

Optimization of Titania Thickness of Dye-Sensitized Solar Cell(DSC) Utilizing Patterning with Electrostatically-Injected Droplet (PELID) Method

Kyousuke Kosugi^{1,2}, Yuki Shimoyama¹, Shinjiro Umez^{1,2}, Yoshihito Kunugi¹, Hitoshi Ohmori²

1: Tokai University, Hiratsuka-shi, Kanagawa, Japan,

2: RIKEN, The Institute of Chemical and Physical Research, Wako-shi, Saitama, Japan

Abstract

Solar cell is one of the key technologies in this century because this has possibility to clear energy problems. In this paper, we tried to pattern titania layer of dye-sensitized solar cell (DSC) utilizing PELID method. The PELID method is an inkjet fabrication method. The PELID method has good merit; that is ability to eject highly viscous liquid. We applied the merit for patterning titania paste on FTO (Fluorine-doped Tin Oxide) glass. The thickness of titania layer was controlled by the time to print. DSC is composed of electrolyte that is sandwiched between FTO glass and Pt electrode. Titania and N3 are patterned on FTO glass. The efficiency is not so high. The main purpose of the study is to improve the efficiency. The fabrication process of the DSC was simple. Titania paste was patterned on FTO glass utilizing doctor blade. The patterned paste was dried and sintered. The thickness of the layer was controlled by the spacer between the doctor blade and the glass. In the former study, the thickness was not changed, however it is essential to determine the thickness to achieve the highest efficiency. Because best thickness will be changed by the chemical characteristics of titania, new fabrication method that can change the thickness easily should be developed. We developed the PELID method.

In this paper, we have optimized of titania layer by controlling the coating time and profile utilizing PELID method. We have demonstrated that optimizing titania layer by PELID method is possible to improve the efficiency of the DSC.

Introduction

Solar cell is one of the clean renewable energy has been attracting attention from the energy and environmental problems. Silicon solar cell with high conversion efficiency has become megatrend today. As the development of solar cells in the future, attachment to the flexible printed electronics devices that further development and future use in developing countries where the sun shines. In recent years, dye-sensitized solar cell^[1-3] highly focused which can be to have the flexibility and design property. However, DSC is still low efficiency and research^[4,5] of from a chemical point of view, such as improvement of the dye and change of type of titanium dioxide (TiO_2) has been reported many, of TiO_2 ^[6-8] studies on manufacturing techniques such as patterning is not performed much. TiO_2 thin film in DSC exert a very important influence on the conversion efficiency. Light pass through TiO_2 thin film of DSC. However, resistance increase too thick of film thickness. Therefore thickness control of TiO_2 thin film is required because of high efficiency. Since TiO_2 is highly viscous, the doctor

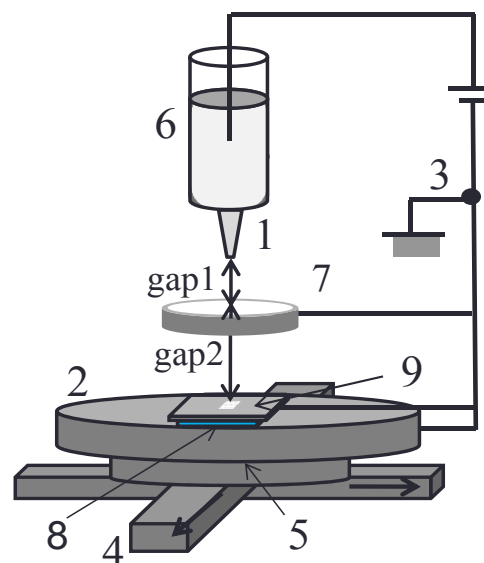


Figure 1. Experimental set-up to pattern titania paste utilizing mask on FTO electrode. (1: water pin electrode, insulative capillary tube filled with TiO_2 paste, 2: plate electrode, 3: high voltage power supply, 4: x-y linear stages, 5: mechanical z-stage, 6: tank, 7: ring electrode, 8: FTO substrate, 9: stainless steel mask)

blade method is the current mainstream, but adjustment of the film thickness is difficult because it depends on the thickness of the spacer by a doctor blade method.

