

# Dye Sensitized Solar Cell Based on Polyethylene Glycol/4,4'-Diphenylmethane Diisocyanate Copolymer Quasi Solid State Electrolyte

Liow Kai Sing<sup>1,a\*</sup>, Coswald Stephen Sipaut<sup>1,b</sup>, Rachel Fran Mansa<sup>1,c</sup>,  
Jedol Dayou<sup>2,d</sup>

<sup>1</sup>Energy and Materials Research Group, School of Engineering and Information Technology, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia.

<sup>2</sup>Energy, Vibration and Sound Research Group (e-VIBS), School of Science and Technology Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu, Sabah, Malaysia.

<sup>a</sup>liow\_kaising@yahoo.com, <sup>b</sup>css@ums.edu.my, <sup>c</sup>rfmansa@ums.edu.my, <sup>d</sup>jed@ums.edu.my

**Keywords:** Dye sensitized solar cell; quasi-solid electrolyte; polyethylene glycol; 4,4'-diphenylmethane diisocyanate.

## Abstract

In this study, quasi-solid state electrolyte (QSE) was prepared by blending the polyethylene glycol (PEG) with molecular weight of 400, 4,4'-diphenylmethane diisocyanate (MDI), potassium iodide (KI) and iodine (I<sub>2</sub>) under a low reaction temperature (50°C) for two hours. QSEs with a different ratio of PEG to MDI were formulated. Adding 15 vol% of MDI into the QSE was found to give the highest open circuit voltage, short circuit current and energy conversion efficient, which were 360 mV, 0.077 mA/cm<sup>2</sup> and 0.02% respectively.

## Introduction

DSSC has received a great attention in the past decades due to its low production cost and high energy conversion efficiency [1,2,3]. However, the application of liquid electrolyte has resulted in the short lifespan of the DSSC due to solvent evaporation and leakage of electrolyte, desorption of weakly adsorbed dyes from the titanium dioxides (TiO<sub>2</sub>) thin film and corrosion of the platinum electrodes [4,5,6,7]. Hence, solid-state electrolyte has been introduced in the later time. However, it showed lower energy conversion efficiency compared to liquid electrolyte based DSSC. It is due to the poor contact between the solid-state electrolyte and the dye sensitized TiO<sub>2</sub> thin film [8] which results in slower dye regeneration rate. Therefore, QSE has been introduced. QSE based on polymer is one of the best candidates due to its flexibility in the end structural design and the 3D polymer network may retain the redox couple within its strongly. Besides, polymer with certain functional groups may help to dissociate the iodide salt which solvent may not be necessary needed. However, the polymer network may hinder the charge transport in the electrolyte and thus results in lower ionic conductivity compared to liquid electrolyte. In this study, copolymer of PEG/MDI was applied to formulate the QSE. The PEG/MDI copolymers were prepared at the different ratio of PEG to MDI. PEG is cheap. Hence, it is widely applied in the solid/quasi-solid electrolyte. However, its high crystallinity has resulted in the poor performance of the DSSC. Therefore, MDI was introduced to reduce the crystallinity of the PEG. Besides, the MDI which contains the nitrogen group is expected to improve the photovoltage of the DSSC. Furthermore, the hard segment (MDI) of the copolymer is expected to provide dimensional stability to the quasi-solid electrolyte.

## Experimental

### Materials

Potassium iodide (KI), iodine (I<sub>2</sub>), polyethylene glycol (average molecular weight, Mw = 400) (PEG 400), PEG 10,000, 4,4'-diphenylmethane diisocyanate (MDI), titanium (IV) chloride for synthesis (TiCl<sub>4</sub>) and nitric acid 65% were purchased from Merck. Titanium (IV) oxide (Aeroxide P25) (TiO<sub>2</sub>) was purchased from Acros Organic. Triton-X and Fluorine doped tin oxide coated glass slide, 7Ω/sq (FTO) were purchased from Sigma Aldrich.

### Preparation of PEG/MDI copolymer quasi-solid electrolyte

0.5M KI was added into the PEG. The mixture was stirred and heated at 60°C for 30 minutes until the KI dissolved. Then, 0.05M I<sub>2</sub> was added into the mixture and stirred for 5 minutes to until it dissolved. After that, MDI was introduced into the mixture slowly. The resulting mixture was stirred and heated at 50 °C for two hours. The ratio of the PEG to MDI was varied as shown in Table 1.

