THE USE OF POLYMER GEL ELECTROLYTE CONTAINING I⁻/I₃⁻ REDOX COUPLE TO ASSEMBLY A SOLID STATE DYE SENSITIZED TiO₂ SOLAR CELL

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ABSTRACT

THE USE OF POLYMER GEL ELECTROLYTE CONTAINING I⁻/I₃⁻ REDOX COUPLE TO ASSEMBLY A SOLID STATE DYE SENSITIZED TiO₂ SOLAR CELL. A solid state dye sensitized TiO_2 nanocrystalline solar cells was assembled employing a polymer gel electrolyte contains of iodide/triiodide (I^-/I_3^-) redox couple. The use of solid electrolyte based on polymer matrix for redox'couples is aimed to overcome several problems of liquid cell, such as leaks of electrolyte that result in degradation of solar cell. TiO_2 nanocrystalline layer was grown on TCO glass substrate by doctor blade technique was stained by synthetic dye Ruthenium 535 for a day. To complete the cell, a polymer gel based on poly(ethylene glycol) (PEG) containing I^-/I_3^- redox couple was sandwiched between a working electrode (nanoporous TiO_2 layer on conductive glass substrate) and a counter electrode (graphite sheet). The solid-state cell does not need a clipp, so the gel polymer electrolyte also acts as a glue to join the electrodes. Two cells assembled with different amount of I^-/I_3^- redox couple used in each cell, one of cell use 20 drops of Iodolyte (contains I^-/I_3^- redox couple) and another cell use 30 drops of Iodolyte solution (purchased from Solaronix, SA). The cells were characterized their photovoltaic performances included: open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), maximum power (P_{max}), fill factor (FF) and energy conversion efficiency.

Key words : Dye-sensitized solar cell, Nanoprous TiO_2 film, Polymer gel electrolyte

ABSTRAK

PENGGUNAAN ELEKTROLIT GEL POLIMER YANG MENGANDUNG PASANGAN REDOKS I⁻/I₃⁻ UNTUK MEMBUAT SEL SURYA PADAT *DYE-SENSITIZED* TiO₂. Sebuah sel surya padat nanokristalin padat *dye-sensitized* TiO_2 dibuat dengan menggunakan elektrolit gel polimer yang mengandung pasangan redoks *iodide/triiodide* (I^-/I_3^-). Penggunaan elektrolit padat berbasis matriks polimer untuk pasangan redoks ditujukan untuk mengatasi masalah dari sel cair, seperti kebocoran elektrolit yang menyebabkan degradasi sel surya. Lapisan nanokristalin TiO_2 yang ditumbuhkan pada substrat gelas TCO dengan teknik *doctor blade* dioles dengan *dye Ruthenium* 535 selama satu hari. Untuk melengkapi sel, suatu gel polimer *poly*(*ethylene glycol*) (*PEG*) yang mengandung pasangan redoks I^-/I_3^- dilapiskan (*sandwich*) diantara elektroda kerja (lapisan TiO_2 *nanoporous* pada substrat gelas konduktif) dan elektroda pembanding (lembaran grafit). Sel padat tidak memerlukan *clipp*, sehingga elektrolit gel polimer juga bertindak sebagai perekat untuk menggabungkan elektroda-elektroda. Dua buah sel dibuat dengan perbedaan jumlah pasangan redoks I^-/I_3^- pada masing-masing sel, salah satu sel menggunakan 20 tetes *iodolyte* (mengandung pasangan redoks I^-/I_3^-) dan sel lainnya menggunakan 30 tetes larutan *iodolyte* (dari *Solaronix*, SA). Sel-sel tersebut dikarakterisasi kinerja fotovoltaik-nya termasuk : *open-circuit voltage* (V_{oc}), *short-circuit current* (I_{sc}), *maximum power* (P_{max}), *fill factor* (FF) dan efisiensi konversi energinya.

