

Effect of ionic conductivity of a PAN–PC–LiClO₄ solid polymeric electrolyte on the performance of a TiO₂ photoelectrochemical cell

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Abstract A nanoparticle TiO₂ solid-state photoelectrochemical cell has been fabricated. The effect of ionic conductivity of a solid electrolyte of polyacrylonitrile (PAN)–propylene carbonate (PC)–lithium perchlorate (LiClO₄) on the performance of a photoelectrochemical cell of indium tin oxide (ITO)/TiO₂/PAN–PC–LiClO₄/graphite has been investigated. A nanoparticle TiO₂ film was deposited onto ITO-covered glass substrate by controlled hydrolysis technique. A solid electrolyte of PAN–LiClO₄ with PC plasticizer prepared by solution casting technique was used as a redox couple medium. The room temperature conductivity of the electrolyte was determined by AC impedance spectroscopy technique. A graphite electrode was prepared onto a glass slide by electron beam evaporation technique. The device shows a photovoltaic effect under illumination. The short-circuit current density, J_{sc} , and open-circuit voltage, V_{oc} , vary with the conductivity of the electrolyte. The highest J_{sc} of 2.82 $\mu\text{A cm}^{-2}$ and V_{oc} of 0.56 V were obtained at the conductivity of $4.2 \times 10^{-4} \text{ Scm}^{-1}$ and at the intensity of 100 mW cm^{-2} .

Keywords Hydrolysis technique · Ionic conductivity · Nanoparticle titanium dioxide · PAN–PC–LiClO₄ · Photoelectrochemical cell

Introduction

Gratzel [1] pioneered a photoelectrochemical solar cell that utilized a liquid electrolyte for reduction and oxidation in the device. Since then, solid-state dye-sensitized solar cells were developed by a lot of research groups in order to replace conventional liquid electrolyte that possesses the problem of shape flexibility and instability [2–5]. Dye-sensitized solar cell utilizing gel polymeric electrolyte was developed by several groups [6–8]. However, the conversion efficiency of the cell utilizing solid or gel polymeric electrolyte is smaller than the cell with liquid electrolyte. This is due to the ionic conductivity of liquid electrolyte is much higher than that of gel electrolyte and solid electrolyte. A non-dye solid-state TiO₂ solar with low conversion efficiency was developed in the work reported in the previous paper [9]. The main challenge for a solid-state cell is to seek a cell with significant conversion efficiency. Our attempt is to choose a solid polymeric electrolyte possessing a high conductivity at room temperature and at ambient temperature of the cell. Therefore, the conversion efficiency of cell could be improved [9]. This paper reports the effect of the conductivity of a polyacrylonitrile (PAN)–propylene carbonate (PC)–lithium perchlorate (LiClO₄) electrolyte on the performance of a solar cell of indium tin oxide (ITO)/TiO₂/PAN–PC–LiClO₄/graphite in terms of open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}).

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Materials and methods

PAN (MW 150,000) and LiClO_4 powder were purchased from Aldrich, N,N-dimethylformamide solvent was purchased from System, and propylene carbonate with 99.9% purity was purchased from Fluka. These materials were used for preparation of a solid polymeric electrolyte of PAN-PC- LiClO_4 . TiO_2 powder was purchased from Alfa Aesar with 97% rutile phase with 99.8% purity. ITO-coated glass with a sheet resistance of 9–15 Ω/sq purchased from Vin Karola instrument, USA was used as a substrate for preparation of TiO_2 thin film. Titanium etoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and potassium chloride (KCl) were purchased from Merck and ethyl alcohol (ethanol) with 99.8% purity was purchased from Fluka. These materials were used for preparation of nanoparticle TiO_2 that were deposited onto TiO_2 thin film. Graphite powder with 99.9% purity and glass slide were used in preparing graphite counter electrode.

ITO-coated glass substrate was cut into a desired size and cleaned using acetone for 15 min and for another 15 min with ethyl alcohol in ultrasonic bath. It was rinsed immediately with ethyl alcohol and cleaned using nitrogen gas to ensure the substrate was cleaned thoroughly. TiO_2 pellet of 13 mm in diameter was prepared by pressing titanium (IV) oxide powder at a pressure of 10 t for 10 min. The TiO_2 films were deposited by electron beam evaporation technique under the vacuum pressure of 2.5×10^{-5} Torr for 1 h. The films were sintered at 450°C for 30 min to get rid of the organic materials and also to achieve the films with porous structure.

