

# Effects of the Alkyl Chain Length of Imidazolium Iodide in the Electrolyte Solution on the Performance of Black-Dye-Based Dye-Sensitized Solar Cells



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## ABSTRACT

Five kinds of electrolyte solutions containing the imidazolium iodide with a different alkyl chain length (DMImI, EMImI, MPImI, DMPImI and HMIImI; DMImI = 1,3-dimethylimidazolium iodide, EMImI = 1-ethyl-3-methylimidazolium iodide, MPImI = 1-methyl-3-*n*-propylimidazolium iodide, DMPImI = 1,2-dimethyl-3-*n*-propylimidazolium iodide, HMIImI = 1-*n*-hexyl-3-methylimidazolium iodide) have been prepared to investigate the effects of the alkyl chain length of the imidazolium iodide on the performance of dye-sensitized solar cells (DSCs) with Black dye and D131. The photocurrent density ( $J_{sc}$ ) increased and the fill factor ( $FF$ ) decreased with increasing the alkyl chain length of the imidazolium iodide. Electrochemical impedance spectroscopic measurements of the DSCs revealed that the conduction band energy of  $TiO_2$  shifted to the positive direction and the diffusion resistance of the redox couple in the electrolyte solution increased with increasing the alkyl chain length of the imidazolium iodide. Therefore, the observed increment of the  $J_{sc}$  value seems to be attributed mainly to the conduction band energy shift of  $TiO_2$ , and the observed decrement of the  $FF$  value would be caused by increasing the diffusion resistance of the redox couple in the electrolyte solution. The conversion efficiency of the DSCs was found to depend on the ion conductivity of the electrolyte solution, which is closely related to the alkyl chain length of the imidazolium iodide. This study demonstrated that the conversion efficiency could be improved by using EMImI instead of the conventional imidazolium iodide (DMPImI) due to the larger ion conductivity with a slightly higher conduction band energy of  $TiO_2$ .

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## Introduction

Dye-sensitized solar cells (DSCs) have attracted significant attention since the pioneering researches were reported in the early 1990's [1–5]. The conversion efficiency of the DSCs have reached recently 13% by employing highly efficient Zn porphyrin sensitizers and polypyridyl cobalt-complex redox mediators [6–8]. Extensive efforts have been thus far devoted to develop highly efficient molecular sensitizers and redox mediators for the efficiency improvement of the DSCs because the conversion efficiency of the DSCs depends strongly on both the sensitizing ability of molecular sensitizers and the electron-transporting ability of redox mediators. On the other hand, it is well known that the conversion efficiency of the DSCs also depends strongly on the electrolyte composition. In general, the electrolyte solutions of the DSCs contain a redox mediator (typically,  $I_2$  and XI; where X is a

cation such as  $Li^+$ ,  $DMPIm^+$  and  $TBA^+$ ;  $DMPIm^+$  = 1,2-dimethyl-3-*n*-propylimidazolium,  $TBA^+$  = tetra-*n*-butylammonium) and several additives such as TBP, GuSCN and NMBl (TBP = 4-*tert*-butylpyridine, GuSCN = guanidinium isothiocyanate, NMBl = 9552; *N*-methylbenzimidazole). The role of each electrolyte component has been disclosed by the systematic studies on the relationship between the electrolyte compositions and the solar cell performances. For example,  $Li^+$  is well known to decrease the conduction band energy of  $TiO_2$ , resulting in the increase of the photocurrent density ( $J_{sc}$ ) [9–11]. On the other hand, TBP and NMBl are also known to raise the conduction band energy of  $TiO_2$ , which results in the improvement of the open-circuit voltage ( $V_{oc}$ ) [12–24]. In addition,  $TBA^+$  is reported to retard the backward electron transfer reaction from the conduction band of  $TiO_2$  to  $I_3^-$  in the electrolyte solution because  $TBA^+$  makes a relatively thicker electrical double layer at the  $TiO_2$  surface, which prevents the approach of  $I_3^-$  to the  $TiO_2$  surface, due to both the relatively bulky structure and the less-adsorptivity to the  $TiO_2$  surface [25]. Therefore, the solar cell performances of the DSCs are improved by adding a moderate concentration of  $TBA^+$  to the electrolyte solution [25]. As described

