



Quasi-solid-state dye-sensitized solar cells assembled with polymeric ionic liquid and poly(3,4-ethylenedioxythiophene) counter electrode



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ABSTRACT

Poly(3,4-ethylenedioxythiophene) nanofibers (PEDOT-NF) with high catalytic activity were synthesized and employed as a counter electrode in dye-sensitized solar cells (DSSCs). A polymeric ionic liquid (PIL) was used as a gelling agent and an iodide source for making a highly conductive gel polymer electrolyte. A quasi-solid-state DSSC assembled with this PIL-based gel polymer electrolyte and PEDOT-NF counter electrode exhibited high conversion efficiency of 8.12% at 100 mW cm⁻².

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1. Introduction

Dye-sensitized solar cells (DSSCs) are promising alternatives to silicon solar cells due to their low cost, easy fabrication and relatively high conversion efficiency [1,2]. Recently, impressive conversion efficiency of 12% has been achieved in a DSSC with a liquid electrolyte [3]. However, leakage or evaporation of liquid electrolyte is a critical problem that limits the long-term operation and practical use of DSSCs [4]. To overcome these problems, considerable efforts have been made to replace liquid electrolytes with gel polymer electrolytes that exhibit high ionic conductivity and improved stability [5–8]. In these gel polymer electrolytes, both cations and anions are mobile, which polarizes the electrolyte and increases the resistance of I⁻/I₃⁻ ions [9]. The use of a single-ion conductive gel polymer electrolyte in which cations are immobilized while anions are highly mobile is therefore highly desirable. A polymeric ionic liquid (PIL) is a single-ion conductor in which cationic or anionic centers are constrained to the polymer backbone. Although extensive research has been devoted to PIL-based electrolytes [10–15], their ionic conductivities are too low for practical applications. Therefore, a PIL-based gel polymer electrolyte with high ionic conductivity is required to achieve high conversion efficiencies in a DSSC. Pt has been used widely as a counter electrode in DSSCs because of its high conductivity and catalytic activity for the reduction of I₃⁻ ions. However, the high cost of Pt has driven the development of other highly efficient and low-cost counter

electrodes. Recently, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted a great deal of attention as a counter electrode due to its high conductivity, catalytic activity, low cost, ease of synthesis and environmental stability [15–20]. However, there are few reports describing highly efficient quasi-solid-state DSSCs based on PIL-based electrolytes and PEDOT counter electrodes. One such study by Kawano et al. [15] reported low conversion efficiency of 1.0–1.5% for DSSCs using PIL-based solid polymer electrolyte and PEDOT counter electrode. Such a low efficiency arose from high resistance of the cell due to the use of solid-state polymer electrolyte and plain PEDOT electrode.

This report details highly efficient quasi-solid-state DSSCs assembled with a PIL-based gel polymer electrolyte and a PEDOT nanofiber (NF) counter electrode. In the PIL, the iodide anions migrate easily, while the imidazolium cations are immobilized. The PIL was important not only for increasing the concentration of I⁻ ions but also in forming the stable gel polymer electrolyte. The resulting DSSC exhibited high conversion efficiency of 8.12%, which was higher than that of the cell with liquid electrolyte and Pt counter electrode.

