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Phosphonium iodide as a donor liquid electrolyte for dye-sensitized solar cells

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Abstract: An efficient triphenylmethylphosphonium iodide-based liquid electrolyte was synthesized and used for the first time as an electrolyte in dye-sensitized solar cells (DSSCs). With the as-synthesized electrolyte, the DSSC yielded an overall light to electricity conversion efficiency of 5.34 to 7.10 %, when the radiant power was tuned from 100 to 10 mW cm⁻². This may be attributed to the limitation of mass transport in the DSSC. The electronic and ionic processes in the DSSC were investigated by electrochemical impedance spectroscopy and linear voltammography, respectively.

Keywords: dye-sensitized solar cells; triphenylmethylphosphonium iodide; mass transport; conversion efficiency.

INTRODUCTION

Dye-sensitized solar cells (DSSCs), which are usually composed of an interconnected nanocrystalline TiO₂ electrode anchored with photosensitizers, a liquid electrolyte typically containing I₃⁻/I⁻ as the redox couple and a Pt counter electrode,¹ have drawn much interest in the past decade. This kind of DSSCs were considered as potential high-efficient and low-cost alternatives to conventional inorganic photovoltaic modules.² Their photovoltage is determined by the difference between the Fermi level of the TiO₂ electrode under illumination and the Nernst potential of I₃⁻/I⁻ in the electrolyte.³ It was concluded that tuning the composition of the electrolyte enhances the open-circuit voltage. Meanwhile, the properties (conductivity, viscosity, *etc.*) of the electrolyte are believed to play a role in the photovoltaic performance of DSSCs by affecting the kinetics of electronic and ionic processes.^{4,5} The designing and preparation of a suitable electrolyte component iodide is critically necessary to improve the performance of DSSCs.

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Recently, imidazolium salt-based electrolytes were successfully applied to dye-sensitized solar cells,^{2,4–7} and sulfonium salts also showed potential application as electrolytes in DSSCs.⁸ However, phosphonium salts as electrolytes for DSSCs have received limited attention, even though they have been used in supercapacitors.⁹ There has only been one paper reporting phosphonium salts, excluding triphenylmethylphosphonium iodide, as electrolytes in DSSCs, and the highest light to electricity conversion efficiency under a light intensity of 8.9 mW cm^{-2} was 5.7%.¹⁰ Furthermore, it was found that triphenylmethylphosphonium iodide was more air-stable than the expensive and water-sensitive LiI,¹¹ which is mostly used in DSSCs. Herein, triphenylmethylphosphonium iodide (TPMI) was synthesized and used for the first time in the electrolyte for DSSCs. Electric impedance spectroscopy was used to investigate the ionic and electronic processes in the DSSC under varied light intensities.

EXPERIMENTAL

Triphenylmethylphosphonium iodide (TPMI) was synthesized according to a literature method.^{12–14} Briefly, a solution of triphenylphosphine (PhP3) (19 mmol, 5.0 g) in dry tetrahydrofuran (THF) was added dropwise to a solution of CH_3I (20 mmol, 2.9 g) in dry THF at room temperature. The reaction mixture was stirred for 12 h and filtered. The white precipitate was then rinsed with dry THF and recrystallized from ethanol/ether. $^1\text{H-NMR}$ (300 MHz; CCl_3D , δ / ppm): 7.61–7.86 (15H, *m*), 1.24 (3H, *m*). The as-synthesized TPMI at a concentration of 0.5 M together with 0.05 M I_2 and 0.6 M 4-*tert*-butylpyridine (TBP) in acetonitrile was used as the electrolyte for the DSSCs.

