



Composite Poly(ethylene oxide) Electrolyte Modified with Ethanol for Dye-sensitized Solar Cells

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ABSTRACT

The composite poly(ethylene oxide) PEO/TiO₂/KI/I₂ in acetonitrile has been introduced as a solid electrolyte for dye-sensitized solar cells (DSSCs). In this work, the influence of ethanol and water as additives in the composite electrolyte on conductivity and photoelectric performance of quasi-solid-state dye-sensitized solar cells will be presented. The average overall energy conversion efficiencies (%) of DSSCs using the composite PEO electrolyte in acetonitrile, acetonitrile with ethanol additive (10% v/v) and acetonitrile with water additive (10% v/v) were 5.60, 5.81 and 2.11, respectively. The ethanol content in acetonitrile was varied to achieve maximum conductivity and energy conversion efficiency. It was found that DSSC composed of the composite PEO electrolyte in 20% v/v ethanol in acetonitrile solution gave the best overall energy conversion efficiency of 6.33%. The long-term storage at room temperature demonstrated that the energy conversion efficiencies of DSSCs gradually decreased to 1% after 2,000 hours.

Keywords: composite poly(ethylene oxide) PEO/TiO₂/KI/I₂, dye-sensitized solar cell, ethanol, water.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) provide an attractive alternative to conventional photovoltaic devices for conversion of solar energy to electrical energy at low production cost and low environmental impact during fabrication. These cells with liquid electrolyte have achieved more than 11% of solar conversion efficiencies under irradiation of AM 1.5 [1]. A dye-sensitized solar cell consists of a dye-sensitized nanocrystalline titanium dioxide film as working electrode, an electrolyte containing a suitable redox-couple and a platinum counter electrode. Energy

conversion in a DSSC occurs when the light is absorbed by a sensitizer and photo-excitation of the dye results in the injection of electrons into the conduction band of TiO₂. Subsequently the dye is regenerated by the electron donor present in the electrolyte. The electrons in the conduction band are collected, flow through the external circuit to arrive at the counter electrode, where they cause the reverse reaction of the redox mediator. Thus, the photoelectrochemical cell is regenerative and the process leads to direct conversion of sunlight into electricity. The use

of liquid electrolytes cause problems such as leakage and volatilization of the liquid, desorption of the attached dyes, and the corrosion of the counter electrode and therefore limits the long-term performance and commercial development of DSSC. Several efforts have been made to find a suitable substitute and polymer based electrolytes have shown promising results [2-4]. Poly(ethylene oxide) (PEO) has been intensively studied as solid polymer electrolyte because it is both chemically stable and polar, which means that it can readily dissolve salts. However, its ionic conductivity is not satisfactory for DSSCs, primarily because of its high crystallinity. The energy conversion efficiency of DSSC employing PEO-KI-I₂ as polymer electrolyte was 2.04% [5]. Many attempts have been made to improve ionic conductivity of PEO polymer electrolyte by incorporating nanoparticle fillers, plasticizers or comonomers [6-10]. Nanocrystalline TiO₂ (Degussa P25 powder) was introduced into a high molecular weight PEO to reduce crystallinity of the polymer. The energy conversion efficiency of DSSC using this polymer was 4.2% at 65 mW cm⁻²[11]. In this work, the influence of ethanol and water as additives in the composite PEO electrolyte on conductivity and photoelectric performance of quasi-solid-state dye-sensitized solar cells was studied. The optimized ratio of acetonitrile with ethanol additive is suggested based on the high conductivity of the composite polymer electrolyte as well as the overall energy conversion efficiency and stability of DSSCs.

2. MATERIALS AND METHODS

2.1 Preparation of Polymer Electrolytes

Composite solid polymer electrolyte consisting of PEO ($M_w \sim 300,000$ g/mol, Sigma-Aldrich), TiO₂ (Degussa P25, 20-30 nm, Germany), potassium iodide (KI) and iodine

(I₂) with a ratio of 61:9:25:5 by weight was prepared in acetonitrile, acetonitrile with ethanol additive (10, 20 and 30% v/v) or acetonitrile with water additive (10% v/v) and then stirred vigorously to form a homogeneous solution.

