

Available online at www.sciencedirect.com



Journal of Power Sources 133 (2004) 293-297



www.elsevier.com/locate/jpowsour

Short communication

Effect of ionic conductivity of a PVC-LiClO₄ based solid polymeric electrolyte on the performance of solar cells of ITO/TiO₂/PVC-LiClO₄/graphite

M.Y.A. Rahman^{a,*}, M.M. Salleh^b, I.A. Talib^b, M. Yahaya^b

^a College of Engineering, Universiti Tenaga Nasional, Kajang, Selangor 43009, Malaysia ^b School of Applied Physics, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia

Received 5 February 2004; accepted 5 March 2004

Abstract

This paper reports the effect of ionic conductivity of the solid polymeric electrolyte of polyvinylchloride–lithium perchlorate (PVC–LiClO₄) on the performance of a solar cell of ITO/TiO₂/PVC–LiClO₄/graphite. Titanium dioxide films have been used as a photoelectrochemical solar cells. The films were deposited onto a ITO-coated glass substrate by a screen printing technique. The electrolytes were prepared by solution casting. The ionic conductivity of the electrolytes was obtained with an impedance spectroscopy technique. ITO and graphite films were chosen as the front and counter electrode of the device, respectively. The graphite films were deposited onto a glass substrate by the electron-beam evaporation technique. The short-circuit current density and open-circuit voltage of the device were found to increase with increasing ionic conductivity of solid polymeric electrolyte of PVC–LiClO₄. The highest short-circuit current density and open-circuit voltage were 0.94 μ A cm⁻² and 186 mV, respectively. The conversion efficiency was low. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ionic conductivity; Photoelectrochemical solar cell; Solid polymeric electrolyte; Titanium dioxide

1. Introduction

O'Regan and Gratzel [1] pioneered a photoelectrochemical solar cell that utilised an ion conductor or electrolyte to transport ions into the solar cell material. Gratzel and his team reported the use of a polymer gel electrolyte [2-4]. The short-circuit current density of the device is $15.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ [2], open-circuit voltage of 0.67 V and efficiency of 6.1%. A liquid electrolyte of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide-0.1 M LiI-0.05 M I₂ in methoxyacetonitrile has been used in the dye-sensitised solar cell as a liquid electrolyte [5]. A short-circuit current density of 15.2 mA cm⁻², an open-circuit voltage of 0.55 V and a conversion efficiency, η of 5.2% were obtained from the cell of an area 0.25 cm² under illumination of $100 \,\mathrm{mW \, cm^{-2}}$ light. A solar cell without dve-sensitiser of structure ITO/TiO₂/liquid electrolyte/ITO utilising 0.5 M ammonium iodide and 0.04 M iodine in 80% water and 20% acetonitrile as a liquid electrolyte produced an opencircuit voltage of 17 mV, short-circuit current density of $1.3 \,\mu\text{A}\,\text{cm}^{-2}$ and low efficiency. The illuminated area was $1.77 \,\text{cm}^2$ under 100 mW cm⁻² of tungsten light source. However, the liquid electrolyte possessed disadvantages such as having heavy weight, shape flexibility and instability. In this work, we used a solid polymeric electrolyte of PVC–LiClO₄ with a different ionic conductivity and TiO₂ films [6,9,12,13] prepared by screen-printing technique as a solar cell material in a non-dye sensitised solar cell of ITO/TiO₂/PVC–LiClO₄/graphite. This paper reports the effect of the ionic conductivity of a solid polymeric electrolyte of PVC–LiClO₄ on the performance of the device (open-circuit voltage and short-circuit current density).

2. Experimental

A solar cell was designed and fabricated using indium-tin oxide (ITO)-covered glass as a substrate. The substrate underwent a routine chemical cleaning using acetone, 2-propanol and distilled water in sequence in an ultrasonic bath, The TiO_2 layer was deposited onto it by

^{*} Corresponding author. Tel.: +60-3-89287262; fax: +60-3-89263506. *E-mail address:* yusri@uniten.edu.my (M.Y.A. Rahman).