2. Experimental

2.1. Synthesis of PMAPII and PEDOT-NF

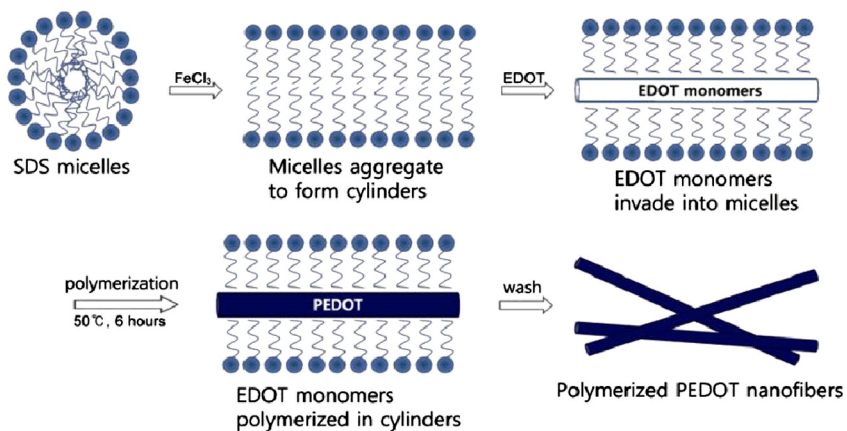
Poly(1-methyl 3-(2-acryloyloxypropyl) imidazolium iodide) (PMAPII) was synthesized as previously reported [21]. 3-Iodopropyl acrylate was obtained by the reaction of 3-iodo-1-propanol and acryloyl chloride with triethylamine in tetrahydrofuran for 24 h at 0 °C. A quaternization reaction of 3-iodopropyl acrylate and *N*-methylimidazole

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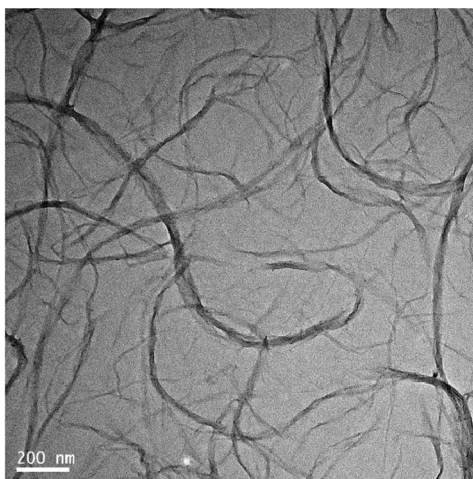
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was performed in ethanol 45 °C for 24 h, and the obtained MAPII monomer was polymerized with azobisisobutyronitrile in dimethyl sulfoxide at 80 °C for 12 h. After polymerization, the resulting solution was added drop by drop to diethyl ether, and the obtained polymer was then washed successively with diethyl ether to remove

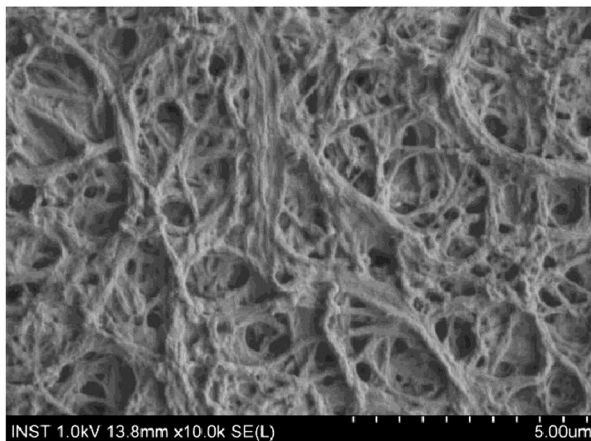
impurities such as residual monomer and initiator. PEDOT-NF was synthesized by chemical oxidative polymerization, shown schematically in Fig. 1(a). An aqueous solution of sodium dodecyl sulfate (SDS) and FeCl_3 was stirred for 1 h at 50 °C to produce micelles with a cylindrical structure. EDOT monomer was then slowly added



a)



b)



c)

Fig. 1. (a) Schematic illustration showing the synthesis of PEDOT-NF, (b) TEM image of the synthesized PEDOT-NF and (c) FE-SEM image of the PEDOT-NF counter electrode.

to the solution, and the polymerization proceeded for 6 h at 50 °C. After polymerization, the resulting PEDOT-NF was filtered, washed several times with methanol and distilled water and re-dispersed in methanol via ultrasonication.

