

## Solid State Dye-Sensitized Solar Cells Employing Polymer Electrolytes : Oligomer Approach

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### 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.  $I/I_3^-$ ) 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. When SPEs are employed, DSSCs suffer from the low overall energy conversion efficiency in the range of 2-3 % at 1 sun condition. The low energy conversion efficiency may come primarily from the low ionic conductivity and the poor interfacial contact between the dye and SPE. Here oligomers have been utilized to overcome the drawbacks on the ionic conductivity and the interfacial contact, expecting much higher energy conversion efficiency in the solid state DSSCs.<sup>1-3</sup>

### Experimental

Three different liquid oligomers (1. PEG oligomer with 4-hydrogen bonding sites at both chain ends (PHB),<sup>1</sup> 2. nanocomposite of oligomer with silica nanoparticles<sup>2</sup> and 3. oligomer blend with high MW PEO<sup>3,4</sup>) 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.

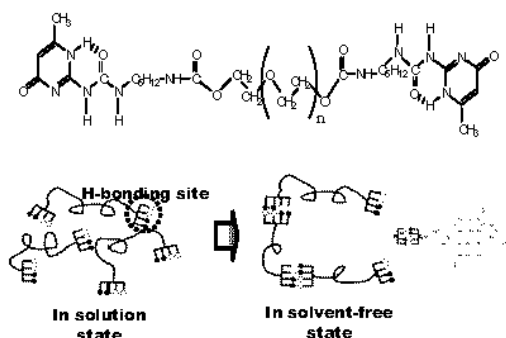


Figure 1. The chemical structure of oligomer with 4 hydrogen bonding sites (PHB)

DSSCs using these electrolytes yielded high values of cell performances such as the increase in both the conversion efficiency and the fill factor, and the better interfacial properties compared to previous results. 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 resistances between polymer electrolyte and the Pt counter electrode were measured by EIS (electrochemical impedance spectroscopy) using IM6e (Zahner) with a symmetric cell composed of two identical Pt coated counter electrodes. The Pt counter electrode was made by thermal decomposition of spin-coated 0.03M  $H_2PtCl_6$  in IPA solution onto the FTO glass substrate ( $8\Omega cm^2$ , Pilkington) and then sintered at 450 °C for 30min. A 50  $\mu m$  thick polyimide tape or 25  $\mu m$  thick Surlyn was placed between the two Pt electrodes and subsequently a polymer electrolyte solution was filled. The active area of the symmetric cell was 0.25cm<sup>2</sup>. The mole ratio of oxygen atoms in the PEO main chain to potassium or imidazolium iodide was fixed at 20/1 ( $XI/I_2 = 10/1$  w/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.

### Results and discussion

The current-voltage (I-V) curves for 3 different electrolytes were shown in Figure 2 and their characteristic values for cell performances were summarized in Table 1.

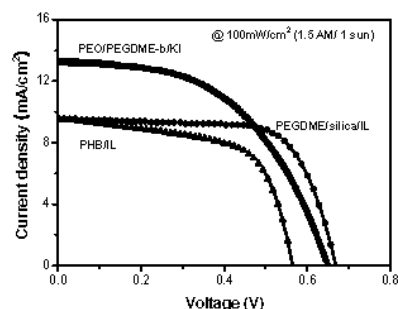


Figure 2. Current-voltage characterization of solid state DSSCs employing polymer electrolytes at 1 sun condition.

Table 1. Characteristics for cell performance at 1 sun condition

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

<sup>a</sup> IL=ionic liquid (MPLI, 1-methyl-3-propylimidazolium iodide)

<sup>b</sup> PHB=Poly(ethylene glycol) with 4 H-bonding sites at both chain ends

The overall energy conversion efficiency for the nanocomposite electrolyte with silica nanoparticles,  $\eta$ , was markedly increased up to 4.5% at 1 sun while it was 1.6% previously.<sup>6</sup> In particular, the oligomer blend with PEO and KI shows very high current density compared to the others, but the fill factor is very low. Here the effect of the cation type has not been clearly understood yet. These results suggest that the "Oligomer Approach" utilizing liquid oligomers, followed by *in situ* solidification, has been very effective in improving the energy conversion efficiency. The increased efficiency could be primarily due to the enlarged interfacial contact area in addition to the increased ionic conductivity.

The relationship between the energy conversion efficiency and the ionic conductivity has been also explored to show the threshold conductivity of near  $1 \times 10^{-4}$  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.

In DSSCs, interfacial properties such as adhesion between the solid polymer electrolyte and the Pt metal may not be good due to the solid-solid contact, resulting in a large interfacial charge transfer resistance. Therefore, we measured the charge transfer resistance,  $R_{CT}(\Omega)$ , along with the series resistance,  $R_s(\Omega)$ , of the polymer electrolyte by electrochemical impedance spectroscopy and summarized in Table 2.

**Table 2.** Charge transfer resistance between PHB electrolyte and Pt counter electrode

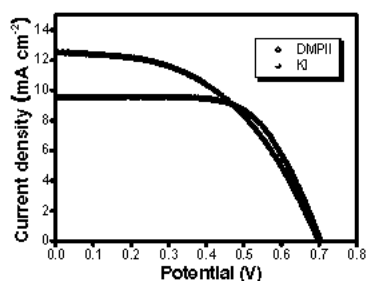
Polymer electrolyte		KI	MPII	DMPII
PHB	$R_s(\Omega)$	18	20	18
	$R_{CT}(\Omega)$	<b>30</b>	22	12

MPII: 1-methyl-3-propylimidazolium iodide

DMPII: 1,4-dimethyl-3-propylimidazolium iodide

The series resistance  $R_s(\Omega)$  does not depend on the salt used, whereas the charge transfer resistance  $R_{CT}(\Omega)$  at the counter electrolyte shows some dependency. The ionic liquids such as MPII and DMPII have much low  $R_{CT}$  values, compared to that of KI.

Figure 3 shows a typical J-V curve for a solid state DSSC with PHB electrolyte, yielding the efficiency of 4.4 % ( $0.45 \text{ cm}^2$ ) at 1 sun condition. The J-V characteristics will be interpreted in terms of the ionic conductivity, the interfacial contact, the recombination rate etc.



**Figure 3.** Current-voltage characterization of solid state dye-sensitized solar cell employing PHB (oligomer with 4 hydrogen bonding sites at both chain ends) electrolyte with two different cations

## Conclusions

Novel solid polymer electrolytes utilizing oligomers provide the high ionic conductivity as well as the good interfacial contact between electrolytes and dye-adsorbed nanocrystalline  $\text{TiO}_2$  layer, resulting in high overall energy conversion efficiency as high as 4.5% at 1 sun: "Oligomer Approach".

The threshold ionic conductivity of about  $10^4 \text{ S/cm}$  was observed in polymer electrolytes in the solid state DSSCs, below which the ionic conductivity may be a main step in determining the efficiency, and above which some factors other than the ionic conductivity such as the interfacial charge transfer resistance may also play an important role. Therefore, the effect of the charge transfer resistance should be investigated to improve the efficiency further in addition to the recombination for the high efficient solid state DSSCs.

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