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Towards fabrication of stable dye sensitized solar cells based on acetonitrile as solvent for the redox couple

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ABSTRACT

The present paper describes the scheme used to fabricate completely sealed dye sensitized solar cell (DSC) and its stability analysis employing acetonitrile as the solvent for redox couple. Since acetonitrile is extremely volatile a perfect sealing is essential to prevent the leakage of electrolyte. The usual hot melt sealing is employed for edge sealing whereas hole sealing is carried out with tooth pick and a UV curable adhesive. The degradation in efficiency is found to be 20% for low efficiency cells whereas, for high efficiency cells it is found to be 45% after 45 days. The leakage of highly volatile acetonitrile through the edge and hole is mainly responsible for the reduction in the performance of the device. Hence a high temperature sealing method is proposed to fabricate stable cells. Copyright © 2014 VBRI press.

Keywords: Dye sensitized solar cell; stability analysis; efficiency, redox couple.

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Introduction

Photo-electrochemical dye sensitized solar cells (DSC), invented by Michel Grätzel and B.O' Regan have attracted considerable attention as a cost effective alternative to conventional silicon based solar cells **[1-5].** DSC consists of a dye sensitized TiO2 photo-electrode, an electrolyte with I^-/I_3^- redox couple dissolved in a suitable solvent and a counter electrode made of a catalytic layer coated on conducting glass substrate. Such solar cells have an impressive conversion efficiency reaching around 11.5% **[6-9].** However, a major drawback of DSCs is the long term stability mainly attributable to the usage of the liquid electrolyte with a highly volatile solvent. Several approaches have been attempted subsequently to overcome these problems, including the use of a p-type semiconductor to conduct away the hole generated in the dye, the use of solid polymer electrolytes and the use of a hole conducting organic material **[10-11].** Even though these cells are industrially much more compatible than the liquid electrolyte based solar cells, the efficiency is much less compared to the latter one.

For DSCs based on liquid electrolyte to be applicable commercially, a life time of 20-25 years is essential which is possible only with the understanding of various degradation mechanisms associated with it. These mechanisms include molecular, cell, module and system level **[12].** Some of the degradation mechanisms in the

molecular level include the reaction of dye with electrolyte components, the excitation of TiO_2 in UV light causing the oxidation of electrolyte or dye and the accumulation of cations such as H^+ and Li^+ **[12-14].** All these problems are greatly accelerated by a defective sealing in the cell level. Additionally, the stability of module and system as such depends on the prevention of degradation in the cell level which again depends on the sealing procedure of the device.

For good stability, a sealing material should satisfy the following requirements: It should not react with any of the components of DSC, especially with the electrolyte since it is highly corrosive. An imperfect sealing can degrade the cell performance either by the evaporation of electrolyte or by the entry of water vapors which accelerates the degradation of dye.

The present paper discusses in detail the process used to fabricate dye solar cells employing acetonitrile as the solvent for electrolyte and the performance evaluation over a period of 45 days (1080 h). Though acetonitrile based electrolytes enable the fabrication of high efficiency cells, it creates problems in the fabrication of industrially compatible stable cells due to its volatile nature. Consequently less volatile methoxypropionitrile is usually used in place acetonitrile. However the efficiency is less in the former case compared to the latter one. In the present paper, the method adopted for hole sealing is different from the conventional method. In addition a high temperature sealing method is suggested for volatile solvents based electrolyte to enable the fabrication of stable cells.

Experimental

Materials

FTO glass (15 Ω/cm^2), N719 dye, Platisol, Surlyn film (60 µm) and Vac n Fill syringe were brought from M/s Solaronix, Switzerland. The Bynel films were obtained from Dupont, USA. P25 TiO_2 was got from Evonic Degussa. UV curable adhesive was from DYMAX Corporation.

