

THE EFFECT OF COUNTER ELECTRODE PREPARATION METHODS TOWARD DYE SENSITIZED SOLAR CELL PERFORMANCE

PENGARUH METODE PENYIAPAN ELEKTRODA BANTU TERHADAP KINERJA SEL SURYA TERSENSITISASI PEWARNA

Pramujo Widiatmoko*, Hary Devianto, Isdiriyani Nurdin, Adriaan, Henry Natanail Purwito

Chemical Engineering Study Program, Faculty of Industrial Technology
Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, Indonesia 40132

*Email: pramujo@che.itb.ac.id

Diterima: 13 Februari 2018

Direvisi: 20 Maret 2018

Disetujui: 27 April 2018

ABSTRAK

Elektroda bantu karbon merupakan alternatif pengganti elektroda platinum yang baik untuk aplikasi sel surya tersensitisasi pewarna (*Dye-Sensitized Solar Cell*, DSSC). Makalah ini menjelaskan pengaruh metode pelapisan elektroda bantu serta jenis karbon pada kinerja DSSC. Elektroda disiapkan menggunakan 3 metode yaitu bilah dokter, batang pengaduk dan pelapisan gelembung. Karbon aktif untuk industri dan medis digunakan dalam penelitian ini. Kinerja DSSC ditentukan berdasarkan data kurva I-V dan spektroskopi impedansi elektrokimia, sementara morfologi lapisan karbon pada elektroda dipelajari menggunakan *Scanning Electron Microscope* dan analisis *Brunauer-Emmett-Teller*. Efisiensi DSSC lebih tinggi diperoleh ketika elektroda bantu disiapkan menggunakan metode bilah dokter dan pelapisan gelembung dengan karbon aktif medis. Perolehan tertinggi efisiensi konversi cahaya ke listrik adalah 3,76%.

Kata Kunci: elektroda berbasis karbon, metoda pelapisan, kinerja DSSC

ABSTRACT

Carbon-coated electrodes is superior substitution for platinum electrodes of Dye-Sensitized Solar Cells (DSSC). This paper describes effect of electrode coating methods as well as carbon types on the performance of DSSC. The electrodes were prepared using 3 methods, i.e. doctor blade, metering rod and bubble deposition. Commercial industrial-grade and medical-grade activated carbon were used in this research. The DSSC performance was measured from I-V curve and electrochemical impedance spectroscopy, meanwhile the morphology of coated carbon electrode was studied from Scanning Electron Microscope and Brunauer-Emmett-Teller analysis. It was found that efficiency of DSSC was higher when the counter electrodes were prepared using doctor blade and bubble deposition methods with medical-grade activated carbon. The highest achievement on light-to-electricity conversion was 3.76%.

Keywords: carbon-based electrode, coating methods, performances of DSSC

INTRODUCTION

Solar energy is a potential new energy source to supply electricity demand in Indonesia. Located on the equator, Indonesia receives intense solar irradiation throughout the year, up to 4.8 kWh/m²/day [1]. This solar energy can be converted directly into electricity using

photovoltaic cells. Application of the photovoltaic cells in Indonesia, however, should consider its monsoon climate. The number of rainy days may reach more than half of month in January to March and one-third in other months. These rainy and cloudy weather causes diffuse light of solar is more common than direct irradiation. It is known that dye-sensitized solar

cells (DSSCs) have advantages over its silicone-based counterparts in utilization of the indirect light [2]. Negligible recombination rate of electron and dye compared with electrons supplied by electrolyte allows the DSSC to work under low light conditions, suggests the possibility for outdoor and indoor usage [3].