2.2 Preparation of Electrodes

The nanocrystalline TiO₂ (Degussa P25) film was prepared by doctor-blade technique. TiO₂ colloidal paste was coated on cleaned fluorine-doped tin oxide (FTO) glass substrate. After drying in air at room temperature, the TiO₂ film electrode was sintered at 450°C for 30 min. The sensitizing dye was adsorbed on the TiO₂ surface by immersing into 0.3 mM solution of bis-tetrabutylammonium salt of Ru^{II} (dc-bpy)₂(NCS)₂ or N719 (Dyesol) in ethanol and kept at 25°C for 24 hours. Afterwards, the TiO₂ film electrode was rinsed with ethanol and dried in the air.

A platinum counter electrode was prepared by spin coating 0.1 mM solution of H₂PtCl₆ in isopropanol on FTO glass substrate and then it was sintered at 400°C for 30 min.

2.3 Fabrication of DSSC

A quasi-solid state dye-sensitized solar cell was fabricated by sandwiching the polymer electrolyte between a dye-adsorbed TiO₂ film electrode and a platinum counter electrode. The polymer electrolyte was spread onto a dye-adsorbed TiO₂ film electrode and heating at 60°C for 5 min to obtain a quasi-solid electrolyte and then was covered with the platinum counter electrode by firmly pressing.

2.4 Characterization Techniques

The electrochemical impedance spectroscopy (EIS) was carried out on a symmetric thin-layer cell composed by sandwiching the composite polymer electrolyte between two platinized FTO electrode. The measurement was performed by using Autolab Potentiostat

PGSTAT 302 with FRA module at the zero bias with the frequency range of 0.05 Hz to 1 MHz.

The DSSCs were illuminated by simulated sunlight from the Xenon arc lamp under AM 1.5 (100 mW cm^{-2}) and measured by a Keithley 236 source-measure unit. The active area of the cell was 1 cm^2 .

3. RESULTS AND DISCUSSION

3.1 Conductivity study

The conductivity of composite polymer electrolyte is an important parameter which affects the photoelectric performance of quasi-solid-state dye-sensitized solar cells. The conductivity values (σ) of composite polymer electrolytes were calculated from the resistance (R_m) using the following equation:

$$\sigma = L / R_m A$$

where L is the thickness of the composite polymer electrolyte ($200 \mu\text{m}$), A is the area of

the electrode (0.25 cm^2) and R_m is the resistance determined from the equivalent circuit obtained from the EIS spectra.

Effect of ethanol and water as additives on conductivity of the composite PEO electrolyte

Figure 1 shows the electrochemical impedance spectra for the composite PEO polymer electrolytes in acetonitrile, acetonitrile with ethanol additive (10% v/v) and acetonitrile with water additive (10% v/v). The conductivity of the composite PEO polymer electrolyte is calculated to be 6.04 mS cm^{-1} , 6.71 mS cm^{-1} and 2.98 mS cm^{-1} , respectively. The conductivity is increased with ethanol as additive in the composite PEO quasi-solid electrolyte at room temperature. Ethanol is a small molecule which solvates PEO by hydrogen bonding formation between the C-O-C groups in PEO and the -OH groups of ethanol and can act as a dispersant to isolate the PEO aggregates. The formation of continuous network through

