produced by the plasma and UV light.

1. Introduction

Recently, dye-sensitized solar cells (DSSCs) has been receiving increasing attention as a low-cost photovoltaic device [1, 2]. The DSSCs have a photoelectrode of a nanoporous TiO_2 film made by sintering TiO_2 paste, applied on a conductive substrate. The optimum sintering temperature of the TiO_2 paste is 450–550 ºC. The high sintering temperature restricts the use of materials with low heat resistance. Flexible, low-cost, and lightweight plastic substrates are also used in addition to glass substrates. However, the energy conversion efficiency of DSSCs with a plastic substrate is much lower than that of DSSCs with a glass substrate because the sintering temperature for the former is limited below 150 ºC [3-7]. To overcome these disadvantages, manufacturing techniques involving a low sintering temperature have been developed particularly for the plastic substrate DSSCs [8-14].

In our previous work, we propose atmospheric pressure non-thermal plasma treatment [15] and ultraviolet (UV) treatment [16]. Those techniques can reduce the annealing temperature from 450 ºC to 250 ºC, while maintaining the energy conversion efficiency. Then we propose a technique of reducing the annealing temperature to 150 ºC, by improving and combining those techniques [17]. In this paper, we analyzed the 150 ◦C-annealed DSSCs by using a frequency response analyzer (FRA), and discussed the impedance of TiO_2 photoelectrode.

Corresponding author: Shungo Zen
e-mail address:zen@streamer.t.u-tokyo.ac.jp

2. Methodology

The DSSC samples were prepared as shown in Fig.1 [17]. TiO_2 paste containing organic binder (JGC Catalysts and Chemicals, PST-18NR) was applied on a fluorine-doped tin oxide (FTO) glass substrate (AGC Fabritech) using screen printing. The area of the TiO_2 film was 5 mm ×5 mm. Then the paste was Hot UV annealed for 18 hours. The thickness of the TiO_2 film was 4 μm after the annealing treatment, which was measured with a Dektak M6 stylus profiler. After the annealed TiO_2 paste was subjected to dielectric barrier discharge (DBD)-treatment, the samples were immersed in a dye solution (Solaronix N-719, 1.9 mM/L in ethanol) for 24 hours at 25 ºC. Then, the substrates were glued to a platinized counterelectrode with a spacer sheet, and electrolyte (Solaronix Iodolyte AN 50) was injected between the substrate and the counterelectrode.

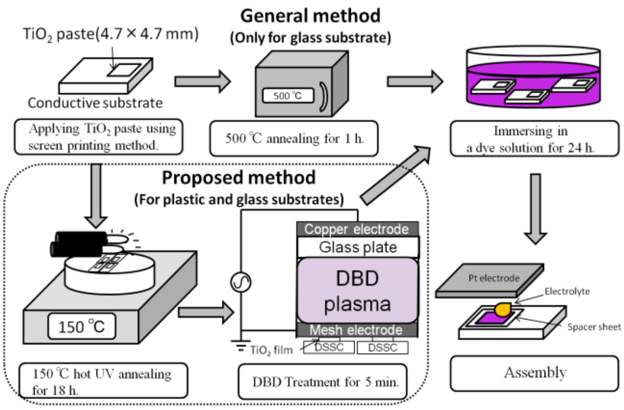

Fig.1 Manufacturing methods for DSSCs. [17]

3. Results and discussion

Electrical impedance of DSSCs was measured by a FRA (Nihon Denkei co. LTD., FRA5022). Figure 2 shows typical Nyquist diagrams (Cole-Cole plot) of DSSCs using 500 ºC annealed samples(A), 150 ºC Hot UV annealed samples without DBD treatment (B), and 150 ºC Hot UV annealed samples with DBD treatment (C). X-axis and Y-axis are the real and the imaginary component of the electrical impedance, respectively. A semicircle was observed in each case in the frequency range of 1-1kHz. Those semicircles are attributed to the electrical impedance at the TiO_2/dye/electrolyte interface [18]. The shape of the semicircle at the case (B) was changed compared with that of the case (A). This indicates that the electron transport resistance of TiO_2 film is not sufficiently low, and the necking of TiO_2 nanoparticles is insufficient. On the other hand, the semicircle at the case (C) remained nearly spherical, which indicates that DBD treatment can reduce the electron transport resistance and promote the necking of Hot UV annealed TiO_2 nanoparticles as well as the 500 ºC annealed samples.