In this paper, we applied the spray mode to pattern titania layer on FTO glass utilizing PELID^[9-13] (Patterning with Electrostatically Injected Droplet) method with high accuracy even in liquid with high viscosity and control the profile of the thin film. We have demonstrated that optimizing titania layer by PELID method is possible the efficiency of the DSC.

Experimental Set-up

Experimental set-up of PELID method was shown in Fig. 1. Small droplets were ejected by electrostatic force when high voltage was applied between nozzle that was filled with conductive liquid and plate electrode. The electrostatic field was controlled by the amplitude of applied voltage and the air gap between the electrodes. Print samples were patterned by the control of voltage application and xy linear stage. We already reported the fundamental characteristics of this inkjet technology. The merits of the inkjet technology were high resolution and ability to eject

highly viscous liquid. Inkjet technology is suitable to find best thickness of titania layer because the thickness is determined by the time to print. Titania paste in this experiment was made as follows. Titania particles (1.85 g) and water (1.0 g) was mixed. Acetylacetone (0.2 ml), Triton-X (1.0 ml) and polyethyleneglycol (0.185 g) were mixed into the paste. Titania is patterned on FTO electrode because FTO electrode is transmissive.

When high voltage is applied, titania paste is ejected like spray because of balance between charge and evaporation of the ejected droplet. In case that the mask was set on the FTO electrode shown in Fig. 1, titania on FTO electrode is patterned in a square shape.

The ejected droplet is separated into relatively small droplets because of balance between charge and evaporation of the ejected droplet when flight of the droplet is long. The experimental set-up shown in Fig.1 is constructed to get uniform titania layer.

Fundamental Characteristics of fabricated TiO_2 layer

Titania is patterned utilizing the PELID method. Fig.2 shows a change of the droplet by the voltage relationship between gap when it is ejected TiO_2 using PELID method. Fig.3 shows patterning results that changing of the droplet. Fig.3(a) and (b) is same result. The line made by drop mode is bold line because ejected large droplets. However, The line by droplet mode become a bold line small droplets combined. On the other hand, TiO_2 paste became bolder line in order to eject into more small droplets and wide range by spray mode (Fig.3(c)). Fig.4 shows the thickness of titania right after the patterning by spray mode when the patterning time is changed. Film thickness and coating time is linearly increased. Fig.5(a),(b) shown photographs of patterned titania. However, profile of thin film become like a mountain that shown Fig.6. This cause is short gap. A lot of TiO_2 is deposited under nozzle because gap is short. This is able to reform by increasing gap. But PELID method cannot precisely patterned TiO_2 because field strength become weak. However, it is possible improved profile of TiO_2 thin films and will be able to increase the gap while keeping the field strength of the nozzle tip by using plate electrodes with a hole. Fig.7 shows improved profile of TiO_2 thin film. Fig.7 shows when not using ring electrodes as a comparison. TiO_2 thin film without plate electrode with a hole became like a mountain. TiO_2 layer by fabricated with using ring electrode is flat.