Counter electrode is an important part of DSSCs for regeneration of the electrolyte. To date, carbon-based electrodes have been extensively studied to substitute the most-suitable-but-expensive platinum-coated electrode. Suzuki et al. have examined nano-carbon materials and showed that single wall nanotube in DSSCs counter electrode have comparable conversion efficiency of 4.5% to sputtered platinum ones [4]. Imoto et al. also reported that carbon counter electrode prepared by doctor blade can surpasses performances of the sputtered Pt-electrode counterpart, depend on the applied coating method of the Pt-electrode [5]. Meanwhile, Dodoo-Arhin et al. prepared electrodes with inkjet-printed graphene and found a lower conversion efficiency (3.0%) compared with the Pt-electrode of 4.4% [6]. These results suggest that along with the carbon types, preparation method of electrodes affects the DSSCs performances. In this paper, study on the

effect of common-and-simple deposition methods which are suitable for commercial production of DSSCs is reported.

EXPERIMENTAL

Fluoride Tin Oxide (FTO) conductive glasses (Techinstro, India) with dimension of 50 x 50 mm were cleaned with water and ethanol, consecutively, prior to be used. All chemicals were used as they are without prior treatment.

Counter Electrode Preparation

Industrial-grade activated carbon (Karbosorb, P.T. Aimtopindo Nuansa Kimia, Indonesia) and medical-grade one (Norit®, Eagle Indo Pharma, Indonesia) were grinded to obtain powder smaller than 100 mesh. Other chemicals were obtained from Merck, U.S.A. The carbon powders were mixed with Dimethylformamide to form carbon pastes. We coated the FTO glasses using three methods, i.e. metering rod, doctor blade, and bubble deposition, as illustrated in Figure 1. The prepared electrodes were then heat-treated in an electric furnace at 100°C for 40 minutes, and subsequently cooled to the room temperature.

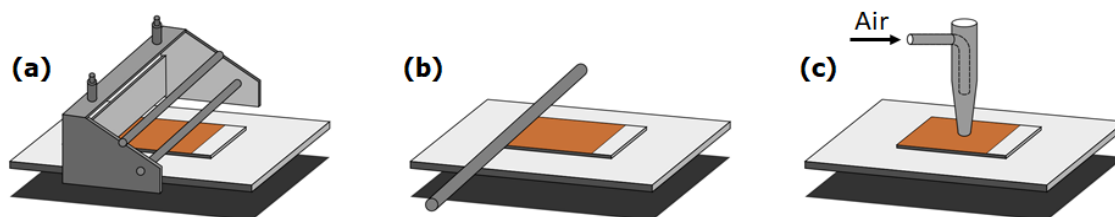


Figure 1. Preparation of Carbon-based Counter Electrodes using (a) Doctor Blade (b) Metering Rod, and (c) Bubble Deposition Methods

Working Electrode Preparation

Working electrodes were prepared from pastes of titanium oxide powder in acetic acid solution. The acetic solution was prepared from glacial acetic acid diluted in aqua DM (e.g. 3 mL glacial acetic acid in 12 mL of aqua DM). Paste of titanium oxide was made from 19 of titanium oxide powder and 30 mL acetic acid solvent. Homogenized paste of titanium oxide was obtained after grinded the mixture in a mortar grinder. The paste was then coated on the conductive glass surface using doctor blade method within area of 25 x 20 mm. Consecutively, the coated conductive glass was heated at 500°C for 30 minutes. After cooled to

room temperature, the working electrode was immersed to dye solution for 24 hours inside a closed impermeable container.

Dye Preparation

The dye solution was prepared by added Eosin Y powder into acetone with formula of 0.0138 g in 20 mL and stirred to make a homogenous solution.

Electrolyte Preparation

Electrolyte used in this work was iodine/triiodide solution. Potassium iodide (KI) salt of 0.496 g was mixed with 0.076 g of iodine powder, then added by 0.5 mL of aqua DM.

Subsequently, the mixture was added with 6 mL of acetonitrile and stirred.

Measuring Methods

Performance of the DSSCs was measured under illumination of a 150 W halogen-lamp (Philips QVF133 Halolite, Indonesia). The samples were placed 200 mm perpendicularly to the lamp. Short circuit current (I_{SC}), open circuit voltage (V_{OC}), and I-V curves were measured by digital multimeter under various loads. To minimize stray lights from other sources, DSSCs were put inside a box and the experiments were conducted inside a dark room. Further, electrochemical characteristic of the DSSCs were analyzed using electrochemical impedance spectroscopy (Gamry Reference 3000, USA).

