

Dye-sensitized solar cells based on composite solid polymer electrolytes

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Received (in Cambridge, UK) 5th August 2004, Accepted 10th November 2004

First published as an Advance Article on the web 20th December 2004

DOI: 10.1039/b412129p

The ionic conductivity of polymer electrolytes and their interfacial contact with dye-attached TiO₂ particles were enhanced markedly by the addition of amorphous oligomer into polymer electrolytes, resulting in very high overall energy conversion efficiency.

Dye-sensitized solar cells (DSSCs) have been under investigation for the past decade due to their attractive features such as high energy conversion efficiency and low production costs.¹ Regenerable redox couples (e.g. I⁻/I₃⁻) are usually dissolved in an organic solvent, which results in high energy conversion efficiency but some drawbacks such as leakage and evaporation of the solvent.^{1–3} Therefore, several attempts have been made to substitute liquid electrolytes with solid or quasi-solid state electrolytes such as solid polymer electrolytes (SPEs),² polymer gel electrolytes (PGEs),⁴ and organic hole-transport materials (HTMs).⁵

SPEs have received considerable attention in recent decades because of their potential applications in electrochemical devices such as solid-state batteries⁶ and separation membranes.⁷ Poly(ethylene oxide) (PEO) has been most intensively studied as a polymer solvent for SPEs because it is both chemically stable and polar, which means that it can readily dissolve salts. However, its ionic conductivity is not satisfactory for solar cell applications primarily because of its high crystallinity. There have thus been many attempts to modify PEO to increase its ionic conductivity by incorporating comonomers or nanoparticle fillers.² Nogueira *et al.* reported that the ionic conductivity of a polymer electrolyte comprising poly(epichlorohydrin-co-ethylene oxide), 9% NaI, and 0.9% (w/w) I₂ was found to be 1.5×10^{-5} S cm⁻¹,^{2a} whereas the ionic conductivity of neat PEO ($M_w = 1,000,000$) is 1.65×10^{-6} S cm⁻¹. DSSCs employing this PEO copolymer electrolyte were found to exhibit a high overall energy conversion efficiency of 1.6% at 100 mW cm⁻². Another approach is the introduction of nanoscale inorganic fillers into highly crystalline polymer matrix in order to reduce the crystallinity of the polymer. For instance, nanocrystalline TiO₂ particles have been introduced into the PEO/LiI/I₂ electrolyte to prevent PEO crystal formation,^{2b} resulting in a high overall energy conversion efficiency of 4.2% at 65.6 mW cm⁻².

Meanwhile, the interfacial contact between dye molecules and polymer electrolytes is a major factor in determining the electron transfer efficiency and consequently the overall conversion efficiency. Thus the penetration of polymer electrolytes into the nanopores of a photoelectrode needs to be maximized in order to promote interfacial contact between the electrolyte and the dye. This is particularly important because high molecular weight

polymers do not readily penetrate into the nanopores of a TiO₂ layer, resulting in poor energy conversion efficiency.

In the present research, we have demonstrated the use of amorphous oligomer (*i.e.* low molecular weight poly(propylene glycol), oligo-PPG) in combination with high molecular weight PEO to provide both a high ionic conductivity and a large interfacial contact area between the electrolyte and the dye. The addition of oligo-PPG into a highly crystalline PEO can increase the ionic conductivity as well as improve the penetration of oligo-PPG electrolytes into the nanopores of the TiO₂ layer.