The TiO_2 nanoparticle layer was deposited onto it by controlled hydrolysis technique, consisting of titanium (IV) etoxide ($\text{Ti}(\text{OC}_2\text{H}_5)_4$) and KCl dissolved in ethyl alcohol. A solar cell of ITO/ TiO_2 /electrolyte/graphite was fabricated using PAN doped with LiClO_4 as a solid electrolyte material. The plasticizer used in the electrolyte as conductivity enhancer was PC. The electrolyte samples were prepared by the solution casting technique for which the percentage by weight of LiClO_4 was varied. The chosen weight percentages of LiClO_4 were 0%, 5%, 10%, 15%, and 20%. The weight of PAN and the volume of PC were fixed at 2 g and 6.6 ml, respectively. The room temperature conductivity of the electrolyte as a function of LiClO_4 content was measured by AC impedance spectroscopy technique. An ITO-covered glass substrate was used as a front transparent electrode with a sheet resistance of 9–15 Ωsq^{-1} and a graphite film was used as a counter electrode. The work function of ITO and graphite are 4.5 and 3.9 eV, respectively. With a high difference in their work function, 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 technique under a vacuum pressure of 2.5×10^{-5} Torr for 1 h at 25°C . The electrolyte film with the conductivity of $9.1 \times 10^{-6} \text{Scm}^{-1}$ corresponding with 5 wt.% LiClO_4 was cut into the rectangular shape to suit the area of TiO_2 film. It was then sandwiched between TiO_2 film and the graphite layer. The device was clamped in order to optimize the contact at the interface of the TiO_2 film-electrolyte and at the electrolyte-graphite. The other photoelectrochemical cells were fabricated using the electrolyte with the conductivity of 1.6×10^{-4} , 2.3×10^{-4} , and $4.2 \times 10^{-4} \text{Scm}^{-1}$. The devices utilized the same TiO_2 film and the counter electrode made of graphite.

The current–voltage characteristics in dark and under illumination at room temperature were obtained using a 237-Keithley high voltage source. The performance under illumination was performed to study a photovoltaic effect in the device. The device was illuminated through a slide projector. A tungsten light source was calibrated by adjusting the light intensity. This was done by adjusting the distance from the cell to the source so that the intensity of 100mW cm^{-2} was obtained. The ambient device temperature was in the range from 25°C to 27°C in a 40% of humidity. Then, the device was applied to a voltage -2V to 2V and the current–voltage curve was displayed on the computer. The intensity of light was controlled by using radiometer and the temperature was measured by using a thermocouple. Thermocouple was used to measure temperature since it can serve as a temperature sensor. Temperature sensor can be used to measure the device temperature and the surrounding temperature. The illuminated cell area was 0.785cm^2 . Figure 1 shows the structure of the cell. The thickness of TiO_2 thin film prepared by electron beam evaporation technique was 100 nm. The thickness of the nanoparticle TiO_2 film prepared by controlled hydrolysis technique was about 145 nm. The thickness of the electrolyte films was in the range 0.2–0.4 mm. The thickness of the graphite film could not be determined

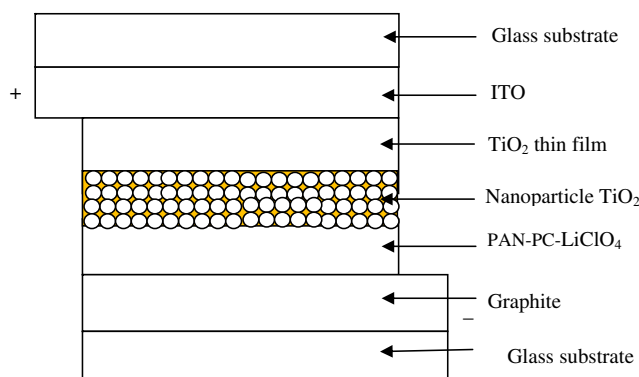


Fig. 1 Structure of the device

since the film prepared by electron beam evaporation technique was very thin. Its thickness was attempted to be determined by ellipsometer, but it did not give response by giving the thickness reading.