RESULT AND DISCUSSION

Characteristics of the Activated Carbons

Carbon powders (before coated on the electrode) were characterized using surface area analyzer (NOVA 2000, Quantachrome Instrument, USA). The result is presented in Table 1. It was found that surface area of the industrial-grade activated carbon ($13.35 \text{ m}^2/\text{g}$) is 2.5 times higher than the medical-grade ones. Meanwhile, average pore-size of the medical-grade activated carbon (13.5 nm) was 1.5 times higher than the industrial-grade ones.

Table 1. Characteristics of Activated Carbons Powder

Activated Carbon Types	Average pore size (nm)	Pore volume (ml/g)	Surface area (m^2/g)
Industrial-grade	9.3	0.031	13.35
Medical-grade	13.5	0.018	5.32

On the surface of counter electrodes, regeneration of I_3^- may follow reaction (1) [5].

Higher surface area of the electrodes is expected to provide higher active sites for the reduction reaction. For small overpotential in dilute electrolyte, the reaction rate increases linearly with increasing of active surface area, may follow the reduction part of Butler-Volmer Equation (2).



$$r_{red} = I_{red} = -n F A k^0 C_{red} \exp[(1 - \alpha) n F (E - E^0)/RT] \quad \dots (2)$$

Pores of the activated carbon potentially enhance the availability of active surface area if only the I^{3-} and I^- ions can penetrate to its inner surface. Mesoporous carbon with pore size between 2 to 50 nm is favorable because can facilitates mass diffusion by internal channel while maintain sufficient surface area for reaction. It is known that the effective hydrodynamic radius of triiodide ion in water is 2.1 \AA [7] and dimension of 3 to 6 \AA (width to length) in acetonitrile [8]. Average pore-size of the industrial and medical-grades activated carbons are 9.3 and 13.5 nm, respectively. Hence, triiodide ions can react in the active channel surface of the pores.

Effect of Carbon Coating Methods on Performance of the DSSCs

Current-Voltage (I-V) characteristic of the prepared DSSCs under illumination is shown in Figure 2. Both industrial and medical-grade carbon electrodes had similar trend of I-V curves when prepared using doctor blade, metering rod, and bubble deposition. Since the carbon materials and size were similar, this result suggested that difference on the performance of DSSCs were mainly caused by the electrode coating methods.

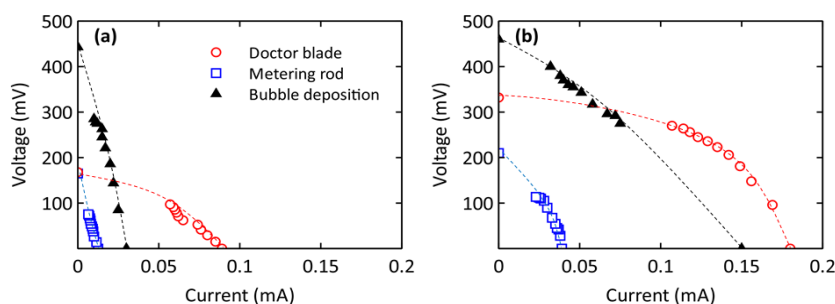


Figure 2. Effect of Coating Methods on I-V Curves of DSSCs Prepared from Commercial (a) Industrial-grade and (b) Medical-grade Activated Carbons

