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Gel polymer electrolytes based on a novel quaternary ammonium salt for dye-sensitized solar cells

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Abstract

Gel polymer electrolytes were prepared with polyacrylonitrile (PAN) and solutions of a novel quaternary ammonium salt, polysiloxane with quaternary ammonium side groups (PSQAS), in a mixture of ethylene carbonate (EC) and propylene carbonate (PC). The influences of PAN content and salt concentration on the ionic conductivity have been investigated. The ionic conductivity can be further improved with the use of the mixtures of KI and PSQAS, which can be expected as inorganic-organic salts. The gel polymer electrolytes were used in the fabrication of the dye-sensitized solar cells with a nanoporous TiO_2 working electrode, *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) complex dye and a counter electrode based on platinized conducting glass. The cells showed open-circuit voltages (V_{oc}) around 0.6 V and short-circuit current densities (J_{sc}) larger than 7.5 mA cm^{-2} under 60 mW cm^{-2} irradiation. The fill factors (FF) and energy conversion efficiencies (η) of the cells were calculated to be higher than 0.56 and 4.4%, respectively.

1. Introduction

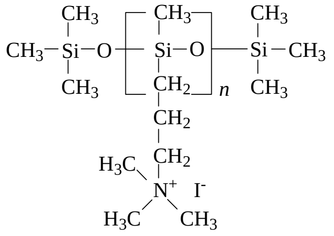
Complexes of poly(ethylene oxide) and alkali salts have been extensively investigated for their potential applications in electrochemical devices [1]. Unfortunately, these electrolytes exhibit very low ionic conductivities at room temperature. It is well known that the incorporation of an organic solvent into a polymer/salt complex is one of the most effective methods to improve the conductivity. Gel polymer electrolytes formed by immobilizing liquid electrolytes in polyacrylonitrile (PAN) showed ionic conductivities higher than 10^{-4} S cm^{-1} at room temperature [2–4].

Dye-sensitized solar cells with high photon-to-current conversion efficiencies and low cost have been reported by Grätzel and coworkers [5, 6]. The electrolyte usually used in these cells is an I^-/I_3^- redox couple in a mixture of ethylene carbonate (EC) and propylene carbonate (PC). The major drawbacks of using liquid electrolytes in dye-sensitized solar cells are difficulty in sealing, leakage of liquid electrolytes and less long-term stability. A solid-state dye-sensitized solar cell with an elastomeric electrolyte based on poly(epichlorohydrin-co-ethylene oxide) has been assembled by Paoli [7]. However, the overall conversion efficiency of the cell was found to be only 0.22%. This may be related to the low ambient conductivity of the electrolyte and the imperfect contact between the solid electrolyte and the nanoporous TiO_2 electrode. Cao et al. have demonstrated that PAN-based gel polymer electrolytes can be used for dye-sensitized solar cells by solution casting technique [8]. Liquid electrolytes generally used for dye-sensitized solar cells have been successfully replaced by a quasi-solid-state electrolyte comprised of PAN with EC and PC as plasticizers [9, 10]. The electrolyte showed an optimum conductivity as high as 2.95×10^{-3} S cm^{-1}. The overall conversion efficiency of the cell using this electrolyte was 2.99%.

Inorganic salts (e.g., LiI, NaI and KI) are usually used in the liquid electrolytes for dye-sensitized solar cells. At room temperature, the solubility of these inorganic salts in the mixtures of EC and PC is limited. Recently, a novel quaternary ammonium salt, polysiloxane with quaternary ammonium side groups (PSQAS), has been successfully synthesized in our laboratory [11]. PSQAS consists of a bulky polycation and anions, and can be expected as an organic salt. The purpose of present study is to characterize the gel polymer electrolytes based on this novel quaternary ammonium salt and investigate its application in dye-sensitized solar cells.

2. Experimental details

The preparation of PSQAS was carried out in two steps. A 0.4 M toluene solution of poly(methylhydrosiloxane)



Scheme 1. Structure of PSQAS.

was reacted with a 50% excess of *N*,*N*-dimethylallylamine at 90 °C for 24 h, in the presence of dicyclopentadienylplatinum(II) chloride ([Pt]/[SiH]=10^{-3}). After toluene and excess *N*,*N*-dimethylallylamine was evaporated under vacuum, the resulting polymer was dissolved in ethanol and quaternized with a large excess of methyl iodide at 40 °C for 24 h. The structure of PSQAS is shown in Scheme 1.