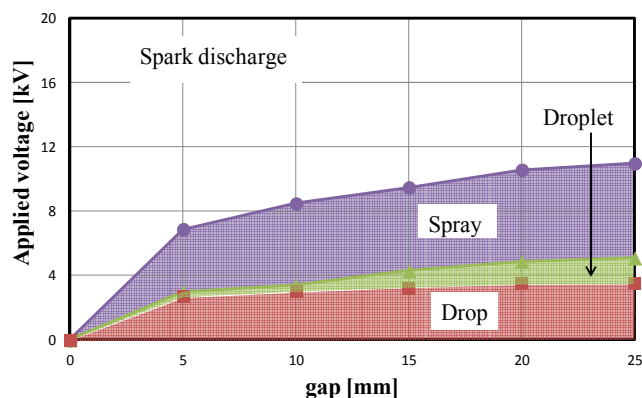


Figure 2. Mode of droplet formation



(a) Drop mode



(b) Droplet mode



(c) Spray mode

Figure 3. Patterning results when printing mode is changed

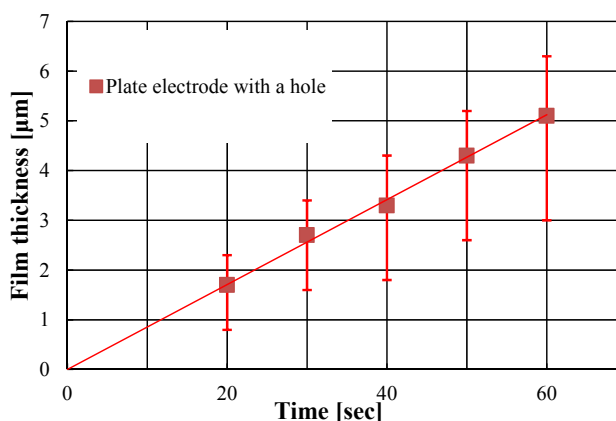
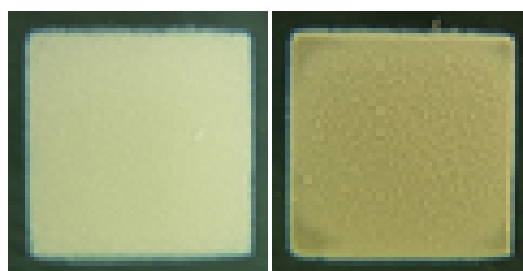
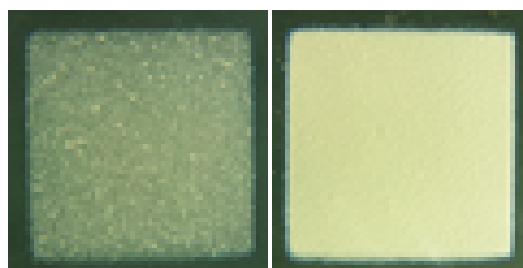


Figure 4. Thickness of patterned titania when the patterning time is changed.



(a) without ring electrode



(b) with ring electrode

Figure 5. Photographs of patterned titania.
(Patterning time: Left:10sec, Right:60sec)

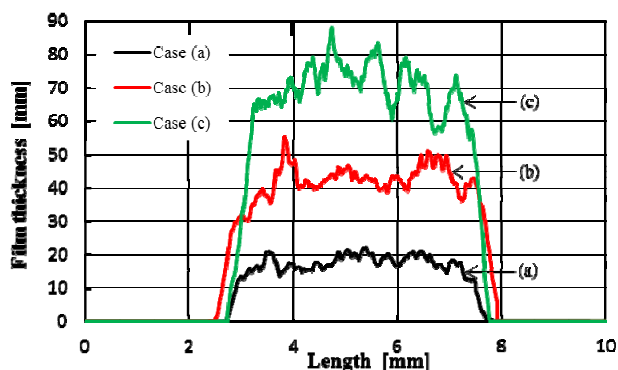


Figure 6. Profile of TiO_2 thin film surface due to the difference in gap (Case(a) gap:20mm, time:70 sec, voltage:8.0kV, Case(b) gap1:0mm, gap2:50mm, time:390 sec, voltage:10kV, Case(c) gap1:0mm, gap2:50mm, time:950 sec, voltage:10kV)

Optimization of Titania layer

Fig.7 and Table.1 show the fundamental characteristics of the fabricated DSC when the thickness of titania layer is changed. J-V curve of DSC is measured under the illumination of simulated AM1.5 solar light at 100 mW/cm^2 light illumination. On the basis of the current-voltage measurements, conversion efficiency (η) of each cell is calculated from current density (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF). J_{sc} is 11.6 mAcm^{-2} and V_{oc} is 0.782 V when the thickness of titania layer is $20 \mu\text{m}$. J_{sc} was 13.7 mAcm^{-2} and V_{oc} is 0.719 V when the thickness of titania layer is $70 \mu\text{m}$. J_{sc} increases when the thickness of titania layer is increased. V_{oc} decreases when the thickness of titania layer is increased. Open circuit voltage and current density are increased when the titania layer thickness are about $45 \mu\text{m}$.