The calculated conversion efficiencies are shown in Table 2. The solar energy-to-electricity conversion efficiency of DSSCs in this work was defined as the ratio of maximum output electrical power to incident light power (I_0) expressed by Equation (3) [9]. Maximum current obtained when short-circuited was the short-circuit current (I_{SC}). The open-circuit voltage (V_{OC}) was potential difference between TiO_2 conduction band edge and electrochemical redox couple in electrolyte [10]. Maximum generated power, P_{max} , is multiplication of the maximum current (I_{max}) with voltage (V_{max}). Overall capacity of the solar cell was evaluated using Fill factor (FF), *i.e.* the ratio of maximum generated power to theoretical maximum power of I_{SC} times V_{OC} .

$$\eta = (I_{SC} V_{OC} FF) / I_0 \times 100\% \quad \dots (3)$$

Low I-V performance of rod coating method is expected from electron transfer problem. The SEM cross-section images of deposited carbon (Figure 3) showed that rod coating method result in loose structure of carbon on the conductive glass. Smaller availability of contact area between the carbon and conductive glass increased the hindrance for electron transfer. In contrary, the doctor blade and bubble methods showed close contact between the carbon layer and the conductive glass, allowed easier electron transfer.

Table 2. Characteristic of Prepared DSSCs

Methods	V_{OC} (mV)	I_{SC} (mA)	V_{max} (mV)	I_{max} (mA)	Fill Factor FF (%)	Efficiency η (%)
Industrial-grade activated carbon						
Doctor blade	168	0.089	97.2	0.059	38.35	0.82
Metering rod	210	0.013	72.3	0.007	19.28	0.14
Bubble deposition	443	0.030	263.0	0.015	29.68	0.72
Medical-grade activated carbon						
Doctor blade	332	0.180	236.0	0.129	50.94	3.25
Metering rod	165	0.039	105.2	0.028	45.78	0.35
Bubble deposition	460	0.150	292.0	0.072	30.47	3.76

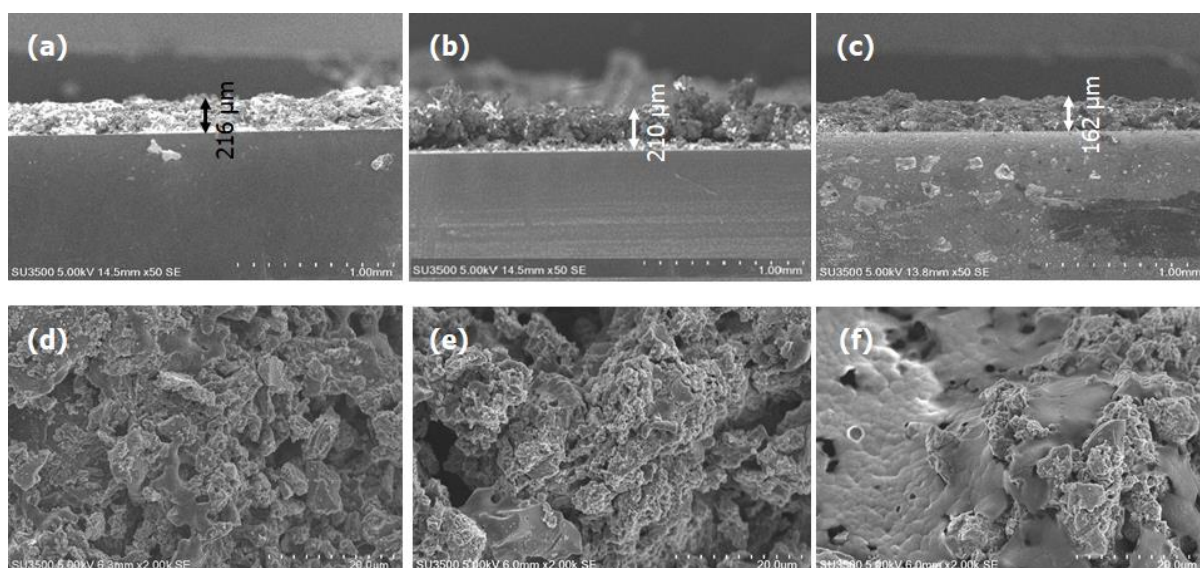


Figure 3. Scanning Electron Microscopy Images (Cross Section and Surface) of the Carbon Counter Electrodes Prepared Using (a, d) Doctor-Blade (b, e) Metering Rod, and (c, f) Bubble Deposition. The Electrodes were Prepared from Medical-Grade Activated Carbon