A mesoporous TiO_2 electrode was prepared by depositing a paste containing TiO_2 nanoparticles (P25, Degussa) and ethyl cellulose in terpineol onto a conducting glass substrate (F-doped SnO_2 , FTO) using a screen-printing technique. The coated substrate was sintered at 450°C in air for 0.5 h. Then, the sintered porous thin film with a thickness of *ca.* $12 \mu\text{m}$ was immersed into a 3×10^{-4} M solution of the dye *cis*-dithiocyanate-*N,N'*-bis(4,4'-dicarboxylate-2,2'-bipyridine) ruthenium(II) (N3) in dry ethanol for about 12 h, after which the dye-anchored film was rinsed with dry ethanol. A platinized counter electrode was prepared by spin-coating an H_2PtCl_6 solution (50 mM in 2-propanol) onto FTO glass and sintering at 390°C for 0.5 h. A sandwich-type solar cell was fabricated by clamping the $\text{TiO}_2/\text{N3}/\text{electrolyte}$ with a counter electrode with two clips. The active electrode area was 0.16 cm^2 .

The electrochemical impedance spectra (EIS) and linear sweep voltammograms were both obtained with an AutoLab model PGSTAT 30 potentiostat. The EIS was obtained in the frequency range of 0.1 Hz to 10^6 Hz with an AC amplitude of 5 mV. Linear sweep voltammograms of symmetric electrochemical cells consisting of two identical platinized FTO separated by Scotch tape of $45 \mu\text{m}$ were used to estimate the apparent diffusion coefficient of I_3^- in the electrolytes of TPMI in acetonitrile. The photovoltaic performance of the DSSC was measured with a Keithley 2400 digital source meter controlled by a computer and a 500 W xenon lamp as the light source to give simulated AM 1.5 irradiation.

RESULTS AND DISCUSSION

The photocurrent-voltage curves of a DSSC employing the N3 dye and the TPMI-based electrolyte under different light intensities are shown in Fig. 1. The

photovoltaic performance parameters under different radiant power are listed in Table I. The highest conversion efficiency of 7.10 % was obtained at a moderate radiant power of 10 mW cm^{-2} . This is the highest efficiency that has been achieved so far for DSSCs under moderate power irradiation with phosphonium salts as the electrolyte. When the light intensity was increased to 100 mW cm^{-2} , the overall energy conversion efficiency was 5.34 %. The reduction of conversion efficiencies with increasing light intensity is related to limitation in the mass transport of triiodide ions between the electrodes in DSSCs.¹⁵

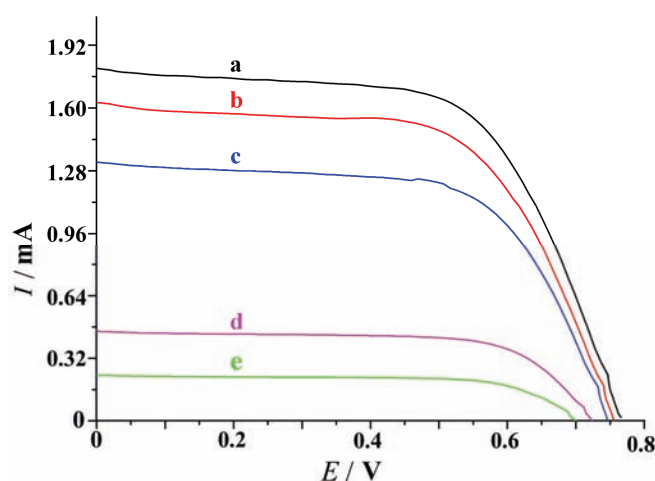


Fig. 1. Photocurrent–voltage characteristics of the DSSC under varied light intensities (AM 1.5): a) 100; b) 80; c) 60; d) 20; e) 10 mW cm^{-2} .