screen-printing a paste, consisting of TiO₂ particles and propylene glycol as organic binder. The films were then cured at 400 °C for 30 min in air to burn out the organic parts and to achieve a porous structure. A solar cell of ITO/TiO₂/electrolyte/graphite was fabricated using polyvinylchloride (PVC) doped with lithium perchlorate (LiClO₄) as the solid electrolyte material. The electrolytes with different ionic conductivity were prepared by the solution casting technique. The ionic conductivity of the electrolyte samples at 40 °C was obtained using impedance spectroscopy. A solar cell of ITO/TiO₂/PVC-LiClO₄/graphite was constructed using ITO-covered glass substrate as a working electrode with a sheet resistance of $2\Omega \operatorname{sq}^{-1}$ and graphite film [14] as a counter electrode. The electronegativity of ITO and graphite are 0.3 and 2.55 on the Pauling scale, respectively. With a high difference in their electronegativity, we can expect a high potential difference between the electrodes and this should lead to a high current generated in the device. The graphite film was deposited onto a glass substrate by electron-beam evaporation under a vacuum pressure of about 3.33×10^{-3} Pa for 1 h at 58 °C. The electrolyte films were cut into the rectangular form for the TiO_2 films. They were then sandwiched between TiO_2 film and the graphite layer. The system was clamped in order to optimise the contact at the interface of the TiO₂ film-electrolyte and electrolyte-graphite. The other solar cell systems were fabricated using different electrolyte samples and utilised the same TiO2 films which were cured at 400 °C for 30 min and using the same counter electrode of graphite. The current-voltage characteristic in dark at room temperature was obtained using a 237 Keithley high voltage source. The current density-voltage, J-V characteristic of 1 cm diameter of the device under illumination of 100 mW cm⁻² light from a tungsten halogen lamp at 40 °C were obtained using a Keithley Voltmeter 175A, Keithley Amperemeter 197A and a load resistance. The major parameters characterising a solar cell, open-circuit voltage and short-circuit current density, were obtained from the J-V curve under illumination.

3. Results and discussion

Fig. 1 shows the current-voltage curve in dark for the five devices utilising solid polymeric electrolytes of PVC-LiClO₄ with different ionic conductivities at room temperature. The devices show rectification. The device with ionic conductivity of $5.8 \times 10^{-7} \,\mathrm{S \, cm^{-1}}$ at room temperature produces the largest current compared to the others. Our earlier expectation is that the device with the highest conductivity of $1.2 \times 10^{-6} \,\mathrm{S \, cm^{-1}}$ will produce the largest current. This might be caused by a poor interfacial contact between the electrolyte and the TiO₂ film. The device with a good interfacial contact will allow more Li⁺ ions from the electrolyte to migrate to the film compared to those with a poor interfacial contact even though their ionic conductivity are high. Also from Fig. 1, it was observed that the current in the reverse bias is larger than that in forward bias for all devices. This result indicates that the current resulted mainly from ClO₄⁻ ion transportation into the graphite counter electrode.

Fig. 2 shows the current–voltage curves of the 1 cm diameter photoelectrochemical solar cells under illumination for five cells of different ionic conductivity. It can be concluded that the current–voltage characteristics obtained from these cells are from photovoltaic effect since the cell behaved like



Fig. 1. Current-voltage characteristics in the dark.



Fig. 2. Current density-voltage curve for the devices with different electrolyte conductivities under illumination of 100 mW cm⁻² light at 40 °C.

a diode [7] according to the results shown in Fig. 1. Furthermore, when a halogen tungsten lamp was switched-off, the ammeter and voltmeter reading suddenly dropped to zero. The temperature that was measured using a thermocouple was decreasing very slowly to room temperature. When the lamp is switched-on again, the ammeter and voltmeter reading increased to the initial reading. This phenomena indicates that the current and voltage obtained from the cell are not from a thermoelectric effect. The low generated current is due to the TiO₂ with a large bandgap (3 eV) and is not so sensitive to visible light [6]. The films absorbs a small quantity of light at a shorter wavelength and more light is converted into heat upon illumination of the cell. From Fig. 2, the highest short-circuit current density is $0.94 \,\mu\text{A cm}^{-2}$ and opencircuit voltage is 186 mV. There results are comparable with the result reported in [16] for which the short-circuit current density generated in the nanocrystalline TiO₂ solar cell without dye-sensitiser was $2.4 \,\mu\text{A cm}^{-2}$ and that reported in [18] was about $0.94 \,\mu\text{A cm}^{-2}$. The current density–voltage curves were obtained by varying the load resistance from 10 to $100 \,\Omega$ which is in series with the internal resistance of the device at an intensity of $100 \,\text{mW cm}^{-2}$ and temperature of 40 °C. It was found that the *J*–*V* curve for all devices did not follow the ideal curve as reported in [19]. This is due to high internal resistance in the devices, resulting in a low current in the devices. The curves shown in Fig. 2 agree well



Fig. 3. Variation of open-circuit voltage with ionic conductivity.



Fig. 4. Variation of short-circuit current density with ionic conductivity.

with those reported in [20,21] for which the current–voltage curve is linear for the photovoltaic cells with high internal resistance.