The SEM images are shown in Fig.8. Fig.8(a) shows of thin film inside which made by Drop mode and Droplet mode. Fig.8(b)

shows the image of thin film which made by Spray mode. Titania paste is of agglomerated state that ejected by Drop mode and Droplet mode. The inside structure of thin film become a little porous. Usually, the TiO_2 film resistance increases with increasing titania layer thickness^[14-15]. Thus, conversion efficiency decreases. On the other hand, the thin film which is made by the Spray mode becomes much porous. It is easier for the electrolyte to penetrate in the titania layer. Amount of dye increases in the TiO_2 thin films in case of the specific surface area is increased. In spite of titania layer thickness is increased, conversion efficiency is increased. These result shows that conversion efficiency is improved by optimizing the film thickness by utilizing PELID method. We achieved high efficiency using P25 TiO_2 .

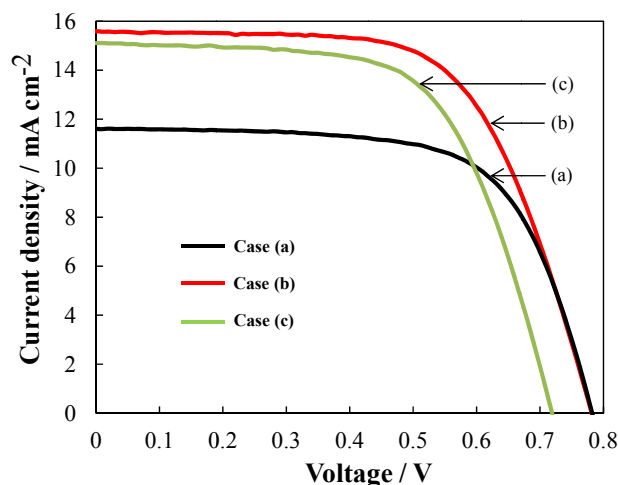


Figure 7. J-V curve of fabricated DSC in case that the patterning time was changed.

(Case(a) gap:20mm, time:70 sec, voltage:8.0kV, Case(b) gap1:0mm, gap2:50mm, time:390 sec, voltage:10kV, Case(c) gap1:0mm, gap2:50mm, time:950 sec, voltage:10kV)

Table.1 Relationship between thickness and efficiency.

Case	Thickness μm	J_{sc} mA cm^{-2}	V_{oc}/V	ff	$\eta/\%$
(a)	20	11.6	0.782	0.66	6.0
(b)	47	15.5	0.779	0.63	7.6
(c)	69	13.7	0.719	0.63	6.2

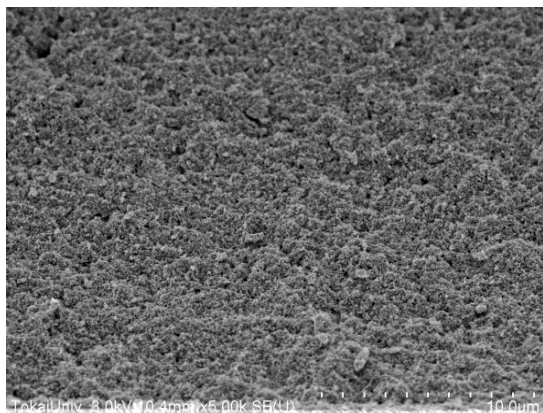


Figure 8. (a) Photograph of thin film inside made by PELID method. (Drop mode)

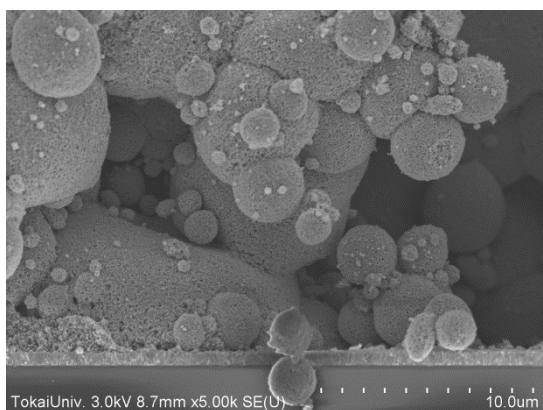


Figure 8. (b) Photograph of thin film inside made by PELID method (Spray mode)

Conclusions

Our inkjet technology, PELID method, is applied to pattern titania paste on FTO electrode. We fabricated titania layer by the Spray mode. It is possible to control the thickness of Titania layer when the time to pattern is changed. Titania layer made by spray mode as compared to other mode is much porous. It is easier for the electrolyte to penetrate in the titania layer and dye is attached when specific surface area is increased. Current density and open circuit voltage are improved by optimizing the film thickness. Optimal film thickness of titania layer is $45\mu\text{m}$ when fabricated by Spray mode. Hence, the efficiency of the preliminary fabricated DSC is about 7.6 %. We have demonstrated that optimizing titania layer by PELID method is possible the efficiency of the DSC.