The electric impedance spectra of a DSSC measured at open circuit voltage (-0.75 V) with and without irradiation in the frequency range $0.1\text{--}10^6 \text{ Hz}$ are presented in Fig. 2. The three semicircles in the high frequency, intermediate and low frequency regions in each impedance spectrum of Fig. 3 can be assigned to the impedance of charge transfer at the Pt/electrolyte interface (Z_1), electron transfer occurring at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (Z_2), and Nernst diffusion within the electrolyte (Z_3), respectively. The charge-transfer resistance Z_1 in the dark and at 40 mW cm^{-2} were both less than $10 \Omega \text{ cm}^2$, indicating a good catalytic performance of the Pt counter electrodes for the reduction of triiodide ions. The impedance Z_2 , characterizing electron transfer from the conduction band of the mesoscopic TiO_2 film to triiodide ions in the electrolyte, was much smaller at 40 mW cm^{-2} than that in the dark even though the potential of the film was the same. The smaller is the impedance Z_2 , the faster is electron recombination under irradiation, which can reduce the efficiency of electron injection from the sensitizer N3 to the conduction band of TiO_2 .⁴ In comparison with the internal resis-

tance of the DSSC,¹⁶ the Warburg diffusion impedance Z_3 can be neglected. In addition, the impedance over 10^6 Hz cannot be measured due to instrumental limitations. The resistances R_s with and without irradiation in the high frequency range $>10^6$ Hz due to the resistance of electrolyte and sheet resistance of FTO were almost the same in Fig. 3, which confirms that R_s was dominated by the sheet resistance of FTO. From Fig. 3 and Table I, it may be proposed that fast electron recombination in the DSSC with irradiation is detrimental to the power conversion efficiency.

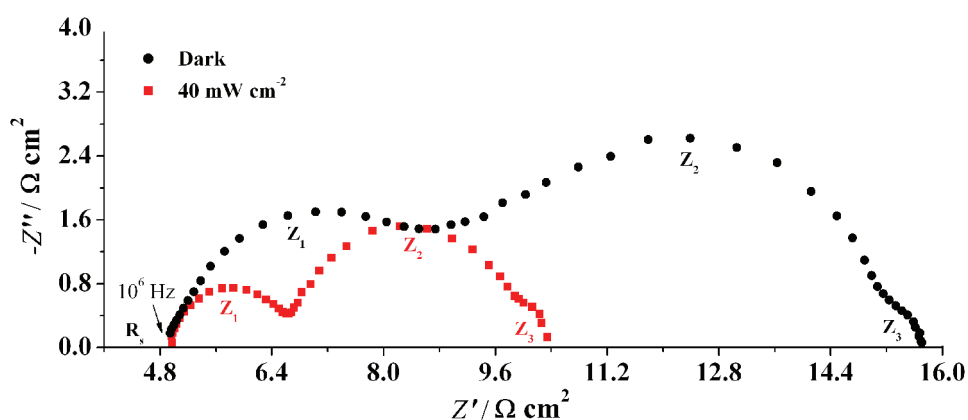


Fig. 2. Electrochemical impedance spectra of a DSSC. Z_1 , Z_2 and Z_3 correspond to the frequency regions: $10^6 - 470$ Hz, $470 - 1.7$ Hz and $1.7 - 0.1$ Hz, respectively, at -0.75 V and 40 mW cm^{-2} (■) and in the dark (●).

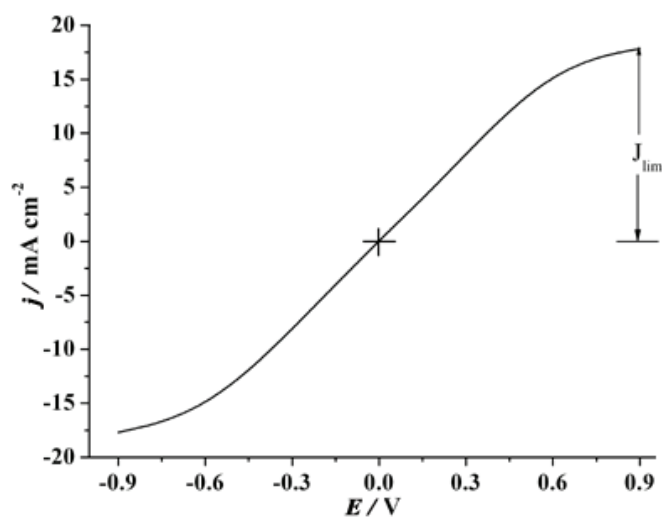


Fig. 3. Characteristic voltammogram for the symmetrical electrochemical cells. Scan rate: 10 mV s^{-1} .