Fabrication of sealed cell

FTO coated glass was used as the substrate for photoanode and counter electrode. Before coating the platinum layer a hole of 0.5 mm diameter was drilled on the counter electrode. Dye sensitized TiO^2 nanocrystalline layer made from a colloidal pate of TiO_2 nanoparticle and microspheres with an active area of 0.47 cm^2 was used as the photo electrode. The preparation procedure adopted is the same as that described in the literature **[15-16].** The sealing gaskets (Surlyn or Bynel) were cut in such a way that its inner dimension is a little higher than the area of the active layer. The counter electrode was then placed on top of the photo-anode in such a manner that the hole should be within the inner dimension of the gasket. The sealing was done with a programmable hot press set at 125 ^OC for Surlyn (150 ^OC for bynel) for duration of 60 s. The sealing quality was examined from the transparency of the polymer foil. The filling of electrolyte was done with special type of Vac n Fill syringe. This will help in removing the air trapped inside the space between the photoanode and the counter electrode in one way and enables the filling of electrolyte in the other way. In order to seal the hole a different procedure was used. The usual procedure of sealing involves the usage of hot melt method. Since acetonitrile has low boiling point this procedure results in the leakage of solvent which necessitates the usage of a non heating method. In the applied method, a tooth pick was inserted into the pre drilled hole and was cut on top to remove the projected portions outside the hole. A drop of UV curable adhesive Dymax was then poured and covered with a microscope cover slide. The entire cell was then kept under UV illumination for 5 min, which resulted in the sealing of the cell. The photograph of the cells made of microspheres (a & b) with sputtered platinum as counter electrode and a fully transparent sealed cell (c& d) made of nanoparticles with solution deposited platinum as counter electrode are shown in **Fig. 1.** The cells made of microspheres were used for stability measurement. Four sealed cells were prepared to perform stability analysis and the results given are average of four cells.

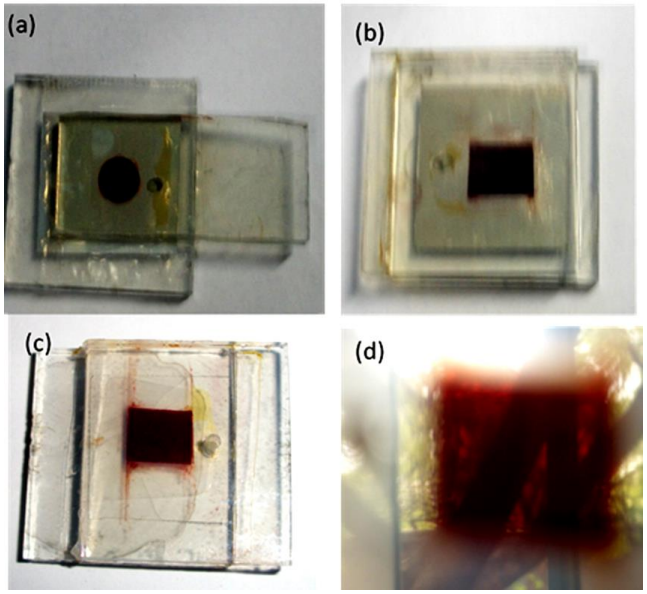

Fig. 1. Cells made of microspheres (a & b) and a fully transparent sealed cell (c & d) made of nanoparticles with solution deposited platinum.

Instrumentation

Photocurrent measurements of the cells were performed with a Keithley model 2420 source meter under illumination (AM1.5, 100 mW/cm^2) using a solar simulator (Newport Class 3A).

Results and discussion

Stability analysis

For stability analysis the cells were kept at room temperature under ambient conditions and the data was taken periodically for 45 days. Immediately after sealing, the efficiency was 7 %. However within a weak the efficiency has come down to 4.8% and stabilized around 4% as shown in **Fig. 2**. The reduction in efficiency is caused by the leakage of electrolyte. Even though sealing

has been done with utmost care, the leakage of solvent could not be prevented. The increase in series resistance (Rs) and the decrease in shunt resistance indicate the solvent leakage which makes the diffusion of ions difficult, giving a high series resistance. Accordingly the FF also reduces. Further the leakage of solvent might have increased the local concentration of I_3^- ions which is responsible for the reduction in voltage **[17].** In order to see the effect of solvent leakage, the electrolyte was kept in a normal bottle with the cap slightly loosen instead of the vacuum tight container and left it in that for 2-3 days and cells were fabricated with that electrolyte **(Fig. 3)**.