The electrolyte consists of PEO ($M_w = 1,000,000$), oligo-PPG ($M_n = 725$), and KI/I₂. The weight ratio of PEO to oligo-PPG was fixed at 4/6. The mole ratio of oxygen atoms in the PEO and PEO + PPG blends to potassium iodide was fixed at 20/1 (KI/I₂ = 10/1 w/w). Transparent glass coated with conductive indium tin oxide (ITO) (16 Ω/□, obtained from Samsung Electro-Mechanics Co. Ltd.) was utilized for preparing DSSCs. For fabrication of photoelectrodes, Ti(IV) bis(ethyl acetoaceto)-diisopropoxide solution (2% w/w in 1-butanol) was coated onto ITO glass and then the glass was heated stepwise to 450 °C. TiO₂ paste (Ti-Nanoxide T, Solaronix) was then cast onto the ITO glass by the doctor-blade technique and sintered at 450 °C for 30 min. The TiO₂ thin film was sensitized overnight with Ru(dcbpy)₂(NCS)₂ dye (535-bisTBA, Solaronix, dissolved in ethanol). Platinum layered counter electrodes were prepared by spin-coating H₂PtCl₆ solution (0.05 mol dm⁻³ in isopropanol) onto ITO glass and then sintering at 400 °C. The cell performances were evaluated after vacuum drying for more than 10 days, without any special sealing. Detailed DSSC fabrication and characterization procedures are well described in recent publications by us.⁸

Fig. 1 shows the WAXS spectra of KI, I₂, PEO₁₀ (pure PEO), and PEO₄PPG₆ (PEO/PPG = 4/6 w/w and M_n of PPG = 725) with and without KI/I₂. It is clearly shown that the intensities in the crystalline peaks for pure PEO (observed at 19.2° and 23.4°) have been drastically diminished with an addition of PPG and a mixture of KI and I₂ (10/1 w/w). Moreover, the crystalline peaks of KI and I₂ also disappeared upon addition of the PEO + PPG blend, indicating that KI and I₂ are completely dissolved in the polymer matrix. The crystallinity (X_c) of the polymer electrolyte was estimated from the melting enthalpy measured by differential scanning calorimetry (DSC).^{2b} The crystallinity of PEO₄PPG₆/KI/I₂ ($X_c = 7.3\%$) was much lower than that of PEO₁₀ ($X_c = 77.2\%$), indicating the drastic decrease in the crystallinity upon incorporation of oligo-PPG. The ionic conductivity was found to increase with the addition of oligo-PPG to PEO, as determined using a four-point probe method for impedance measurements; the ionic conductivity of the PEO₄PPG₆/KI/I₂ electrolyte is $2.57 \times$

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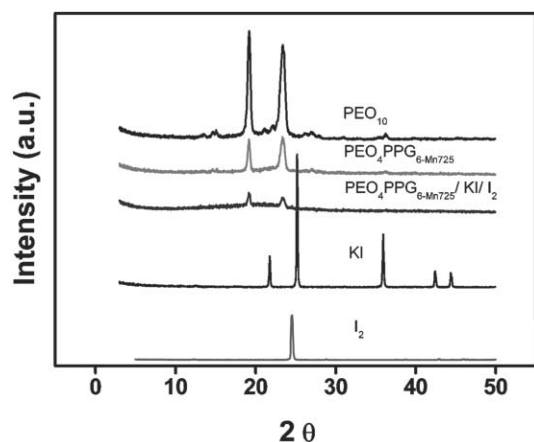


Fig. 1 WAXS spectra of PEO₁₀, PEO₄PPG₆, PEO₄PPG₆/KI/I₂, KI, and I₂.

10^{-5} S cm⁻¹ at room temperature, nearly 14-fold higher than that of PEO/KI/I₂, which is 1.87×10^{-6} S cm⁻¹. The increase in the ionic conductivity was mostly attributable to the prevention of PEO crystal formation and the chain mobility enhancement upon addition of oligo-PPG.