The thickness of carbon layers (Figure 3) prepared using doctor blade, metering rod, and bubble deposition methods were 216, 210, and 162 μm , respectively. The electric current produced from DSSC prepared using bubble deposition method was smaller than doctor blade ones. Excessive amount of electrolyte on the electrode was supposed to reduce the electrolyte reduction rate [11]. Checking the porosity of carbon layer using ASTM C20-00 (2015) standard, the apparent porosity of bubble deposited layer was much smaller (0.32) compared with doctor blade one (0.71). This difference might come from the addition of more solvent in the bubble deposition methods to reduce its viscosity. Using similar amount of electrolyte, the flooding phenomena (due to excessive amount of electrolyte) would preferably occur on the bubble deposited electrode.

Further, the DSSCs with bubble deposition method showed the highest open circuit voltage. The bubble deposited counter electrodes had the thinnest layer of 162 μm . Thinner layer of counter electrode layer was supposed to reduce I_3^- concentration on the surface of counter electrode [11], reduce diffusion rate of I_3^- into electrode. The electrons tended to accumulate in electrodes due to higher resistance, increase charge transport resistance [10]. As a result, cell's open circuit voltage increased.

The medical-grade activated carbon showed higher activity (about 5.3 times higher on its Peak Power) than the industrial-grade ones despite its lower surface area (5.32 to 13.35 m^2/g). Average pore size of medical-grade carbon was higher (13.5 to 9.3 nm), however the electrolyte and dye could diffuse into pores of both activated carbons. It was supposed that conductivity of the activated carbon plays its role. Medical-grade activated carbon contained activated carbon, gelatin, titanium dioxide and iron oxide. Electrical resistivity of carbon was $60 \times 10^{-5} \Omega\text{m}$, while electrical resistivity of iron oxide is $5 \times 10^{-5} \Omega\text{m}$ (Heck, 1974). Therefore, internal electrical resistance of the medical-grade activated carbon medicine became lower, increasing the cell performance.

To confirm the effect of deposition methods, further analysis was performed on the DSSCs using Electrochemical Impedance Spectroscopy (EIS) within frequency range of 10 mHz to 10 kHz under illumination. The EIS was analyzed for the DSSCs prepared using medical-grade activated carbon only because they show better I-V performance than the industrial-grade counterpart. Figure 4 shows Nyquist plot of the DSSCs with various deposition methods.

Typically, there were three semicircles in the EIS spectra of DSSCs which were attributed to charge transfer (at high frequency), transport and recombination of electron in the TiO_2 conduction band (at medium frequency) and Nernst diffusion impedance of redox species (at low frequency). Intercept of the first semicircle in real axis represented the ohmic series resistance (R_s) of the DSSCs. Main contributor to the R_s are sheet resistance of electrode substrate and the resistance of electrolyte solution [12]. The charge transfer resistance (R_{CT}) was combination of resistance of $\text{TiO}_2/\text{electrolyte}$ and $\text{C}/\text{electrolyte}$ interfaces, identified as the second semicircle. On the carbon counter electrode, the charge transfer resistance associated with the redox reaction involving Γ^- and I_3^- . Meanwhile in $\text{TiO}_2/\text{electrolyte}$, the resistance came from electron transport through diffusion and recombination. The third semicircle represented diffusion of I_3^- in electrolyte.