Gel polymer electrolytes were prepared with PAN and liquid electrolytes. The liquid electrolytes were obtained by dissolving PSQAS, KI or a mixture of KI and PSQAS in a binary solvent (EC:PC = 8:2 by weight). The concentrations of PSQAS and KI in the liquid electrolytes were varied from 0 to 2.25 M and 0 to 0.5 M, respectively. Weighted PAN and liquid electrolytes were mixed together and stirred for 2 h at room temperature to ensure wetting of the PAN powder. Then the mixture was sealed in a bottle and heated at 80 °C until a viscous liquid was obtained. The liquid was subsequently cooled down to room temperature. The content of PAN was 0, 5, 10, 15, 20, 25 wt % of the final electrolytes.

The ionic conductivity was measured using HIOKI LCR 3520 Hi TESTER at 1 kHz. The sample was placed in a poly(tetrafluoroethylene) spacer ring compressed between two stainless steel electrodes and sealed in a testing cell. Measurements were carried out over the temperature interval 30–80 °C. Before each measurement was made, the sample was kept at constant temperature for 30 min.

The photoelectrochemical properties of the dye-sensitized solar cells using the gel polymer electrolytes proposed in this paper were studied by measuring current–voltage (*I*/*V*) characteristics at room temperature. TiO_2 films were prepared by spreading the TiO_2 colloid obtained from the hydrolysis of titanium isopropoxide on fluorine-doped SnO_2 conducting glass and sintering at 450 °C for 30 min. The TiO_2 electrodes were obtained by dipping the TiO_2 films in the ethanol solution of *cis*-di-(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) complex for 12 h. The platinized counter electrodes were prepared by spreading the solution of H_2PtCl_6 in isopropanol on fluorine-doped SnO_2 conducting glass and sintering at 390 °C for 10 min. The gel polymer electrolytes for dye-sensitized solar cells consist of 10 wt. % PAN and the liquid electrolytes with 0.6 M PSQAS or 0.3 M KI/0.3 M PSQAS. The concentration of I_2 in the liquid electrolytes was maintained to be 0.03 M. The gel polymer electrolytes were sandwiched between the nanoporous TiO_2 electrode and the counter electrode. The *I*/*V* curves were monitored and recorded with a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273) and an X-Y recorder. A 250 W tungsten halogen lamp was used as the light source and the active cell area was 0.20 cm^2. The incident light intensity calibrated by using a photometer (UDT Instruments 350) was 60 mW cm^{-2}.

3. Results and discussion

The influence of PAN content on the ionic conductivity of the gel polymer electrolytes containing the liquid electrolyte with 0.1 M PSQAS is shown in Figure 1. The ionic conductivity tends to decrease with the increase in PAN content. This result may be explained by the increase in the viscosity of the electrolytes and hence the decrease in the mobility of the charge carriers with the addition of PAN [12]. The ionic conductivity of the liquid electrolyte with 0.1 M PSQAS was 1.48×10^{-3} S cm^{-1} at 30 °C. At room temperature, the electrolyte containing 5 wt % PAN was highly viscous liquid and no gel formed. The addition of 10 wt % PAN to the liquid electrolyte resulted in gel formation, while the ionic conductivity decreased to 9.23×10^{-4} S cm^{-1}. The electrolyte prepared with 25 wt % PAN was rigid solid and showed ionic conductivity of 3.08×10^{-4} S cm^{-1}. The use of rigid solids as polymer electrolytes for dye-sensitized solar cells is quite unfavorable because of the incomplete wetting of the nanoporous TiO_2 electrode, which will ultimately lead to lower conversion efficiency [8]. For the electrolytes under study, the optimum PAN content is believed to be 10–15 wt % in terms of both ionic conductivity

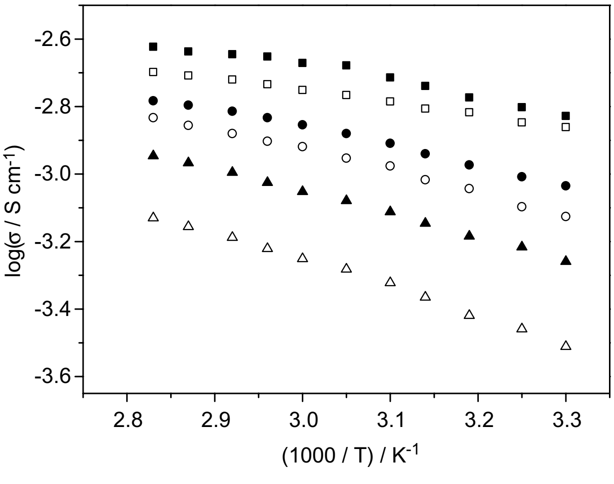


Fig. 1. Temperature dependence of the ionic conductivity of the gel polymer electrolytes. PSQAS concentration was maintained at 0.1 M. PAN content: (■) 0,(□) 5, (●) 10, (○) 15, (▲) 20 and (△) 25 wt %.

and the contact between the polymer electrolytes and the nanoporous TiO_2 electrode.

