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Influence of salts on ionic diffusion in oligomer electrolytes and its implication in dye-sensitized solar cells

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Abstract

The diffusion coefficients of I^- and I_3^- in poly(ethylene glycol) (PEG) oligomer electrolytes as a function of salt type and salt concentration were measured. It was found that the diffusion coefficient of I_3^- in PEG oligomer electrolytes with potassium iodide (KI) was much lower than that with imidazolium iodide (MPII) because of the difference in the interactions of polar oxygen atoms in the PEG oligomer with K^+ or MPI^+. In addition, it was also confirmed that this phenomenon affected the recombination process, electron lifetime and consequently, the performance of the DSSCs.

Keywords: Dye-sensitized solar cell; Ionic diffusion; Poly(ethylene glycol); Non-volatile electrolyte

1. Introduction

Over the past few decades, there has been a considerable body of research generated regarding dye-sensitized solar cells (DSSCs), which have many advantages such as a high energy conversion efficiency and a low production cost [1]. The majority of the work has focused on the improvement of the cell performance, resulting in a very high energy conversion efficiency (∼11%) [2]. This high efficiency has been obtained by incorporating common liquid electrolytes such as acetonitrile and propionitrile, which are normally volatile. Such volatile liquid solvents face some drawbacks, and thus the need for an alternative nonvolatile liquid electrolyte has been stressed. Such typical examples employ ionic liquids, volatile liquids with gelators or oligomers [3–5].

In our previous studies, we introduced oligomer electrolytes, followed by *in situ* self-solidification upon solvent evaporation, resulting in solid state DSSCs with a high energy conversion efficiency [6–8]. Oligomers are typically liquid at room temperature with a molecular weight in the range of 500–1000 and have a negligible vapor pressure at room temperature. Although oligomers can be used as the alternative electrolytes of DSSCs, there have been a few studies about transport phenomena through the oligomer electrolytes. It is expected that the transport phenomena through the oligomer electrolyte would be different than those of common liquid electrolytes, for instance, due to structural changes upon introduction of iodine salts. Accordingly, it is desirable to investigate the transport phenomena through oligomer electrolytes, in particular, the ionic and the electronic diffusion behavior.

In this work, the diffusion coefficients of I^- and I_3^- in oligomer electrolytes as a function of salt type and salt concentration were measured, and their effect on the performance of the DSSCs was also examined.

2. Experimental

Poly(ethylene glycol dimethyl ether) (PEGDME, $M_W = 500$ g/mol) was used as a host-material and 1-methyl-3-propylimidazolium iodide (MPII), an ionic liquid, and potassium iodide (KI), a metal salt, were used as salts. The

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molar ratio of oxygen atom in ether groups of PEGDME to the iodide was fixed at 20 and 40, and the content of iodine was fixed at 10 mol% with respect to the salt. Each electrolyte was denoted by MPII 20, MPII 40, KI 20 and KI 40. A rheometer (DV-III+, Brookfield) was used to measure the viscosity of the electrolytes at 25 °C and in order to investigate the diffusion coefficients of both iodide and triiodide in the electrolytes, the anodic and cathodic steady-state currents were measured using a scanning electrochemical microscope (SECM, CHI900).

