

A comparative study of gel polymer electrolytes based on PVDF-HFP and liquid electrolytes, containing imidazolinium ionic liquids of different carbon chain lengths in DSSCs[☆]

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Abstract

The photoelectrochemical characteristics of titanium dioxide (TiO₂)-based dye-sensitized solar cells (DSSCs) containing gel polymer electrolyte (GPE) and organic liquid electrolyte (OLE) were studied in detail. GPE was prepared by adding poly(vinylidene fluoride-co-hexafluoro propylene) (PVDF-HFP) to imidazolinium ionic liquids (IILs) of the type, 1-methyl-3-alkyl imidazolinium iodides (alkyl is C_nH_{2n+1}, where $n = 3\text{--}10$) in methoxy propionitrile (MPN) and the OLE contained the above molten salt in MPN. The IILs were synthesized in the laboratory and characterized by ¹H nuclear magnetic resonance spectroscopy (NMR). The conductivities (σ) of both GPE and OLE decrease with increase in chain length (n) of the alkyl group of IILs; however, the effect is more drastic in the former case. The performance of the DSSCs containing OLE increases with the increase in alkyl chain length of IIL from C3 to C7, whereas, there is a linear decrease in the efficiency of the DSSCs incorporated with GPE containing IIL of alkyl chain length from C3 to C10. The change in short circuit current density (J_{SC}) determines the cell efficiency as the V_{OC} of the DSSCs remains almost the same with increase of alkyl chain length of IILs for both the electrolytes. The change in J_{SC} values and the consistency of the V_{OC} of the DSSCs for both the electrolytes may be explained on the basis of increase in viscosity of IILs from C3 to C10 and the dominating role of the 4-tertiary butyl pyridine (TBP), respectively, on the phenomenon of charge recombination.

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1. Introduction

Because of the possible low production cost and the expected high-energy conversion efficiency, dye-sensitized solar cells (DSSCs) with nanocrystalline TiO₂, organic dyes and an electrolyte become a large-scale prevalent material for light harvesting [1]. These solar cells usually employ

liquid electrolytes containing I[−]/I₃[−] redox couple as supporting electrolyte in order to reduce the dye cation, generated by the injection of the photo-excited electron. However, as far as long-term stability of the solar cell is considered, use of the liquid electrolytes must be avoided as the organic solvents evaporate slowly leading to decrease in cell performance. Hence, in order to improve the long-term stability of the solar cell, gel polymer electrolytes (GPEs) such as poly(acrolonitrile) [2–4], poly(ethylene glycol) [5], poly(oligoethylene glycol methacrylate) [6], poly(siloxane-co-ethylene oxide) [7], poly(butylacrylate) [8] and poly(vinylidene fluoride-co-hexafluoro propylene) (PVDF-HFP) [9,10] with different plasticizers have been employed. Among them, PVDF-HFP shows relatively high ionic

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conductivities at room temperature and they are stable in the presence of TiO_2 and Pt nanoparticles.

Imidazolinium iodides have been used as liquid [11–13] and quasi-solid-state electrolytes [11,12,14–16] in the solar cells. They contribute to enhancement of conductivity of I^-/I_3^- electrolyte and their multilayer adsorption on the TiO_2 surface leads to the enhancement in electron diffusion coefficient [17]. In this study, the photovoltaic performance of the DSSCs fabricated with GPE and organic liquid electrolyte (OLE), both incorporated with imidazolinium ionic liquids (IILs) of the type 1-methyl-3-alkyl imidazolinium iodides (alkyl is $\text{C}_n\text{H}_{2n+1}$, where $n = 3\text{--}10$) in methoxy propionitrile (MPN), have been compared under identical experimental conditions. This study brings a direct comparison on the performance of DSSCs containing different chain length of IILs in both liquid and gel systems and this is different from other Refs. [9,10].

2. Experimental section

2.1. Materials

Anhydrous LiI, I_2 , poly(ethylene glycol) (PEG), 4-tertiary butyl pyridine (TBP) and MPN were obtained from Merck. Tetrabutylammonium iodide (TBAI, +98%) and titanium (IV) isopropoxide (+98%) were purchased from Acros and used as received. The N3 dye was the commercial product obtained from Solaronix S.A., Aubonne, Switzerland.