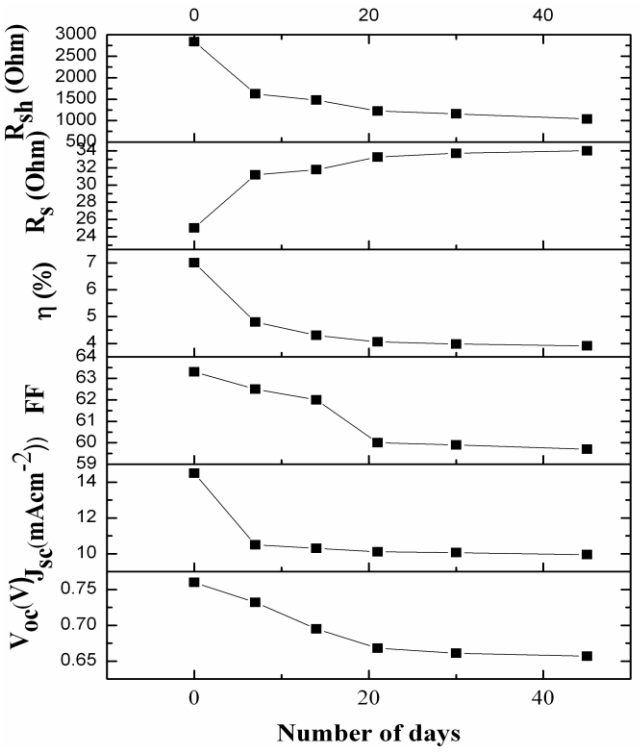

Fig. 2. Stability data of high efficiency cell.

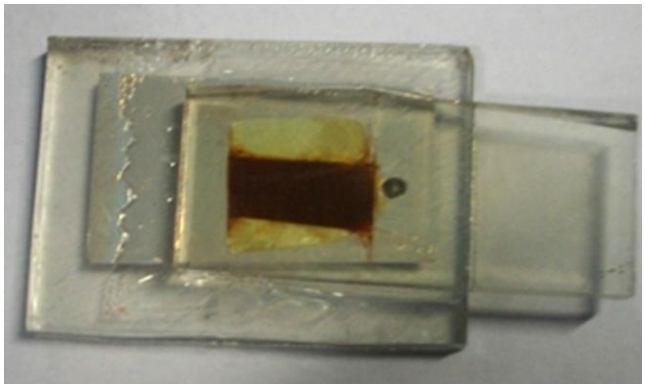

Fig. 3. Sealed cell with concentrated electrolyte.

Immediately after sealing, the efficiency was around 4.02 % and it was maintained without much variation for a period of 45 days as shown in **Fig. 4.** From the data it is clear that the efficiency degradation comes mainly from the reduction in photo voltage and the variation in all the other photovoltaic parameters was marginal, in contrast to the high efficiency cell which shows a wide variation initially. The low efficiency was ascribed to the use of a concentrated electrolyte. The overall efficiency reduction within 45 days was found to be 20% in the present cell whereas in case of high efficiency cell it was 45%.

