Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2013, Article ID 617126, 5 pages
http://dx.doi.org/10.1155/2013/617126

Research Article

Dye-Sensitized Solar Cells with Optimal Gel Electrolyte Using the Taguchi Design Method

Jenn-Kai Tsai,[1] Wen Dung Hsu,[2] Tian-Chiuan Wu,[1] Jia-Song Zhou,[1] Ji-Lin Li,[1] Jian-Hao Liao,[1] and Teen-Hang Meen[1]

[1] *Department of Electronic Engineering, National Formosa University, Yunlin 632, Taiwan*
[2] *Department of Materials Science and Engineering, National Cheng Kung University, Tainan City 701, Taiwan*

Correspondence should be addressed to Jenn-Kai Tsai; tsaijk@nfu.edu.tw

Received 11 September 2013; Accepted 10 October 2013

Academic Editor: Liang-Wen Ji

The Taguchi method was adopted to determine the optimal gel electrolyte used in dye-sensitized solar cells (DSSCs). Since electrolyte is a very important factor in fabrication of high performance and long-term stability DSSCs, to find the optimal composition of gel electrolyte is desired. In this paper, the common ingredients used in the liquid electrolyte were chosen. The ingredients then mixed with cheap ionic liquids and poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) was added to form colloidal electrolyte (gel). The optimal composition of each materials in the gel electrolyte determined by Taguchi method consists of 0.03 M I_2, 0.15 M KI, 0.6 M LiI, 0.5 M 4-tertbutylpyridine (TBP), and 10% PVDF-HFP dissolved in the acetonitrile and 3-methoxypropionitrile (MPN) solution with volume ratio of 2 : 1. The short circuit current density of 14.11 mA/cm^2, the conversion efficiency (η) of 5.52%, and the lifetime of over 110 days was observed for the dye-sensitized solar cell assembled with optimal gel electrolyte. The lifetime increases 10 times when compared with the conventional dye-sensitized solar cell assembled with liquid electrolyte.

1. Introduction

Since the pioneering work of Grätzel and O'Regan in 1991, dye-sensitized solar cells (DSSCs) have become one of the promising devices in photovoltaic application, because of low fabrication cost, good stability, and compatibility with flexible substrates [1–3]. Conventional dye-sensitized solar cell has the structure of porous titanium dioxide layer as the dye adsorbed on the TiO_2 surface and an organic liquid, I^-/I_3^- solution as electrolyte top on the TiO_2 layer, and the two layers are sandwiched in between bottom electrode made of ITO (SnO_2) and top electrode made of platinum thin film. However, due to the loss of liquid electrolyte through the leakage or evaporation, the lifetime of dye-sensitized solar cells is limited, which causes the problem for commercialization. To solve this issue and enhance durability, gel or quasisolid-state electrolytes mixed with ionic liquids were used to improve the sealing and minimize the loss of electrolytes [4–6]. Since the electrolyte is an important factor affecting the conversion efficiency of DSSC, to find an optimized composition of the mixture is crucial.

The mixture is usually composed of polymers and ionic liquids. In order to determine the optimized composition of each material, Taguchi method which takes multifactors into consideration is the most powerful tool for statistical design of this kind of experiments for improvement of the product and the process. It is a simple, systematic and powerful method to increase the experiment quality. The advantage of this method is to reduce both product cost and number of experiments [7–9]. The method starts from identifying the impact factors in the experiments and then does the experiments by systematically adjusting the quantity of each factor and assuming that the interaction between the factors is orthogonal.

In this study the optimized mixture was determined by Taguchi method. The mixture was composed of seven materials, iodine (I_2), lithium iodide (LI), potassium iodide (KI), 4-tertbutylpyridine (TBP), 3-methoxypropionitrile (MPN), acetonitrile (ACN), and PVDF-HFP. The other common ionic liquids as 1,2-dimethyl-3-propylimidazolium iodide (DMPII) [10] and N-methylimidazole (NMBI) [11] were not employed in this study due to the fact that were more expensive. The quantity of each material was controlled in two levels. The optimized constitute of the most suitable gel electrolyte used in DSSC was identified with minimum number of experiments. DSSC with the best efficiency of 5.52% was observed in AM 1.5 illuminations.

