



# Black-Dye-Based Dye-Sensitized Solar Cells using the Electrolyte Solutions Containing a Quaternary Phosphonium Iodide with a Various Alkyl Chain Length



Hironobu Ozawa<sup>1</sup>, Ayako Urayama, Hironori Arakawa\*

Department of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 12-1, Ichigaya-Funagawara, Shinjuku, Tokyo, 162-0826, Japan

## ARTICLE INFO

### Article history:

Received 22 July 2015

Received in revised form 26 August 2015

Accepted 30 October 2015

Available online 14 November 2015

### Keywords:

Dye-sensitized solar cells

Quaternary phosphonium iodide

Alkyl chain length

Backward electron transfer

## ABSTRACT

Solar cell performances of the cosensitized dye-sensitized solar cells (DSCs) with Black dye and D131 using the electrolyte solution containing a quaternary phosphonium iodide with a various alkyl chain length have been evaluated by the photoelectrochemical and the electrochemical impedance spectroscopic measurements. Effects of the difference of the central atom between the quaternary phosphonium iodide and the quaternary ammonium iodide on the solar cell performances have been clarified. The DSC using the electrolyte solution containing tetrabutylphosphonium iodide showed higher  $J_{sc}$  value and lower  $V_{oc}$  and  $FF$  values compared to those of the DSC using the electrolyte solution containing tetrabutylammonium iodide. In addition, effects of the alkyl chain length of the quaternary phosphonium iodide on the solar cell performances have been also investigated. The blocking effect of the quaternary phosphonium cation for the access of  $I_3^-$  to the  $TiO_2$  surface was found to be improved with increasing the alkyl chain length. The highest conversion efficiency (11.3%) could be obtained in the cosensitized DSC with Black dye and D131 using the electrolyte solution containing a moderate concentration of tetraoctylphosphonium iodide under AM 1.5 (100 mW/cm<sup>2</sup>) irradiation. This study demonstrated that the quaternary phosphonium iodide with a longer alkyl chain is also effective for the improvement of the conversion efficiency of the DSCs due to both the improvement of the electron lifetime in the  $TiO_2$  photoelectrode and the slight increment of the conduction band energy of the  $TiO_2$ .

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Continuous efforts have been devoted to improve the light-to-electrical energy conversion efficiency of dye-sensitized solar cells (DSCs) for the commercialization of DSCs [1–4]. Recently, the conversion efficiency of the DSCs has reached to 13% by using the combination of the efficient Zn porphyrin sensitizer and the suitable polypyridyl cobalt-complex redox mediator [5,6]. Development of both the highly efficient sensitizers and the redox mediators, redox potentials of which are tuned suitably, is a most efficient and direct way to increase the conversion efficiency of the DSCs. On the other hand, promotion of the backward electron transfer reaction from the conduction band of  $TiO_2$  to  $I_3^-$  in the electrolyte solution is considered to be one of the major pathways which decreases the conversion efficiency of the DSCs. Therefore,

retardation of this backward electron transfer reaction is also an important issue to improve the conversion efficiency of the DSCs. In this regards, various attempts have been thus far carried out to suppress the electron leakage from the  $TiO_2$  photoelectrodes. For example, surface passivation of the  $TiO_2$  photoelectrodes by a metal-oxide insulator thin over layer has been reported to suppress effectively the electron leakage from the  $TiO_2$  photoelectrodes [7–19]. This method is actually effective for the suppression of the electron leakage, however, preparation of the surface-passivated  $TiO_2$  photoelectrodes requires a detailed technique with great care, which would raise the production cost of the DSCs. On the other hand, some additives in the electrolyte solution are reported to retard effectively the electron leakage as well due to their blocking effect for the access of  $I_3^-$  to the  $TiO_2$  surface [20–24]. We have also reported recently that the backward electron transfer reaction from the conduction band of  $TiO_2$  to  $I_3^-$  is suppressed effectively by using the electrolyte solution containing a moderate concentration of a quaternary ammonium iodide such as TBAI and THAI (TBAI = tetrabutylammonium iodide, THAI = tetraheptylammonium iodide) [25,26]. These quaternary ammonium cations are

\* Corresponding author.

E-mail address: [h.arakawa@ci.kagu.tus.ac.jp](mailto:h.arakawa@ci.kagu.tus.ac.jp) (H. Arakawa).