The better penetration of electrolytes into the nanopores of the TiO₂ layer and consequently more interfacial contact area would be expected if the coil size of a polymer is smaller than the pore size. The coil size of polymer chains in a good solvent is commonly represented by the radius of gyration, which can be expressed approximately by $R_g = C(M_w)^{1/2}$, where M_w is the molecular weight in g/mol and C is constant ($C = 0.063$ (nm/(g/mol)^{1/2}) for PEO).⁹ The radii of gyration of PEO and oligo-PPG are determined as approximately 63.0 and 1.7 nm, respectively, assuming that the C value of PPG is the same as that of PEO. The pore size of the TiO₂ layer was obtained by the Brunauer–Emmett–Teller (BET) method from the N₂-desorption isotherm using the BJH method.¹⁰ The average pore diameter and the specific surface area were 16.5 nm and 76.9 m²/g, respectively. Thus it is expected that oligo-PPG ($M_n = 725$ and $R_g = 1.7$ nm) may preferentially penetrate into the nanopores of the TiO₂ layer because of their smaller size compared to that of the nanopore, resulting in increased interfacial contact area, whereas high molecular weight PEO ($M_w = 1,000,000$ and $R_g = 63$ nm) may not penetrate into the nanopore readily but mostly stays outside of the TiO₂ layer. Therefore, it is expected that the oligo-PPG concentration in the nanoporous TiO₂ layer is somewhat higher than in the bulk electrolyte layer. The difference in the polymer/oligomer composition of the two layers could be minimized by a multiple coating method, employing a diluted and subsequently a highly concentrated polymer electrolyte solution. The relative concentration of oligo-PPG to PEO was fixed at 4/6. The Pt coated ITO electrode is then superposed upon it. The assembled cell is subsequently pressed for vacuum drying to prevent the formation of bubbles due to the rapid evaporation of organic solvent as well as to obtain a very thin polymer electrolyte layer. The thickness of the electrolyte layer largely depends on the properties of polymer electrolytes (*e.g.* viscosity, molecular weight of polymer or oligomer, and blending ratios (polymer/oligomer) *etc.*). In the case of the PEO₄PPG₆ electrolyte, the thickness between the front of the TiO₂ layer and the counter electrode was

5–6 μm while the average thickness of the TiO₂ layer was 25 μm ($t_{\text{TiO}_2} = 25$ μm). The TiO₂ layer was obtained *via* successive coating and sintering processes (total 4 times). Thus, total thickness excluding ITO glasses was about 30 μm.

Fig. 2 shows cross-sectional FE-SEM photomicrographs of TiO₂ nanocrystalline photoelectrodes. When only high molecular weight PEO was used, the TiO₂ nanoparticles maintain their original size (*i.e.* diameter = ~20 nm) and shape, as shown in Fig. 2(a), and do not seem to be adequately coated with polymer electrolyte, suggesting poor penetration of the electrolyte materials into the nanopores and thus poor contact between the electrolyte and the dye molecules. When oligo-PPG was added into the polymer electrolyte at a concentration of 20% (w/w), an improvement in the interfacial contact between the TiO₂ nanoparticles and the electrolyte was achieved, as is evident in Fig. 2(b). The size of the TiO₂ nanoparticles apparently increases due to the adsorption of the electrolyte materials onto the surfaces. When the oligo-PPG concentration was increased further to 60% (w/w), the cross-section of the particles became apparently smooth and homogeneous, and the typical TiO₂ nanoparticle shape was not observed (Fig. 2(c)). This is because the TiO₂ particles are covered by the oligo-PPG at this concentration, resulting in more interfacial contact between the electrolyte and the dye-adsorbed TiO₂ particles.

Fig. 3 shows the J - V curves (measured at 100 mW cm⁻²) of DSSCs employing PEO and PEO + oligo-PPG electrolytes. The photoelectrochemical performance characteristics (short-circuit current J_{sc} (mA cm⁻²), open-circuit voltage V_{oc} (V), fill factor ff and overall energy conversion efficiency η) are listed in Table 1. J_{sc} and V_{oc} were measured using a Keithley Model 2400 and a 1000 W Xenon lamp (Oriel, 91193). The light was homogeneous up to 8 in. × 8 in., and its intensity (or radiant power) was adjusted with

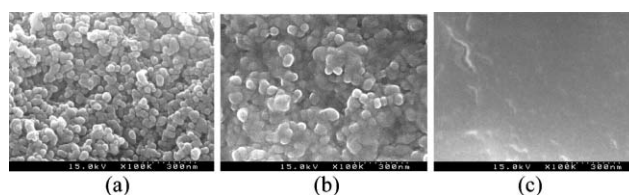


Fig. 2 Cross-sectional FE-SEM images of the nanocrystalline TiO₂ layers incorporating polymer electrolytes varying PPG ($M_n = 725$) content in PEO ($M_w = 1$ M): (a) PEO₁₀; (b) PEO₈PPG₂; (c) PEO₄PPG₆.