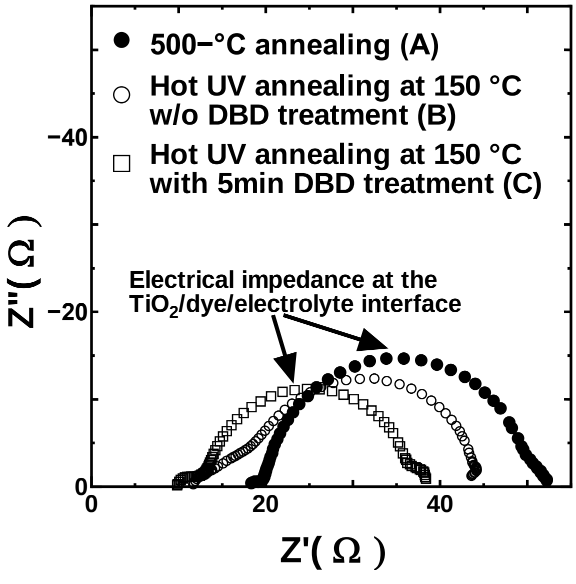

Fig.2 Typical Nyquist diagrams of DSSCs using different manufacturing methods.

4. Conclusion

We analyzed the 150 ◦C annealed DSSCs by using a frequency response analyzer (FRA). It was shown that the necking of 150 ºC Hot UV annealed TiO_2 nanoparticles is insufficient compared with 500 ºC annealed samples. It was also shown that DBD treatment can reduce the electron transport resistance and promote the necking of Hot UV annealed TiO_2 nanoparticles as well as 500 ºC annealed samples.

Acknowledgments

This work is partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sport, Science and Technology.

References

[1] B. O'regan, and M. Grätzel, Nature, **353** (1991)737.
[2] M. Grätzel, Nature, **414(**2001)338.
[3] T. Miyasaka, and Y. Kijitori, J. Electrochem. Soc., **151**, (2004)1767.
[4] S. Uchida, M. Timiha, H. Takizawa, and M. Kawaraya, J. Photochem. Photobiol. ,**164**(2004)93.
[5] T. Miyasaka, M. Ikegami, and Y. Kijitori, J. Electrochem. Soc., **154**(2007)455.
[6] L. Y. Lin, P. C. Nien, C. P. Lee, T. W. Tsai, M. H. Yeh, R. Vittal, and K. C. Ho, J. Phys. Chem. C., **114**(2010)21808.
[7] A. Vomiero, V. Galstyan, A. Braga, I. Concina, M. Brisotto, E. Bontempi, and G. Sberveglieri, Energy En viron. Sci., **4**(2011)3408.
[8] X. C. Zhao, H. Lin, X. Li, and J. B. Li, Electrochim. Acta., **56**(2011)6401.
[9] T. Yamaguchi, N. Tobe, D. Matsumoto, and H. Arakawa, Chem. Commun., **45**(2007)4767.
[10]Z. S.Wang, H. Kawauchi, T. Kashima, and H. Arakawa, Coordin. Chem. Rev., **248**(2004)1381.
[11]K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, Sol. Energ. Mater. Sol. C., **64**(2000)115.
[12]T. Yamaguchi, N. Tobe, D. Matsumoto, T. Nagai, and H. Arakawa, Sol. Energ. Mater. Sol. C., **94**(2010)812.
[13]T. N. Murakami, Y. Kijitori, N. Kawashima, and T. Miyasaka, Chem. Lett., **32**(2003)1076.
[14]T. N. Murakami, Y. Kijitori, N. Kawashima, and T. Miyasaka, J. Photochem. Photobiol. A., **164(**2004)187.
[15]S. Zen, Y. Teramoto, R. Ono, and T. Oda, Jpn. J. Appl. Phys., **51(**2012)056201.
[16]S. Zen, D. Saito, R. Ono, and T. Oda, Chem. Lett., **42(**2013)624.
[17]S. Zen, Y. Ishibashi, and R. Ono, Appl. Phys. Lett., **104**(2014)213904.
[18]L. Han, N. Koide, Y. Chiba, and T. Mitate, Appl. Phys. Lett., **84**(2004)1690495.