<sup>1</sup> Present address: Education Center Global Leaders in Molecular Systems for Devices, Kyushu University, 774, Motooka, Nishi-ku, Fukuoka 819-0395, Japan.

relatively bulky and less adsorptive for the  $\text{TiO}_2$  surface, therefore, they make a relatively thick electrical double layer at the  $\text{TiO}_2$  surface. As a result, the electron leakage from the  $\text{TiO}_2$  photoelectrodes is retarded effectively due to the lower concentration of  $\text{I}_3^-$  at the  $\text{TiO}_2$  surface [20–24]. This method for the retardation of the electron leakage by using the additives is more simple and easy way compared to the above mentioned surface passivation method, therefore, further investigations should be carried out to achieve the low-cost production of the high-performance DSCs.

In this study, quaternary phosphonium iodides have been employed instead of quaternary ammonium iodides to reveal the effect of the central atom on the retardation of the electron leakage from the  $\text{TiO}_2$  photoelectrodes. In addition, the effect of the alkyl chain length of quaternary phosphonium iodide on the retardation of the electron leakage has been also investigated because the bulkiness of the quaternary phosphonium cation is considered to be a most important parameter for the retardation of the electron leakage. Here we report the solar cell performances of the cosensitized DSCs with Black dye and D131, which exhibit the conversion efficiency beyond 11.0% when the thick  $\text{TiO}_2$  photoelectrodes are employed, using the electrolyte solutions containing the quaternary phosphonium iodides with a various alkyl chain length.

## 2. Results and Discussion

At first, solar cell performances of the cosensitized DSCs with Black dye and D131 using the electrolyte solution containing TBAI or TBPI (TBPI = tetrabutylphosphonium iodide) have been evaluated. In this measurement, electrolyte solutions with a simple composition (0.05 M  $\text{I}_2$ , 0.3 M 4-*tert*-butylpyridine, and 0.7 M TBAI or TBPI) have been employed to clarify the effect of the difference of the central atom between TBAI and TBPI on the solar cell performances. As summarized in Table 1, the conversion efficiency of the DSC using TBPI (6.2%) was found to be higher than that of the DSC using TBAI (5.9%). Interestingly,  $J_{sc}$  value was remarkably larger and  $V_{oc}$  and  $FF$  values were meaningfully smaller in the case of the DSC using TBPI compared to those of the DSC using TBAI. This difference would be arisen from the difference of the central atom between TBPI and TBAI, therefore, further investigations using the SLIM-PCV (stepped light-induced transient measurements of photocurrent and photovoltage) and the EIS (electrochemical impedance spectroscopic) measurements have been conducted to reveal the effect of the difference of the central atom between TBPI and TBAI on the solar cell performances of the DSCs.

As shown in Fig. 1a, the electron lifetime in the  $\text{TiO}_2$  photoelectrode of the DSC using TBPI was found to be shorter than that of the DSC using TBAI at the matched  $V_{oc}$  value. This result suggests that the efficacy of  $\text{TBP}^+$  ( $\text{TBP}^+$  = tetrabutylphosphonium cation) for the suppression of the backward electron transfer reaction from the  $\text{TiO}_2$  photoelectrode to  $\text{I}_3^-$  is inferior to that of  $\text{TBA}^+$  ( $\text{TBA}^+$  = tetrabutylammonium cation), even though the molecular size of each cation seems to be almost equal. In addition,  $V_{oc}$  value of the DSC using TBPI was lower than that of the DSC

