

Fabrication of Semi-quasi Solid DSSC using Spiro Material as Hole Transport Material

L Safriani, W P Primawati, C Mulyana, T Susilawati, and A Aprilia

Physics Department, Faculty of Mathematic and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung Sumedang Km. 21, Jatinangor, Sumedang 45363, Indonesia

E-mail : lusi.safriani@phys.unpad.ac.id

Abstract. Dye Sensitized Solar Cells (DSSC) has been emerging a promising development in recent years. DSSC is a low-cost solar cell belonging to the third generation of solar cells. However, the conversion efficiency of DSSC is still far behind compared to silicon based solar cells. To produce long stability of DSSC, the used of solid state electrolyte is recommended instead of liquid electrolyte, though solid state DSSC also has problem relating to a lack of pore-filling hole transport material into mesoporous TiO_2 . In this work an attempt to improve performance of DSSC has been done by adding hole transport material into mesoporous TiO_2 layer and optimizing fabrication method. In the first part of the work, we used low T_g material spiro-TAD and spiro-TPD as hole transport material with mosalyte and hybrid polymer as gel electrolyte to obtain a semi-quasi solid DSSC. In the second part, we modified fabrication method by annealing process before spin-coated spiro material into dye-coated TiO_2 substrate. Current-voltage measurement of semi-quasi solid DSSC was performed using halogen lamp. We found that the used of spiro-TPD as hole transport give the best power conversion efficiency $\eta = 2.03\%$ of semi-quasi solid DSSC.

1. Introduction

Recently, the development of dye-sensitized solar cells (DSSC) attracts many researchers due to its achievement of DSSC performance that has reached efficiency as high as 18.7% [1] with some modification on its electrode. There are three main components of DSSC i.e. a dye-sensitized photoanode, an electrolyte and counter electrode [2]. Fine tuning any of these components have resulted in increasing of DSSC's efficiencies [3]. A dye-sensitized photoanode contain of a semiconductor material which always been TiO_2 (anatase) mesoporous to hold dye. Dye itself is a material act as photo-sensitizer which is adsorbed on the semiconductor surface. On this layer, an excitation of charge transfer dye results in injection of an electron into conduction band of semiconductor layer.

Normally an electrolyte is a liquid electrolyte based on the I_3^-/I^- redox couple [4]. However, the use of liquid electrolyte shows some disadvantages such as sealing problems and long-term durability, solvent evaporation and leakage of volatile organic solvent [4,5]. One alternatives to liquid electrolyte is quasi-solid electrolyte, ionic liquids (e.g. 1-propargyl-3-methylimidazolium iodide, bis(imidazolium) iodides and 1-ethyl-1-methylpyrrolidinium) and polymer gel (e.g.



poly(ethyleneoxide), poly(vinylidene fluoride) and polyvinyl acetate) containing redox couples are commonly used as quasi-solid electrolytes to overcome leakage problems [6,7,8].

One of factors that could inhibit the efficiency of DSSC is related to charge transport especially hole transport in porous TiO_2 . The incomplete pore-filling of hole transport materials into porous TiO_2 , leads to poor dye-regeneration and reduces device efficiency [9]. A good candidate material for a transparent hole transport material is small molecules so it will be easy to penetrate into porous TiO_2 layer. Organic material based on spiro material has been used as hole transport material in DSSC [10] due to its charge transport properties [11]. In this research, combination of gel electrolyte and spiro material was used to form semi-quasi solid DSSC to overcome the solvent evaporation problem and increase device performance.

2. Experimental methods

Fabrication of DSSC based on combination of gel electrolyte and spiro material was divided into three steps. Firstly, photoanode was prepared using screen printing on FTO substrate. One layer of Ti Nanooxide T/SP was deposited FTO substrate and subsequently followed by Ti Nanooxide MC/SP and Ti Nanooxide T/SP. It was then gradually annealed until 500°C for 30 minutes on hotplate to produce mesoporous TiO_2 layer. Secondly, photoanode was immersed on Ruthenium dye (535-bisTBA; purchased from Solaronix) and chenodeoxylic acid (1:10). After overnight, FTO/ TiO_2 /Ru-dye was rinsed by acetonitrile several times to remove residue of dye molecules. Hole transport material (HTM) based on spiro material dissolve in chlorobenzene was spin-coated on FTO/ TiO_2 /Ru-dye. Two kind of spiro material were used in this experiment, 2,2',7,7'-tetra-kis(diphenylamino)-9,9'-spirobifluorene (spiro-TAD) and 2,2',7,7'-tetra(m-tolyl-phenylamino)-9,9'-spirobifluorene (spiro-TPD) which purchased from Lumtec. Drilled platinum coated FTO substrate (Pt/FTO) was used as counter electrode and stack together with working electrode FTO/ TiO_2 /Ru-dye separated by hot melt surlyn film having thickness $25\ \mu\text{m}$. Finally, gel electrolyte which mixed between co-polymer TMSPMA and ionic liquid electrolyte mosalyte (purchased from Solaronix) was injected to the hole of Pt/FTO side and then sealed with transparent tape to avoid leaking. To investigated performance of device, current voltage (J-V) characteristics was measured using source lamp with power input $36.5\ \text{mW}/\text{cm}^2$ integrated with Yokogawa GS 200 DC voltage-current source and Yokogawa digital multimeter 7555.

