Alkylpyrrolidiniumtrialkoxysilyl iodides as organic iodide sources for dye-sensitised solar cells

Naomi A. Lewcenko,[a] Matthew J. Byrnes,[a] Yi-Bing Cheng,[b] Shaik M. Zakeeruddin,[c] Michael Grätzel*[c] and Leone Spiccia*[a]

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Two new alkylpyrrolidiniumtriethoxysilyl iodides have been developed as iodide sources for DSSCs; the compound with an undecyl spacer between the siloxane and the pyrrolidinium moieties furnished higher open circuit voltages than the propyl analogue and higher efficiencies at low light intensity.

Dye-sensitised solar cells (DSSCs) have been an intensively investigated renewable energy technology since their initial report in 1991 by O'Regan and Grätzel.[1] The design of the DSSC is a relatively simple one, consisting of a high band-gap semiconductor material, coated with a mono-layer of a highly absorbent dye which injects electrons into the semiconductor following irradiation with light. The electrons pass through conductive glass to the counter electrode, reducing a redox couple which then regenerates the oxidised dye, thereby completing the circuit. A large body of research has been reported relating to the effects that each component has on the device. In particular, the variation in DSSC performance with different semiconductors, dyes, redox couples and electrolytes has been widely studied.

Due to its intimate relationship with every part of the cell, the electrolyte is one of the most influential components of DSSCs. It comes as no surprise to discover that changing the composition of the electrolyte has significant ramifications for cell performance. For example, cell performance can be affected by the interaction of cations present in the electrolyte with the surface of the titania. Lithium ions have been shown to decrease the open circuit voltage (V_{oc}) while increasing the short circuit current (J_{sc}) because Li^+–titania interactions lead to a lower conduction band potential (CBP).[2–7] Electrolyte cations have also been shown to influence the kinetics of cell degradation,[8,9] and to play an important role in the electron lifetimes of the device.[4,10–12] Moreover, the cation is capable of interacting with the sensitiser, resulting in a bathochromic shift in the spectrum of the bound dye.[13] These studies have demonstrated the instrumental role that cations play in the performance of the cell, and as such, the development of new types of cations for DSSCs is an important avenue of research.

Previous investigations with larger cations have focussed on the planar and aromatic imidazolium cation[14–21] and on bulkier tetraalkylammonium cations.[6,11] We recently prepared a series of alkylammoniumtriethoxysilyl iodides, of which **1** and **2** (Fig. 1) functioned as efficient iodide sources in DSSCs.[22] Cells constructed with **1** and **2** in the electrolytes showed reasonably high open circuit voltages (V_{oc}) and short circuit currents (J_{sc}) with good overall efficiencies, especially at low sunlight levels. These siloxanes were used to prepare hybrid organic–inorganic iodide sources for use in DSSCs.[23]

These promising results stimulated our interest in new types of organic iodide sources for DSSCs and, with this objective in mind, two new organic iodides, **3** and **4**, have been developed. To gain insight into the effects of these compounds on the performance of the DSSCs, two disparate length alkyl spacers (undecyl (C11) *vs.* propyl (C3)) were incorporated to provide a contrast between the two cations.

The synthesis of compounds **3** and **4** was adapted from procedures used to prepare related compounds,[24–27] and full synthetic details will be included in a subsequent publication.

The results of DSSC testing using the new iodide sources under standard testing conditions are summarised in Table 1. The iodide sources were first tested at 1.0 M concentration. The results obtained in MPN (methoxypropionitrile) indicated that, although the V_{oc} values are considerably higher for the cells made using the undecyl derivative **4**, the lower J_{sc} values coupled with lower fill factors result in poor overall efficiencies compared to the propyl analogue **3** at all light intensities. Changing the solvent to a 3 : 1 mixture of acetonitrile : valeronitrile (denoted ACN) yielded similar device efficiencies at 0.1 Sun. At higher light intensities, however, even when using ACN, poorer fill factors for **4** led to poorer efficiencies in spite of the higher potentials and similar short circuit current.