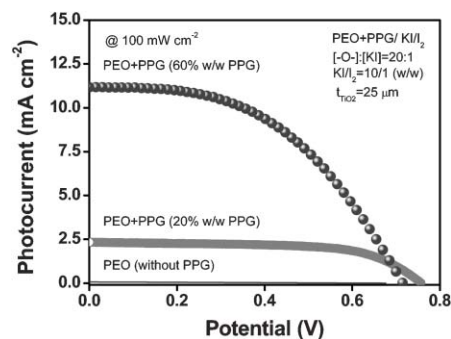


Fig. 3 J - V curves measured at 100 mW cm⁻² of DSSCs ($t_{\text{TiO}_2} = 25$ μm) employing PEO₁₀/KI/I₂, PEO₈PPG₂/KI/I₂, and PEO₄PPG₆/KI/I₂ electrolytes.

Table 1 Ionic conductivities (σ) and performance characteristics of the solar cells employing PEO₁₀/KI/I₂ and PEO₄PPG₆/KI/I₂ electrolytes at 100 mW cm⁻² ($t_{\text{TiO}_2} = 25 \mu\text{m}$)

Electrolyte	$\sigma (\times 10^6, \text{S cm}^{-1})$	$V_{oc}(\text{V})$	$J_{sc}(\text{mA cm}^{-2})$	$ff(-)$	$\eta(\%)$
PEO ₁₀ /KI/I ₂	1.87	0.68	0.06	0.26	0.01
PEO ₄ PPG ₆ /KI/I ₂	25.7	0.72	11.2	0.48	3.84

a Si solar cell (Fraunhofer Institute for Solar Energy System; Mono-Si + KG filter; Certificate No. C-ISE269) for 1 sun light intensity (100 mW cm⁻²) that was double-checked with an NREL-calibrated Si solar cell (PV Measurements Inc.) Moreover, increase in temperature inside the cell during the measurement was prevented by using a cooler.

The overall conversion efficiency dramatically increases upon the addition of oligo-PPG, mostly due to the increase of the current density. The best results we obtained for DSSC ($t_{\text{TiO}_2} = 25 \mu\text{m}$) employing PEO + PPG/KI/I₂ are J_{sc} of 11.2 mA cm⁻², V_{oc} of 0.72 V, ff of 48%, and η of 3.84% at 100 mW cm⁻². It is obvious that the increase in the current density upon the addition of oligo-PPG primarily arises from the increased interfacial contact between the electrolyte and the dye as well as from the increase in the ionic conductivity of the polymer electrolyte. It should be noted that when oligo-PPG was added to the PEO electrolyte the increase of η was much more prominent than that of the ionic conductivity; the former increased 380-fold (at 100 mW cm⁻²) whereas the latter only 14-fold, suggesting the importance of interfacial contact in determining the overall energy conversion efficiency.

In conclusion, we have achieved a remarkably high cell efficiency of ~3.84% at 100 mW cm⁻². The excellent cell performance resulting from the addition of amorphous oligomer is primarily due to the enhancement of the ionic conductivity and more importantly the enlarged interfacial contact area between the dye-attached TiO₂ particles and the polymer electrolyte. Although the influence of the miscibility of this polymer-oligomer blend on the photovoltaic characteristics has not been significantly considered in this communication, the partial phase separation may be rather helpful for the penetration of oligomer into the TiO₂ layer. Note that the concept of this study can be extended to various

polymer-oligomer blend systems. Thus, we have been investigating the use of several polymer-oligomer blend systems, especially with oligomers having various terminal groups, for DSSC application and the detailed results will be reported at the earliest date.

The authors gratefully acknowledge financial support from the Korea Science & Engineering Foundation (KOSEF) through the Creative Research Initiatives Program.

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