3. Results and Discussions

Absorption spectrum of TiO_2 layer combined with Ru-dye and spiro material is presented in figure 1. It is clearly shown that TiO_2 /Ru-dye/spiro material layer has higher absorption compared to TiO_2 /Ru-dye layer which due to the addition of both spiro-TPD and spiro-TAD. An absorption at around 500 nm (visible region) is correlated to Ru-dye absorption.

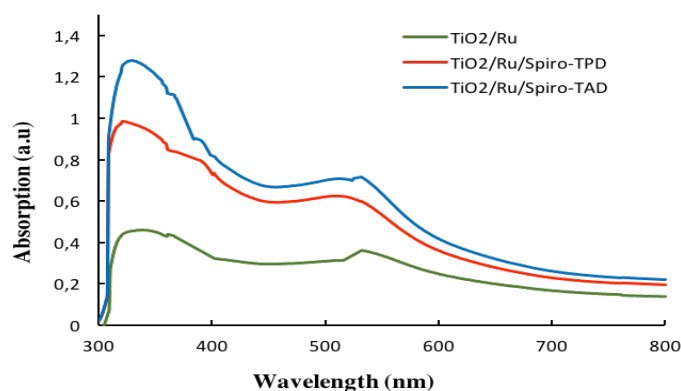


Figure 1. Absorption spectrum of TiO_2 /Ru-dye and TiO_2 /Ru-dye/spiro material

Current density-voltage characteristics of DSSC with structure FTO/TiO₂/Ru-dye/spiro material (HTM)/gel electrolyte/Pt-FTO was carried out under irradiated of halogen lamp with 0.3 mW/cm² as power input and shown di figure 2. All parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill Factor (FF) and efficiency (η) which observed and calculated were presented in table 1.

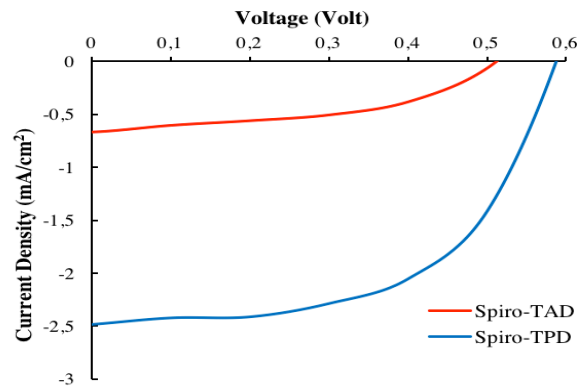


Figure 2. J-V curve of DSSC with different spiro material as HTM

Table 1. Parameters of DSSC with different spiro material as hole transport material (HTM)

Spiro material (HTM)	J_{sc} (mA/cm ²)	V_{oc} (Volt)	FF (%)	η (%)
Spiro-TAD	0.67	0.51	45	0.24
Spiro-TPD	2.48	0.59	56	1.86

Energy conversion efficiency η obtained for semi-quasi solid DSSC with spiro-TAD and spiro-TPD as HTM are 0.24% and 1.86% respectively. A lower efficiency of DSSC with spiro-TAD as HTM correlated with its energy level which lower than that of Ru-dye. This could inhibit charge transfer from Ru-dye to highest occupied molecular orbital (HOMO) of spiro-TAD. On the other hand, spiro-TAD has a higher HOMO level than RU-dye to facilitate charge transfer and increase the efficiency.

In order to enhance performance of DSSC with structure FTO/TiO₂/Ru-dye/spiro material (HTM)/gel electrolyte/Pt-FTO, we did two kind modification in fabrication method. In previous result, mesoporous TiO₂ layer was resulted from coating of three times Ti Nanooxide, but this cause a thick mesoporous TiO₂ layer which could prevent a penetration of Ru-dye. To optimize the penetration process of Ru-dye into mesoporous TiO₂ layer, Ti Nanooxide was deposited on FTO substrate twice and followed by annealing process as described in previous section. We also did annealing process before spin coating of spiro material into dye-coated TiO₂ substrate to remove air bubbles which trapped inside mesoporous TiO₂ layer. Current density-voltage characteristics and parameters device produced from optimized fabrication methods is presented in figure 3 and table 2 respectively.