2.2. Cell assembly

Nanocrystalline TiO₂ paste (Ti-Nanoxide T20/SP, Solaronix) was cast onto fluorine-doped tin oxide (FTO) glass with a doctor blade and sintered at 450 °C for 30 min. The thin film was sensitized overnight in a *cis*-diisothiocyanato-*bis*(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis(tetrabutyl ammonium) (Ruthenium 535 bis-TBA, Solaronix) dye solution. The PEDOT-NF dispersed in methanol was ultrasonicated for 3 min to form a stable dispersion. The counter electrode was then prepared by spin coating the PEDOT-NF solution onto the FTO glass and vacuum drying at 60 °C for 2 h. Its thickness was optimized to be 200 nm. To prepare the gel polymer electrolyte, a different amount of PMAPII was added to the liquid electrolyte. The liquid electrolyte was a solution of 0.05 M I₂ and 0.05 M 4-*tert*-butylpyridine dissolved in γ -butyrolactone; no iodide salts were added. The gel polymer electrolyte was directly cast onto the TiO₂ electrode. The cell was then fabricated by sealing the TiO₂ electrode and PEDOT-NF counter electrode together using a hot-melt film.

2.3. Measurements

The ionic conductivity of the gel polymer electrolyte was measured from 100 Hz to 100 kHz using an impedance analyzer (Zahner Elektrik IM6). The photovoltaic performance of the DSSCs was evaluated using a xenon light source (100 mW cm⁻²) with an AM 1.5 filter in a solar simulator. The light intensity was calibrated with an NREL-calibrated Si solar cell (PV Measurements, Inc.). A black mask with a 0.25-cm² aperture was placed over the cells during irradiation, and an anti-reflection glass was placed on the front glass cover over the cells. AC impedance measurements of DSSCs were performed using an impedance analyzer over a frequency range of 10 mHz to 100 kHz at open circuit under 1 Sun illumination.

3. Results and discussion

Typical TEM image of the PEDOT-NF is shown in Fig. 1(b). The PEDOT-NF structures were small in diameter (10–50 nm) with a high aspect ratio (>100). The 1-D structure of the PEDOT-NF allows a smaller grain boundary than in bulk PEDOT, resulting in more efficient electron transfer [18,22]. Consequently, the electronic conductivity of the PEDOT-NF was as high as 83 S cm⁻¹. The nanofibrous structure of PEDOT-NF with its high conductivity and large surface area is expected to behave as a counter electrode with high catalytic activity. Fig. 1(c) shows an FE-SEM image of the PEDOT counter electrode coated onto FTO glass. The electrode was porous, with a rough network structure that can facilitate the penetration of electrolyte for redox reactions.

Fig. 2(a) shows the ionic conductivity of gel polymer electrolytes as a function of PMAPII content. Ionic conductivity increased with PMAPII content up to 16 wt.% and then decreased at higher levels. PMAPII is the only iodide source because no iodide salt was added to the gel polymer electrolyte. Accordingly, the initial increase in ionic conductivity with PMAPII content can be ascribed to an increase in the number of free I⁻/I₃⁻ ions. The decrease in ionic conductivity beyond 16 wt.% PMAPII was attributed to a decrease in ionic mobility. A stable gel without fluidity was obtained at PMAPII contents greater than 16 wt.%, as shown in the inset. At 16 wt.% PMAPII, the ionic conductivity was fairly high (4.9×10^{-3} S cm⁻¹). Fig. 2(b) shows the photocurrent density–voltage curves of the DSSCs assembled with PEDOT-NF counter electrode, and Table 1 summarizes the photovoltaic performance of DSSCs with PEDOT-NF or Pt counter electrodes.