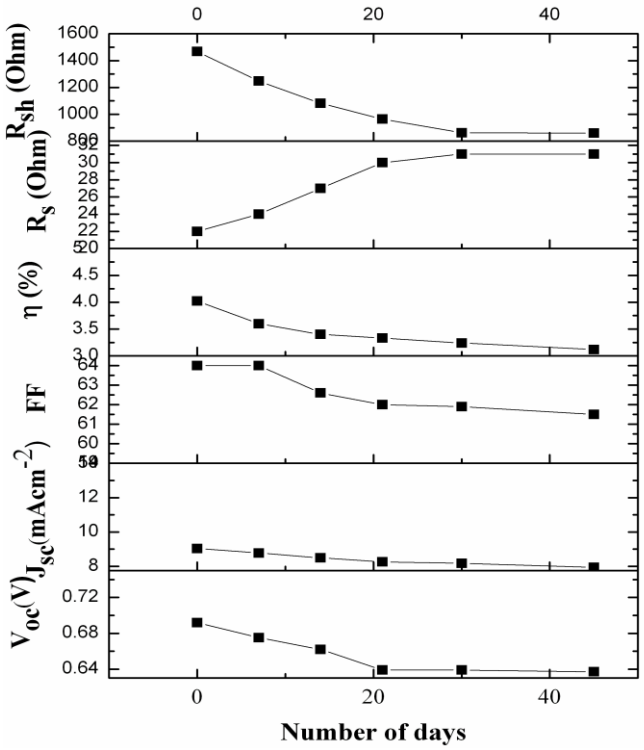

Fig. 4. Stability data for cells fabricated with concentrated electrolyte.

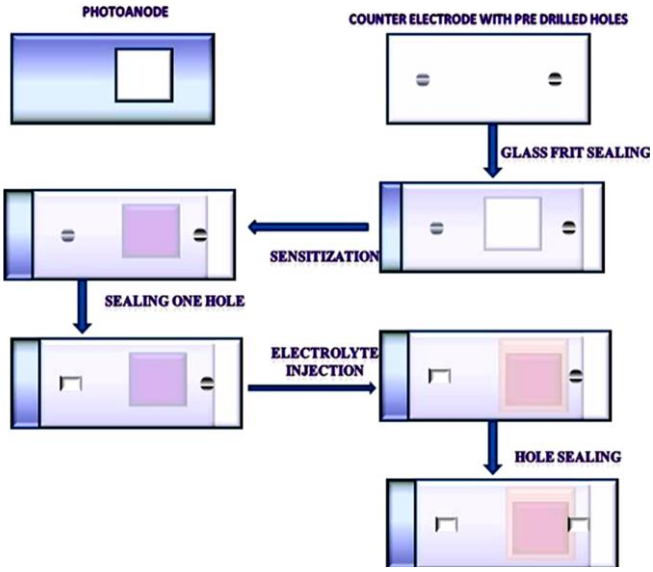

Fig. 5. Schematic diagram illustrating the proposed procedure for making sealed cells.

Proposal for making stable solar cells

Based on the attempts made to fabricate a perfectly sealed cell, the adopted sealing procedure is found to be insufficient for acetonitrile based electrolyte. Hence in order to get a highly stable cell with volatile solvent the

fabrication procedure has to be redefined. In case of sealed cells the electrolyte can be leaked either through edge or through the hole. A proper edge sealing will enhance the stability of the cell, since it contributes the major pathway for electrolyte evaporation as well as the entry of moisture.

Another important problem to be addressed while sealing is the exposure of dyed electrode before it is assembled into the cell. This problem will not be there in case of open cells; where immediately after the sensitization cell is assembled so that the exposure of dye loaded electrode alone is prevented. However the different steps involved in the fabrication of sealed cells causes the exposure of dyed electrode before being assembling the cell and it accelerates the decay of dye. One solution for the aforesaid problem is to do the sealing procedure inside a glove box in a dark room. Another solution is to load the dye after edge sealing. In the applied technology, since the sealing was carried out after dye loading, high temperature sealing methods such as glass frit sealing cannot be used. If the sensitization is done after sealing, the interaction of dye loaded electrode to light and moisture can be prevented. Thus the sensitization after sealing on one hand reduces the interaction of dye loaded electrode with moisture and light and on the other hand facilitates the application of high temperature sealing methods. Though the method sounds fine, the sensitization of electrode after sealing is really tricky. It involves the design of some suitable equipment to ensure the continuous circulation of dye solution through the two holes in the counter electrode for a long time. The same set up can be used for removing the un attached dye by circulating anhydrous ethanol. Once dye loading is over, one hole can be sealed and the electrolyte can be injected through the other hole. The schematic representation of the procedure is illustrated in **Fig. 5**. The first hole can be sealed by hot melt sealant and microscope cover slide and the second hole can be sealed by UV curable Dymax.