Kata kunci : Sel surya dye-sensitized, film nanoporous TiO_2, elektrolit gel polimer

INTRODUCTION

Alternative energy sources, such as solar and wind power, have received increasing attention over the past decades in order to replace the environmentally damaging and diminishing fossil fuels. Solar power is obviously one of the most attractive renewable energy sources. Up to now, the main photovoltaic (PV) devices have been based on solid-state junctions, usually made of silicon, and take advantage of the development of the semiconductor industry [1,2].

Recently, a challenging new generation of solar cells based on sensitized nanocrystalline oxides and conducting electrolytes have been developing. The so called dye sensitized nanocrystalline solar cells (DSSCs) are currently attracting widespread

attention as low cost alternative to conventional inorganic photovoltaic devices based on silicon p-n junction for light-to-electricity conversion [1,3-8]. A typical dye-sensitized solar cell consists of nanoporous TiO_2 electrode on the transparent conducting glass substrate covered with a monolayer of sensitizing dye, a redox electrolyte (e.g. I^-/I_3^-) and a counter electrode such as platinized conductive glass forms a sandwich [3-5].

The principle of such devices is based upon the injection of an electron from a photoexcited state of the sensitizer dye into the conduction band of the semiconductor electrode, commonly TiO_2 film. Working principle of the dye-sensitized solar cell is described at Figure 1. Photon is absorbed by the sensitizer dye anchored to the surface of TiO_2, generate electrons to the excited state quenched by electrons injection into the conduction band of TiO_2, then are transported to the charge collector. The original state of the sensitizer dye is restored by electron donation from redox system, commonly iodide/triiodide (I^-/I_3^-). The iodide (I^-) ion, donating an electrode to the sensitizing dye, is regenerated in turn by reduction of triiodide (I_3^-) ion at the counter electrode. The two photoseparated charges flows in different direction in external circuit providing the electrical current in an external load [3,6].
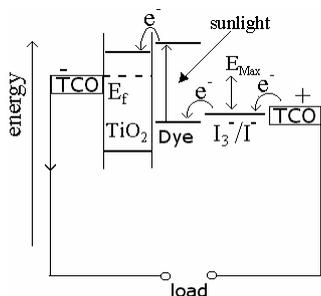

Figure 1. Principle of dye sensitized solar cell

The early configuration, the cell use a liquid electrolyte containing a redox couple, commonly iodide/triodide (I^-/I_3^-) in the organic solvent, called as Grätzel solar cell, the inventor of the cell [3], that results in an overall energy conversion of 10%. Higher energy conversion efficiency (11.1%) of dye-sensitized solar cell have been reported by Chiba et.al. [9]. Unfortunately, the use of liquid electrolyte causes several problems like sublimation of the iodine or leaks of the electrolyte that result in difficulty of hermetic sealing, so that used a solid electrolyte instead of liquid electrolyte [6-8].

Modification of the Grätzel solar cell (liquid cell) to a solid-state cell is aimed to solve the problems of stability and both short-term and long-term sealing problems of solar cells. The concept can be realized employing a solid organic such as PEDOTs [10] or inorganic semiconductor such

as CuI [11], CuSCN [12] or NiO [13] as hole conductor. Another concept can be used is a polymer gel electrolyte containing a redox couple, commonly I^-/I_3^-. Several kinds of polymer used including PEO [6,14,15], PAN [14,16,17], and PEG [7,18].

In this report, we assembly a solid state dye-sensitized solar cell based on solid electrolyte employing a gel poly(ethylene glycol) (PEG) containing I^-/I_3^- redox couple. The cell was formed into sandwich structure without a clipp as like to the liquid system, so the gel electrolyte also acts as glue to join the electrodes.
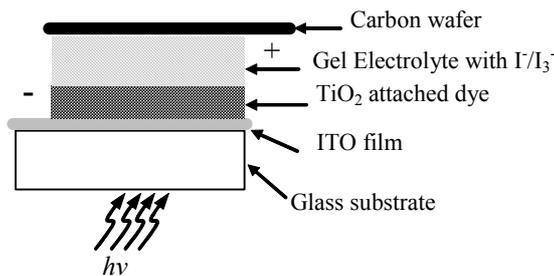

Figure 2. Structure of dye-sensitized solar cell

Polymer electrolytes are attracting widespread as solid-state alternative to liquid and crystalline electrolytes for device applications, ranging from secondary lithium batteries [19,20] to electrochromic displays [21], and photoelectron- chemical cells [8,14-18]. Polymer electrolytes have reasonable ionic conductivities and eliminate the problems of sealing and solvent leakages in the any devices that results in a good stability of devices, specially for photoelectrochemical devices.