1-Alkyl-3-methylimidazolium iodide (Scheme 1) [18] were prepared by the quaternization reaction of 1-methylimidazole (Fluka) with an equimolar amount of the corresponding alkyl iodide (RI) (Fluka) at 120°C for 12 h in cyclohexane, where $\text{R} = \text{C}_n\text{H}_{2n+1}$ ($n = 3\text{--}10$). The products were washed with diethyl ether to remove remains of the starting materials and dried under vacuum at 75°C for 4 h, and the purity was confirmed by 400 MHz ^1H FT nuclear magnetic resonance spectroscopy (NMR) instrument (Bruker Avance) in CDCl_3 .

2.2. Preparation of TiO_2 thin films and the cell assembly

The preparation of TiO_2 precursor and the electrode fabrication were carried out based on the previous literature [19] except after autoclave treatment, where the solution was concentrated to 13 wt% and two types of pastes, namely, P1 and P2 were prepared by the addition of 30 wt% (with respect to TiO_2) of poly (ethylene glycol) (PEG) having molecular weights of 20,000 and 200,000,

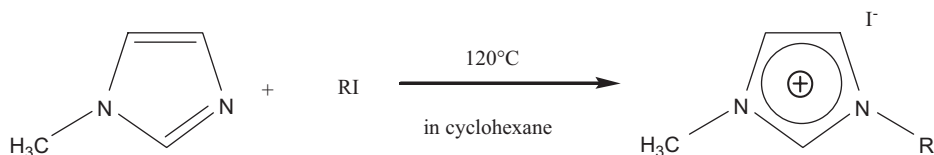
respectively, to the above solution in order to control the pore diameters and to prevent the film from cracking during drying [20]. P2 was coated over P1 on a fluorine-doped tin-oxide (FTO) glass ($R_{\text{sh}} = 25 \Omega/\square$, Sinonar Corp., Hsinchu, Taiwan), using glass rod. This bilayer TiO_2 film is an efficient light-harvesting material, as confirmed from the previous study carried out in this laboratory [20].

An active area of 0.25 cm^2 was selected from sintered electrode and the electrodes were immersed in $3 \times 10^{-4} \text{ M}$ solution of cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II) (N3) containing acetonitrile and tertiary butanol (in the volume ratio of 1:1) for 24 h. The OLE and GPE contain an optimized electrolyte composition of 0.6 M of IILs/0.2 M LiI/0.08 M of I_2 /0.5 M of TBP and 5 wt% PVDF-HFP/0.8 M of IILs/0.12 M of I_2 /0.2 M of TBP in MPN, respectively. The specified composition of the electrolyte was sprayed on both the dye-immobilized photoanode and Pt-sputtered (thickness of Pt is 100 nm) FTO glass and they are physically sandwiched together using cell holders.

2.3. Instrumentation

The photoelectrochemical characterizations of the DSSCs were carried out by using an AM 1.5 simulated light radiation. The light source was a 450 W Xe lamp (Oriel, #6266) equipped with a water-based IR filter and AM 1.5 filter (Oriel, #81075). Conductivity measurement of solution was performed by electrochemical impedance spectroscopy (EIS) with two Pt electrodes conductance cell where the area of each Pt electrode is 1 cm^2 and the distance between the two electrodes is 1 cm. The cell constant is 0.55 cm^{-1} , as calibrated from the standard aqueous KCl solution. Photoelectrochemical characteristics of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands) under constant light illumination of 100 mW/cm^2 .

The photovoltage transients of assembled devices were recorded with a digital oscilloscope (LeCroy, model LT322). Pulsed laser excitation was applied by a frequency-doubled Q-switched Nd:YAG laser (Spectra-Physics laser, model Quanta-Ray GCR-3-10) with 2 Hz repetition rate at 532 nm and 7 ns pulse width at half height. The beam size was larger than 0.25 cm^2 to cover the area of the device with incident energy of 1 mJ/cm^2 . The average lifetime of electron can be estimated approximately by fitting a decay of the open-circuit voltage transient with



Scheme 1.

$\exp(-t/\tau_e)$, where t is the time and τ_e is an average time constant before recombination.