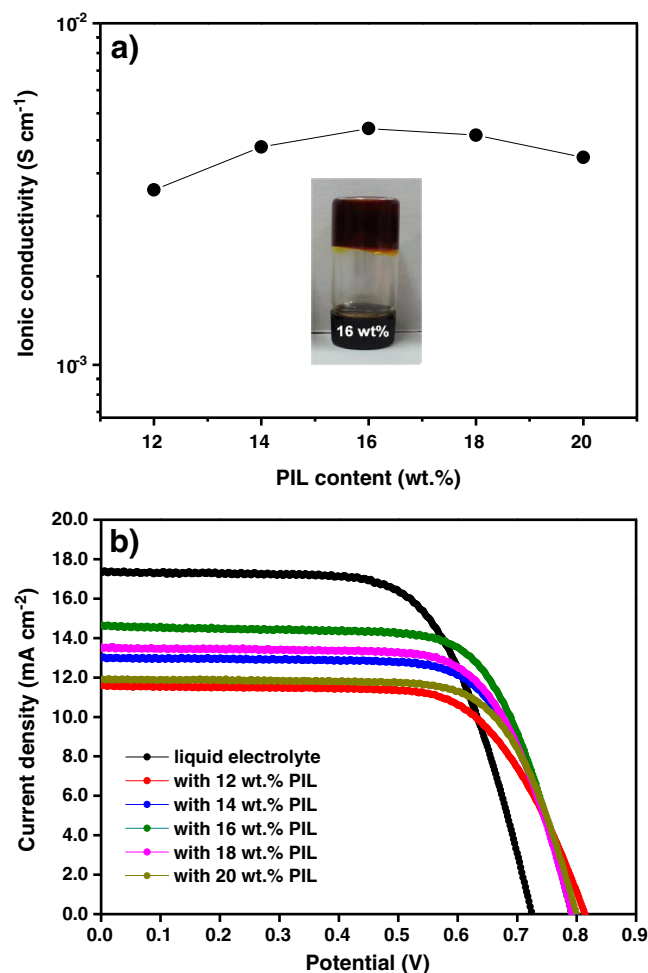


Fig. 2. (a) Ionic conductivities of PIL-based gel polymer electrolytes as a function of PIL content and (b) photocurrent-voltage curves for DSSCs assembled with PEDOT-NF counter electrode.

Note that the liquid electrolyte contained 0.5 M LiI as an iodide source. The open circuit voltages of the DSSCs with gel polymer electrolyte were higher than those of the liquid electrolyte-based DSSC. The short-circuit current densities (J_{sc}) of DSSCs assembled with gel polymer electrolyte increased with PMAPII content up to 16 wt.% and decreased at higher levels. The small J_{sc} values obtained with low PMAPII content were related to an insufficient concentration of I⁻ ions and hence a low charge-transfer reaction rate for the I⁻/I₃⁻ redox couple at the electrodes. The decrease in J_{sc} beyond 16 wt.% PMAPII can be attributed to the reduction in ionic mobility. The DSSC assembled with the PIL-based gel polymer electrolyte and

Table 1
Photovoltaic performance of DSSCs assembled with different counter electrodes.

Counter electrode	Electrolyte	J_{sc} (mA cm ⁻²)	V_{oc} (V)	Fill factor	η (%)
PEDOT-NF	Liquid electrolyte	17.3	0.73	0.67	8.34
	12 wt.% PIL	11.6	0.81	0.68	6.39
	14 wt.% PIL	13.0	0.80	0.71	7.31
	16 wt.% PIL	14.7	0.79	0.70	8.12
	18 wt.% PIL	13.6	0.79	0.70	7.53
	20 wt.% PIL	11.9	0.80	0.72	6.85
Pt	Liquid electrolyte	16.6	0.73	0.60	7.20
	12 wt.% PIL	10.5	0.81	0.61	5.13
	14 wt.% PIL	12.0	0.82	0.62	6.02
	16 wt.% PIL	14.3	0.80	0.60	6.85
	18 wt.% PIL	12.7	0.80	0.61	6.15
	20 wt.% PIL	11.2	0.80	0.61	5.49