The DSSCs employing the oligomer electrolytes were prepared as follows and then the performances of the cells were measured. A photoelectrode consisted of a TiO_2 blocking layer and a nanocrystalline TiO_2 on a transparent fluorine-doped tin oxide glass (SnO_2:F, FTO) (sheet resistance 8 Ω/□, Pilkington). To prepare the TiO_2 blocking layer, an edge of the FTO glass was capped with adhesive tape to provide a non-coated area for electrical contact, and then a Ti(IV) bis(ethyl acetoacetato)–diisopropoxide solution (2%, w/w in 1-butanol) was spin-coated on the FTO glass. After removing the tape, the electrode was sintered at 450 °C for 30 min. To control the thickness of the nanocrystalline TiO_2, the substrate was covered on two parallel edges with the tape. TiO_2 paste (18NR-T, STI) was then cast with a glass rod sliding over the tape-covered edges and annealed at 450 °C for 30 min in air. The thickness of the TiO_2 layer was 12.1 μm as measured by a surface profiler (P-10, Tencor). The TiO_2 electrodes were dipped into a solution consisting of 0.3 mM $Ru(dcbpy)_2(NCS)_2$ dye (535-bisTBA, Solaronix) in acetonitrile and *tert*-butyl alcohol (volume ratio, 1:1) for 24 h. A Pt counter electrode was prepared by spin-coating the H_2PtCl_6 solution (0.01 mol dm^{-3} in isopropanol) onto FTO glass and then sintering at 400 °C for 20 min. In order to control the space between the photo and counter electrode, a spacer with a thickness of 30 μm was inserted. The oligomer electrolyte was cast onto the TiO_2 electrode and then covered with the Pt electrode. The *J*–*V* curves of the DSSCs employing the oligomer electrolytes were measured at 1 sun (100 mW/cm^2, AM 1.5) using a Keithley Model 2400 and a 1000 W Xenon lamp (91193, Oriel). The active area of the DSSCs was about 0.49 cm^2.

Moreover, the electron lifetimes in the TiO_2 electrodes of the cells were measured using stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) [9]. For SLIM-PCV, a diode laser (λ = 635 nm) was operated at the voltage of 3.00 V and stepped down to 2.90 V, and ND filters were used to verify the laser intensity. Only when the TiO_2 electrode was thinner than the diffusion length of the electrons in the TiO_2 electrode was the measurement reliable. Therefore, the thickness of the TiO_2 layer was fixed at about 6 μm. Other conditions have been explained in detail at a previous publication [9].

3. Results and discussion

The properties of the oligomer electrolytes such as the type and concentration of the salts are listed (Table 1). Without salt, the viscosity of PEGDME was 31 cP at 25 °C. Salt addition increased viscosity of each electrolyte and the viscosities of MPII 20, MPII 40, KI 20, and KI 40 were 55, 45, 124 and 59 cP, respectively. When MPII was applied, the viscosity did not largely increase with the salt concentration. On the contrary, the viscosity sharply increased with the salt concentration when KI was employed. These results may arise from the differences of the coordination interactions between the ether groups in the oligomer and cations including MPI$^+$ and K$^+$. The interactions between ether groups and MPI$^+$ were relatively weak, while those between ether groups and K$^+$ were strong, resulting in physical cross-linking and thereby the increase in the viscosity. In addition, the viscosity difference between MPII 40 and KI 40 was not large while the viscosity of KI 20 was a double of MPII 20. It can be thought that MPII 40 and KI 40 contain a smaller amount of salt and thus the viscosity increase due to salt addition is not significant.

Table 1
Properties of oligomer electrolytes according to type and concentration of salts

Oligomer electrolyte	Viscosity (cP)	Diffusion coefficient (10^{-7} cm^2/s)	
		I^-	I_3^-
MPII 20	55	2.58	2.41
MPII 40	45	3.15	2.87
KI 20	124	2.21	0.53
KI 40	59	3.55	0.77

An ultramicroelectrode technique using SECM has frequently been used to measure the ionic diffusion coefficients of I^- and I_3^- [10–12]. Steady-state voltammograms of the oligomer electrolytes are shown in Fig. 1 and the diffusion coefficients of I^- and I_3^- were calculated from steady-state current (I_{SS}) using the following equation.

$$I_{ss} = 4nFDCr$$

where *n* is the electron number per molecule, *F* is the Faraday constant, *D* is the diffusion coefficient of I^- or I_3^-, *C* is the bulk concentration of electroactive species, and *r* is the radius of Pt ultramicroelectrode that is 5 μm.