The effect of PSQAS concentration in the liquid electrolytes entrapped in PAN matrix on the ionic conductivity is shown in Figure 2. In these electrolytes, the PAN content was held to be 15 wt %, while the PSQAS concentration was varied from 0.1 to 2.25 M. The dependence of the ionic conductivity of the present gel polymer electrolytes on salt concentration is similar to that reported by others [13, 14]. The ionic conductivity rises to a maximum and then decreases with further increase in PSQAS concentration. The highest ionic conductivity was observed at 1.0 M PSQAS in the overall range of temperatures studied. At 30 °C, an ionic conductivity as high as 2.06×10^{-3} S cm^{-1} was achieved for the gel polymer electrolyte with 1.0 M PSQAS. The initial increase in the ionic conductivity is attributed to the increase in the number of charge carriers with the increase in PSQAS concentration. The viscosity of the ionic environment may be increased with the addition of a polymeric salt, resulting in a decrease in the ionic mobility. Therefore, the increase in the number of charge carriers will be offset not only by the formation of ion pairs or ion clusters but also by the decrease in the ionic mobility. The latter two effects begin to dominate at high salt concentrations, leading to the decrease in the ionic conductivity.

To improve the existing conductivity, gel polymer electrolytes containing inorganic-organic salts were prepared and their conductive behaviours were investigated. The inorganic-organic salts consist of KI and PSQAS. Figure 3 shows the variation of the ionic conductivity as a function of PSQAS concentration for the inorganic-organic systems. In these electrolytes, the KI concentration was held at 0.3 or 0.5 M, while the PSQAS concentration was varied from 0 to 1.5 M. As PSQAS concentration is increased, the ionic conductivity reaches a maximum and then decreases. The inorganic-organic salt systems with 0.5 M KI are more conductive than the systems with 0.3 M KI. However, further addition of KI leads to phase separation and has little effect on the ionic conductivity. The highest ambient conductivity equal to 3.4×10^{-3} S cm^{-1} appeared at 0.1 M PSQAS for the electrolytes with 0.5 M KI, while the maximum ambient conductivity of the electrolytes with 0.3 M KI was found to be 2.65×10^{-3} S cm^{-1} at 0.3 M PSQAS. Therefore, the total concentration of KI and PSQAS corresponding to the maximum ambient conductivity is expected to be 0.6 M. Figure 4 presents the dependence of the ionic conductivity measured at 30 °C on the salt composition of the inorganic-organic salt systems, in which the total concentration of KI and PSQAS was maintained at 0.6 M. The ionic conductivity as a function of KI concentration for the inorganic salt systems is also shown in Figure 4. The ionic conductivity of both systems goes through a maximum as the KI concentration

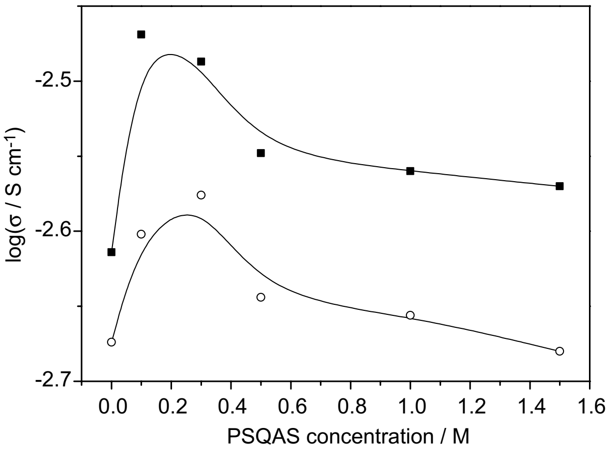


Fig. 3. Ionic conductivity as a function of PSQAS concentration of the gel polymer electrolytes with (○) 0.3 M and (■) 0.5 M KI. PAN content was maintained at 15 wt %.

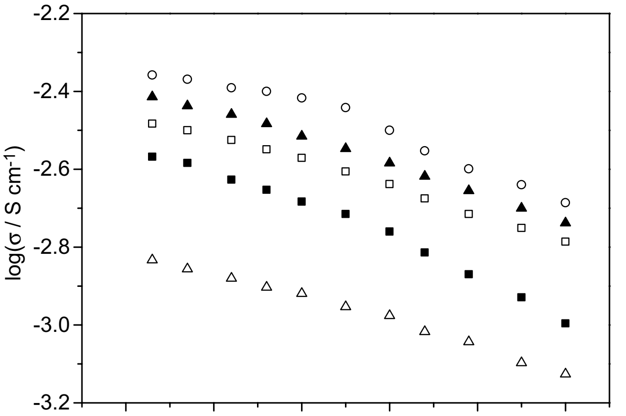


Fig. 2. Temperature dependence of the ionic conductivity of the gel polymer electrolytes containing the liquid electrolytes. PAN content was maintained to be 15 wt %. PSQAS concentration: (○) 1.0, (▲) 1.5, (□) 0.5, (■) 2.25 and (△) 0.1 M.

