STABILITY OF DYE SENSITIZED SOLAR CELLS BASED ON A GEL POLYMER ELECTROLYTE COMPLEXED WITH POLYMETHYLMETHACRYLATE

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ABSTRACT

Many efforts have been made to increase the performance of dye sensitized solar cells (DSSCs) using liquid electrolytes. But these types of cells have unsolved critical problems such as leakage and evaporation of volatile organic solvents due to the presence of liquid electrolytes. Thus DSSCs based on gel polymer electrolytes (GPEs) have been attracting as a group of better alternative for substituting liquid electrolyte based DSSCs. This paper is based on a study carried out to investigate the stability of a DSSC fabricated with a GPE based on poly (methylmathacrylate) (PMMA), ethylene carbonate (EC), propylene carbonate (PC), sodium iodide (NaI) and iodine (I_2). GPE was prepared by using different salt amounts and keeping PMMA, EC and PC amounts constant. The composition 100 PMMA: 150 EC: 150 PC: 65 NaI: 55 I_2 (weight basis) showed the highest room temperature conductivity of 2.09×10^{-3} S cm^{-1}. It showed an ionic transference number of 0.9. DSSCs in the configuration fluorine doped conductive titanium oxide (FTO) / glass / TiO_2 / dye / GPE / Pt / glass configuration was fabricated and their performance was observed with time. They showed an average open circuit voltage of 596 mV and a short circuit current density of 3.0 mA cm^{-2}. Fill factor and efficiency were 0.3 and 0.5% respectively. Values of open circuit voltage and short circuit current density decreased with time. Possible desorption and photo-degradation of the attached dyes, corrosion of the Pt counter electrode and building up of internal impedance are some reasons for decreasing performance of DSSCs.

Keyword: Gel polymer electrolyte, Polymethylmetacrylate, Dye sensitized solar cell, Stability

1. INTRODUCTION

A dye sensitized solar cell (DSSC) is a photo-electrochemical cell (PEC) utilizing photovoltaic material sensitized with dye, an electrolyte and a counter electrode. In the past decades, high efficient DSSCs based on nanocrystalline TiO_2 by photoexcited dye molecules have been attracting many researchers' interests as potential competitive alternative to traditional photovoltaic devices[1]. Ease of fabrication, low production cost and reasonable energy conversion are some of the advantages of DSSCs[2]. Much research activities have been carried out on DSSCs based on liquid and solid electrolytes. A liquid electrolyte has a very high conductivity, but it has a high risk of leakage and also some other critical problems. The low conductivity of solid electrolytes is a major issue to be employed for many applications[3]. In order to overcome these problems, gel polymer electrolytes (GPEs) have been considered for applications due to their merits of appreciable conductivities and good mechanical properties[3,4]. GPEs are consisting of a polymer network, a salt and a solvent / mixture of solvents. Most of DSSCs depend on I^-/I_3^- redox couple as it assists regeneration of the photoexcited dye. In this research, GPE samples consisting of polymethylmethacrylate (PMMA) / ethylene carbonate (EC) / propylene carbonate (PC) and different concentrations of the salt, sodium iodide (NaI) and iodine (I_2) were prepared. Ionic conductivity of the sample and the stability of the DSSC based on GPE were investigated.

2. EXPERIMENTAL

2.1 Preparation of the gel polymer electrolytes

Poly (methylmethacrylate) (PMMA, Aldrich, 350 000 Mw), ethylene carbonate (EC, Aldrich, 98%), propylene carbonate (PC, Aldrich, 99%), sodium iodide (NaI, Fluka, 99%) and iodine (I_2, Aldrich) were used as received. Several samples were prepared by varying salt concentration and keeping PMMA, and EC/PC amounts constant. I_2 was added as one tenth of the total mole amount of salt. The required amounts of PMMA, EC, PC and NaI were weighed and magnetic stirring was done at 60 °C for 2 hours until a homogeneous solution was obtained. After that, I_2 was added. Then, the hot viscous homogeneous solution was pressed in between two well cleaned glass plates and it was kept in a desiccator for 24 h. Different samples were prepared by varying the salt concentration.

2.2 AC impedance measurements

A GPE sample of having a diameter of 14 mm was cut and sandwiched in between two stainless steel (SS) electrodes in a spring loaded sample holder. Impedance measurements

were taken in the frequency range from 400 kHz to 0.01 Hz using Metrohm Autolab impedance analyzer. Data were gathered from 28 $^{\circ}$C to 50 $^{\circ}$C.