2. Materials and Methods

The gel electrolyte studied in this work containing I_2 (Osaka, Japan), LiI (Aldrich, USA), KI (Hanawa, Japan), TBP (Aldrich, USA), 3-methoxypropionitrile (MPN) (Fluka, China), acetonitrile (Avantor, USA), and PVDF-HFP (Aldrich, USA) was prepared, and the Taguchi method was used to determine the optimized composition of each component. The mixture was then heated to 80°C and became a liquid-type electrolyte.

The 10 wt% TiO_2 paste was prepared by mixing nanocrystalline TiO_2 nanoparticles (NPs) (Degussa, P25, the average nanoparticle diameter was about 25–30 nm), tert-butyl alcohol, and deionized water. The paste then scraped on transparent indium-tin-oxide (ITO) glass by doctor balding process to form TiO_2 thick film. The film was annealed under air at 150°C for 90 min to decompose the organic compounds and then the temperature increased to 350°C for 30 min to assist the interconnection of TiO_2 NPs. After that the TiO_2 thin films were immersed in 0.3 mM N3 dye at 45°C for 90 min. The Pt thin film was grown on ITO glass by an electroplating process prepared for as counter electrode. Then the counter electrode was placed on the top of the TiO_2 thin film and bonded by a 50 μm-thick hot-melt polymer spacer. Finally, the previously prepared gel electrolyte was injected into the cell by capillary forces through an injecting hole drilled in the counter electrode. Finally, the hole was covered and sealed with a piece of hot-melt polymer to prevent electrolyte leakage. The liquid-type electrolyte then cooled and became a gel electrolyte. The resulting active electrode area was approximately 0.25 cm^2 (0.5 cm × 0.5 cm). The schematic image of the DSSC structure is shown in Figure 1.

The current-voltage characteristics of samples were measured by Keithley 2400 source meter (Keithley Instruments, Inc., Ohio, USA) under simulated sunlight (SAN-EI XES-40S1, San Ei Brand, Japan), AM 1.5 radiation at 100 mW/cm^2.

Table 1 shows the composition of gel electrolyte and factor symbols used in the Taguchi method. The reason that the seven materials were chosen for fabrication of the gel electrolytes is explained as follows.

(1) Iodine (I_2, factor A), lithium iodide (LiI, factor B), and potassium iodide (KI, factor C) are the most popular materials used as the electrolyte in DSSC to produce the redox I^-/I_3^-, in which the redox energy level matches the highest occupied molecular orbital (HOMO) energy level of the dye, and hence speeds up the carrier diffusion in the organic liquid solvent. In addition LiI would improve the current density of DSSC. The LiI would decompose to Li^+-e pair while be absorbed on the TiO_2 surface by attracting the conduction band electrons. The Li^+-e pairs can migrate toward or away from the TiO_2 nanoparticle surface improving the conductivity of TiO_2 layer and enhance the current density of DSSC. Besides, the materials are relatively cheap and easy to obtain.

(2) 4-Tertbutylpyridine (TBP, factor D) was used to avoid the TiO_2 nanoparticles which are not covered by the dye molecules directly contacted with the electrolyte. The contact would result in high leakage current through transport of excited electrons in TiO_2 layer to electrolyte.

(3) 3-Methoxypropionitrile (MPN, factor E) and acetonitrile (factor F) are the common solvent used to prepare the electrolyte. Acetonitrile was employed due to its high ionic conductivity and effective electrolyte leakage-proof.

(4) PVDF-HFP (factor G) is a useful material to gel liquid electrolyte to overcome the electrolyte leakage problem. In addition, it also can improve the dissociation of lithium iodide to enhance the iodide ion concentration [12].