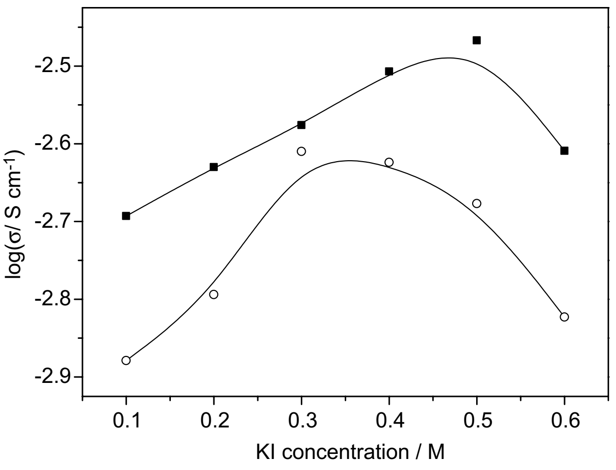


Fig. 4. Dependence of ionic conductivity on KI concentration for the gel polymer electrolytes containing (○) KI and (■) inorganic-organic salts. The total concentration of PSQAS and KI was held to be 0.6 M in the inorganic–organic salt systems. PAN content was maintained to be 15 wt %.

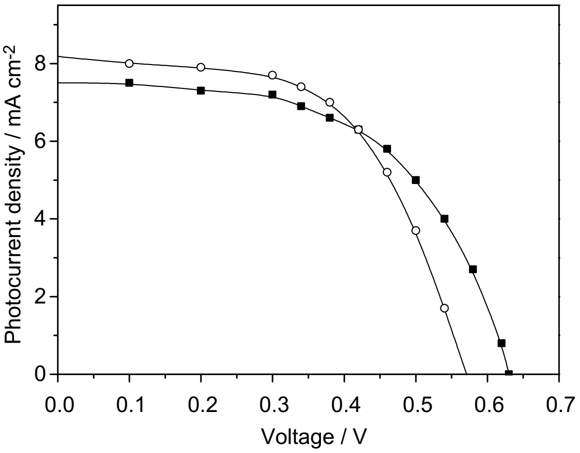


Fig. 5. Current–voltage curves of the cells fabricated using gel polymer electrolytes containing (■) PSQAS (0.6 M) and (○) the inorganic-organic salt (0.3 M KI/0.3 M PSQAS).

is increased. The variation of the KI concentration corresponding to the maximum conductivity is probably due to the ion-dipole interaction between KI and quaternary ammonium groups [15,16]. Preliminary results show that the use of inorganic-organic salts will lead to an increase in the ionic conductivity.

Figure 5 shows the I/V curves for the dye-sensitized solar cells fabricated using the gel polymer electrolytes based on PSQAS. The ambient conductivity of the gel polymer electrolyte containing the liquid electrolytes with 0.6 M PSQAS was 2.97×10^{-3} S cm^{-1}, while the gel with 0.3 M KI/0.3 M PSQAS showed ionic conductivity of 3.62×10^{-3} S cm^{-1} at 30 °C. The cell fabricated using the electrolyte with 0.6 M PSQAS generated a short-circuit current density (J_{sc}) of 7.5 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.63 V. J_{sc} of 8.2 mA cm^{-2} and V_{oc} of 0.57 V were obtained for the cell using the electrolyte with 0.3 M KI/0.3 M PSQAS. The relatively high V_{oc} of the cell with the electrolyte containing 0.6 M PSQAS is probably due to the absorption of the polycations dissociated from PSQAS on the TiO_2 electrode, which impedes the recombination of electrons. The fill factors and energy conversion efficiencies of the cells were calculated to be higher than 0.56 and 4.4%. These values are found to be satisfactory in comparison with those reported by others [8–10]. Optimization of the electrolyte composition with respect to the ionic conductivity and the photoelectrochemical properties of the solar cells is still in progress.

4. Conclusion

Gel polymer electrolytes based on a novel quaternary ammonium salt have been prepared. The ionic conductivities of these electrolytes were determined by PAN content and salt concentration in the liquid electrolytes contained in the polymer matrix. The ionic conductivity can be further improved by the use of the mixtures of KI and PSQAS. Dye-sensitized solar cells using these electrolytes had energy conversion efficiencies higher than 4.4% under 60 mW cm^{-2} irradiation.

Acknowledgement

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