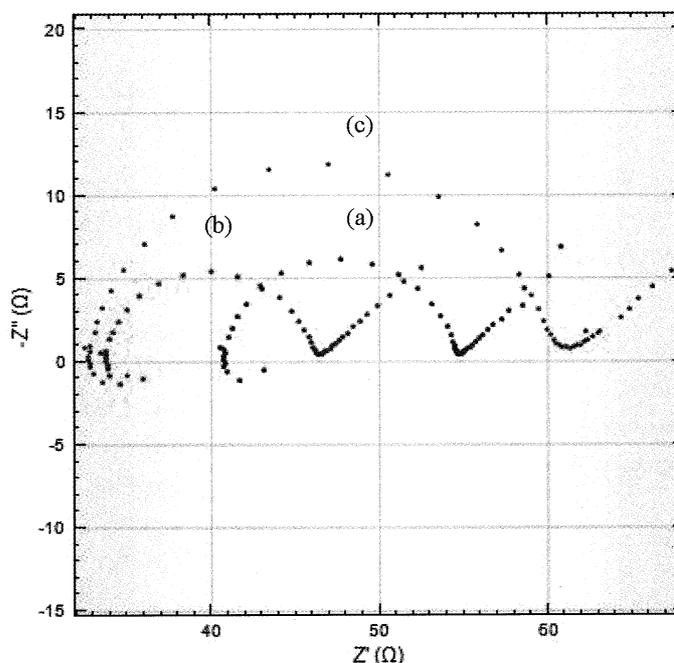


Figure 1. Electrochemical impedance spectra for composite PEO polymer electrolyte in acetonitrile (a), acetonitrile with ethanol additive (b) and acetonitrile with water additive (c).

cross-linking creates free space and voids which facilitate ion transport in the electrolyte [12].

Effect of ethanol concentrations on conductivity

The conductivity of the composite PEO polymer electrolyte changes with different concentration of ethanol 10, 20 and 30% v/v.

It can be seen from Figure 2 that the conductivity of the electrolyte initially increases with increasing ethanol additive content. At 20% v/v ethanol in acetonitrile the maximum conductivity of 7.05 mS cm⁻¹ is obtained. As the concentration of ethanol in acetonitrile is greater than 20% v/v, the conductivity decreases.

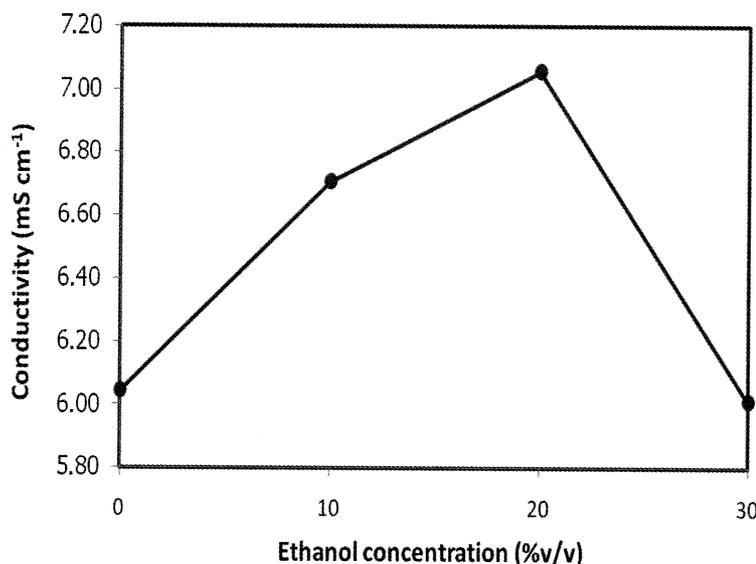


Figure 2. The conductivity dependence on ethanol concentration in acetonitrile.

3.2 Performance of Dye-sensitized Solar Cells

The photovoltaic characteristics of DSSCs is defined as

$$FF = \frac{P_{\max}}{J_{sc} V_{oc}} = \frac{I_{\max} V_{\max}}{J_{sc} V_{oc}}$$

The overall energy conversion efficiency (%) of DSSC is calculated using

$$\eta = \frac{P_{\max}}{IA} = \frac{J_{sc} V_{oc} FF}{IA}$$

where FF is fill factor, J_{sc} is short-circuit current, V_{oc} is open circuit voltage, I_{\max} is the current for maximum power output, V_{\max} is the voltage for maximum power output, P_{\max}

is maximum electrical power obtained, I is intensity of incident illumination and A is cell area.