Table 1: Gel electrolyte parameters and factors of Taguchi method.

Factor symbol	Parameter	Level 1	Level 2
A	I_2	0.03 M	0.06 M
B	LiI	0.3 M	0.6 M
C	KI	0.15 M	0.1 M
D	TBP	0.5 M	0.8 M
E	MPN	1 mL	2 mL
F	Acetonitrile	1 mL	2 mL
G	PVDF-HFP	10 wt%	5 wt%

In the Taguchi method, a modified orthogonal array of L_8 is found to be appropriate and hence it was chosen. The orthogonal array (L_8) is shown in Table 2 where the experiments are divided into 8 groups and number 1 represents level 1 shown in Table 1 (so as 2). The experimental design using the orthogonal array L_8 of Taguchi's method provides a simple, efficient, and systematic approach for optimal design of experiments to assess the performance, quality, and cost. The error would be small and the cost of experiments would be economical. Each experiment group was duplicated three times in order to estimate the random error.

3. Results and Discussion

Figure 2 shows the conversion efficiencies of DSSCs of 8 experiment groups. The results demonstrate that the conversion efficiency of the duplicates of each experiment group is very closely indicating that the random errors are small and the fabrication processes of DSSC are reliable. The 1st experiment group has the highest conversion efficiency of 4.37% among all the groups.

Table 2: Experimental layout and results using the modified L_8 orthogonal array.

Group	Factor A	B	C	D	E	F	G	η_{avg}	S/N_{LTB}
1	1	1	1	1	1	1	1	4.08	12.20
2	1	1	2	2	2	2	1	2.98	9.49
3	2	2	1	1	2	2	1	3.80	11.56
4	2	2	2	2	1	1	1	2.48	7.76
5	1	2	1	2	2	1	2	3.19	10.06
6	1	2	2	1	1	2	2	3.15	9.95
7	2	1	1	2	1	2	2	2.17	6.70
8	2	1	2	1	2	1	2	2.64	8.39

Table 3: The analysis results of each parameter and the optimal design parameters of the electrolyte composition.

Parameter	I_2	LiI	KI	TBP	MPN	ACN	PVDF-HFP
Factor Symbol	A	B	C	D	E	F	G
Level 1 S/N	10.421	9.192	10.129	10.524	9.152	9.599	10.205
Level 2 S/N	8.603	9.833	8.895	8.501	9.872	9.426	8.774
$S/N_{max} - S/N_{min}$	1.82	0.64	1.23	2.02	0.72	0.17	1.44
Ranking	2	6	4	1	5	7	3
Optimum	0.03 M	0.6 M	0.15 M	0.5 M	1 mL	2 mL	10 wt%

Taguchi defined that the optimal operator combination is to minimize variances of quality characteristics resulted from signal-to-noise ratio (S/N ratio). It was used for the larger-the-better (LTB) evaluated by using the following equation:

$$\frac{S}{N_{LTB}} = -10 \log \left[\frac{1}{n} \sum_{i=1}^{n} \left(\frac{1}{y_i} \right)^2 \right], \quad (1)$$

where n is the number of tests and y_i denotes the respective characteristic, which is the conversion efficiency in this study. Then, the measured values of quality characteristics obtained through the experiments will be transformed into S/N ratio by using (1). Table 2 shows the average conversion efficiencies (η_{avg}) and the S/N ratio of each experiment group. The maximum average conversion efficiency and S/N ratio appear in the 1st experiment group with the value of 4.08 and 12.19, respectively. Since the S/N ratio represents the signal-to-noise ratio of conversion efficiencies, the larger the ratio the higher consistent the data. By comparison of the difference of S/N ratio between level 1 and level 2 of the same material, the degree of the influence of seven materials can be ranked. Table 3 shows the further analysis. The results indicate that the TBP, which is used to avoid the TiO_2 nanoparticles that are not covered by the dye molecules directly contact with the electrolyte, gives the most impact on the performance of conversion efficiency. If the TBP is over added in the mixture, the electronic transport is hindered and lowering the conversion efficiency. The seven materials are