TABLE I. Photovoltaic performance of the DSSC with TPMI-based electrolyte under various irradiation powers (AM 1.5), P , incident power; V_{oc} , open circuit voltage; j_{sc} , short circuit current density; η , power conversion efficiency

$P / \text{mW cm}^{-2}$	V_{oc} / mV	$j_{sc} / \text{mA cm}^{-2}$	FF	$\eta / \%$
10	700.9	1.4	0.69	7.10
20	724.5	2.9	0.68	7.09
60	747.5	8.3	0.63	6.52
80	755.9	10.3	0.61	5.94
100	765.5	11.3	0.62	5.34

In order to further elucidate the mass transport in the DSSC, a symmetric FTO/Pt/electrolyte/Pt/FTO electrochemical cell was employed to determine the apparent diffusion coefficient of triiodide, which was considered as the current-limiting species due to their lower concentration in the electrolyte (the molar ratio of I^- to I_3^- is 1:10). The characteristic linear sweep voltammetry curve of the TPMI based electrolyte is presented in Fig. 3. The resemblance between the anodic and cathodic limiting current plateaus indicates steady-state conditions. The apparent diffusion coefficient (D_{app}) of triiodides can be calculated from the limiting current densities according to the equation, $J_{lim} = 2nFC_0D_{app}/d$,¹⁷ where $n = 2$ is the electron-transfer number required for the reduction of triiodide to iodide, F is the Faraday constant, C_0 the bulk concentration of triiodide ions and d the thickness of the cell. From the data shown in Fig. 3, the diffusion coefficient of triiodide in the TPMI based electrolyte at room temperature was determined to be about $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is roughly half of that of the LiI electrolyte in acetonitrile giving a larger current density of 16.8 mA cm^{-2} .^{18,19} This sheds light on the cause of the smaller current density of 11.3 mA cm^{-2} in the DSSC based on TPMI liquid electrolyte and, consequently, the relatively low power conversion efficiency of 5.34 % at 100 mW cm^{-2} , AM 1.5.

CONCLUSIONS

In conclusion, triphenylmethylphosphonium iodide as an I^- donor in acetonitrile was for the first time used in a DSSC and the energy conversion efficiency at 10 mW cm^{-2} (AM 1.5) was up to 7.10 %. The ionic and electronic processes in the DSSC were investigated *via* electric impedance spectroscopy and cyclic voltammogram. It was found that the rapid electron recombination at high intensities of irradiation was detrimental to the power conversion efficiency. The short-circuit current densities at high intensity irradiation were related to the mass transport of I_3^- , which has a diffusion coefficient of $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This is valuable information for the design and improvement of the electrolyte components for DSSCs.

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ИЗВОД
 ФОСФОНИЈУМ-ЈОДИД КАО ДОНОР У ТЕЧНОМ ЕЛЕКТРОЛИТУ
 ЗА СОЛАРНЕ ЋЕЛИЈЕ СЕНЗИБИЛИСАНЕ БОЈОМ

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Синтетисан је ефикасан течан електролит на бази трифенилметилфосфонијум-јодида и по први пут је коришћен као електролит за соларне ћелије сензибилисане бојом. Са овим електролитом соларна ћелија је показала укупан степен конверзије светлосне енергије у електричну између 5,34 и 7,10 %, при снази зрачења у опсегу од 100 до 10 mW cm⁻². Овај резултат се може приписати ограничењима у преносу масе у соларној ћелији. Електронски и јонски процеси у соларној ћелији су испитивани спектроскопијом електрохемијске импеданције и линеарном волтаметријом, респективно.

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