### Preparation of DSSC

The FTO glass was cleaned under sonication by detergent solution (10 minutes), followed by acetone (10 minutes) and ethanol (10 minutes). Then the cleaned FTO glass was treated with 40mM TiCl<sub>4</sub> at 70 °C for 30 minutes. After that, TiO<sub>2</sub> paste was prepared by blending 0.5g of TiO<sub>2</sub> with 2mL nitric acid (0.1M), 0.25g PEG 10,000 and two drops of Triton X-100 in an agate mortar for 15 minutes. Then, the TiO<sub>2</sub> paste was allowed to equilibrate for 5 minutes. After that, the TiO<sub>2</sub> paste was coated onto an FTO glass by doctor-blade technique and successive sintering at 450°C for 30 minutes. The TiO<sub>2</sub> coated FTO glass was treated with 70mM TiCl<sub>4</sub> at 70 °C for 30 minutes and sintered at 450°C for 30 minutes. Then, it was sensitized overnight (24 hours) with blueberry dye extract. After that, the QSE was added onto the dye sensitized TiO<sub>2</sub> film and heated in an oven at 60°C for 30 minutes. To prepare the counter electrode, FTO glass was coated with carbon black by using a candle. The carbon black coated FTO glass is then heated at 200°C for 15 minutes. After that, the counter electrode and photoanode were assembled by using two binder clips.

### Measurement

The conductivity of the electrolytes was measured by digital conductivity meter (Wissenschaftlich Technische Werkstätten, LF330). The open circuit voltage (V<sub>oc</sub>) and short circuit current (J<sub>sc</sub>) were measured by using multimeter and potentiometer under a metal halide lamp (75 watt). The fill factor (FF) and energy conversion efficiency (η%) of the DSSC were calculated by using the Eq. 1 and Eq. 2.

$$FF = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100 \quad (2)$$

where J<sub>sc</sub> is the short-circuit current density (mA/cm<sup>2</sup>); V<sub>oc</sub> is the open-circuit voltage (mV); J<sub>max</sub> (mA/cm<sup>2</sup>) and V<sub>max</sub>(mV) are the maximum current density and voltage obtained at the point of maximum power output from the J-V curve and P<sub>in</sub> is the incident light power (mW/cm<sup>2</sup>).

## Results and discussion

According to Table 1, the  $J_{sc}$  was very low. This may due to the  $TiO_2$  films were too thin and therefore the dyes uptake were less. Besides, there were bubbles in the  $TiO_2$  paste that coated on the FTO glass. It resulted in large pores formation of the  $TiO_2$  films after sintering. The large pores formed increased the direct contact of the FTO glass with the electrolyte in which short circuit may happen.

According to Table 1, the conductivity of the QSE decreased as the content of the MDI introduced increased. This may due to the increase of the QSE viscosity. From Table 1 and Fig. 1, the  $J_{sc}$  was first increased as the MDI content increased. It showed that, the  $J_{sc}$  was not mainly depending on the conductivity [9]. The increase of the  $J_{sc}$  may due to the increase of the diffusion coefficient of the triiodide ions upon the introducing of the MDI. Besides, the introducing of the MDI may reduce the crystallinity of the PEG. Furthermore, the lone pair electron of the phenyl group and oxygen atom in the MDI may improve the ion movement and electron transfer in the electrolyte. However,  $J_{sc}$  started to decrease after reaching a maximal value. This may due to the increase of the electrolyte viscosity.

The increased of the  $V_{oc}$  may due to the MDI is a nitrogen containing compound. The nitrogen containing part of the MDI adsorbed on the  $TiO_2$  surface and resulted in a negative shift of the conduction band of  $TiO_2$ . Besides, the negative shift of the conduction band may reduce the charge recombination rate. The FF decreased as the MDI introduced. This may due to the increase of the viscosity of the electrolyte which resulted in poorer electrolyte penetration into the  $TiO_2$  film.

Table 1 Performance of DSSC with different electrolyte formulation

Electrolyte	PEG:MDI [mL]	Conductivity ( $\mu\text{S}/\text{cm}$ )	$V_{oc}$ [mV]	$J_{sc}$ [ $\text{mA}/\text{cm}^2$ ]	FF	$\eta$ [%]
0	20:0	356.3	295	0.053	0.31	0.015
1	19:1	188.7	300	0.052	0.27	0.013
2	18:2	98.7	305	0.061	0.26	0.015
3	17:3	45.1	360	0.077	0.24	0.025
4	16:4	20.4	275	0.051	0.24	0.011
5	15:5	-	270	0.044	0.24	0.010