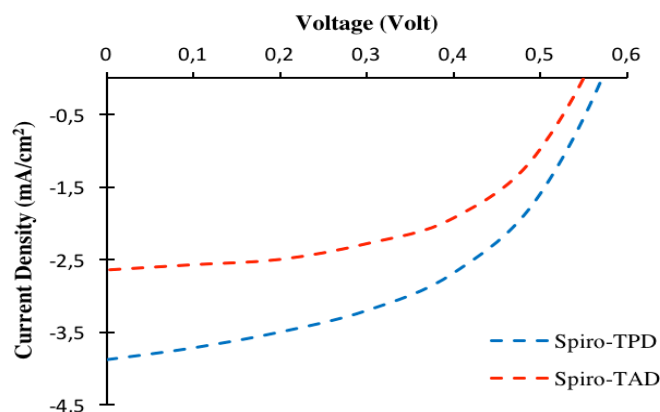


Figure 3. J-V curve of DSSC with different spiro material as HTM produced from optimized fabrication methods

Table 2. Parameters of DSSC with different spiro material as hole transport material (HTM) produced from optimized fabrication methods

Spiro material (HTM)	J_{sc} (mA/cm ²)	V_{oc} (Volt)	FF (%)	η (%)
Spiro-TAD	2.64	0.55	33	0.97
Spiro-TPD	3.88	0.57	48	2.03

Based on current density-voltage characteristic, it is clearly shown that after optimized fabrication method device, efficiency η is increased both for device with spiro-TAD and spiro-TPD as HTM. Twice coating process resulted thinner mesoporous TiO₂ layer so that Ru-dye penetrated in all area of mesoporous TiO₂ layer and prevented empty space of Ru-dye. Annealing process before spin-coated of spiro material also give contribution to broaden contact area between Ru-dye and spiro material to ease charge transfer from Ru-dye to spiro material. Therefore, the combination between the used of HTM based on spiro material and modification process that have been done could be one of the ways to increase power conversion efficiency of semi-quasi solid DSSC.

4. Conclusions

Semi-quasi solid DSSC have been fabricated using gel electrolyte and spiro material as hole transport material. In order to enhance device performance, the optimized fabrication methods were done by making thinner mesoporous TiO₂ layer to ease Ru-dye penetration into TiO₂ layer, and by anneal the TiO₂/Ru-dye layer before spin-coated of spiro material to broaden contact area between Ru-dye and spiro material. The highest power conversion efficiency, $\eta = 2.03\%$, is resulted from device which fabricated with optimized methods and used spiro-TPD as hole transport material.

5. Acknowledgement

Authors gratefully acknowledges the financial support from Universitas Padjadjaran under research PUPT (Program Unggulan Perguruan Tinggi) with contract No. 431/UN6.3.1/PL/2016.

References

- [1] Jiazang C, Bo L, Jianfeng Z, Jianghong Z, Zhenping Z. 2012 *J. Phys. Chem. C* **116** 14848
- [2] Ali N, Hussain A, Ahmed R, Wang M.K, Zhao C, Ul Haq B and Fu Y Q 2016 *Renewable and Sustainable Energy Reviews* **59** 726
- [3] Obotowo I N, Obot I B and Ekpe U J 2016 *Journal of Molecular Structure* **1122** 80

- [4] Bastianini M, Vivani R, Nocchetti M, Costenaro D, Bisio C, Oswald F, Meyer T B and Marchese L 2014 *Solar Energy* **107** 692
- [5] Ye M, Wen X, Wang M, Iocozzia J, Zhang N, Lin C and Lin Z 2015 *Materials Today* **18** 155
- [6] Bai S, Bu C, Tai Q, Liang L, Liu Y, You S, Yu Z, Guo S and Zhao X 2013 *ACS Appl. Mater. Interfaces* **5** 3356
- [7] Achari M B, Elumalai V, Vlachopoulos N, Safdari M, Gao J, Gardner J M and Kloo L 2013 *Phys. Chem. Chem. Phys.* **15** 17419
- [8] Wang L, Zhang H, Wang C and Ma T 2013 *ACS Sustain. Chem. Eng.* **1** 205
- [9] Yuan W, Zhao H, Baker and G L 2014 *Organic Electronics* **15** 3362
- [10] Saragi T P I, Spehr T, Siebert A, Fuhrmann-Lieker T and Salbeck J 2007 *Chem. Rev.* **107** 1011
- [11] Saragi T P I, Fuhrmann-Lieker T and Salbeck J 2006 *Adv. Funct. Mater.* **16** 966