Roles of terminal groups of oligomer electrolytes in determining photovoltaic performances of dye-sensitized solar cells†

Moon-Sung Kang,[a] Young Jin Kim,[a] Jongok Won[b] and Yong Soo Kang*[a]

The effect of terminal groups of oligomer electrolytes on the photovoltaic performance of dye-sensitized solar cells (DSSCs) have been systematically investigated to show that the terminal group plays a critical role in determining the concentration of I_3^-, ionic conductivity, flatband potential and consequently the energy conversion efficiency.

Dye-sensitized solar cells (DSSCs) have been paid much attention for the past decades due to their attractive features such as high energy conversion efficiency (*i.e.* ~10.5%) and low energy production costs.[1] DSSCs are composed of three major parts of the photoelectrode including a dye-attached nanocrystalline TiO_2 layer, a counter electrode with a platinum catalyst layer, and an electrolyte mediating ion transfer between the electrodes. Electrolytes consist of salts (*i.e.* alkali metal or imidazolium iodides and iodine), dissolved in an electrolyte medium to form redox couples such as I^-/I_3^-. Liquid solvents such as acetonitrile have been commonly employed as an electrolyte medium and result in high energy conversion efficiency. However, DSSCs employing liquid electrolytes have drawbacks such as leakage and evaporation of the solvent.[1–3] Many efforts have been thus made to substitute liquid electrolytes with solid or quasi-solid state electrolytes by using solid polymer electrolytes (SPEs)[3–5] or polymer–gel electrolytes (PGEs).[6] Recently, medium molecular weight oligomers have been also successfully used to prepare solid state DSSCs, showing high energy conversion efficiency of η = 4.5% (@ 1 sun, AM 1.5) primarily due to the deeper penetration of electrolyte materials, followed by *in situ* self-solidification, and higher ionic conductivity.[4,5]
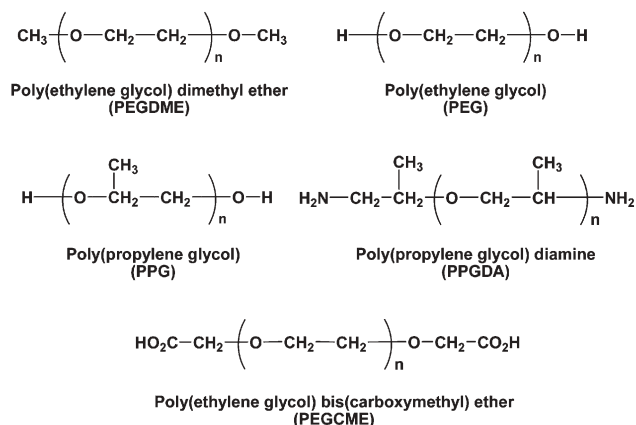
Generally SPE-DSSCs suffer from low energy conversion efficiency compared to liquid electrolyte ones, resulting mostly from low ionic conductivity and small interfacial contact area between electrolyte and dye, primarily due to poor penetration of the electrolyte material into the nanopores of the TiO_2 layer. Thus, there have been many attempts to improve the ionic conductivity of polyethers-based polymer electrolytes comprising poly(ethylene glycol) (PEG), poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO) by incorporating comonomers or nanoparticle fillers.[3] Moreover, the importance of the interfacial contact has been particularly emphasized in determining the energy conversion efficiency.[4,5] For instance, if the coil size of a polymer solvent as an electrolyte medium is bigger than the pore size of the nanocrystalline TiO_2 layer, the electrolyte may not readily penetrate deep into the TiO_2 nanopores, resulting in poor interfacial contact. If the coil

size of the polymer solvent is smaller than the pore size of the nanocrystalline TiO_2 layer, the electrolyte may readily penetrate deep into the TiO_2 nanopores, resulting in good interfacial contact. The coil size of polymer chains in a good solvent depends on its molecular weight, and is commonly represented by the radius of gyration R_g = $C(M_w)^{1/2}$, where M_w is the molecular weight in g mol^{-1} and C = 0.063 (nm (g mol^{-1})$^{-1/2}$) for PEO.[7] The average pore diameter of the TiO_2 layer obtained by the Brunauer–Emmett–Teller (BET) method from the N_2-desorption isotherm was approximately 16.5 nm[8] (corresponding to the molecular weight of PEO of approximately 18 000 g mol^{-1}). Therefore, deeper penetration of the electrolyte into the TiO_2 layer could be achieved by a polymer medium having its coil size smaller than 16.5 nm, *i.e.*, the use of an oligomer having a medium molecular weight is suggested for improvement in the interfacial contact and consequently the energy conversion efficiency.