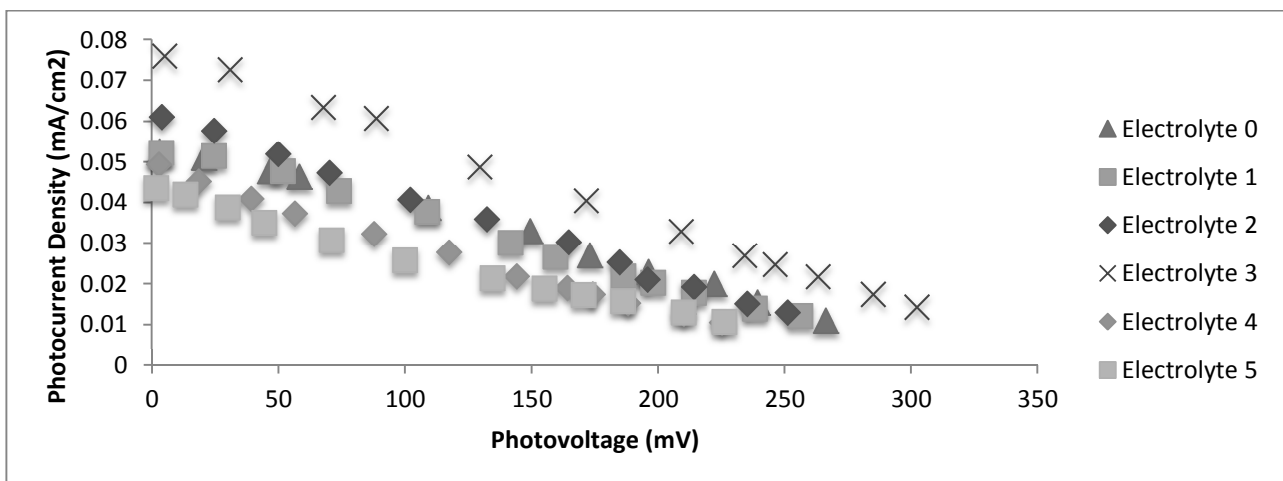


Figure 1 Performance of DSSC with different electrolyte formulation

## Conclusions

Quasi-solid electrolytes based on different formulations of PEG/MDI copolymer were prepared. The energy conversion efficiency of the DSSC increased upon the introduction of the MDI. It was due to the reducing of the PEG crystallinity and plasticizing effect of the MDI. Besides, the nitrogen containing MDI can improve the Voc of the DSSC.

## Acknowledgment

This research is supported by the Malaysian Ministry of Education under the research grant number ERGS0019-TK-1/2012, and is greatly acknowledged.

## References

- [1] B. O'Regan, M. Gratzel, *Nature* 353 (1991) 737–740.
- [2] O.A. Ileperuma, M.A.K.L. Dissanayake, S. Somasunderam, L.R.A.K. Bandara, *Sol. Energy Mater. Sol. Cells* 84 (2004) 117–124.
- [3] Y.L. Lee, Y.J. Shen and Y.M. Yang. A hybrid PVDF-HFP/nanoparticle gel electrolyte for dye-sensitized solar cell applications. *Nanotechnology* 19(2008) 455201 (6pp)
- [4] J.R. Durrant and S.A. Haque. 2003. *Nat. Mater.*2362
- [5] Z.P. Huo, S.Y. Dai, K.J. Wang, F.T. Kong, C.N. Zhang, X. Pan, X.Q. Fang. Nanocomposite gel electrolyte with large enhanced charge transport properties of an  $I_3^-/I^-$  redox couple for quasi-solid-state dye-sensitized solar cells. *Solar Energy Materials & Solar Cells* 91 (2007) 1959–1965
- [6] RF Mansa, ARA Yugis, KS Liow, STL Chai, MC Ung, Jedol Dayou, CS Sipaut. A Brief Review on Photoanode, Electrolyte, and Photocathode Materials for Dye-Sensitized Solar Cell Based on Natural Dye Photosensitizers. *Developments in Sustainable Chemical and Bioprocess Technology* (2013) 313-319.
- [7] Rachel Fran Mansa, Gobinat Govindasamy, Yan Yan Farm, Hafeza Abu Bakar, Jedol Dayou & Coswald Stephen Sipaut. Hibiscus flower extract as the natural dye sensitizer for dye-sensitized solar cell. *Journal of Physical Science* (2013).
- [8] J. Wu, S. Hao, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fang, S. Yin, T. Sato, *Adv. Funct. Mater.* 17 (2007) 2645
- [9] Y.F. Zhou, W.C. Xiang, S.Chen, S.B. Fang, X.W. Zhou, J.B. Zhang, Y. Lin. Influences of poly(ether urethane) introduction on poly(ethylene oxide) based polymer electrolyte for solvent-free dye-sensitized solar cells. *Electrochimica Acta* 54 (2009) 6645–6650.