Conclusion

The DSC efficiency is highly dependent on the procedure used for sealing. In order to get high efficiency, sealing procedures have to be optimized. Also the long term stability is strongly correlated with the electrolyte constituents such as additives and solvent. For acetonitrile based solvent, sealing procedures adopted is found to be inadequate to maintain its high efficiency. Hence a suitable method of sealing is proposed. Though the procedure involves some complexity, the method will be suitable for fabricating highly stable cells.

Reference

1. O'Regan, B.; Grätzel, M.; *Nature*. **1991,** *353*, 737. **DOI:** 10.1038/353737a0.
2. Grätzel, M.; *Nature* **2001,** *414*, 338. **DOI:** 10.1038/35104607.
3. Hagfeldt, A.; Grätzel, M.; *Chem. Rev*. **1995**, *95*, 49. **DOI:** 10.1021/cr00033a003.
4. Grätzel, M.; *J. Photochem. Photobio*. **2004,** *A 164*, 3. **DOI:** 10.1016/j.jphotochem.2004.02.023.
5. Intelligent Nanomaterials", Wiley-Scrivener Publishing, USA, ISBN 978-04-709387-99, **2012**
6. Nazeeruddin, M.K.; Angelis F.D.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M.; *J. Am. Chem.Soc.* **2005,** *127*, 16835. **DOI:** 10.1021/ja052467l.
7. Gao, F.; wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S.M. ; Gra¨ tzel, M.; *J. Am. Chem. Soc*. **2008**, *130* , 10720. **DOI:** 10.1021/ja801942j
8. Chen, C.Y.; Wang, M.; Li, J.Y.; Pootrakulchote, N.; Alibabaei, L.; Ngoc-le, C.; Decoppet, J.D.; Tsai, J.H.; Gra¨ tzel, C. ; Wu, C.G.; Zakeeruddin, S. M.; Gra¨ tzel. M.; *ACS Nano* **2009,** *3*, 3103. **DOI:** 10.1021/nn900756s.
9. Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L.; *Jpn. J. Appl. Phys.* **2006**, *45*, L638. **DOI:** 10.1143/JJAP.45.L638.
10. Tennakone, K.; Kumara, G.R.R.A.; Kumarasinghe, A.R.; Wijayantha, A.R.; Sirimanne, P.M.; *Semicond. Sci. Technol.* **1995,** *10*, 1689. **DOI:** 10.1088/0268-1242/10/12/020.
    Tiwari, A.; Valyukh, S. (Eds), In Advanced Energy Materials, WILEY-Scrivener Publishing LLC, USA, **2014**.
11. Bach, U.; Lupo, D.; Comte, P.; Moser, J.E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Gratzel, M.; *Nature* **1998**, *395*, 583. **DOI:** 10.1038/26936.
12. Harikisun, R.; Desilvestro, H.; *Solar Energy*. **2011,** 85, 1179. **DOI:** 10.1016/j.solener.2010.10.016.
13. Pettersson, H.; Gruszecki, T.; *Sol. Energy Mater. Sol. Cells.* **2001,** *70*, 203. **DOI:** 10.1016/S0927-0248(01)00025-3.
14. Arakawa, H.; Yamaguchi, T.; Okada, K.; Matsui, H.; Kitamura, T.; Tanabe, N. ; *Fujikura Tech. Rev*. **2009**, *38* , 55. http://www.fujikura.co.jp/00/gihou/gihou38e/38e_11.html.
15. Chen, D.; Huang, F.Z.; Cheng, Y.B.; Caruso, R.A.; *Adv. Mater*. **2009,** *21*, 2206. **DOI:** 10.1002/adma.200802603.
16. Mathew, A.; Rao, G.M.; Munichandraiah, N.; *Mater. Chem. Phys.* **2011**, *127*, 95. **DOI:** 10.1016/j.matchemphys.2011.01.032.
17. Mathew, A.; Rao, G.M.; Munichandraiah, N.; *Electrochim. Acta*. 2013**,** *87*, 92. **DOI:** 10.1016/j.electacta.2012.08.104.