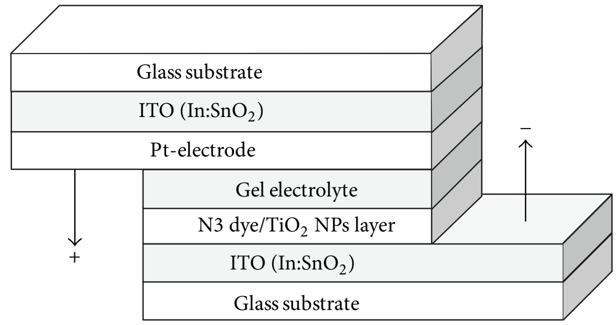

Figure 1: The schematic device structure of TiO_2 nanoparticles dye-sensitized solar cell using the gel electrolyte.

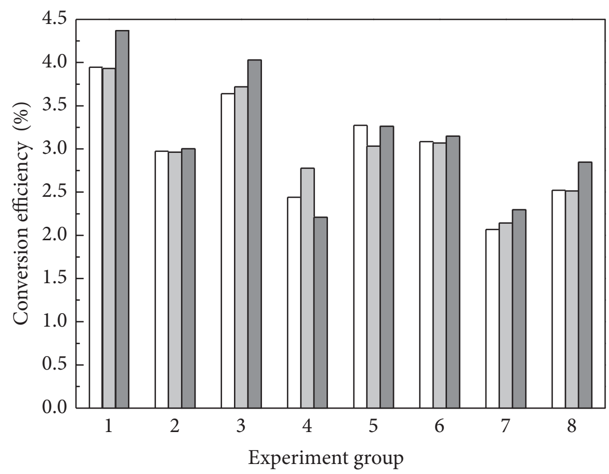

Figure 2: The conversion efficiency distribution of dye-sensitized solar cells using different gel electrolyte.

ranked as TBP, I_2, PVDF-HFP, KI, MPN, LiI, and ACN from high to low by the sequence of their degree of influence.

After further analysis, the optimal operator combinations can be located, according to the S/N_{max} ratio. The optimal design of experiment parameters are I_2 of 0.03 M, LiI of 0.6 M, KI of 0.15 M, TBP of 0.5 M, MPN of 1 mL, ACN of 2 mL, and PVDF-HFP of 10 wt%, as arranged and shown in Table 3. Current densities against voltage (J-V) characteristics of the DSSCs prepared by the optimal parameters under AM 1.5 sunlight are shown in Figure 3. The photovoltaic properties of the DSSCs using the optimal operator combinations, the gel electrolyte of 1st and 6th experiment groups, are summarized in Table 4. The short-circuit current density is 12.17 mA/cm^2 and the open-circuit voltage is 0.71 V. The fill factor (F.F.) was calculated using

$$\text{F.F.} = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}}, \quad (2)$$

where J_{max} is the current density at maximum power output, J_{SC} the current density at short circuit, V_{max} the voltage at maximum power output, and V_{OC} the voltage at open circuit. The fill factor calculated using (2) for the optimum electrolyte

Table 4: Characteristics of DSSCs fabricated using the optimal operator combination, experiment groups 1 and 6 gel electrolyte.