In the case of PEG or its derivatives, its molecular weight of a few thousand (especially under M_w = 2000 g mol^{-1}) is recommended to prepare highly efficient SPE-DSSCs. Since oligo-PEGs in the range of 400–500 g mol^{-1} are usually in the liquid state at room temperature, their solidification is necessary for preparing solid-state DSSCs, where it has been done, for instance, by forming a network structure with fumed silica nanoparticles[5a] and also by blending with high molecular weight PEO.[4] The solidification or gelation of PPO with triethoxysilane terminal groups *via* the sol–gel route has also been suggested.[6c] Interestingly highly efficient solid-state DSSCs have been prepared by employing a supramolecular electrolyte made from oligo-PEG (M_w = 1000 g mol^{-1}) containing quadruple hydrogen bond sites at both chain ends (*i.e.* 2(6-isocyanatohexylamino-carbonyla-mino)-6-methyl-4[1H]-pyrimidinone).[5b] The solid-state DSSCs employing SPEs mentioned above exhibited very high photo-voltaic performances (*i.e.* η = 4.5% (@ 1 sun, AM 1.5),[5a] η = 3.84% (@ 1 sun, AM 1.5),[4] η = 4% (@ 0.9 sun),[6c] and η = 3.34% (@ 1 sun, AM 1.5)[5b]). These results show that the use of oligomers as an electrolyte medium followed by *in situ* self solidification is very effective in preparing highly efficient solid-state DSSCs: the "oligomer approach". However, we have found that the terminal functional groups of the oligomer chain ends play a critical role in determining the energy conversion efficiency. In this communica-tion, therefore, we demonstrate the roles of the terminal groups of the oligomers on the photovoltaic characteristics of DSSC.

Scheme 1 shows chemical structures of the oligomers with different terminal groups (*i.e.* –CH_3, –OH, –NH_2, and –COOH) employed in this study. We have utilized the liquid-state oligomers (at room temperature) having similar molecular weights of 350– 500 g mol^{-1} (PEGDME (M_w = 500); PEG (M_w = 400); PPG

Scheme 1 Oligomers with different terminal groups.

Table 1 Ionic conductivities (σ), flatband potentials (V_{Fb}, $V_{Fb/TiO2} = -1.22$ V) and photovoltaic characteristics of the DSSCs employing oligomer-based electrolytes (under illumination of 100 mW cm^{-2})

Base polymer	$\sigma \times 10^5$/ S cm^{-1}	V_{Fb}/V	V_{oc}/V	J_{sc}/mA cm^{-2}	ff	η (%)
PEGDME	9.34	−1.096	0.572	10.360	0.527	3.12
PEG	5.71	−0.667	0.517	6.772	0.559	1.96
PPG	2.50	−0.694	0.529	4.295	0.310	0.71
PPGDA	2.13	−0.994	0.443	1.769	0.199	0.16
PEGCME	4.05	−0.335	0.298	3.696	0.528	0.58

($M_w = 425$); PPGDA ($M_w = 400$); PEGCME ($M_w = 350$)) to minimize the influence of the molecular size and the crystallinity on the photovoltaic performances of DSSCs.

The molar ratio of the oxygen atom in the oligomer to KI was fixed at 20 : 1 and KI : I$_2$ = 10 : 1 w/w. Transparent fluorine-doped tin oxide glass (SnO$_2$:F, FTO) (sheet resistance 8 Ω □$^{-1}$, purchased from Pilkington) was utilized for preparing DSSCs. For fabrication of photoelectrodes, Ti(IV) bis(ethyl acetoacetato)--diisopropoxide solution (2% w/w in 1-butanol) was coated onto the FTO substrate and then the glass was heated stepwise to 450 °C. TiO$_2$ paste (Ti-Nanoxide T, Solaronix) was then cast onto the FTO glass by a doctor-blade and sintered at 450 °C for 30 min. The TiO$_2$ 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 H$_2$PtCl$_6$ solution (0.05 mol dm^{-3} in isopropanol) onto FTO glass and then sintering at 400 °C for 20 min. Solvent-free oligomer electrolyte was cast onto the TiO$_2$ layer of photoelectrode and then Pt-layered FTO was superposed upon it.

