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Quaternary ammonium polyiodides as ionic liquid/soft solid electrolytes in dye-sensitized solar cells

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Abstract

Four new quaternary ammonium iodides, $(Me_2Pe_2N)I$, $(Me_2Hex_2N)I$, $(Et_2Pe_2N)I$ and $(Et_2Hex_2N)I$, were synthesized and studied as electrolytes in dye-sensitized solar cells. All compounds were solids at room temperature. Influence of varying amounts of elemental iodine and the effect of *tert*-butylpyridine (TBP) on the performance of the cell was also studied. Addition of iodine lowered the melting points of the resulting polyiodides. From the ammonium iodides only $(Me_2Hex_2N)I:I_2$ (10:1) was liquid at the room temperature and the others were soft solids. Under illumination from a halogen lamp source at 10 mW cm^{-2} intensity, the highest power conversion efficiency of 2.4% was obtained with the $(Me_2Hex_2N)I:I_2$ (10:1) liquid electrolyte containing TBP, which may be compared to an efficiency of 5.4% obtained from similar cells with traditional 3-methoxypropionitrile based electrolyte tested under identical conditions. The best efficiency with soft solid electrolyte, $(Et_2Hex_2N)I:I_2$ (10:1) with TBP, was 2.3%.

Keywords: Dye-sensitized solar cell; Ionic liquid; Quaternary ammonium iodide; Polyiodide

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention over the past decade since they have been reported to have a high light into electricity conversion efficiency (up to 11%) [1,2] and potential for low-cost production [3–6]. Typical DSSC consists of two conductive transparent glasses, ruthenium dye-sensitized TiO_2 film, a platinum catalyst layer and a liquid electrolyte containing I^-/I_3^- redox couple. Best efficiencies for the cells were obtained by using organic liquid electrolytes. Due to the high vapour pressure of these solvents leakage of electrolyte becomes a problem and thus several attempts have been made to replace it. Ionic liquids [7–13], nanocomposites [14–17], polymer gels [18–28] and solid-state materials [29–37] have been introduced to replace the organic liquid electrolytes. Wang et al. [12] have tested the low-viscosity solvent-free 1-ethyl-3-methylimidazolium selenocyanate as pure ionic liquid electrolyte in DSSC and reached a power conversion efficiency of 7.5% in full sunlight. The same group has introduced photochemically and electrochemically stable nanocomposite gel electrolyte based on silica nanoparticles solidifying imidazolium-based ionic liquid electrolyte yield an efficiency of 7.0% [14]. Gelators of low-molecular-weight compounds have both good solubility upon heating and they produce smooth gelation of organic liquids at quite low concentrations. Conductivity in these electrolytes is not significantly reduced by the gelation process. Komiya et al. [28] have used an oligomer [poly(ethylene oxide-*co*-propylene oxide) trimethacrylate] having three polymerizable reactive groups as ion conducting polymer gel electrolyte. By using this stable oligomer a three-dimensional network structure has been formed and the cell performance of 8.1% was achieved. Compared to solar cells with ionic liquids, nanocomposites and polymer gels, somewhat lower efficiencies have been obtained when all-solid-state electrolytes were used. Efficiency of 5.0% has been reached by using *N*-methyl-*N*-butylpyrrolidinium iodide doped succinonitrile plastic crystal electrolyte in DSSC [36].

In this paper we report a study of new quaternary $R_2R'_2N^+I^-$ ammonium iodides (R = methyl or ethyl and R′ = pentyl or hexyl) with iodine and TBP as ionic liquid/soft solid electrolytes in DSSC.

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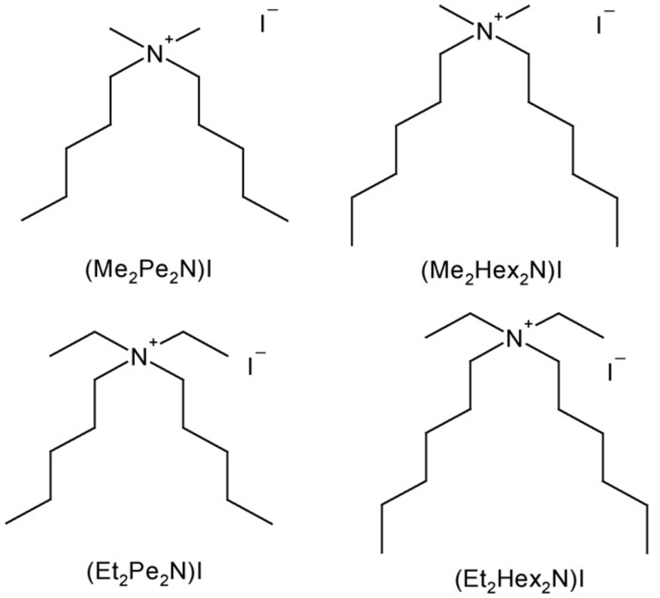

Scheme 1. Molecular structures of the synthesized quaternary ammonium iodides.