3. Results and discussion

Fig. 1 shows the photovoltaic characteristics of the DSSCs based on GPE and OLE containing IILs of different carbon chain lengths. From Fig. 1a, it is understandable that open-circuit voltages of the DSSCs (V_{OC}) do not vary very much by incorporating IILs of different carbon chain lengths (C3–C10). (V_{OC} changes from 0.69 to 0.71 V for OLEs and 0.65 to 0.68 V for GPEs.) The short-circuit densities (J_{SC}) of the DSSCs varied significantly for IILs containing carbon chain length from C3 to C10. For example, the J_{SC} value of the DSSCs based on OLE increases with increase in alkyl group of IIL from C3 to C8 and then decreases, whereas, a linear decrease in J_{SC} is observed for GPE-containing IIL with alkyl group from C3 to C10 (Fig. 1b). On the other hand, there was only little variation in fill factors (FF) of the DSSCs when the chain length of alkyl groups of IIL was varied for both OLE and GPE (Fig. 1c). In the similar manner, the efficiencies of the DSSCs based on GPE decrease from C3 to C10, whereas, a linear increase and decrease on the performances of the

DSSCs were noted for the IILs from C3–C7 to C8–C10, respectively, with OLE (Fig. 1d).

It is well known that the V_{OC} values of the DSSCs are related to the difference between the Fermi level for electrons in the TiO_2 electrode and the redox potential of I^-/I_3^- . Actually, the increase of alkyl chain length would increase electron density in the TiO_2 by suppressing charge recombination, causing the increase of Fermi level. Fig. 2a shows the photovoltage transients induced by pulse laser (532 nm) radiation for TiO_2 electrodes in different pure IILs and Fig. 2b brings the correlation between electron lifetime (τ_e) and viscosity of the pure IILs used in this study. Though there is an increase of electron recombination lifetime from C3 to C10, presence of 4-tertiary butyl pyridine (TBP) nullifies this effect. Because of this reason, there is not much difference in the V_{OC} of the DSSCs containing both OLE and GPE [18].

This characteristic variation in the J_{SC} (Fig. 1b) and conversion efficiency (Fig. 1d) of the DSSCs containing IIL may be correlated with different conductivities and viscosities of individual IIL. The relationship between the conductivity of both GPE and OLE with different IILs vs. the viscosity of pure IIL is shown in Fig. 3. It is well known that the IILs are highly viscous liquids and their viscosities increase with increase in chain length of alkyl group. This is