EXPERIMENTAL METHOD

Materials

Poly(ethylene glycol) with average molecular weight 4000 (PEG-4000), chloroform, acetyleacetone, ethanol, Triton X-100, Nanocrystalline TiO_2 Powder (Degussa P25) were all A.R. grade. Sensitizing dye Ruthenium-513 and electrolyte solution (Iodolyte) containing of redox couple were purchased from SOLARONIX, SA.

Conducting glass plates (ITO glass, Indium doped tin oxide over-layer, sheet resistance 8Ω cm^{-2}, purchased from Visiontek Co., UK) were used as a substrate for precipitating TiO_2 porous film on and were cut into 2 cm x 1.5 cm sheets.

Preparation of Electrolyte Gel

The gel polymer electrolyte based on poly(ethylene glycol) was used as matrix for a redox couple I^-/I_3^- containing in the Iodolyte solution (Solaronix, SA). Amount of 7 g PEG was diluted with 25 mL chloroform solution to form a gel polymer, then

added several drops of Iodolyte solution (Solaronix, SA). The mixing solution was stirred continously while heated at 80^0C for 1 h until a homogen solution obtained.

Assembly of Solid State Solar Cell

Nanoporous TiO_2 film was manufactured by following procedure. Firstly, a TiO_2 colloid was prepared by diluted 0,5 g Nanocrystalline TiO_2 powder (P25 Degussa) with 0,5 ml acetylacetone, to the solution added a few drops of emulsification reagent of Triton X-100 to form a TiO_2 colloid.

A conducting glass sheet (ITO) was immersed in an ethanol solution for 24 h to remove any impurities. A plastic adhesive tape (Schott) was fixed on the four sides of conducting glass sheet to restrict the thickness and area of TiO_2 porous film. The TiO_2 colloid was dropped on the ITO glass plate by using a doctor scraping technique. The process was done for three times to form a thick TiO_2 film. Finally, the TiO_2 porous film was solidified and sintered by firing the conducting glass sheet at 450 ^{0}C in a furnace for 30 min.

After cooled to 80 ^{o}C, the TiO_2 film was immersed in a 5.0×10^{-4} M absolute ethanol solution of Ruthenium complex dye for 24 h to adsorb the dye adequately, the other impurities were washed up with anhydrous ethanol and dried in moisture-free air. After that, a TiO_2 porous film electrode adsorbed dye was prepared.

A solid-state dye-sensitized solar cell was assembled in a sandwich structure, where a gel polymer electrolyte containing I⁻/I₃⁻ redox couple sandwiched between two electrodes (anode and cathode). Several drops of gel polymer electrolyte was distributed onto the surface of the dye-staining porous TiO_2 film electrode (anode) by a glass rod, then a carbon sheet (cathode) pressed on the top of TiO_2 electrode to form a sandwich structure. The cell was stored for a day until the electrodes were clipped together. This solid-state cell does not need a clipp, so the gel polymer electrolyte also acts as a glue to join the electrodes.

Photovoltaic Measurments of Solar Cell

The photovoltaic test of solid state dye sensitized solar cells was carried out by measuring the *I-V* character curves under irradiation of directly sunlight at 12 P.M. The incident sunlight intensity and the active cell area is 37 mWcm^{-2} and 1,5 cm^2, respectively. The photovoltaic performances of solar cell can be described by the values of the open circuit voltage (V_{OC}), short circuit current (I_{SC}), fill factor (FF) and conversion efficiency (η) obtained from these curves.