2. Experimental

2.1. Synthesis

Quaternary ammonium iodides, $(R_2R'_2N^+)I^-$, were synthesized by using a synthetic route where dimethylformamide (R = methyl) or diethylformamide (R = ethyl) is treated with pentyliodide or hexyliodide (R′ = pentyl or hexyl) in the presence of potassium carbonate [38]. As a result, dimethyldipentylammonium iodide $(Me_2Pe_2N)I$, dimethyldihexylammonium iodide $(Me_2Hex_2N)I$, diethyldipentylammonium iodide $(Et_2Pe_2N)I$ and diethyldihexylammonium iodide $(Et_2Hex_2N)I$ (Scheme 1) were obtained. All reactants and other chemicals are commercially available and were used as received.

All the reagents were placed in the reaction flask. The reaction mixture was stirred at 80 °C temperature for 72 h. After cooling down to RT the mixture was filtered and the filtrate was evaporated. Evaporation of filtrate gave the raw product as a white or yellow powder. The product was extracted by dissolving it to dichloromethane and the final product was obtained by evaporation of the filtrate. The powder was dried in vacuum over night. All compounds were solids at room temperature.

2.2. Characterization of the electrolytes

The elemental analyses were carried out with Vario EL III CHN elemental analyser by using sample weights of 3–7 mg. The thermal properties of the compounds (especially the melting points of the quaternary ammonium iodides and polyiodides after the addition of the iodine) were examined with a Perkin-Elmer PYRIS 1 differential scanning calorimetry (DSC). The measurements were carried out (under nitrogen atmosphere with flow rate of 50 ml/min) using 50 μl sealed aluminium sample pans with pinholes. The temperature calibration was made using three standard materials (*n*-decane, In, Zn) and the energy calibration by using an indium standard. The samples were heated at a rate of 10 °C/min from −50 °C up to the temperature of 110 °C. The sample weights used in the measurements were about 3–6 mg.

2.3. Preparation of the dye-sensitized solar cell

Dye-sensitized TiO_2 films were made on conductive glass substrate (F-doped SnO_2, 15 Ω/sq). The films were spread from anatase TiO_2 paste (Solaronix SA) by doctor-blading technique and an adhesive tape as a frame. After spreading, the film was left to dry in air for few minutes and heated at ~450 °C for 30 min. A second TiO_2 layer was prepared similarly on top of the first layer to obtain a film thickness about 10 μm. The heated films were cooled down to ~80 °C and then immersed in a 0.3 mM ruthenium 535-bis TBA (Solaronix) solution (solvent: *tert*-butanol and acetonitrile, 1:1 vol%) overnight for dye-sensitization. Sensitized films were rinsed with acetonitrile prior cell assembly.

Counter electrode was made by spraying 5 mM H_2PtCl_6 (Aldrich) in 2-propanol onto heated (80 °C) conducting glass substrate (F-doped SnO_2, 8 Ω/sq) followed by heating in an oven for 15 min while the temperature increased from room temperature to 385 °C and then held at 385 °C for 10 min [39].

The polyiodide salts were prepared by adding the iodine to the quaternary ammonium iodides in the following iodide:iodine

Table 1
The quaternary ammonium iodides and polyiodides used as electrolytes in dye-sensitized solar cells, their melting point (presented as peak maximum value) and the appearance at room temperature