Effect of ethanol and water as additives in the composite PEO electrolyte on performance of DSSCs

The photovoltaic characteristics of DSSCs employing the composite PEO solid electrolytes are presented in Table 1. The average overall energy conversion efficiencies (%) of DSSCs using composite PEO electrolytes in acetonitrile, acetonitrile with ethanol additive (10% v/v) and acetonitrile with water additive (10% v/v) were 5.60, 5.81 and 2.11, respectively. The best overall energy

conversion efficiency achieved in the DSSC with ethanol as additive is consistent with the highest conductivity of the electrolyte. This result indicates that the conductivity dictates

the mobility of the I^-/I_3^- redox couple in the composite polymer electrolyte and thus has a direct bearing on the overall energy conversion efficiency of DSSC.

Table 1. Photovoltaic performance of dye-sensitized solar cells based on composite PEO polymer electrolyte in acetonitrile (ACN), acetonitrile with ethanol additive (10% v/v) and acetonitrile with water additive (10% v/v).

Sample	σ (mS cm ⁻¹)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
ACN	6.04	9.53	738	0.80	5.60
ACN+EtOH	6.71	10.01	749	0.78	5.81
ACN+water	2.98	4.89	769	0.56	2.11

Effect of ethanol concentrations in the composite PEO electrolyte on performance of DSSCs

The photovoltaic characteristics of DSSCs using the composite PEO solid electrolyte with various concentrations of ethanol additive are shown in Table 2. With increasing ethanol additive content from 0 to 20 %v/v, the short-circuit current increases from 9.53 to 10.28 mA cm⁻², most probably due to the enhancement of the conductivity of the composite polymer electrolyte which increase from 6.04 ms cm⁻¹ to 7.05 ms cm⁻¹. With ethanol content greater than 20% v/v, the current is decreased to 9.04 mA cm⁻² as with a decrease in conductivity to 6.01 ms cm⁻¹. The decrease of conductivity may be due to the reduced concentration of I^-/I_3^- anions in the electrolyte caused by less solubility of KI in ethanol than in acetonitrile and excess

ethanol may disrupt the cross-linking networks between ethanol, PEO, TiO₂ and salt dissociation. The performance of a DSSC is determined by an efficient transport of iodide and triiodide in the electrolyte. DSSCs fabricated with composite PEO polymer electrolyte in acetonitrile with ethanol additive of 20 % v/v has shown to be the best condition, the short-circuit current (J_{sc}) is 10.28 mA cm⁻², the open circuit voltage (V_{oc}) is 737 mV, the fill factor (FF) is 0.84 and the overall energy conversion efficiency (%) is 6.33%. These results agree with those of poly(ethylene oxide)-poly(vinylidene fluoride) (PEO-PVDF)/TiO₂/LiI/I₂ electrolyte modified with 12.4 wt% ethanol to give maximum conductivity of 1.57 mS cm⁻¹ and optimized conversion efficiency of 5.77% [13].

Table 2. Photovoltaic performance of dye-sensitized solar cells based on composite PEO polymer electrolyte in acetonitrile with various concentrations of ethanol additive.

Ethanol(% v/v)	σ (mS cm ⁻¹)	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
0	6.04	9.53	738	0.80	5.60
10	6.71	10.01	749	0.78	5.81
20	7.05	10.28	737	0.84	6.33
30	6.01	9.04	733	0.65	4.30