RESULTS AND DISCUSSION

Morphology and XRD Pattern of TiO₂ Electrode

A scanning electron micrograph of TiO_2 film deposited by casting on a conducting glass sheet is given in Figure 3. Based on the scanning electron microspopy (SEM) image, the TiO_2 film shows a highly nanoporous morphology and interconnectivity among the TiO_2 particles with porosity is >50%. Such a porous structure permits not only the adsorption of a greater number of dye molecules, but also better wetting of the film by electrolyte. Together, these features result in a perfect penetration of the I⁻/I₃⁻ redox couple into the TiO_2 film that can enhances the performances of the solar cell.
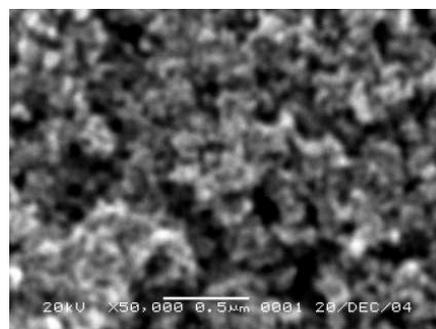

Figure 3. SEM picture of nanoporous TiO_2 film

Figure 4 shows the SEM image of the cross-section of TiO_2 film after calcinations at 450 ^{o}C for 1 h. The thickness of porous film is about 12 μm measured based on the scale on the cross-section image. The magnified cross-section image between conducting glass and TiO_2 film clearly indicated that perfect adherence had been formed and the small TiO_2 particles seemed to grow from the surface of the conducting glass. The good adherence of nanoporous TiO_2 film onto the surface of conducting glass substrate provides a favorable electricity contiguity resulting in decreasing resistance loss and easy electron transfer from TiO_2 film to the conductive substrate then flows to external circuit.

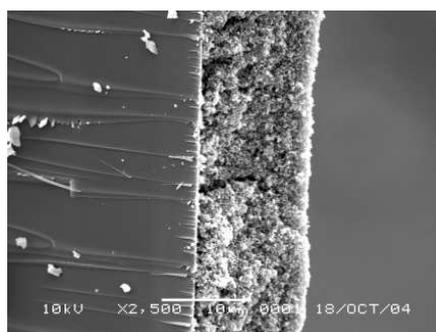The structural characteristic of TiO_2 films was studied by x-ray diffraction (XRD). The XRD pattern of

Figure 4. Cross-section of TiO_2 film on glass substrate

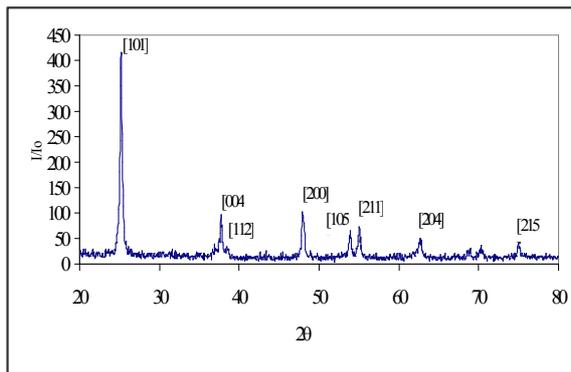## Photovoltaic Characteristics of the Solar Cell

Figure 5. XRD pattern of TiO$_2$ film

TiO$_2$ film is shown at Figure 5, clearly shows that the deposited TiO$_2$ film consisted anatase-type crystal has the excellent performance for DSSCs compared with rutile and brookite types [10].

The XRD profile showed that preferential orientation of the TiO$_2$ crystallites as recognized from the extremely enhanced relative peak intensity for the [101] diffraction at around $2\theta = 25°$. Based on the preferential orientation indicated the film have grown with two direction *a*-axis and *c*-axis paralell to the substrate.