Sample	Ratio of iodine	Melting point [°C]	Appearance at RT
$(Me_2Pe_2N)I$		90.5 (Peak onset 86.4)	White powder
$(Me_2Hex_2N)I$		51.6 (Peak onset 45.1)	White sticky powder
$(Et_2Pe_2N)I$		98.8 (Peak onset 94.8)	Light yellow powder
$(Et_2Hex_2N)I$		78.4 (Peak onset 72.6)	Light yellow powder
$(Me_2Pe_2N)I:I_2$	10:1	39.7	Dark gray solid
$(Me_2Hex_2N)I:I_2$	10:1	[a]	Dark reddish brown liquid
$(Et_2Pe_2N)I:I_2$	10:1	61.7	Soft dark gray solid
$(Et_2Hex_2N)I:I_2$	10:1	63.7	Brown solid
$(Et_2Hex_2N)I:I_2$	50:1	69.6	Yellowish brown solid
$(Et_2Hex_2N)I:I_2$	100:1	70.5	Light yellowish brown solid

[a] Liquid in the measured temperature range from −50 °C to 110 °C.

weight ratios of 1:1, 5:1, 10:1, 50:1 and 100:1 and then heated to the melting point of the appropriate quaternary ammonium iodide (Table 1) for mixing the iodide salt and the added iodine. After mixing the electrolyte was cooled down to the room temperature. *Tert*-butylpyridine (TBP) was added to some of the electrolytes so that the concentration of TBP was 0.5 M. A hot-melt polymer foil (Surlyn 1702, DuPont) was used as a spacer frame between the electrodes. The empty volume between electrodes was filled with an electrolyte and pressed together with clamps. Finally, a silver paste was added on clean areas of conducting glass to enhance conductivity and to ensure good contact during measurements. Fabricated DSSCs had surface area of 0.8–1.0 cm^2.

Calibrated mono-Si reference solar cell with KG3 filter was used to adjust the illumination. Samples were illuminated with a halogen lamp (Solux) source at ca. 10 mW cm^{-2} intensity. No mask was used around the photoactive area, the dye-TiO_2 film, or the reference solar cell in measurements. Current–voltage curves were measured by using a Keithley 2400 source measurement unit with LabView 6.1 software.

3. Results and discussion

3.1. Characterization of the electrolytes

Studied quaternary ammonium iodides had melting point below 100 °C and therefore they are classified as ionic liquids [40–44]. However, none of them are liquid at room temperature. Addition of elemental iodine (I_2) clearly lowered the melting point of the resulting polyiodide electrolytes. The properties of the quaternary ammonium iodides and polyiodides are shown in Table 1. One of the polyiodides proved to be liquid at room temperature [$(Me_2Hex_2N)I:I_2$ (10:1)] and the rest of the polyiodides were soft solids having iodide:iodine ratio of 10:1. However, their melting points also remained very close to room temperature, as can be seen from the differential scanning calorimetry measurements. The low melting points could have also been expected from their soft nature at room temperature.

The elemental analyses were performed for all ammonium iodides and polyiodides to confirm the purity of the iodide salts and to estimate the correctness of the mixing ratio between the iodide salt and the pure iodine (Table 2). The experimental and calculated values of elemental analysis are in good agreement with each other indicating the excellent purity of the quaternary ammonium iodides and the successful mixing of the iodine with the ammonium iodides.

Table 2
The results of the elemental analysis

Sample	Ratio of iodine	C_{exp}	C_{calc}	H_{exp}	H_{calc}	N_{exp}	N_{calc}
$(Me_2Pe_2N)I$		45.9	46.0	9.1	9.0	4.4	4.5
$(Me_2Hex_2N)I$		49.6	49.3	9.7	9.5	4.0	4.1
$(Et_2Pe_2N)I$		49.0	49.3	9.6	9.5	4.0	4.1
$(Et_2Hex_2N)I$		51.7	52.0	9.9	9.8	3.8	3.8
$(Me_2Pe_2N)I:I_2$	10:1	42.3	41.8	8.4	8.2	3.9	4.1
$(Me_2Hex_2N)I:I_2$	10:1	45.6	44.8	8.7	8.6	3.8	3.7
$(Et_2Pe_2N)I:I_2$	10:1	43.8	44.8	8.3	8.6	3.6	3.7
$(Et_2Hex_2N)I:I_2$	10:1	48.0	47.3	9.2	8.9	3.4	3.5
$(Et_2Hex_2N)I:I_2$	50:1	50.5	49.6	9.6	9.4	3.6	3.6
$(Et_2Hex_2N)I:I_2$	100:1	51.8	51.5	9.9	9.7	3.6	3.8