The photovoltaic characteristics (J-V curves measured at 100 mW cm^{-2}) of DSSCs employing different oligomer-based electrolytes are shown in Fig. 1. The photoelectrode flatband potential V_{Fb} (V), short-circuit current density J_{sc} (mA cm^{-2}),
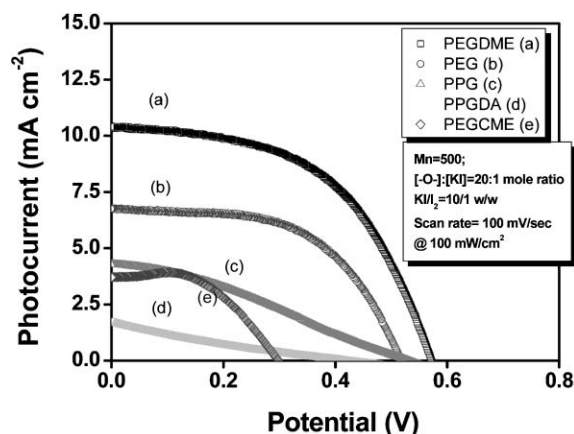
open-circuit voltage V_{oc} (V), fill factor ff and overall energy conversion efficiency η (%) and the ionic conductivity (σ) of the electrolytes are summarized in Table 1. The photovoltaic characteristics were measured by using a potentiostat/galvanostat (263A, EG&G Princeton Applied Research) and a 150 W Xenon lamp (Oriel) under 100 mW cm^{-2} illumination (1 sun, AM 1.5). Ionic conductivity was measured using a lab-made four-point probe conductivity cell connected to an impedance analyzer (IM6, Zahner). An Ag/AgCl reference electrode, a platinum-wire counter electrode, UV–Vis spectrophotometer (8453, Agilent) and a potentiostat/galvanostat were used for measuring the flatband potential of TiO$_2$-layered photoelectrodes (effective area = 0.5 cm^2).[9] The photovoltaic characteristics of the DSSCs are largely dependent upon the nature of the terminal groups of oligomers. Among them, the DSSC employing a PEGDME-based electrolyte shows the best efficiency, indicating that the chemically inactive methyl group (–CH$_3$) of PEGDME is particularly effective in improving the energy conversion efficiency compared to the others. Moreover, the ionic conductivity of PEGDME-based electrolyte is the highest among the electrolytes considered, suggesting the higher chain mobility of PEGDME than those of the others because the hydrogen bond formation between the terminal groups possibly reduces the flexibility of the oligomer chains (please see ESI†).

We also carried out wide angle X-ray scattering (WAXS) experiments with Cu K$_\alpha$ radiation to characterize the solubility of KI and I$_2$ in the oligomers. FT-Raman spectra for the electrolytes containing the oligomers were also recorded at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman at a resolution of 1 cm^{-1}, with a neodymium-doped yttrium aluminium garnet (Nd^{3+}:YAG) laser operating at 1.064 μm. For characterizations in the solid-film state, the oligomers were blended with high molecular weight PEO ($M_w = 1\,000\,000$). The weight ratio of PEO to oligomer was fixed at 4 : 6. The molar ratio of oxygen atoms in PEO and the PEO + oligomer blends to KI was fixed at 20 : 1 (KI : I$_2$ = 10 : 1 w/w). WAXS spectra in Fig. 2 show that the salt compounds were completely dissolved in all electrolyte systems, indicating that the difference in the concentrations of I$^-$ and I$_3^-$ can be ignored in explaining the variances in the photovoltaic performances. Meanwhile, FT-Raman spectra confirm the formation of triiodide (I$_3^-$) and polyiodides (I$_{2n+1}^-$, $n = 2$, 3, 4…) in the electrolytes. As shown in Fig. 3, two symmetric stretching peaks assigned to I$_3^-$ at around 113 cm^{-1} and polyiodides (e.g. I$_5^-$) at around 141 cm^{-1} were observed except for the PEO/PPGDA system (f). The intensity of the former peak is much higher than that of the latter, showing that iodide species are present mostly as I$_3^-$. Moreover, the band attributed to vibration of molecular iodine around 180–210 cm^{-1} was not