Absorbance Spectra of Ruthenium Complex Dye

The assembled solar cell devices use a synthetic dye based on Ruthenium complex named Ruthenium 535 (purchased from Solaronix, SA). Before used as a dye for the solar cell, Ruthenium complex solution (5,0 x 10^{-4}M in absolute ethanol solution) was tested its absorpstion characteristic by UV-Vis spectroscopy.

The molecules of the dye shows a two specific absorption bands, that are around 400 nm and 530 nm, as shown at Figure 6. The absorption spectra of the dye explains that the dye can absorps two specific spectra of electromagnetic wave, violet-blue spectrum and green spectrum that can enhances performances of the solar cells.
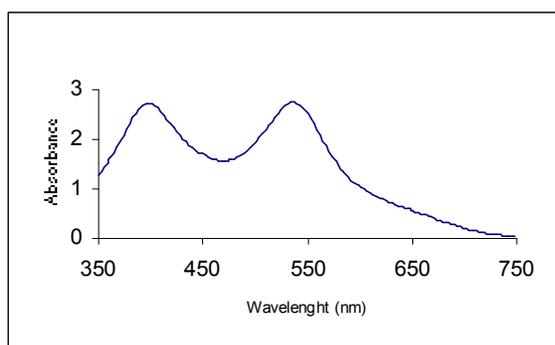
The photocurrent voltage (*I-V*) curves for a dye-sensitized solar cell that employs the gel polymer electrolyte are shown in Figure 4. These curves were measured under direct sunlight with intensity of 37 mWcm^{-2} measured by radiometer.

The photovoltaic performances of solar cell can be described by the values of the open circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor (FF) and conversion efficiency (η) obtained from these curves. The fill factor can be calculated by the following relationship :

$$ FF = \frac{V_{max} . I_{max}}{V_{oc} I_{sc}} \quad \text{................................} \quad (1) $$

where P_{max} is the maximum electrical power obtained; I_{SC} and V_{OC} are the short-circuit current and open-circuit voltage, respectively. The conversion efficiency of the dyesensitized solar cell is obtained from the following equation :

$$ \eta(\%) = \frac{V_{max} I_{max}}{P_{in}} x100 = \frac{V_{oc} I_{sc} . FF}{P_{in}} x100 \quad ..... \quad (2) $$

where P_{in} is the incident light power, and I_{max} and V_{max} are the current and voltage in the *I–V* curves, respectively, at the point of maximum power output.

The I-V curves at Figure 7 show the dependence of photocurrents (I) and photovoltage (V) for solar cell on concentration or amount of redox couple in electrolyte that result in a different characteristic for solar cells, as shown in Table 1. The curves show an ideal I-V characteristic of solar cell, where the parameters of solar cells can be determined from this curves. The cell with 20 drops of Iodolyte solution (contains a redox couple) have a lower performance (i.e. the overall energy conversion efficiency, see Table 1) than another cell with 30 drops of Iodolyte.

Generally, an increase of concentration of redox couple contains in electrolyte results in an increasing phocurrent, as shown in the curves, the cell with higher amount of Iodolyte used resulted in a higher short-circuit
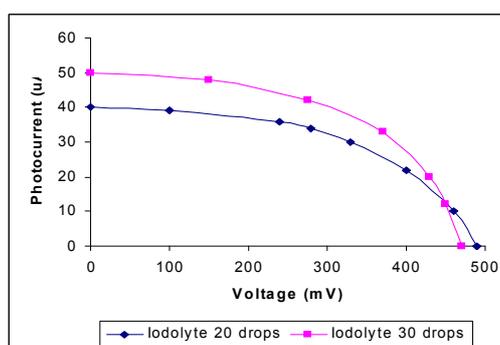

Figure 6. Absorption spectra of the Ruthenium complex dye

Figure 7. I-V characteristics of two solar cell devices, with Iodolyte (a) 20 drops and (b) 30 drops.

Table 1. Parameters of solar cell outputs.