Results and discussion

Figure 2 shows SEM micrograph of nanoparticle TiO₂ film. The film is homogeneous since its grain size is identical. It was observed that all grains are closely packed to each other with the uniform grain size. From Fig. 2, the average grain size of the nanoparticle TiO₂ was estimated using the scale located at the lower left corner of SEM micrographs. The average grain size was estimated by taking the diameter for five grains. The average grain size for the TiO₂ films is 76 nm. The porous structure of the TiO₂ films is observed and the Li⁺ ions interact easily with the TiO₂ particles.

Table 1 illustrates the variation of the electrolyte conductivity at room temperature with the LiClO₄ salt content. From the table, it was found that the electrolyte conductivity increases with the salt content up to the certain level and then drops. The behavior of the electrolyte conductivity with the salt content was discussed in detail in the previous work [10]. The increase in conductivity with LiClO₄ content is due to the increase in the availability of mobile ions which is Li⁺. From Table 1, the lowest conductivity of 3.4 × 10⁻⁶ Scm⁻¹ is obtained at 0% by weight of LiClO₄ and the highest value of 4.2 × 10⁻⁴ Scm⁻¹ is obtained at 10% by weight of LiClO₄; while at 15% by weight of LiClO₄, the conductivity decreases to 2.3 × 10⁻⁴ Scm⁻¹. This can be due to the formation of non-conducting ion pairs within the concentration range of the LiClO₄ salt. This causes constraint in the polymer segmen-

Table 1 Variation of room temperature conductivity, σ , of PAN-PC-LiClO₄ with LiClO₄ content

wt.% LiClO ₄	σ (Scm ⁻¹)
0	3.4 × 10 ⁻⁶
5	9.1 × 10 ⁻⁶
10	4.2 × 10 ⁻⁴
15	2.3 × 10 ⁻⁴
20	1.6 × 10 ⁻⁴

tal motion and might also increase the crystalline nature of the electrolyte, leading to the decrease in the charge carrier mobility. When the salt content in the electrolyte is further increased, the distance between ions will decrease and it will result in the interaction between ion Li⁺ and ClO₄ become more apparent and the formation of ion pairs eventually occur in the electrolyte.

Figure 3 shows the current–voltage curve for the four devices utilizing the electrolyte with different conductivity in dark at room temperature. The device with the conductivity of 4.2 × 10⁻⁴ Scm⁻¹ produces the largest current compared to the devices with the lower conductivity in both forward and reverse bias. However, the difference in current in all devices is small. It is concluded the conductivity of the electrolyte does not significantly affect the dark current in the device. Generally, the devices allow a small current to be generated which is in the range of 14–18 μ A. This might be caused by a poor interfacial contact between the electrolyte and the TiO₂ film [9]. The poor interfacial contact results in a high internal resistance, leading to a low current in the devices. From Fig. 3, it was also observed that the current in the reverse bias was slightly larger than that in forward bias for all devices. This result indicates that the current that flow towards the