using TBAI at the matched electron density (Fig. 1b). This result indicates that the conduction band energy of the  $\text{TiO}_2$  photoelectrode of the DSC using TBPI was lower than that of the DSC using TBAI. Therefore, this result explains reasonably both the observed increment in the  $J_{sc}$  value and decrement in the  $V_{oc}$  value for the DSC using TBPI. Judging from these two results, the adsorptivity of  $\text{TBP}^+$  to the  $\text{TiO}_2$  surface seems to be weaker than that of  $\text{TBA}^+$  because the blocking effect of  $\text{TBP}^+$  against the access of  $\text{I}_3^-$  to the  $\text{TiO}_2$  surface was inferior to that of  $\text{TBA}^+$ . In addition, the positive charge density of  $\text{TBP}^+$  is considered to be larger than that of  $\text{TBA}^+$  since the conduction band energy of the  $\text{TiO}_2$  photoelectrode in the DSC using TBPI was lower than that of the DSC using TBAI. Fig. 1c shows the Nyquist plots of the DSCs under the irradiation and the open-circuit condition obtained from the EIS measurements. Generally, three semicircles were observed in the Nyquist plots when measurements were conducted for the efficient DSCs. These three semicircles are considered to indicate the internal resistances of the DSCs as follows [27–31]. The semicircle at the higher frequency region corresponds to the interfacial resistance at the counter electrode ( $R_1$  resistance). The semicircle at the middle frequency domain is considered to be the interfacial resistance at the  $\text{TiO}_2$ -dye-electrolyte interface ( $R_2$  resistance), and the semicircle at the lower frequency region is the diffusion resistance of the redox couple in the electrolyte solution ( $R_3$  resistance). In this study, single-layered  $\text{TiO}_2$  photoelectrodes, the  $R_2$  resistances of which are relatively larger, were employed. Therefore, the semicircles at the middle frequency region ( $R_2$  resistances) were quite large, and hence they overlapped to the semicircles at the lower frequency region ( $R_3$  resistances). As shown in Fig. 1c, the overlapped semicircle of  $R_2$  and  $R_3$  resistances of the DSC using TBPI was obviously smaller than that of the DSC using TBAI. The viscosity of the ionic liquid of quaternary phosphonium iodide is reported to be lower than that of the corresponding quaternary ammonium iodide [32,33], therefore, the smaller  $R_2$  and  $R_3$  resistances of the DSC using TBPI seem to be attributed to the lower viscosity of the electrolyte solution. Considering from the above results, quaternary phosphonium iodides are also effective additives for the improvement of the conversion efficiency the cosensitized DSCs with Black dye and D131 although the positive effect of the quaternary phosphonium iodide for the improvement of the solar cell performances is different from that of quaternary ammonium iodide.

Second, nine kinds of electrolyte solutions containing various concentrations of TBPI have been prepared (EL1~EL9 in Table 2), and the solar cell performances of the cosensitized DSCs with Black dye and D131 using each electrolyte solution have been evaluated to determine the optimum electrolyte composition (Table 3). As summarized in Table 2, concentrations of DMPIml (DMPIml = 1,2-dimethyl-3-propylimidazolium iodide), LiI, and TBPI varied gradually as the total concentration of  $\text{I}^-$  was fixed at 0.7 M. By employing the electrolyte solution which does not contain TBPI (EL1), 7.8% conversion efficiency was obtained in the cosensitized DSC with a thin  $\text{TiO}_2$  photoelectrode (8  $\mu\text{m}$ ). The  $J_{sc}$  value was increased, and the  $V_{oc}$  and  $FF$  values were decreased slightly by replacing of 0.1 M DMPIml into TBPI (EL2). As a result, the conversion efficiency improved to 8.3%. Further replacement of DMPIml into TBPI resulted in the gradual decrease of the  $J_{sc}$  value without changing the  $V_{oc}$  and  $FF$  values (EL3~EL5). The conversion efficiency was found to decrease gradually with increasing the concentration of TBPI above 0.1 M. As shown in Fig. 2a, the electron lifetime in the  $\text{TiO}_2$  photoelectrode was improved largely by replacing the 0.1 M DMPIml into TBPI, and the electron lifetime improved further with increasing the TBPI concentration. This result suggests strongly that the backward electron transfer reaction from the conduction band of  $\text{TiO}_2$  to  $\text{I}_3^-$  was retarded effectively by  $\text{TBP}^+$ . On the other hand, the conduction band energy

**Table 1**

Solar cell performances of the cosensitized DSCs with Black dye and D131 using the electrolyte solutions containing TBAI or TBPI.<sup>a</sup>

Additive	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	$FF$	$\eta$ (%)
TBAI	12.0	0.758	0.647	5.89
TBPI	14.4	0.711	0.604	6.18

<sup>a</sup> The electrolyte is an acetonitrile solution containing 0.05 M  $\text{I}_2$ , 0.3 M 4-*tert*-butylpyridine, and 0.7 M additive. Irradiation was carried out by a solar simulator AM 1.5 (100 mW/cm<sup>2</sup>).  $\text{TiO}_2$  film thickness and active area were 7  $\mu\text{m}$  and 0.25 cm<sup>2</sup>, respectively.

Download English Version:

<https://daneshyari.com/en/article/183245>

Download Persian Version:

<https://daneshyari.com/article/183245>

[Daneshyari.com](https://daneshyari.com)