

고분자 전해질을 이용한 고체형 염료감응 태양전지

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New Polymer Electrolytes for Solid State Dye-Sensitized Solar Cells

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Abstract : The solid state dye-sensitized solar cells (DSSCs) employing polymer electrolytes show high overall energy conversion efficiency as high as 4.5% at 1 sun conditions. The improved efficiency may be primarily due to the enlarged interfacial contact area between the electrolyte and dyes in addition to the increased ionic conductivity, which were done by utilizing liquid oligomers, followed by in situ self-solidification, to form the solid DSSCs : "Oligomer Approach". The effect of the charge transfer resistance at the counter electrode side on the efficiency has also been investigated.

1. Introduction

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. 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. Therefore, several attempts have been made to substitute liquid electrolytes with solid or quasi-solid state electrolytes such as solid polymer electrolytes (SPEs), polymer gel electrolytes (PGEs), and organic hole-transport materials (HTMs). SPEs have received considerable attention in recent decades because of their potential applications in electrochemical devices such as solid-state batteries and separation membranes. Poly(ethyleneoxide)(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 and they suffer from the

low overall energy conversion efficiency in the range of 2-3 % at 1 sun condition. The low efficiency has been markedly increased by the improvements in both the ionic conductivity through polymer electrolyte and the interfacial contact between the nanoporous TiO₂ layer and polymer electrolyte.

2. Experimental

Three different liquid oligomers (1. PEG oligomer with 4-hydrogen bonding sites at both chain ends,¹ 2. nanocomposite of oligomer with silica nanoparticles² and 3. oligomer blend with

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high MW PEO³⁻⁴) have been utilized to increase the ionic conductivity and to improve the interfacial contact, and subsequently *self-solidified* to make solid polymer electrolytes: *Oligomer Approach*. This approach has both advantages of liquid and solid states. The chemical structure of oligomer with 4 hydrogen bonding sites (PHB) is in Figure 1. The oligomers are in separated coils at the solution state, but become solid by *self-solidification* due to the hydrogen bonding between the coils upon evaporation of the solvent used.

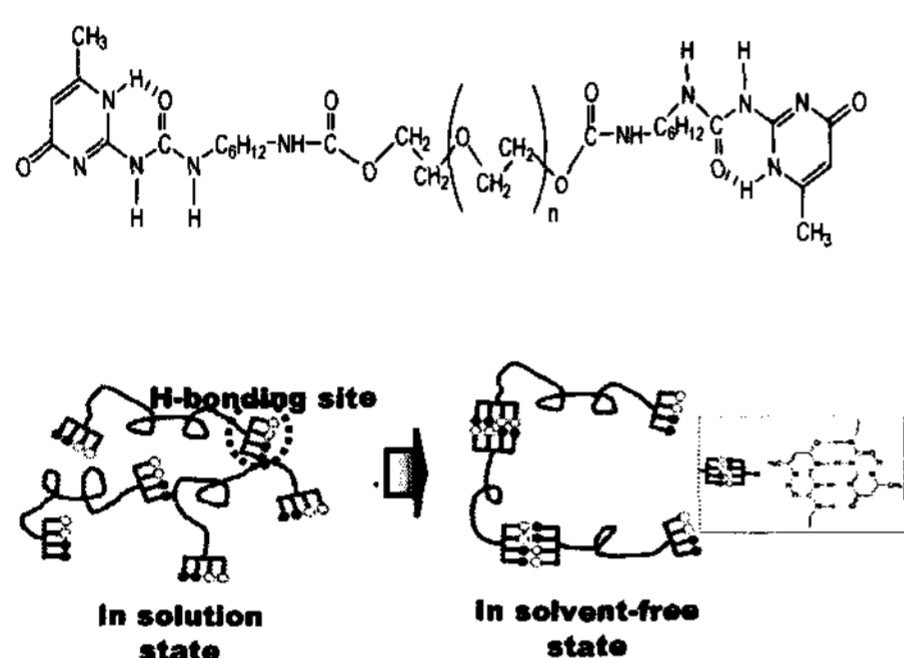


Figure 1. The chemical structure of oligomer with 4 hydrogen bonding sites (PHB)