Fig. 1 J-V curves measured at 100 mW cm^{-2} of DSSCs employing oligomer/KI/I$_2$ electrolytes.
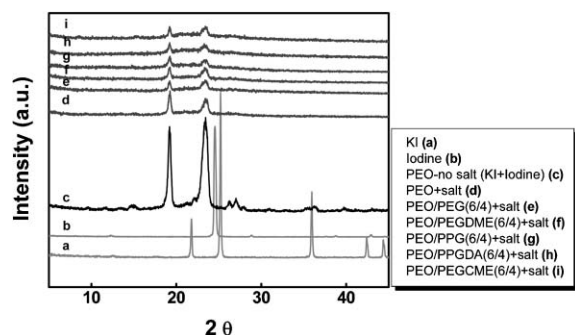
Fig. 2 WAXS spectra of salt compounds (KI and I_2), bare PEO (M_w = 1 M), and polymer electrolytes composed of PEO (M_w = 1 M)/oligomer and KI/I_2.
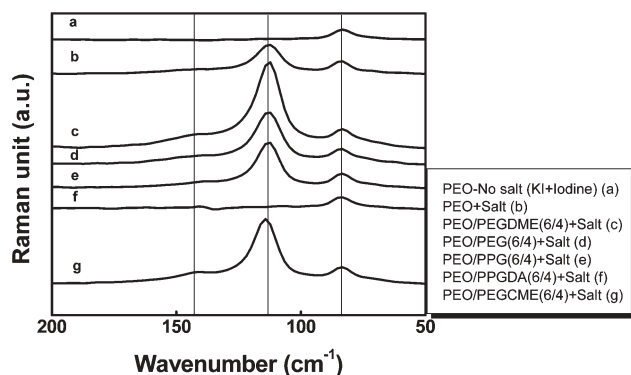

Fig. 3 FT-Raman spectra of bare PEO (M_w = 1 M) and polymer electrolytes composed of PEO (M_w = 1 M)/oligomer and KI/I_2.

observed, indicating the complete dissolution of I_2 in the electrolytes. In the case of the PEO/PPGDA electrolyte, however, the formation of I_3^-/I_5^- species in the medium seems to be greatly reduced due to the complex formation between the terminal amines (–NH_2) and iodides. It has been known that the primary amine groups of Lewis base can form a complex with iodide species (I_3^- or I_2) of Lewis acid. An example of the complex formation is shown in eqn (1):[10]

$$\text{Oligomer-}NH_2 + I_3^- \rightarrow \text{Oligomer-}NH_2I^+ + 2I^-. \quad (1)$$

Therefore, it is believed that the photovoltaic performances of the PPGDA-based electrolyte are quite different from those of the others due to the complexation of iodides with the terminal amine groups (mainly due to the limitation of I_3^- formation). On the other hand, the acidic groups (–COOH, $i.e.$ in PEGCME) hardly affect the change in the concentrations of I_3^- and polyiodides. However, the acidity of PEGCME results in a large flatband potential shift ($i.e.$ +0.88 V $vs.$ Ag/Ag$^+$; 0.5 M LiClO$_4$/0.2 M

tetrabutyl ammonium perchlorate dissolved in CH_3CN, oligomer content = 2.5% w/w) as shown in Table 1, resulting in a decrease in the open-circuit potential ($i.e.$ under Fermi level pinning, $V_{oc} = |V_{Fb} - V_{red}|$, where V_{red} is the standard reduction potential of a redox couple).[9] Moreover, PPG is an inferior precursor to PEG for SPEs because its ionic conductivity is commonly lower than that of PEG, resulting in low J_{sc}.[11,12]

In conclusion, we have investigated the effects of the different terminal groups of the oligomers commonly utilized as precursors for SPEs on the photovoltaic characteristics of DSSCs. Our results demonstrate that the terminal groups significantly affect the photovoltaic characteristics by changes in ionic conductivity, flatband potential and I_3^- concentration. We have concluded that low molecular weight PEO, $i.e.$ oligo-PEO with chemically-inactive alkyl terminal groups is the most desirable as a precursor of SPEs for solid-state DSSC applications.

Moon-Sung Kang,[a] **Young Jin Kim,**[a] **Jongok Won**[b] **and Yong Soo Kang**[*a]
[a]*Center for Facilitated Transport Membranes, Korea Institute of Science & Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, South Korea. E-mail: yskang@kist.re.kr; Fax: +82 2 958 6869; Tel: +82 2 958 5362*
[b]*Department of Applied Chemistry, Sejong University, Seoul, 143-747, South Korea*

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