The steady-state currents of I^- for the both the KI and MPII cases were comparable, while the steady-state current of I_3^- was much smaller for KI than that for MPII. This means that the diffusion coefficient of I_3^- in the KI electrolyte was selectively

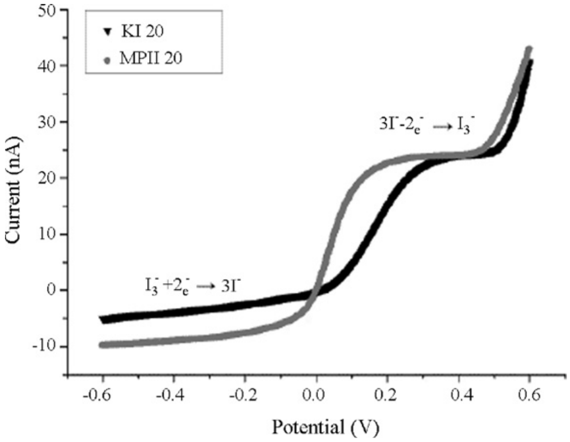

Fig. 1. Steady-state voltammograms measured at a scan rate 5 mV/s of oligomer electrolytes.

Table 2
Performance characteristics of DSSCs employing oligomer electrolytes at 100 mW/cm^2

Oligomer electrolyte	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η (%)
MPII 20	0.61	8.47	0.62	3.24
MPII 40	0.63	6.72	0.55	2.32
KI 20	0.64	8.32	0.50	2.67
KI 40	0.67	7.06	0.45	2.10

decreased. The reason for this phenomenon may be the difference of the coordination interactions of the polar oxygen groups in the oligomer with the cations. K^+ was able to coordinately interact with oxygen groups rather strongly, whereas the interactions between the MPI^+ and the oxygen groups were relatively weak. Accordingly, the rather strong interactions between K^+ and oxygen polar groups result in the physical cross-links among the polymeric chains [13], and thereby the increase in the chain stiffness and the glass transition temperature [13]. It is expected that stiff polymeric chains lead to the size selective diffusion of a large diffusant, whereas a small diffusant shows only slight size-selective diffusion behavior. Therefore, the diffusion coefficient of I_3^- is much lower in the physically cross-linked and stiffened polymeric chains for the KI system, compared to the MPII system, primarily because I_3^- is of larger size than I^-. In addition, it was also found that the diffusion coefficients of both cases of KI and MPII decreased with the salt concentration as expected. This can be rationalized by the increase in the viscosity with increasing salt concentration.

The influence of the ionic diffusion on the performance of DSSCs employing the oligomer electrolytes was investigated. The *J*–*V* curves of the DSSCs (at fixed molar ratio of oxygen atoms to the cations of 20, KI 20 and MPII 20) are shown in Fig. 2, and Table 2 summarizes the open-circuit voltage (V_{OC}), short-circuit photocurrent density (J_{SC}), fill factor (FF) and overall energy conversion efficiency (η) of the DSSCs. It was found that the cells with KI electrolytes showed a larger open-circuit voltage than those with MPII electrolytes. This fact may be associated with the diffusion coefficient of I_3^-. If the diffusion coefficient of I_3^- is small, the collision frequency between the electrons in the TiO_2 electrode and I_3^- in the electrolyte also decreases, resulting in a decrease in the recombination rate and an increase in the lifetime of the electrons [9,14–16]. It is well known that the slow recombination rates result in a higher open-circuit voltage [17–19]. Consequently, DSSCs using KI electrolytes would have a large V_{OC}. In addition, it can be seen that V_{OC} decreased with increasing salt concentration. This was caused by the rapid recombination rate due to the increased concentration of I_3^-.

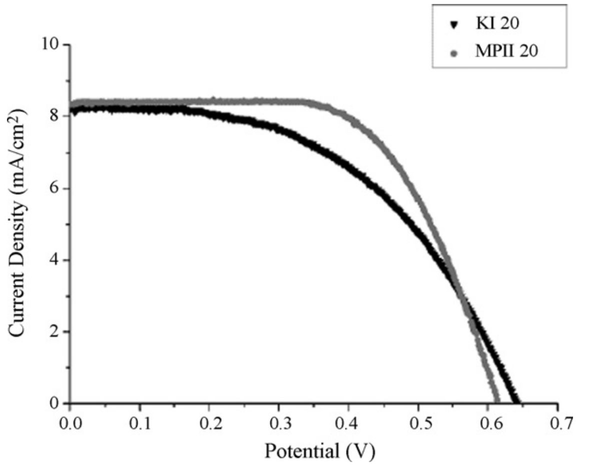

Fig. 2. *J*–*V* curves measured at 100 mW/cm^2 of the DSSCs employing oligomer electrolytes.