DSSCs using this electrolyte yielded high value of cell performance such as increased in conversion efficiency and fill factor as well as better interfacial properties compared to DSSCs employing previously reported polymer electrolytes. To investigate cation effect on the cell performance of PHB electrolyte, we have used several kinds of measurement such as photovoltaic characterization, stepped light-induced transients of photocurrent and voltage (SLIM-PCV) and electrochemical impedance spectroscopy (EIS).

Charge transfer resistance between polymer electrolyte and Pt counter electrode could be measured by EIS (electrochemical impedance spectroscopy) measurement using IM6e (Zahner) with symmetric cell composed of two same Pt coated counter electrode. Pt counter electrode was made by thermal decomposition of spin-coated 0.03M H₂PtCl₆ in IPA solution onto the FTO glass substrate (8Ωcm⁻², Pilkington) and then sintered at 450°C for 30min. A 50 thickness of imide tape or

25μm thickness of Surlyn was placed at the gap between the two same Pt electrodes. The active area of symmetric cell was 0.25cm² and then filled with polymer electrolyte. The mole ratio of oxygen atoms in the PEO main chain to potassium or imidazolium iodide was fixed at 20/1 (XI/I₂=10/1w/w). The charge transfer resistances were obtained after solvent drying in air at 40°C for 1~2 days to fabricate all solid state cell.

3. Results and discussion

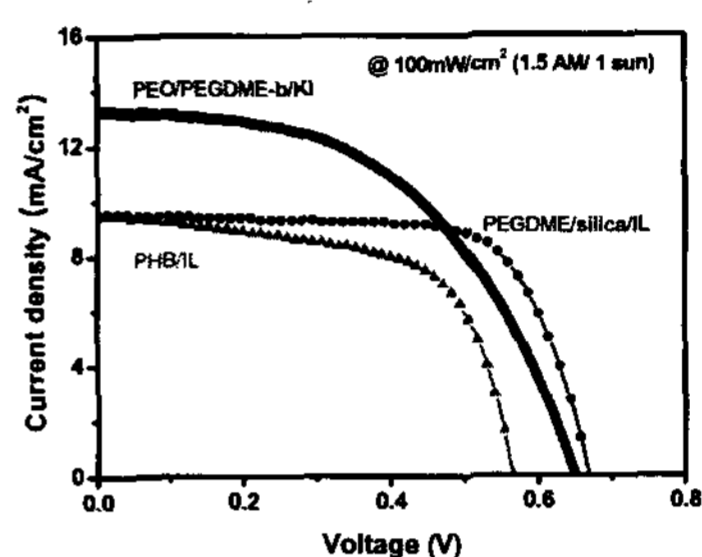


Figure 2. Current-Voltage Characterization of solid state DSSCs employing polymer electrolytes with oligomer approach

	Jsc (mA/cm ²)	Voc (V)	FF	η (%)
PEO/PEGDME-KI	13.23	0.65	0.51	4.42
PEGDME/silica/IL ^a	9.58	0.67	0.70	4.50
PHB/IL ^b	9.53	0.57	0.62	3.34

^a IL = ionic liquid

(MPII ; 1-methyl-3-propylimidazolium iodide)

^b PHB = Poly(ethylene glycol) with Hydrogen Bonding end-groups

In DSSCs, interfacial properties are more important than bulk properties because of all processes such as photogeneration, separation and charge recombination take place at the heterointerface. Therefore, we have investigated these crucial interfacial properties by electrochemical impedance spectroscopy. Also we have examined electron transport phenomena in TiO₂ mesoporous structure of solid-state DSSCs employing polymer electrolytes. This is a major

part to determine the overall cell performance of DSSCs.