From the results shown in Figs. 3 and 4, it was found that the open-circuit voltage and short-circuit current density of the devices increase with ionic conductivity. This is because the charge transfer through the interface between the electrolyte with higher conductivity and activated layer of TiO₂ is more efficient. Higher ionic conductivity will result in more Li^+ ions migrating from the electrolyte to the TiO₂ film in order to decrease the potential in Helmholtz layer in the TiO_2 film [17]. With the lower potential, it is easier for the light to excite more electrons from the valence band to the conduction band of TiO2 films when illuminated. This leads to the enhancement of the current generated in the device and consequently increase in the voltage. The shortcircuit current density obtained from the cell utilising the solid electrolyte is lower than that obtained from the one using liquid electrolyte [6]. This is because the ionic conductivity in liquid electrolyte is much higher than that in the solid medium. Generally, the conversion efficiency obtained from these devices are very low: Fig. 4. The efficiency of the cell can be improved by depositing an organic dye sensitiser on the TiO₂ film [1-5,8-11,13-15] which can absorb more light at a higher wavelength. The excited molecules in the dye will send more electrons into the conduction band of the TiO₂ film when illuminated.

4. Conclusions

The performance of the photoelectrochemical solar cells increases with ionic conductivity of the solid polymeric electrolyte. The preliminary J-V characteristics under illumi-

nation of the TiO_2 solar cell proved encouraging and will lead to more extensive work to improve performance of the device.

Acknowledgements

The authors are thankful to IRPA grant: 03-02-02-0020-SR003/07-06 granted by Ministry of Science and Technology to UKM where this work was carried out.

References

- [1] O'Regan, M. Gratzel, Nature 353 (1991) 737.
- [2] P. Wang, S.M. Zakeeruddin, J.E. Moser, M.K. Nazeeruddin, T. Sekiguchi, M. Gratzel, Nature 2 (2003) 402.
- [3] J.R. Durrant, S.A. Haque, Nature 2 (2003) 362.
- [4] R.F. Service, Science 300 (2003) 1219.
- [5] K. Hara, Y. Tachibana, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, Solar Energy Mater. Solar Cell. 77 (2003) 89.
- [6] M.M. Salleh, M. Yahaya, Mursyidah, in: Proceedings of the Seventh Asian Conference on Solid State Ionics, Materials and Devices, vol.737, 2000.
- [7] A.L. Fahrenbruch, R.H. Bube, Fundamentals of Solar Cells: Photovoltaic Solar Energy Conversion, Academic Press, New York, 1983.
- [8] S. Takenaka, Y. Maehara, H. Imai, M. Yoshikawa, S. Shiratori, Thin Solid Films, in press.
- [9] K. Miyairi, E. Itoh, Y. Hashimoto, Thin Solid Films, in press.
- [10] Q.-H. Yao, Y.-Y. Huang, L.-Q. Song, B.-W. Zhang, C.-H. Huang, Z.-S. Wang, F.-Y. Li, X.-S. Zhao, Solar Energy Mater. Solar Cell. 77 (2003) 319.
- [11] S.-S. Kim, J.-H. Yum, Y.-E. Sung, Solar Energy Mater. Solar Cell. 79 (2003) 495.
- [12] W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S.-H. Baeck, E.W. Mc-Farland, Solar Energy Mater. Solar Cell. 77 (2003) 229.
- [13] P.M. Sirimanne, T. Shirata, L. Damodare, Y. Hayashi, T. Soga, T. Jimbo, Solar Energy Mater. Solar Cell. 77 (2003) 15.

- [14] K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J.-I. Nakamura, K. Murata, T. Wada, Solar Energy Mater. Solar Cell. 79 (2003) 489.
- [15] S. Ito, T. Kitamura, Y. Wada, S. Yanagida, Solar Energy Mater. Solar Cell. 76 (2003) 3.
- [16] I. Zumeta, R. Espinosa, J.A. Ayllon, X. Domenech, R. Rodriguez-Clemente, E. Vigil, Solar Energy Mater. Solar Cell. 76 (2003) 15.
- [17] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Arakawa, Solar Energy Mater. Solar Cell. 70 (2001) 151.
- [18] T. Yohannes, O. Inganas, Solar Energy Mater. Solar Cell. 51 (1998) 193.
- [19] T.L. Chu, S.S. Chu, J. Britt, C. Ferekids, C. Wang, C.Q. Wu, H.S. Ullal, IEEE Electr. Dev. Lett. 13 (5) (1992) 303.
- [20] A.K. Ghosh, D.L. Moral, T. Feng, R.F. Shaw, C.A. Rowe Jr., J. Appl. Phys. 45 (1) (1973) 230.
- [21] J.P. Dodelet, H.P. Pommier, M. Ringuet, J. Appl. Phys. 53 (6) (1982) 4270.