The proposed equivalent circuits however varied with materials and preparation methods of DSSCs [12,13,14,15]. In this research, interpretation was done by fitting the spectra to an equivalent circuit as in Figure 5, adapted from Fabregat-Santiago, et al. [13]. The series resistance R_s of cells using the doctor blade, metering rod, and bubble methods were 56.48, 47.96, and 87.77 Ω , respectively. The charge transfer in counter electrode might represented with parallel circuit of resistor, R_{CT} and constant phase element, $CPE3$. In the bubble deposition, the R_{CT} was higher (179.5 Ω) compared to doctor blade and metering rod (2.49 and 18.83 ohm, respectively). Capacitive parameter of the bubble deposited layer was significantly higher (347.5 compared to 2.26×10^{-6} and $3.80 \times 10^{-4} \text{S.s}^a$), which would result in a high charge transfer resistance.

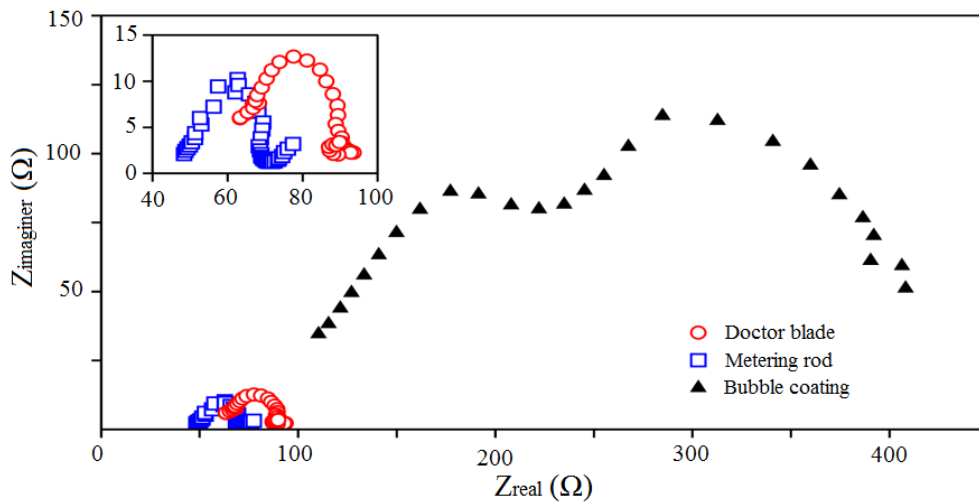


Figure 4. EIS Nyquist Plots of from the DSSCs Prepared Using Various Deposition Methods. Medical-grade Activated Carbon was Used

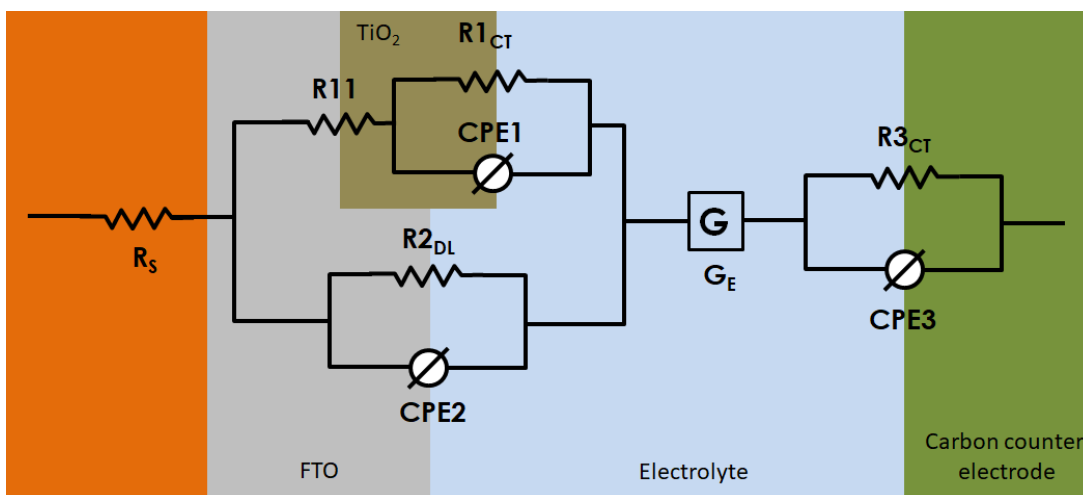


Figure 5. Equivalent Circuits of the DSSCs

The charge transfer on the carbon counter electrodes/electrolyte itself was further evaluated using symmetrical cells. The result showed that the charge transfer resistance in the bubble deposited counter electrode was higher (130.8 Ω) compared to the metering rod and doctor blade ones (6.7 and 30.4 Ω , respectively). It was supposed that layered carbon which covered the particles (as in Figure 3.f) decreased the availability of charge transfer area.