The relationship between the energy conversion efficiency and the ionic conductivity has been also explored to show the threshold conductivity of near $1 \times 10^{-4} \text{S/cm}$, above which the ionic conductivity may not be critical in improving the energy conversion efficiency, but other factors such as the interfacial resistance at the junctions of electrodes and electrolyte.

Table 1. Charge transfer resistance between PHB electrolyte and Pt counter electrode

Polymer electrolyte		KI	MPII	DMPII
PHB	R_s	18	20	18
	R_{CT}	30	22	12

Charge transfer resistance of interface between solid polymer electrolyte and Pt counter electrode is very important to determine cell performance of DSSCs. Because solid polymer electrolyte has lower ionic conductivity and diffusion coefficient than liquid electrolyte has. Besides, relatively slow redox reaction is occurred at solid polymer electrolyte/Pt counter electrode interface and solid polymer electrolyte is less compatible with platinum counter electrode than liquid electrolyte. These suggest that the charge transfer resistance could also be an important parameter in determining the overall energy conversion efficiency for solid state DSSCs in addition to the ionic conductivity, which depends on the type of cations used and the electrolyte media. As a result, decrease of R_{CT} in polymer electrolytes will induce increase of current density of DSSCs and photovoltaic performance ultimately.

As shown above Table 1, metal salt and ionic liquid have different behavior in the polymer electrolytes. Metal salt such as LiI, NaI, KI and polar site of polymer electrolyte attract and coordinate with each other, whereas almost no interaction occurred between ionic liquid and polar site of polymer electrolyte. In addition, R_{CT} with metal iodide based polymer electrolyte is higher

than that with imidazolium iodide.

Figure 4 shows a typical J-V curve for a solid state DSSC with PHB electrolyte, yielding the efficiency of 4.4% (0.45 cm^2) at 1 sun condition. The J-V characteristics are interpreted in terms of the ionic conductivity, the interfacial contact, the recombination rate etc.

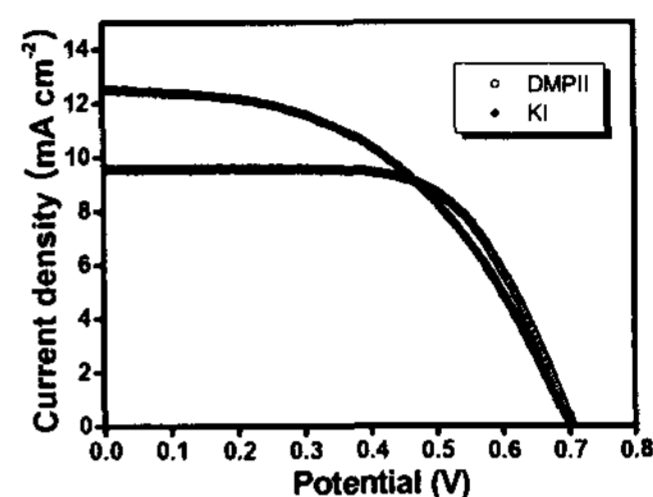


Figure 4. Current-Voltage Characterization of solid state dye-sensitized solar cell employing PHB (polymer with hydrogen bonding site) electrolyte with two different cations

4. Conclusions

Novel solid polymer electrolytes provide high ionic conductivity as well as good interfacial contact between electrolyte and dye-adsorbed nanocrystalline TiO_2 layer.

In summary, the threshold ionic conductivity of about 10^{-4}S/cm was observed in polymer electrolytes and DSSCs using PHB (oligomer with H-bonding site) electrolyte yielded high cell performance (4.36% @1sun, 0.45 cm^2). In addition, interfacial contact between polymer electrolyte and both electrodes of DSSC play an important role in improving the cell efficiency and cations of polymer electrolyte are very important determining electron transport in TiO_2 photoanode, diffusion of redox couple (I^-/I_3^-) and charge transfer at the counter electrode. The importance of the charge transfer resistance at the counter electrode has been emphasized in the solid state dye-sensitized solar cells.

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