3.2. Performance of electrolytes in dye-sensitized solar cells

The influence of addition of TBP in the $(Me_2Hex_2N)I:I_2$ and $(Et_2Hex_2N)I:I_2$ electrolytes (iodide:iodine ratio of 10:1) to concentration of 0.5 M of TBP was studied first. Addition of a small amount (~70 μl/ml) of TBP in the electrolyte had no observable effect on composition of electrolyte. Characteristic parameters (FF, V_{OC}, I_{SC} and η) of these cells are listed in Table 3. In all cases TBP improved photocurrent, voltage and solar cell efficiency. TBP has been widely used as an additive in conventional organic liquid electrolytes since it increases the open-circuit voltage (V_{OC}) in DSSC [4,45]. After addition of TBP for cells containing the $(Me_2Hex_2N)I:I_2$ electrolyte, which was liquid at room temperature, the efficiency improved from 1.7% to 2.4%. For soft solid $(Et_2Hex_2N)I:I_2$ electrolyte the efficiency improved from 2.1% to 2.3%.

The efficiency of the solar cell as a function of iodine concentration in the electrolyte was also studied. Electrolytes with different iodide:iodine weight ratios of 1:1, 5:1, 10:1, 50:1 and 100:1 of $(Et_2Hex_2N)I:I_2$ were prepared and used as an electrolyte in the DSSC. Results are summarized in Table 4.

The best solar cell efficiency (2.3%) was achieved by having iodide:iodine ratio of 10:1 in $(Et_2Hex_2N)I$ ionic liquid. Clearly lower efficiencies were obtained with iodide:iodine ratios of 5:1, 50:1 and 100:1. The efficiency decreased to almost zero 1:1 ratio of iodine and ionic liquid. The addition of iodine increases the photocurrent rapidly until maximum is reached. Further addition of iodine reduces photocurrent [46] (Table 4). As iodide:iodine ratio 10:1 showed the best performance it was used to compare performances of different quaternary ammonium iodide electrolytes (see chapters below).

Table 3
The influence of TBP addition to the solar cell parameters[a] in $(Me_2Hex_2N)I:I_2$ and $(Et_2Hex_2N)I:I_2$ electrolytes

Electrolyte	TBP [M]	FF [%]	V_{OC} [V]	I_{SC} [mA cm^{-2}]	Efficiency [%]
$(Me_2Hex_2N)I:I_2$	0.5	49	0.60	0.80	2.4
$(Me_2Hex_2N)I:I_2$	–	45	0.56	0.65	1.7
$(Et_2Hex_2N)I:I_2$	0.5	43	0.62	0.86	2.3
$(Et_2Hex_2N)I:I_2$	–	49	0.56	0.77	2.1

Both electrolytes contained iodide:iodine weight ratio of 10:1.

[a] Measurements were made using a halogen lamp illumination source at ca. 10 mW cm^{-2}.

Table 4
The effect on the solar cell performance[a] with different amount of iodine in (Et$_2$Hex$_2$N)I electrolyte containing TBP

Electrolyte	Salt–iodine ratio	FF [%]	V_{OC} [V]	I_{SC} [mA cm^{-2}]	Efficiency [%]
(Et$_2$Hex$_2$N)I:I$_2$	1:1	0.8	0.03	0.00	0.0
(Et$_2$Hex$_2$N)I:I$_2$	5:1	35	0.51	0.49	0.7
(Et$_2$Hex$_2$N)I:I$_2$	10:1	43	0.62	0.86	2.3
(Et$_2$Hex$_2$N)I:I$_2$	50:1	46	0.60	0.64	1.8
(Et$_2$Hex$_2$N)I:I$_2$	100:1	45	0.61	0.47	1.3

[a] Measurements were made using a halogen lamp illumination source at ca. 10 mW cm^{-2}.