Stability of DSSCs

DSSC uses organic dye may suffer from degradation and then less stable compared to silicone-based solar cell. Therefore, stability test was conducted to determine the lifetime of DSSC. Figure shows that daily electrolyte addition enables the DSSC to perform optimally. However, without electrolyte addition, the cell performance decreased drastically. The volatile liquid electrolyte caused this phenomenon. After 5 days, there was no structure damage was found on the DSSC. It proved that cell stability toward time was influenced by electrolyte amount inside the DSSC.

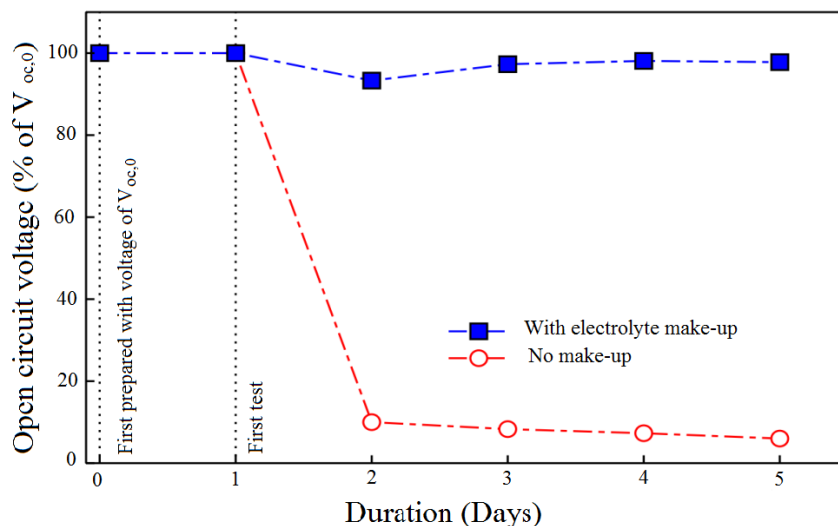


Figure 6. Open Circuit Voltage of DSSCs During Stability Test

Lee et al. reported that DSSC performance can be kept up for 60 days without any electrolyte addition by using polymer seal [16]. The seal will prevent contact between ambient air with DSSC electrolyte, avoid evaporation, and maintain optimum cell performance. However, this lifetime is still shorter than silicone-based solar cell of which has 20 years lifetime in average. Therefore, further development of the DSSC stability should be done by choosing the suitable polymer for the seal material. The material should totally prevent the contact to atmospheric and be inert (or less reactive) to Iodine electrolyte.

CONCLUSION

Coating methods of doctor-blade, metering rod, bubble deposition have been studied to prepare DSSC counter electrodes. The doctor-blade and bubble deposition methods showed higher light-to-electricity conversion efficiency than the metering rod. Based on the I-V curve analysis, however, the doctor-blade method could provide the best performance. Therefore, we concluded that the doctor-blade method is the best method for mass-production of carbon counter electrode from slurry. Because stability of the DSSCs depends on the electrolyte present inside cells, further studies for cell sealing is required.

ACKNOWLEDGEMENT

Authors gratefully thank Mhd. Ridho Utomo, Hilham Zamriko Koto, Saumi Febrianti Khairunnisa, and Lydia Ignacia for their kind helps. We also thank P.T. Aintopindo Nuansa Kimia for the commercial-grade activated carbon.