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above, each electrolyte component plays a crucial role for achieving a higher conversion efficiency, therefore, the optimization of the electrolyte composition is required to obtain the best performance of the DSCs. In this context, optimization of the electrolyte composition in the cosensitized DSCs with Black dye and D131, which exhibit the conversion efficiency higher than 11%, has been carried out in our group. The conversion efficiency of such cosensitized DSCs was increased by using the electrolyte solution containing a moderate concentration of TBAI, which can suppress effectively the backward electron transfer reaction as mentioned above [26]. Moreover, 12.0% efficiency could be achieved by employing the electrolyte solution containing a moderate concentration of THAI (THA<sup>+</sup> = tetra-*n*-heptylammonium) [27]. In the study, the efficacy of the quaternary ammonium cation toward the retardation of the backward electron transfer reaction has been found to depend on the alkyl chain length of the quaternary ammonium cation [27]. Since THA<sup>+</sup> has four alkyl chains longer than those of TBA<sup>+</sup>, THA<sup>+</sup> can suppress the backward electron transfer reaction more effectively than TBA<sup>+</sup>. Therefore, the electron lifetime in the TiO<sub>2</sub> photoelectrode is improved effectively, which results in the enhancement of the *J*<sub>sc</sub> value.

On the other hand, typical electrolyte solutions of the DSCs contain an imidazolium iodide with the concentration much higher than those of the other electrolyte components. It is reported that the viscosity and the ion conductivity of the electrolyte solutions are closely related to the molecular size of the imidazolium cation [28–32], and these two parameters of the electrolyte solutions affect directly the diffusion coefficient of the redox couple (I<sup>-</sup>/I<sub>3</sub><sup>-</sup> couple) in the electrolyte solution. Therefore, the molecular sizes of the imidazolium iodide seem to affect largely the performances of the DSCs. In this regard, effects of the alkyl chain length of the imidazolium iodide on the performance of the DSC should be investigated in detail for the efficiency improvement of the DSCs. In this study, the relationship between the alkyl chain length of imidazolium iodide and the performance of the cosensitized DSC with Black dye and D131 has been investigated for further efficiency improvement. This study demonstrated that conversion efficiency of the DSC depends on the ion conductivity of the electrolyte solution, which is closely related to the alkyl chain length of the imidazolium iodide. Moreover, the conversion efficiency could be improved by using EMImI (EMImI = 1-ethyl-3-methylimidazolium iodide, Fig. 1) instead of the conventional imidazolium iodide (DMPImI).

## Results and discussion

In this study, five kinds of electrolyte solutions containing an imidazolium iodide with a different alkyl chain length (DMImI, EMImI, MPImI, DMPImI and HMIImI; DMImI = 1,3-dimethylimidazolium iodide, EMImI = 1-ethyl-3-methylimidazolium iodide, MPImI = 1-methyl-3-*n*-propylimidazolium iodide, DMPImI = 1,2-dimethyl-3-*n*-propylimidazolium iodide, HMIImI = 1-*n*-hexyl-3-methylimidazolium iodide, shown in Fig. 1) have been prepared,

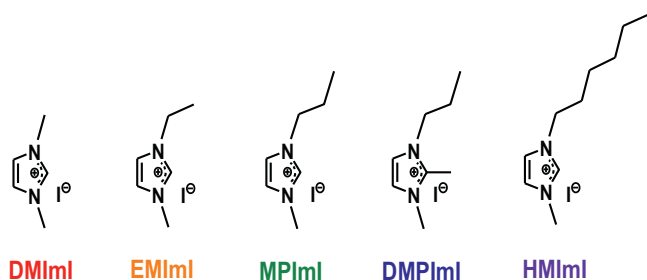


Fig. 1. Structures of DMImI, EMImI, MPImI, DMPImI and HMIImI.