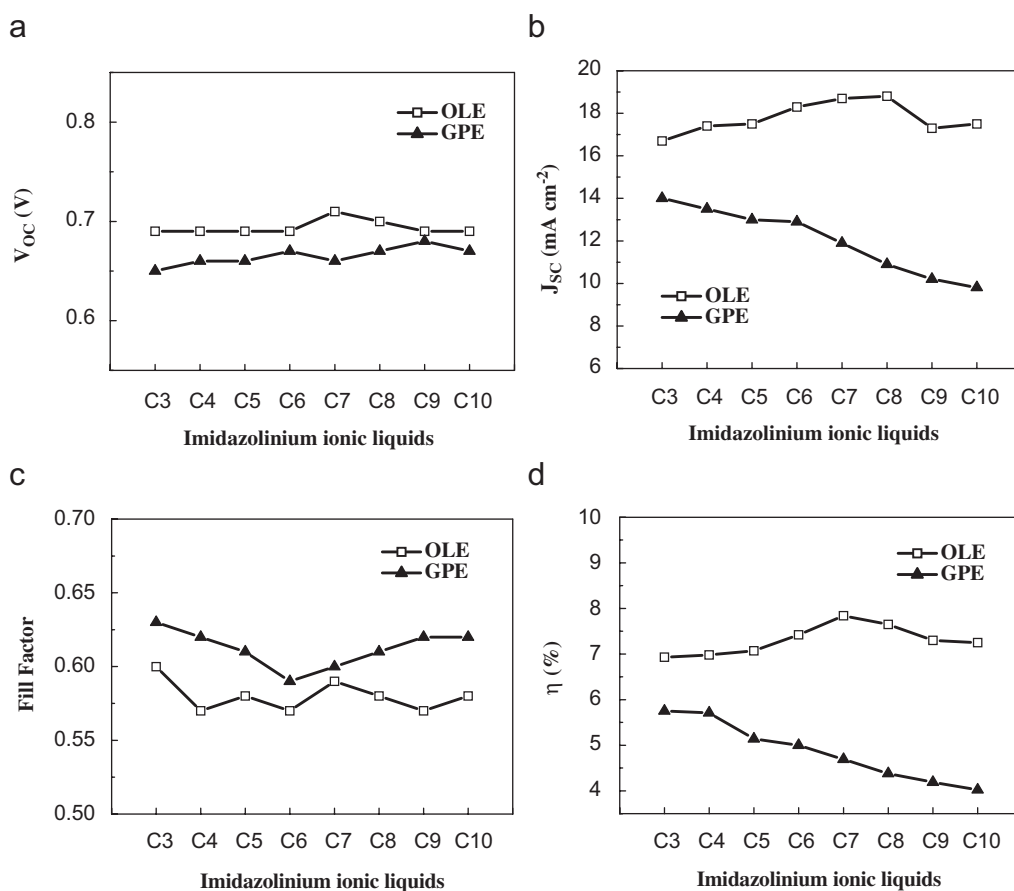


Fig. 1. Photovoltaic characteristics such as (a) V_{OC} (b) J_{SC} (c) FF, and (d) η of the DSSCs containing OLE and GPE incorporated with IILs of different carbon chain lengths from C3 to C10.

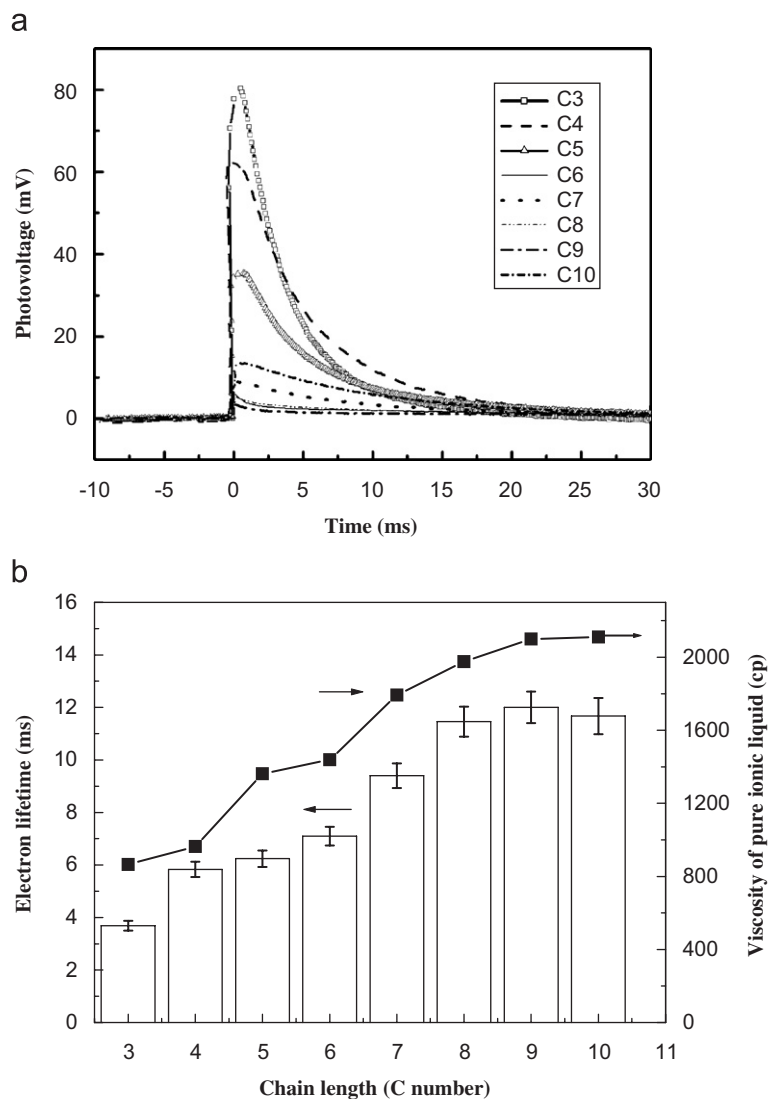


Fig. 2. (a) Photovoltage transients induced by pulse laser (532 nm) radiation for the TiO₂ electrodes in the GPE with IILs containing different alkyl chain lengths (C3–C10). (b) Relationship between electron lifetimes in the TiO₂ electrode and the viscosity of IILs under the same condition.