REFERENCES

- [1] Nurliyanti, V., Pandin, M., Pranoto, B., "Pembuatan Peta Potensi Energi Surya". *Pusat Penelitian dan Pengembangan Teknologi Ketenagalistrikan, Energi Baru, Terbarukan, dan Konservasi Energi*, 2012.
- [2] Barber, Greg, "Utilization of Direct and Diffuse Sunlight in a Dye-Sensitized Solar Cell – Silicon Photovoltaic Hybrid Concentrator System". *Journal of Physical Chemistry Letters*, 581-585, 2011.
- [3] Law M., et al., "Nanowire Dye-Sensitized Solar Cells", *Nature Materials*, 4, 455, 2005.
- [4] Suzuki, K., Yamaguchi, M., Kumagai, M., Yanagida S, "Application of Carbon Nanotubes to Counter Electrodes of Dye-sensitized Solar Cells", *Chemistry Letter CSJ*, 32 (1), 2003.
<https://doi.org/10.1246/cl.2003.28>
- [5] Imoto, K., Takahashi, K., Yamaguchi, T., Komura, T., Nakamura, J., Murata, K., "High Performance Carbon Counter Electrode for Dye-Sensitized Solar Cells",

- Solar Energy Materials & Solar Cells*, 2003, 79 (4), 459-469.
- [6] Dodoo-Arhin, D, Howe, R. C. T., Hu, G., Zhang, Y., Hiralal, P., Bello, A., Amaratunga, G., Hasan, T., "Inkjet-printed graphene electrodes for dye-sensitized solar cells", *Carbon*, 2016, 105, 33-41.
- [7] Cao Y., Zhang, J., Bai, Y., Li, R., Zakeeruddin, S. M., Gratzel, M. and Wang, P., "Dye-Sensitized Solar Cells with Solvent-Free Ionic Liquid Electrolytes", *J. Phys. Chem. C*, 112, 13775–13781, 2008.
- [8] Sakane, H., Mitsui, T., Tanida, H., Watanabe, I., *J. Synchrotron Radiat*, **8**, 674, 2001.
- [9] Hara, K., Sato, T., Katoh, R., Furube, A., Ohga, Y., Shinpo, A., Suga, S., Sayama, K., Sugihara, H., Arakawa, H., "Molecular Design of Coumarin Dyes for Efficient Dye-Sensitized Solar Cells", *J. Phys. Chem. B*, 107, 597-606, 2003.
- [10] Cahen, D., Hodes, G., Graetzel, M., Guillemos J., *The Journal of Physical Chemistry B*, 104, 2053, 2000.
- [11] Desilvestro, Hans, "What Physical Factors Affect Current-Voltage Characteristics of Dye Solar Cells", *Dyesol*, 2008.
- [12] Sarker, S., Ahammad, A. J. S., Seo, H. W., Kim, D. M., "Electrochemical Impedance Spectra of Dye-Sensitized Solar Cells: Fundamental and Spreadsheet Calculation", *International Journal of Photoenergy*, 17, 2014.
- [13] Fabregat-Santiago, F., Bisquert, J., Palomares E., et al., "Correlation between photovoltaic performance and impedance spectroscopy of dye-sensitized solar cells based on ionic liquids", *The Journal of Physical Chemistry C*. 111 (17), 6550–6560, 2007.
- [14] Wang, Q., Moser, J., and Gratzel, M., "Electrochemical Impedance Spectroscopic Analysis of Dye-Sensitized Solar Cells", *J. Phys. Chem. B*, 109, 14945-14953, 2005.
- [15] Lee, K. J., Kim, J. H., Kim, H. S., Shin, D. S., Yoo, D. W. Kim, H. J., "A study on a solar simulator for dye sensitized solar cells", *International Journal of Photoenergy*, pages 11, 2012.
- [16] Lee, W. J., Ramasamy, E., Lee, D. Y., Song, J. S., "Performance variation of carbon counter electrode based dye-sensitized solar cell", *Solar Energy Materials & Solar Cells*, 92, 814-818, 2008.