Acknowledgement

The authors would like to express their thanks to Mr. Masafumi Ogawa and Mr. Takumi Hasegawa. This work was sup-

ported by grants of Special Grants from Tokai University and MEXT/JSPS [KAKENHI Grant Number: 25420224] and NEC C&C Foundation

References

- [1] B. O Regan, M. Grätzel: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, *Nature*, 353, 737(1991).
- [2] A. Hagfeldt and M. Grätzel: Molecular Photovoltaics, *Acc. Chem. Res.*, 33, 269(2000).
- [3] H.Arakawa, J. Surface Finish. Soc. Jpn., 59, 167 (2008) (in Japanese)
- [4] S.Ferrere, B. A. Gregg: Large increases in Photocurrents and solar conversion efficiencies by UV illumination of dye sensitized solar cells, *J. Phys. Chem. B* 105, 7602-7605(2001)
- [5] J. Spivack: Improved efficiency of dye sensitized solar cells by treatment of the dyed titania electrode with alkyl(trialkoxysilanes, *Solar Energy Materials & Solar Cells* 90, 1296-1307 (2006)
- [6] L. Yeji and K. Misook: The optical properties of nanoporous structured titanium dioxide and the photovoltaic efficiency on DSSC, *Mater. Chem. Phys.* 122, 284, (2010)
- [7] Y. Yamamoto, M. Kawayaya, H. Segawa, S. Uchida, J. Kano, F. Saito, K. Tsujimoto, T. Saito, and S. Ito: 10% Efficiency Dye-sensitized Solar Cell using P25 TiO_2 Nanocrystalline Electrode Prepared by Bead-milling Method, *Chem. Lett.* 40, 1220 (2011)
- [8] S. Nikraz, D. J. Phares, and H. Wang: Mesoporous Titania Films Prepared by Flame Stabilized on a Rotating Surface: Application in Dye Sensitized Solar Cell, *J. Phys. Chem. C* 116, 5342 (2012)
- [9] H. Kawamoto, et al.: Fundamental Investigation on Electrostatic Inkjet Phenomena in Pin-to-Plate Discharge System, *J. Imaging Sci. Technol.*, 49, 19-27 (2005)
- [10] S.Umezu, et al.: Fundamental characteristics of printed cell structures utilizing electrostatic inkjet phenomena, *Sens. Actuators A*, 166, 251-255 (2011)
- [11] S.Umezu, et al.: Fundamental Characteristics of Bioprint on Calcium Alginate Gel, *Jpn. J. Appl. Phys.* 52, 05DB20-1- 05DB20-4 (2013)
- [12] S.Umezu: BioCell print utilizing patterning with electrostatically injected droplet (PELID) metod, *J. Artif. Life Robotics* 17, 59 (2012)
- [13] S. Umezu, Y. Kunugi, and H. Ohmori: Dye-Sensitized Solar Cell Utilizing Electrostatic Inkjet, *Jpn. J. Appl. Phys.* 52, 05DC23-1-05DC23-5 (2013)
- [14] M. G. Kang, et al.: Dependence of TiO_2 Film Thickness on Photocurrent-Voltage Characteristics of Dye-Sensitized Solar Cells, *Bull. Korean Chem.* 25, 5 (2004)
- [15] I.Shin, et al.: Analysis of TiO_2 thickness effect on characteristics of a dye-sensitized solar cell by using electrochemical impedance spectroscopy, *Current Appl. Phys.* 10, S422-S424 (2010)

Author Biography

KOSUGI, Kyousuke received the BE (2012) degrees in Mechanical Engineering from Tokai University. He is now a master course student at Tokai University. His research interests include imaging technology and Dye-sensitized Solar Cell utilizing PELID(Patterning with Electrostatically-Injected Droplet) method.