2.3 DC polarization test

A circular shape sample was sandwiched in between two stainless steel (SS) blocking electrodes in a sample holder and current drop across the sample was measured with time under a 1 V dc potential.

2.4 Preparation of TiO_2 electrode

Titanium dioxide (TiO_2-0.2 g) was measured and ground for about one minute. Then, three drops of acetic acid were added and grinding was continued for several minutes. One drop of triton x and three drops of acetic acid were added. Then, six drops of acetic acid and few drops of ethanol were added into the mixture. This TiO_2 paste was applied on an area of 0.25 cm^2 of well cleaned fluorine doped conductive titanium oxide (FTO) glass strips. Those electrodes were sintered for 45 minutes at 450 $^{\circ}$C. Sintered electrodes were immersed in ruthenium dye for 24 h before fabricating DSSC.

2.5 Fabrication and characterization of dye sensitized solar cell (DSSC)

The GPE sample which has the highest RT conductivity was selected for cell fabrication. The DSSCs based on the configuration glass /FTO / TiO_2/ dye / GPE / Pt / glass were fabricated. Photocurrent and photovoltage were measured during 2910 minutes under the illumination of 100 mW cm^{-2}. This was done to investigate the stability of the DSSC.

3. RESULTS AND DISCUSSION

3.1 Optimizing gel polymer electrolyte composition

100 PMMA / 150 EC / 150 PC / 60 NaI /55 I_2 composition was selected as the starting GPE composition. Different samples were prepared by varying salt concentration and keeping PMMA and EC / PC amounts constant. Variation of the salt concentrations and conductivities of different samples are shown in Fig. 1.
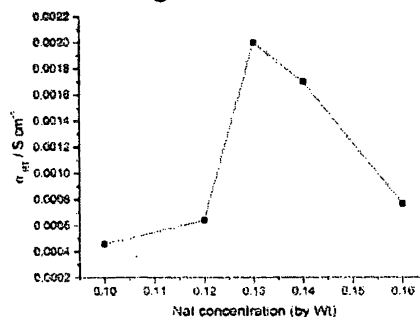

Figure 1: Variation of RT conductivity with different salt concentrations

The conductivity was calculated using equation 1.

$$\sigma = \frac{1}{R_b \times A}$$ (1)

where σ is the conductivity of the sample, R_b is bulk electrolyte resistance, 1 is thickness of the sample and A is area of the electrolyte.

When increasing the salt concentration, the conductivity increases due to the enhancement of charge carrier concentration. Then, it reached a maximum value of 2.09×10^{-3} S cm^{-1}. After that, conductivity decreases because concentration of free charge carriers is decreased due to ion aggregation and formation of ion pairs[5]. The sample having the highest room temperature conductivity was taken for the DC polarization test as well as for assembling the DSSC.

3.2 Conductivity – temperature variation of gel polymer electrolytes (GPEs)

The variation of conductivity plotted against the reciprocal temperature for different GPE samples by varying salt amounts are shown in the Fig. 2. When the temperature increases, the mobility of charge carriers tend to increase. It is due to increase of energy with higher temperatures[5, 6]. The nonlinear shape of the curves can be explained by the Vogel-Tamman-Fulcher (VTF) equation[4].

$$\sigma = AT^{-1/2} \exp(-E_a(T - T_0))$$ (2)

where E_a is the pseudo activation energy, T_0 is related to the glass transition temperature, A is a pre exponential factor.
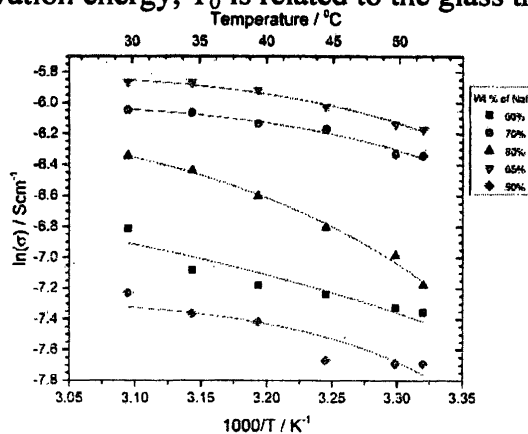

Figure 2: Conductivity variation of GPEs with reciprocal of temperature

The behaviour which follows VTF equation points out the fact that conducting mechanism in the GPE may take place via ion movement inside the free volumes.