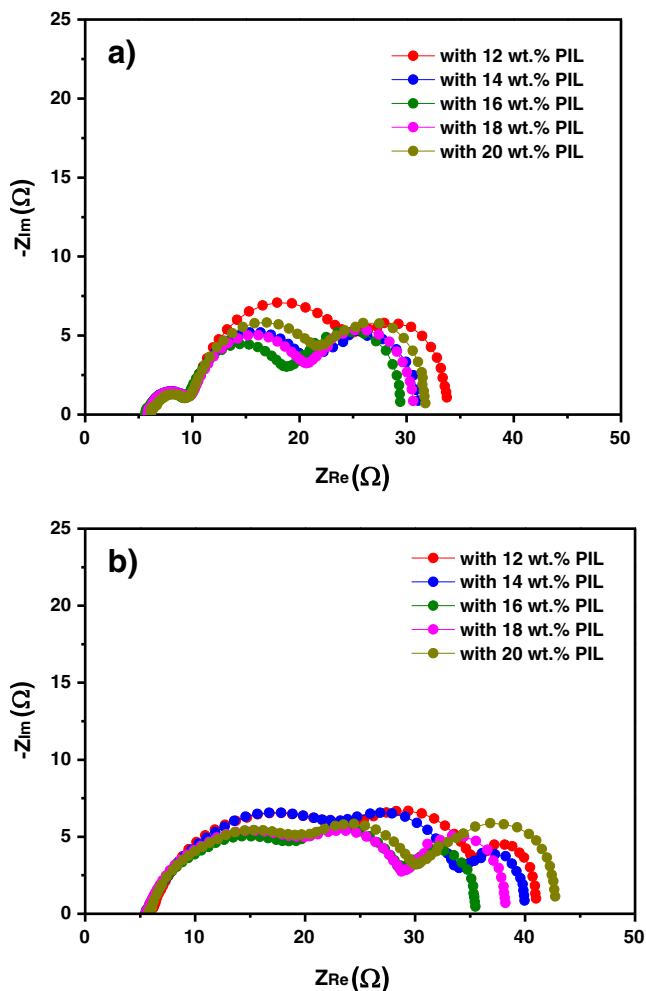


Fig. 3. AC impedance spectra assembled with PIL-based electrolytes and different counter electrodes. (a) PEDOT-NF and (b) Pt counter electrode.

PEDOT-NF electrode exhibited maximum conversion efficiency of 8.12%. Both J_{sc} and the fill factor of the DSSCs with PEDOT-NF electrode were higher than those of cells employing Pt, resulting in higher conversion efficiency. This is ascribed to the relatively high efficiency of the charge-transfer reaction at the PEDOT-NF electrode. Compared to Pt electrode, the PEDOT-NF electrode showed higher redox current in the cyclic voltammograms, due to the large catalytic active site toward the reduction of I_3^- ions, as reported earlier [20]. Notably, the quasi-solid-state DSSC with PIL-based gel electrolyte (16 wt.% PMAPII) and PEDOT-NF electrode exhibited higher conversion efficiency (8.12%) than did the cell containing liquid electrolyte and a Pt electrode (7.20%). A solid-state DSSC with PIL-based solid polymer electrolyte and PEDOT-NF electrode showed a low conversion efficiency of 1.78%, likely due to the low ionic conductivity of solid polymer electrolyte ($2.2 \times 10^{-4} \text{ S cm}^{-1}$).

The AC impedance results of cells with PEDOT-NF and Pt electrode are compared in Fig. 3. All of the spectra exhibit three semicircles, which can be assigned to an electrochemical reaction at the counter electrode (R_{ct1}), the charge transfer reaction at the TiO_2 electrode (R_{ct2}) and the Warburg diffusion of I^-/I_3^- [23,24]. The cell containing 16 wt.% PIL exhibited the lowest electrolyte resistance and interfacial resistances (R_{ct1} and R_{ct2}). This result indicates that the addition of an appropriate amount of PMAPII not only reduces the electrolyte

resistance but also improves the charge transfer reaction at both TiO_2 electrode and counter electrode (Pt or PEDOT-NF). Interestingly, the R_{ct1} values of cells assembled with PEDOT-NF were much lower than those of Pt-based cells, suggesting a faster reduction rate of I_3^- ions at the PEDOT-NF counter electrode. Due to its low surface resistance, good adhesion and large catalytic active site, the PEDOT-NF electrode exhibited high catalytic activity and low charge-transfer resistance for the I^-/I_3^- redox reaction, resulting in higher conversion efficiency than the Pt-based cell.

4. Conclusions

PIL and PEDOT-NF were synthesized and employed in DSSCs. A quasi-solid-state DSSC was assembled with a highly conductive PIL-based electrolyte and a PEDOT-NF counter electrode, yielding relatively high conversion efficiency of 8.12%. This was higher than that obtained in an analogous cell containing a liquid electrolyte and a Pt counter electrode.

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