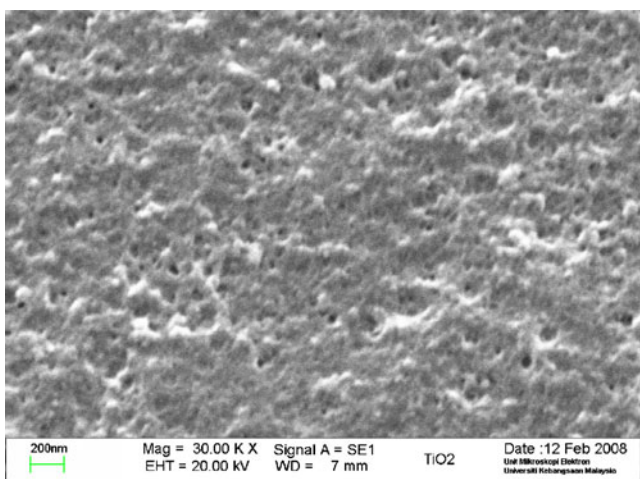


Fig. 2 SEM micrograph of nanoparticle TiO₂ film

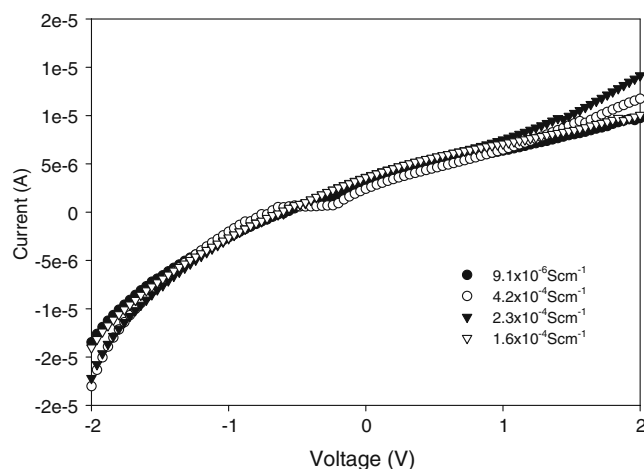


Fig. 3 Current–voltage curve for the devices with the variation of electrolyte conductivity in the dark

graphite counter electrode is quite dominant than that toward the ITO front electrode. This is because the graphite electronegativity, 2.6 on the Pauling scale, is greater than that of ITO, which is 0.4 on the Pauling scale.

Figure 4 shows the current density–voltage curves of the 0.785 cm² illuminated area of the solar cells under illumination for five variations of electrolyte samples. The current density decreases with the increasing voltage since the internal resistance in the device was high. The current density–voltage curve deviates from an ideal current density–voltage curve. The current density–voltage curves shown in Fig. 4 were quite similar to that reported by the previous researcher [11, 12] who developed a photogalvanic cell and a polymer solar cell, respectively, for solar energy conversion and storage. The device with the highest electrolyte conductivity shows the largest current–voltage than that with lower conductivity. It was also found that the device with the electrolyte conductivity of $9.1 \times 10^{-6} \text{ Scm}^{-1}$ shows higher current density–voltage than those with the conductivity of 1.6×10^{-4} and $2.3 \times 10^{-4} \text{ Scm}^{-1}$. Figure 4 also shows almost the same behavior of current density–voltage for the devices with the electrolyte conductivity of 9.1×10^{-6} and $4.2 \times 10^{-4} \text{ Scm}^{-1}$. The figure also shows the device with the electrolyte conductivity of $3.4 \times 10^{-6} \text{ Scm}^{-1}$ possesses higher current density–voltage compared with the device with the electrolyte conductivity of 2.3×10^{-4} and $4.2 \times 10^{-4} \text{ Scm}^{-1}$, respectively. This behavior might be caused by the resistance at the interfacial contact of graphite/electrolyte/TiO₂ of the device with smaller conductivity which is about the same or even smaller compared with the device with higher conductivity.

The photovoltaic parameters such as short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) were obtained from the intersection axis of current–density and voltage,

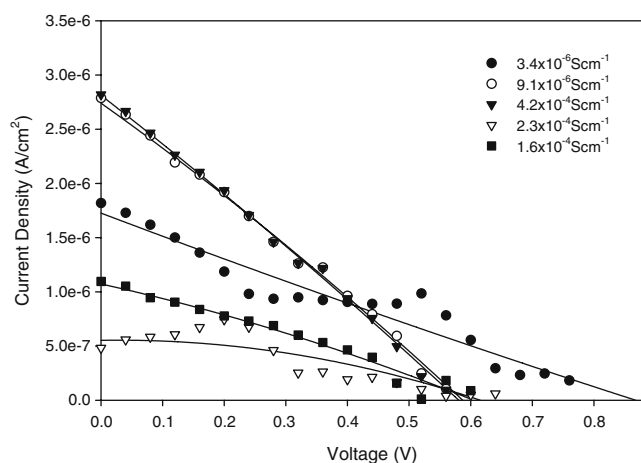


Fig. 4 Current density–voltage curve for the devices with the variation of electrolyte conductivity under illumination of 100 mWcm⁻² light

Table 2 Variation of photovoltaic parameter of the device with the conductivity of electrolyte