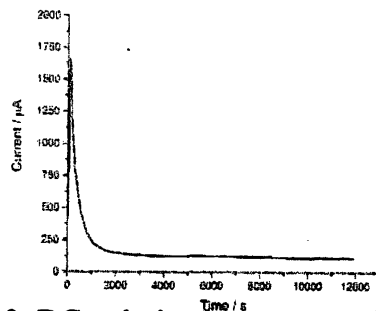## 3.3 Calculation of transference numbers

Figure 3: DC polarization curve with blocking electrodes

The sudden drop of current is due to blocking of ions and the steady state current is due to electrons[6]. Ionic transference number was calculated using following equation.

$$t_i = \frac{I_0 - I_s}{I_0} \qquad (3)$$

Where, I_0 is the initial current and I_s is the steady state current.

The value of ionic transference number is 0.9. This shows that the GPE sample is purely an ionic conductor[6].

3.4 Investigating the stability of the DSSC

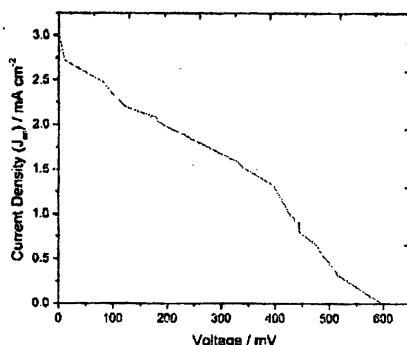Fig. 4 shows the I-V characteristics curve of the DSSC under an irradiation of 100 mWcm^{-2} at t=0s.

Figure 4: I-V characteristics curve at t=0s

The value of open circuit voltage (V_{oc}) was 596 mV and short circuit current density (J_{sc}) was 3 mA cm^{-2}. The values of fill factor (FF) and efficiency (η) 0.3 and 0.5% were calculated. FF and efficiency were calculated by using the following equations.

$$FF = (J_{max} \times V_{max}) / (J_{sc} \times V_{oc}) \qquad (4)$$

$$\eta = ((J_{max} \times V_{max}) / P_{in}) \times 100\% \qquad (5)$$

where J_{max} is the current density at maximum power output, V_{max} is the voltage at maximum power output and P_{in} is the power of incident light

3.5 Stability of the dye sensitized solar cell

Variations of V_{oc} and J_{sc} are shown in Figure 5 and 6. After 2910 minutes, values of V_{oc} and J_{sc} were measured as 257 mV and 0.02 mA cm^{-2} respectively.
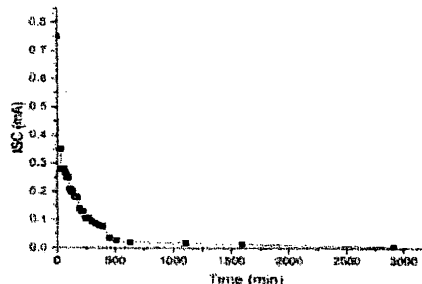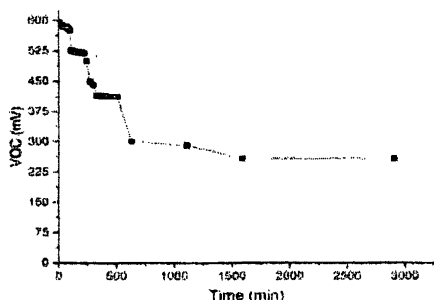

Figure 5: Variation of V_{oc} with time   Figure 6: Variation of J_{sc} with time

When time passes, the performance of DSSC decreases. This is because possible desorption and photo-degradation of the attached dyes, corrosion of the Pt counter electrode[1,7]. And also, the solvent evaporation may cause in less-long term stability and decrease in performance of the DSSCs. Building up of internal impedance and solubility of NaI salt in an organic solvents is limited at RT are critical problems for less long term stability of DSSCs.

4. CONCLUSION

GPEs were prepared by keeping PMMA, EC, PC, amounts constant and varying salt concentration and I_2. Highest RT conductivity was 2.09×10^{-3} S cm^{-1} and it was obtained with the composition 100 PMMA: 150 EC: 150 PC: 65 NaI: 55 I_2 (by weight). Conductivity-temperature variation shows that conductivity of GPE follows VTF equation. Ionic transference number is 0.9 and it proves that the GPE is purely an ionic conductor. The drop of V_{oc} and J_{sc} was very high in 2910 minutes. The possible reasons may be desorption and photo-degradation of the attached dyes, corrosion of the Pt counter electrode, solvent evaporation and building up internal impedance. And also, the solvent evaporation and solubility of NaI salt in an organic solvent is limited at RT may cause in less-long term stability and decrease in performance of the DSSCs.

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