3.3 Stability of DSSCs

The stability of DSSCs fabricated with the composite PEO electrolyte in acetonitrile, acetonitrile with ethanol additive of various concentrations and acetonitrile with water additive was observed by measuring the photovoltaic characteristics during interval of storage time. Figure 3 depicts the changes in the overall energy conversion efficiency (%) of DSSCs as a function of storage time at room temperature. It demonstrated that the initial decrease in energy conversion efficiency as a function of storage time during the first 48-200 hours is faster than the later time (200-2,000 hours) of storage. The efficiency of DSSCs fabricated with the composite PEO electrolytes in acetonitrile and acetonitrile

with ethanol additive gradually decreased to about 1% after 2,000 hours of storage whereas those fabricated with composite PEO electrolyte in acetonitrile with water additive showed the least stability and the efficiency decreased to 0.61%. This could be attributed to a weak interaction of ethanol molecule with the composite PEO network which results in decreasing crystallinity of the polymer and enhancing ion mobility, however on storage at room temperature without sealing the device, the ethanol molecule leaked from the network causing decrease in efficiency to about 1%. This value agrees with the earlier work on a solvent-free composite PEO/TiO₂/LiI/I₂ electrolyte which gave the overall conversion efficiency of 0.96% [14].

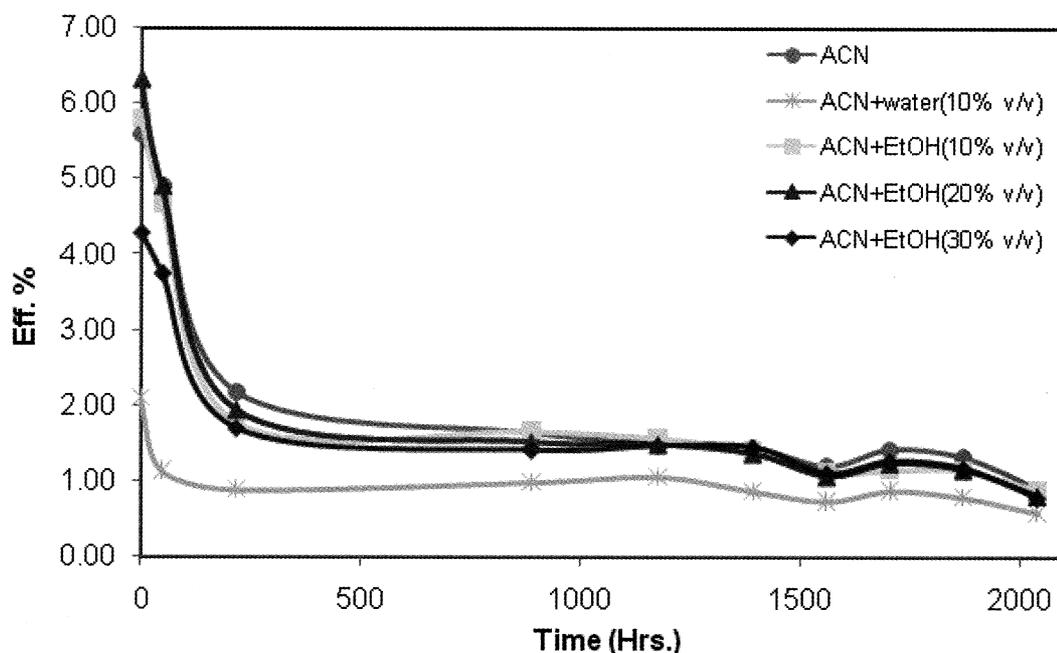


Figure 3. Stability of DSSCs fabricated with composite PEO polymer electrolyte in acetonitrile, (ACN), acetonitrile with ethanol additive and acetonitrile with water additive.

4. CONCLUSIONS

The composite poly(ethylene oxide) PEO/TiO₂/KI/I₂ electrolyte in acetonitrile with ethanol additive demonstrated an increase in ionic conductivity of the solid polymer electrolyte and an improvement in the overall energy conversion efficiency from 5.60 to 6.33%. This could be due to a weak interaction of solvent molecules with the composite PEO network resulting in a quasi-solid electrolyte with reducing crystallinity of the polymer, thus creating more channels for the iodide/triiodide ions mobility. However the efficiency of the DSSCs gradually decreased to 1% after 2,000 hours of storage at room temperature without sealing. Further work is investigated to improve the stability of DSSCs by changing the viscosity of the composite quasi-solid PEO-based electrolyte to retain the solvent molecules in the polymer network.

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