Electrolyte	V_{OC} (V)	J_{SC} (mA/cm^2)	V_m (V)	J_m (mA/cm^2)	$F.F.$ (%)	H (%)
Optimum	0.71	14.11	0.48	11.51	55.14	5.52
Group 1	0.72	11.86	0.45	9.70	51.43	4.37
Group 6	0.69	10.90	0.40	8.241	43.84	3.30

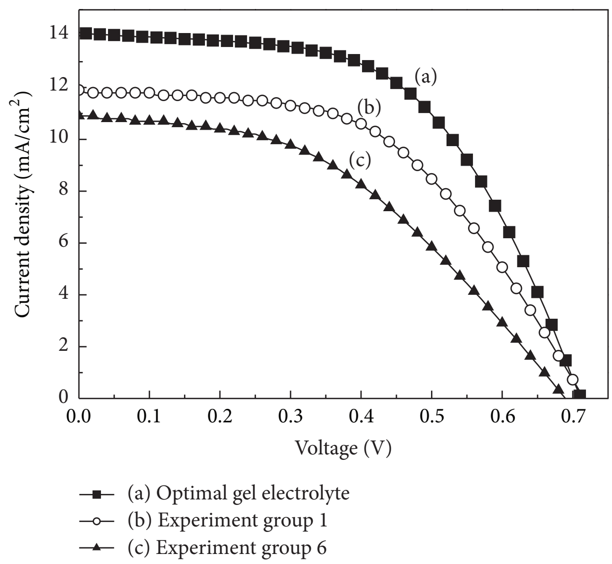

Figure 3: J-V curves of DSSCs using (a) the optimal combination and (b) 1st and (c) 6th experiment group gel electrolytes.

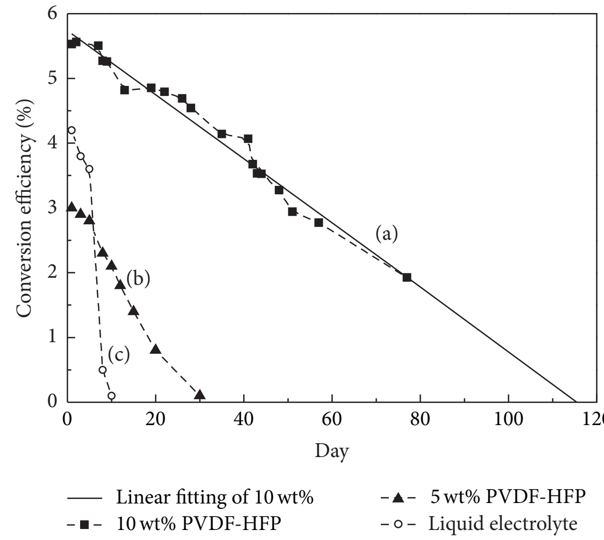

Figure 4: The lifetime of DSSCs uses the different concentrations of gel electrolyte, (a) 10 wt% PVDF-HFP (optimal operator combination), (b) 5 wt% PVDF-HFP (6th experiment group), and (c) the common liquid electrolyte comparison chart.

DSSC is 55.8%. The photoelectric conversion efficiency (η) is calculated by

$$\eta = \frac{J_{SC} \times V_{OC} \times \text{F.F.}}{P_{in}}, \quad (3)$$

where P_{in} is total incident power density. The conversion efficiency for the optimum electrolyte DSSC calculated using (3) is 5.52%. It is enhanced over 26.3% compared to the 1st experiment group. The result demonstrates that the Taguchi experiment design method is very useful in this study.

Figure 4 shows the electrolyte effect on the lifetime of DSSCs characterized by the power conversion efficiency associated with time. The lifetime of DSSC, fabricated by the 6th experiment group, used the gel electrolytes with PVDF-HFP concentration of 5 wt% was about 30 days. On the other hand the lifetime of DSSC, fabricated by the optimal gel electrolyte, of PVDF-HFP concentration of 10 wt% was over 80 days and the lifetime is expected to be 110 days as the conversion efficiency becomes zero. In general the lifetime of the DSSC with liquid electrolyte was about one week to ten days, however, by replacing the liquid electrolyte with the gel electrolyte, the lifetime of DSSC increases over ten times. Therefore, the DSSCs using gel electrolytes present a better performance in lifetime compared to those assembled with classical liquid electrolyte.