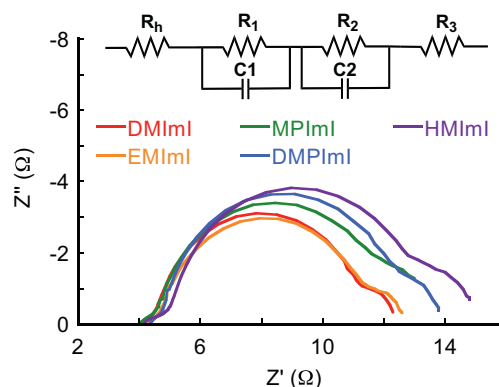


Fig. 2. Nyquist plots of the DSCs with five kinds of electrolyte solutions under the irradiation and the open-circuit conditions.

and the performance of the cosensitized DSC with Black dye and D131 using each electrolyte solution has been evaluated. The viscosity of imidazolium iodide is reported to increase with increasing the alkyl chain length at the same temperature because Van der Waals forces between the alkyl chains induce the aggregation of imidazolium iodides [28–33]. Since the viscosity of the electrolyte solution of the DSC is one of the quite important parameters to obtain a higher conversion efficiency, internal resistances of the DSCs with five kinds of electrolyte solutions prepared in this study have been investigated by the electrochemical spectroscopic (EIS) measurements. Fig. 2 shows Nyquist plots of the DSCs with five kinds of electrolyte solutions under the irradiation condition. The internal resistances, especially the  $R_3$  resistances corresponding to the diffusion resistances of the redox couple in the electrolyte solution, increased largely with increasing the alkyl chain length of the imidazolium iodide (Table 1). This result suggests that a longer alkyl chain of the imidazolium iodide retards the redox-couple diffusion in the electrolyte solution. We reported recently that the redox-couple diffusion is retarded by the quaternary ammonium cation with relatively longer alkyl chains in the electrolyte solution [26,27]. Therefore, the alkyl chain of the imidazolium iodide seems to have the same effect to the quaternary ammonium iodide.

The ion conductivity ( $\sigma$ ) of five kinds of electrolyte solutions, calculated from the results of the EIS measurements [34], decreased with increasing the alkyl chain length of the imidazolium iodide (Table 1). As shown in Fig. 3, the ion conductivity of the electrolyte solution was found to increase drastically at the molecular weight of imidazolium iodide below 253. This result suggests that the presence of the alkyl chain longer than *n*-propyl one increases largely the viscosity of the electrolyte solution under

Table 1

Internal resistances of the DSCs and the ion conductivity of the electrolyte solution containing various kinds of imidazolium iodide<sup>a</sup>.

Imidazolium iodide	MW <sup>b</sup>	$R_2^c$ ( $\Omega$ )	$R_3^d$ ( $\Omega$ )	$\sigma^e$ ( $\times 10^{-3}$ S/cm)
DMImI	224.0	6.67	1.32	15.2
EMImI	238.1	6.75	1.83	10.9
MPImI	252.1	7.15	3.19	6.4
DMPImI	266.1	7.39	3.19	6.3
HMIImI	294.2	7.62	3.99	5.0

<sup>a</sup> The electrolyte was a mixed solution of acetonitrile and THF (95:5, v/v) containing 0.05 M I<sub>2</sub>, 0.02 M LiI, 0.6 M imidazolium iodide, 0.3 M TBP, and 0.05 M THAI. Irradiation was carried out by a solar simulator AM 1.5 (100 mW/cm<sup>2</sup>). TiO<sub>2</sub> film thickness and active area were 42  $\mu$ m and 0.25 cm<sup>2</sup>, respectively.

<sup>b</sup> molecular weight of imidazolium cation.

<sup>c</sup>  $R_2$  is the interfacial resistance at the TiO<sub>2</sub>/dye/electrolyte interface.

<sup>d</sup>  $R_3$  is the diffusion resistance in the electrolyte solution between two electrodes.

<sup>e</sup>  $\sigma$  was calculated by using the  $R_3$  value listed in this Table.

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