σ (Scm ⁻¹)	J_{sc} (μAcm^{-2})	V_{oc} (V)
3.4×10^{-6}	1.80	0.85
9.1×10^{-6}	2.81	0.60
1.6×10^{-4}	1.10	0.52
2.3×10^{-4}	0.48	0.64
4.2×10^{-4}	2.82	0.56

respectively. The variation of J_{sc} and V_{oc} with the electrolyte conductivity is illustrated in Table 2. The electrolyte with the highest conductivity shows the highest J_{sc} . This might be caused by more mobile redox couple taking place in the electrolyte with higher conductivity. The redox couple of the electrolyte is Li⁺ and ClO₄⁻. Faster electrons from the external circuit was captured by Li⁺, the faster ClO₄⁻ captured the holes. The faster the regeneration of electron–holes pair taking place in the TiO₂ film, the faster the oxidation–reduction in the cell. The Li⁺ is reduced to Li at the interface of graphite/PAN–PC–LiClO₄, following the reduction equation:



Li will intercalate into graphite to occupy its sites. Then, it will deposit on the graphite electrode. ClO₄⁻ will donate electrons to holes at the interface of TiO₂/PAN–PC–LiClO₄ following the oxidation equation,



Holes will then recombine with electrons donated by ClO₄⁻ which is oxidized to ClO₄ following Eq. (2). ClO₄⁻ will then intercalate into TiO₂ to occupy its sites [13]. The electrons will occupy the vacancies in the valence band of TiO₂ left by the electrons which have been excited to the conduction band of TiO₂. These processes were repeated upon the illumination of the photoelectrochemical cell. These processes were recycled faster when the device utilized the higher conductivity of the electrolyte [9]. From Table 2, it was also found that the device with the electrolyte conductivity of $9.1 \times 10^{-6} \text{ Scm}^{-1}$ shows higher J_{sc} than the devices with the conductivity of 1.6×10^{-4} and $2.3 \times 10^{-4} \text{ Scm}^{-1}$. The resistance at the interfacial contact of the device with smaller conductivity was smaller than the devices with higher conductivity. The higher internal resistance of the device, the lower the current generated in the device [9]. The J_{sc} obtained from the photoelectrochemical cell developed from this work was comparable with the one developed by other researcher [5], ranging from 2 to 5 $\mu\text{A cm}^{-2}$.

Conclusions

We have fabricated a solar cell of ITO/TiO₂/PAN-PC-LiClO₄/graphite utilizing PAN-PC-LiClO₄ as the electrolyte. Its performance was tested in the dark and under the illumination of 100 mW cm⁻² light. The device shows the photovoltaic effect under the illumination. The dark current does not change with the electrolyte conductivity. The cell performance such as J_{sc} varies with the electrolyte conductivity. The device with the electrolyte conductivity of $4.2 \times 10^{-4} \text{Scm}^{-1}$ shows the highest J_{sc} of $2.82 \mu\text{A cm}^{-2}$ and V_{oc} of 0.56 V. Further investigation is to obtain an electrolyte with higher conductivity at ambient temperature of the cell and hence, improve the J_{sc} and consequently the conversion efficiency of the cell.

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References

1. Gratzel M (2001) *Nature* 414:338
2. Yang L, Zhang Z, Fang S, Gao X, Obata M (2006) *Sol Energy* 81:717
3. Howie WH, Harris JE, Jennings JR, Peter LM (2007) *Sol Energy Mater Sol Cells* 91:424
4. Karthikeyan CS, Peter K, Wietasch H, Thelakkat M (2007) *Sol Energy Mater Sol Cells* 91:432
5. Mohamad SA, Yahya R, Ibrahim ZA, Arof AK (2007) *Sol Energy Mater Sol Cells* 91:1194
6. Wang P, Zakeeruddin SM, Moser JE, Nazeruddin MK, Sekiguchi T, Gratzel M (2003) *Nature Materials* 2:402
7. Lan Z, Wu J, Lin J, Huang M (2006) *J Power Sources* 164:921
8. Kim JY, Kim TH, Kim DY, Park NG, Ahn KD (2008) *J Power Sources* 175:692
9. Rahman MYA, Salleh MM, Talib IA, Yahya M (2004) *J Power Sources* 133:293
10. Rika, Ahmad A, Rahman MYA, Salleh MM (2009) *Physica B* 404:1359
11. Lal C (2007) *J Power Sources* 164:926
12. Watt AAR, Blake D, Warner JH, Thompson EA, Tavenner EL, Dunlop HR, Meredith P (2005) *J Phys D: Appl Phys* 38:2006
13. Rahman MYA, Salleh MM, Talib IA, Yahya M (2007) *Curr Appl Phys* 7:449