4. Conclusion

In this study, the Taguchi method is adopted to determine the optimal composition of gel electrolyte in the assembly of dye-sensitized solar cells. The development procedure can be more efficient by using Taguchi experimental design method. The lifetime was found ten times longer than conventional DSSC by replacing liquid electrolyte with optimal gel electrolyte. The DSSC with optimal gel electrolyte had the short circuit current density of 12.17 mA/cm^2, the open-circuit voltage of 0.71 V, fill factor of 55.8%, the conversion efficiency of 5.52%, and the lifetime of over 110 days.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors are grateful to Tung-Lung Wu and Jun-Hong Shih for their assistance and National Formosa University for providing financial support in this project.

References

[1] B. O'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.

[2] M. Grätzel, "Photoelectrochemical cells," *Nature*, vol. 414, pp. 338–344, 2001.

[3] M. K. Nazeeruddin, A. Kay, I. Rodicio et al., "Conversion of light to electricity by *cis*-X_2bis(2,2′-bipyridyl-4,4′-dicarboxylate)ruthenium(II) charge-transfer sensitizers (X = Cl^-, Br^-, I^-, CN^-, and SCN^-) on nanocrystalline TiO_2 electrodes," *Journal of the American Chemical Society*, vol. 115, no. 14, pp. 6382–6390, 1993.

[4] T. M. W. J. Bandara, M. A. K. L. Dissanayake, and B.-E. Mellander, "Dye sensitized solar cells with poly(acrylonitrile) based plasticized electrolyte containing MgI_2," *Electrochimica Acta*, vol. 55, no. 6, pp. 2044–2047, 2010.

[5] D. Kuang, P. Wang, S. Ito, S. M. Zakeeruddin, and M. Grätzel, "Stable mesoscopic dye-sensitized solar cells based on tetracyanoborate ionic liquid electrolyte," *Journal of the American Chemical Society*, vol. 128, no. 24, pp. 7732–7733, 2006.

[6] J. E. Benedetti, A. D. Gonçalves, A. L. B. Formiga et al., "A polymer gel electrolyte composed of a poly(ethylene oxide) copolymer and the influence of its composition on the dynamics and performance of dye-sensitized solar cells," *Journal of Power Sources*, vol. 195, no. 4, pp. 1246–1255, 2010.

[7] C. Chan, W. Hsu, C. Chang, and C. Hsu, "Preparation and characterization of gasochromic Pt/WO_3 hydrogen sensor by using the Taguchi design method," *Sensors and Actuators B*, vol. 145, no. 2, pp. 691–697, 2010.

[8] T. Tsai, "Improving the fine-pitch stencil printing capability using the Taguchi method and Taguchi fuzzy-based model," *Robotics and Computer-Integrated Manufacturing*, vol. 27, no. 4, pp. 808–817, 2011.

[9] H. Lee, C. Han, Y. Sung, S. S. Sekhon, and K. Kim, "Gel electrolyte based on UV-cured polyurethane for dye-sensitized solar cells," *Current Applied Physics*, vol. 11, no. 1, pp. 158–162, 2011.

[10] H. Chen, C. Lin, Y. Lai et al., "Electrophoretic deposition of ZnO film and its compression for a plastic based flexible dye-sensitized solar cell," *Journal of Power Sources*, vol. 196, no. 10, pp. 4859–4864, 2011.

[11] H. Yang, J. Liu, Y. Lin, J. Zhang, and X. Zhou, "PEO-imidazole ionic liquid-based electrolyte and the influence of NMBI on dye-sensitized solar cells," *Electrochimica Acta*, vol. 56, no. 18, pp. 6271–6276, 2011.

[12] J. H. Kim, Y. S. Chi, and T. J. Kang, "Optimization of quasi-solid-state dye-sensitized photovoltaic fibers using porous polymer electrolyte membranes," *Journal of Power Sources*, vol. 229, pp. 84–94, 2013.