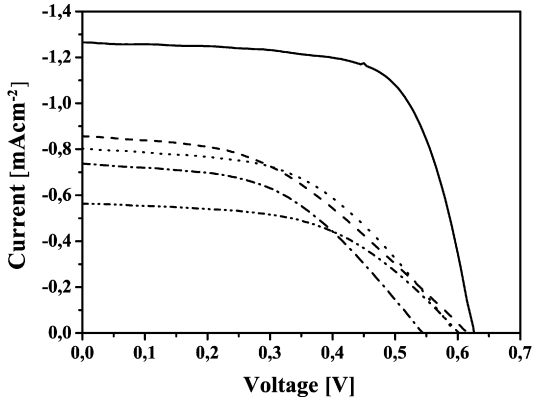

Fig. 1. Current–voltage curves of dye-sensitized solar cells with different electrolytes: Organic liquid based reference (—), (Et$_2$Hex$_2$N)I:I$_2$ (- - -), (Me$_2$Hex$_2$N)I:I$_2$ (· · ·), (Me$_2$Pe$_2$N)I:I$_2$ (- · · -) and (Et$_2$Pe$_2$N)I:I$_2$ (- · · · -). All quaternary ammonium polyiodide electrolytes contained iodide:iodine ratio of 10:1 (weight ratio) and TBP. Measurements were made using a halogen lamp illumination source at ca. 10 mW cm^{-2}.

Also other quaternary ammonium iodides (Me$_2$Pe$_2$N)I, (Me$_2$Hex$_2$N)I and (Et$_2$Pe$_2$N)I were used as electrolytes with salt–iodine ratio of 10:1 and TBP in dye-sensitized solar cells. The current–voltage curves of the cells containing (Me$_2$Pe$_2$N)I:I$_2$, (Me$_2$Hex$_2$N)I:I$_2$, (Et$_2$Pe$_2$N)I:I$_2$ and (Et$_2$Hex$_2$N)I:I$_2$ electrolytes are shown in Fig. 1 and characteristics of the cells (FF, V_{OC}, I_{SC} and η) are listed in Table 5. The best efficiency of 2.4% was achieved by using the electrolyte which was liquid at room temperature, (Me$_2$Hex$_2$N)I:I$_2$ electrolyte (see Table 1). From the soft solid electrolytes (Et$_2$Hex$_2$N)I:I$_2$ showed the best efficiency (2.3%). As seen in Table 5, the length of hydrocarbon chain in ammonium iodides has also an effect on performance in DSSCs. Hexyl-substituted ammonium iodides (Me$_2$Hex$_2$N)I:I$_2$ and (Et$_2$Hex$_2$N)I:I$_2$ exhibited clearly better efficiencies (2.4% and 2.3%) than pentyl-substituted ammonium iodides (Me$_2$Pe$_2$N)I:I$_2$ and (Et$_2$Pe$_2$N)I:I$_2$ (1.9% and 1.8%). All studied quaternary ammonium polyiodide electrolytes were compared with the liquid based electrolyte consisting of 0.1 M LiI, 0.05 M I$_2$, 0.3 M TBP, 0.5 M 1-hexyl-3-methylimidazolium iodide (HMII was synthesized according to ref. [47]) in 3-methoxypropionitrile.

Table 5
Characteristics of DSSC[a] with different ionic liquid electrolytes

Electrolyte	FF [%]	V_{OC} [V]	I_{SC} [mA cm^{-2}]	Efficiency [%]
Reference	68	0.63	1.27	5.4
(Me$_2$Hex$_2$N)I:I$_2$	49	0.60	0.80	2.4
(Et$_2$Hex$_2$N)I:I$_2$	43	0.62	0.86	2.3
(Me$_2$Pe$_2$N)I:I$_2$	48	0.55	0.74	1.9
(Et$_2$Pe$_2$N)I:I$_2$	52	0.61	0.56	1.8

All quaternary ammonium polyiodides contained iodide:iodine ratio of 10:1 and TBP.

[a] Measurements were made using a halogen lamp illumination source at ca. 10 mW cm^{-2}.

4. Conclusions

Four new quaternary R$_2$R$'_2$N$^+$I$^-$ ammonium iodides were studied as ionic liquid/soft solid electrolytes in dye-sensitized solar cell. All synthesized ammonium iodide compounds were solids at room temperature. Addition of iodine lowered the melting point of the resulting electrolytes. The (Me$_2$Hex$_2$N)I:I$_2$ (10:1) electrolyte proved to be liquid at room temperature, the rest showed melting points near room temperature. Addition of *tert*-butylpyridine clearly improved the solar cell performance and the best efficiency 2.4% was obtained with the (Me$_2$Hex$_2$N)I:I$_2$ electrolyte under illumination from a halogen lamp source at 10 mW cm^{-2}. From the soft solid electrolytes, (Et$_2$Hex$_2$N)I:I$_2$ showed the best efficiency, 2.3%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.07.008.

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