Parameters	Cell 1 (20 drops Iodolyte)	Cell 2 (30 drops Iodolyte)
Open-circuit voltage (V_{oc})	490 mV	470 mV
Short-circuit current (I_{sc})	40 μA	50 μA,
Maximum power output (P_{max})	9,9 μW	12,2 μW
Fill factor (*FF*)	50,5%	51,9%
Conversion efficiency (η)	0,018%.	0,02%.

photocurrent (I_{sc}) than another one with lower amount of Iodolyte. This considered due to the increase in conductivity of the electrolyte with increasing redox couple (I^-/I_3^-) in the cell [22]. An increase of short-circuit photocurrent with redox couple also suggests that I^- diffusion from the bulk electrolyte into the inside of the nanoporous TiO_2 electrode and/or of I_3^- produced by oxidation of I^-, from within the nanoporous TiO_2 electrode into the counter electrode, are the rate determining steps under these conditions [22]. According to the following equation (Equation (3)), I_3^- concentration increases with increasing I^- concentration.

$$I^- + I_2 \Leftrightarrow I_3^- \qquad \text{...................................} \quad (3)$$

On the other hand, increase in redox couple concentrations result in decrease an open-circuit photovoltage (V_{oc}). V_{oc} for dye-sensitized solar cells with an iodine redox electrolyte is represented by the following equation [22]:

$$V_{oc} = \frac{kT}{e} \ln\left(\frac{I_{inj}}{n_{cb} k_{et} [I_3^-]} \right) \qquad \text{.................} \quad (4)$$

where I_{inj} is the injection current from dye to semiconductor, n_{cb} is the carrier (electron) density on the conduction band of semiconductor, and k_{et} represents the rate constant of reduction of I_3^- to I^- (back electron tranfer reaction, represented by Eq. (5)).

$$I_3^- + 2e_{cb} \Leftrightarrow 3I^- \qquad \text{.......................................} \quad (5)$$

According to Eq. (4), V_{oc} decreases with an increasing back electron transfer reaction. Decrease in V_{oc} with increasing Iodolyte concentration is explained by the enhanced back electron transfer reaction.

The DSSCs assembled with the gel polymer electrolyte reports a lower I_{sc} than the DSSC with a liquid electrolyte. The lower value of I_{sc} in the DSSC with gel polymer electrolyte may originate from its lower ionic conductivity. Unfortunately, in this research, the electrical conductivity of gel electrolyte was not measured. A higher resistance to ion migration reduces the supply of I_3^- to the counter-electrode. This causes

depletion of I_3^- and also retards the kinetics of dye regeneration, and therefore, decreases the I_{sc} [22]. On the other hand, when a gel polymer electrolyte is used in the DSSC, the polymer contacted on the surface of TiO_2 suppresses the back electron-transfer from the conduction band of TiO_2 electrode to the I_3^- in the gel polymer electrolyte, which results in high value of V_{oc}.

In the DSSCs assembled with gel polymer electrolyte, the organic solvent containing I^-/I_3^- redox couple is well encapsulated in the gel polymer electrolyte. Moreover, the electrolyte can promote a strong interfacial contact between the dye-adsorbed TiO_2 electrode and the platinum counter electrode. This gives a more stable performance than that of the DSSC assembled with liquid electrolyte. From these findings, it is expected that the solid-state dye-sensitized solar cell constructed with gel polymer electrolyte is a promising candidate for a practical solar cell with good durability.

CONCLUSION

Gel polymer electrolyte based on the poly(ethylene glycol) (PEG) containing a redox couple (I^-/I_3^-) was prepared successfully. The gel polymers encapsulated the electrolyte solution well without solvent leakage and maintains good mechanical properties that allowed application in the dye-sensitized solar cell. A dye-sensitized solar cell employing the gel polymer electrolyte gives an open-circuit voltage around 0.5V and short-circuit current of 40-50 μA for an incident directly sunlight intensity of 37 mWcm⁻². This yields a conversion efficiency around 0,02%. Use of the gel polymer electrolyte in the DSSCs improves cell stability by suppressing solvent evaporation, but gives a slightly lower short-circuit current.

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