Fig. 3(a) shows the electron lifetime of the cells employing oligomer electrolytes as a function of electron charge density. Here the electron charge density was calculated by using the equation in reference [20]. At the same charge density, the apparent electron lifetime of the cells incorporating KI showed about 10 times longer value than the cell with MPII. As expected, the electron lifetime decreased with the concentration of I_3^-. From this, it can be concluded that the V_{OC} values of the cells employing oligomer electrolytes increase with the decreasing diffusion coefficient and concentration of I_3^- because of the retarded recombination process between the electrons in the TiO_2 electrode and I_3^- [16]. However, the cells employing KI electrolytes showed the difference in V_{OC} only 0.03–0.04 V when compared with those employing MPII electrolytes. To look into this result, the V_{OC} was compared as a function of electron density. The dependence of the open-circuit voltage on the photo-induced charge density would suggest the band-edge

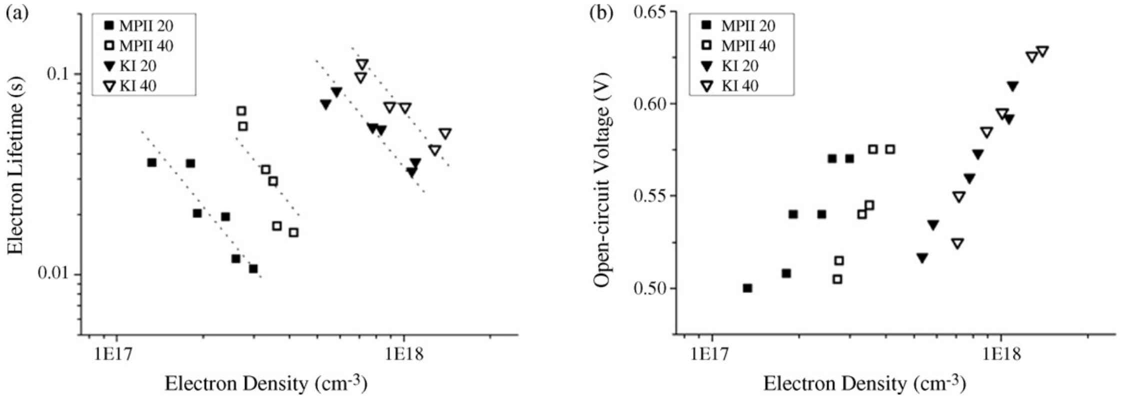

Fig. 3. (a) Electron lifetime in TiO_2 electrode and (b) open-circuit voltage of DSSCs employing oligomer electrolytes as a function of electron charge density.

movement in TiO_2 mesoporous films [21]. A higher open-circuit voltage at a constant charge density indicates upward movement of the conduction band-edge, while a lower open-circuit voltage indicates a downward movement. Fig. 3(b) shows that the cell employing MPII electrolyte can contribute to band-edge movement, 70 mV shift to negative potentials due to the effect of cation with large size [18]. This band-edge movement of MPII presumably compensates for the relatively fast recombination process and then results in comparable V_{OC} which is only 0.03 V less than the cells with KI electrolyte.

4. Conclusions

It was found that the diffusion coefficients of I^- and $I_3{}^-$ in the oligomer electrolyte were selectively affected by the type of salts. This phenomenon resulted from the difference of the coordination interaction between polar groups in the oligomer and the cations of the salts. In addition, it was confirmed that this also affected the recombination process, electron lifetime and consequently, the performance of the DSSCs.

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