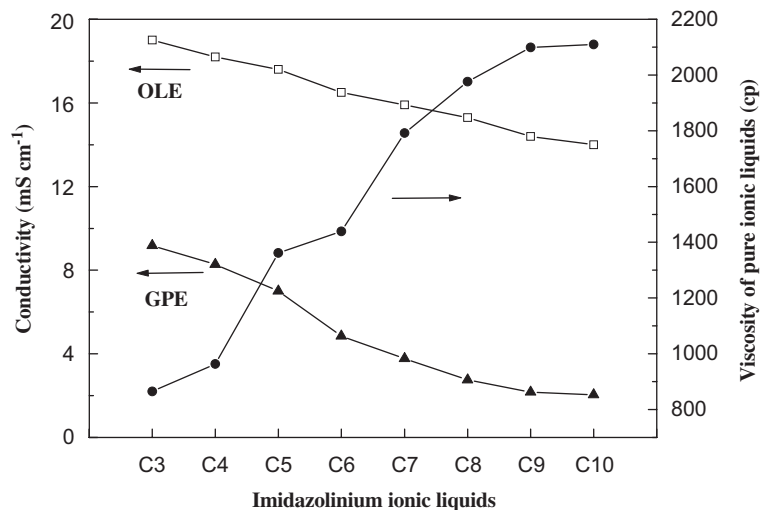


Fig. 3. Plots of conductivity of OLE and GPE vs. the viscosity of IILs containing different alkyl chain lengths (C3–C10).

because of high van der Waals forces of attraction functioning between the molecules and this lowers diffusion of ions. Since the diffusion of ions in a liquid depends on its viscosity, the conductivity of the liquid decreases with increase in the viscosity. From Fig. 3, it is noted that IIL containing propyl group (C3) shows maximum conductivity in both the GPE and OLE and the conductivity decreases from C3 to C10. Naturally, higher conductivity values are obtained for OLE than the GPE irrespective of the different IILs.

From the previous literature, it has been observed that the diffusion coefficient of electrons injected in a TiO_2 electrode (D_e) increases as a result of the multilayer adsorption of imidazolinium cations [21]. When the chain length of alkyl group in IIL increases, the carbon–carbon will have more chance to encounter, the van der Waals forces will increase in the presence of the longer chain length. The aggregation of these imidazolinium cations will be more and this leads to high D_e value. As a consequence of this, the J_{SC} value of the DSSC also increases. Though the conductivity decreases with increases in the chain length of IIL, both the effect of τ_e and D_e overcome this. Consequently, the conversion efficiency of the DSSCs-containing OLE increases from C3 to C7. However, for GPE containing IILs from C3 to C10, a linear decrease in the performance of the DSSCs is observed. This may be correlated with the weak adsorption of imidazolinium cations on the TiO_2 electrode as a result by trapping of IIL in polymer cages formed by the host matrix in GPE.

4. Conclusions

A comparative study on the photoelectrochemical characteristics of the DSSCs-containing PVDF-HFP as GPE and OLE both incorporated with different IILs containing different carbon chain lengths from C3 to C10 in MPN was carried out in this work. The conductivities (σ) of both GPE and OLE decrease with increase in chain length of the alkyl group of IILs. The V_{OC} of the DSSCs remains almost stable with increase of alkyl chain length of IILs for both the electrolytes and this is related with the dominating role of the TBP on the charge recombination behavior. The performance of the DSSCs based on OLE increases with the addition of IILs from C3 to C7, whereas, there is a linear decrease in the efficiency of the DSSCs incorporated with GPE electrolytes containing IILs of different carbon chain lengths from C3 to C10. This may be explained on the basis of increase in both electron lifetime and the diffusion coefficient of electron, and is in consistent with increase in viscosity of IILs.

Acknowledgments

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