It became apparent that **4** showed great promise in terms of the larger V_{oc} but that the poor fill factors needed addressing. Consequently, the organic iodide concentration was decreased to 0.6 M, closer to that in standard electrolytes and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) was added to assist charge transport. As can be gleaned from Table 1, for **3** in ACN, the optimised electrolyte resulted in

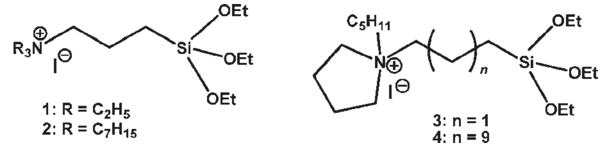

Fig. 1 Structures of the alkylammoniumtrialkoxysilyl iodides, **1** and **2**, and the new pyrrolidinium iodides, **3** and **4**.

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[a] School of Chemistry, Monash University, Victoria 3800, Australia. E-mail: leone.spiccia@sci.monash.edu.au; Fax: +61 3 9905 4597
[b] School of Engineering, Monash University, Victoria 3800, Australia
[c] Laboratory for Photonics & Interfaces, EPFL, CH1015 Lausanne, Switzerland. E-mail: michael.graetzel@epfl.ch; Fax: +41 2 1693 6100

Table 1 Summary of the photovoltaic performance of **3** and **4**[a]

Electrolyte	Sun intensity	V_{oc}/mV	J_{sc}/mA cm^{-2}	FF	% η
3MPN 1.0	0.1	644	1.5	0.73	7.4
	0.5	685	7.8	0.61	5.7
	1.0	699	13.9	0.52	5.0
4MPN 1.0	0.1	724	1.2	0.63	5.8
	0.5	758	6.0	0.48	4.6
	1.0	769	10.5	0.39	3.1
3ACN 1.0	0.1	677	1.5	0.74	8.0
	0.5	720	7.9	0.64	6.9
	1.0	735	14.2	0.54	5.7
4ACN 1.0	0.1	713	1.5	0.70	8.0
	0.5	754	8.0	0.52	6.0
	1.0	768	14.5	0.39	4.3
3MPN 0.6	0.1	671	1.4	0.75	7.4
	0.5	709	7.2	0.66	6.4
	1.0	723	12.4	0.60	5.4
4MPN 0.6	0.1	702	1.3	0.76	7.5
	0.5	745	6.7	0.68	6.4
	1.0	759	11.0	0.63	5.2
3ACN 0.6	0.1	703	1.4	0.79	8.0
	0.5	751	7.2	0.73	7.5
	1.0	768	13.1	0.69	6.9
4ACN 0.6	0.1	745	1.5	0.75	8.5
	0.5	790	7.7	0.68	7.9
	1.0	806	13.9	0.62	7.0
PMII 0.6	0.1	814	1.13	0.80	7.8
	0.5	864	6.21	0.78	7.9
	1.0	881	11.52	0.76	7.7

[a] **3MPN** or **4MPN 1.0**: 1.0 M **3** or **4**, 0.15 M I_2, 0.50 M *N*-butylbenzimidazole in 3-methoxypropionitrile (MPN). **3ACN** or **4ACN 1.0**: 1.0 M **3** or **4**, 0.03 M I_2, 0.50 M *tert*-butylpyridine in 3 : 1 acetonitrile–valeronitrile, (ACN : VN). **3MPN** or **4MPN 0.6**: 0.60 M **3** or **4**, 0.15 M I_2, 0.50 M *N*-butylbenzimidazole, 0.25 M EMITFSI in MPN. **3ACN** or **4ACN 0.6**: 0.60 M **3** or **4**, 0.03 M I_2, 0.50 M *tert*-butylpyridine, 0.25 M EMITFSI in ACN : VN 3 : 1. **PMII 0.6**: 0.60 M 1-propyl-3-methylimidazolium iodide (PMII) with 0.03 M I_2, 0.50 M *tert*-butylpyridine in ACN : VN 3 : 1.

slightly better cell performance at 0.1 sunlight and more significant improvements at higher sunlight levels. For example, at 1.0 Sun the efficiency increased from 5.7% to 6.9%, mainly as a consequence of an improved fill factor. Some improvements in DSSC performance were observed at 0.5 and 1.0 Sun for the analogous MPN-solvent systems. In striking contrast, DSSC efficiencies for the optimised electrolyte with **4** as the sole iodide source were much improved for both solvents and over the range of light intensities. At 1.0 Sun, the efficiency of DSSCs with the ACN-based electrolyte increased from 4.3% (**4ACN 1.0**) to 7.0% (**4ACN 0.6**) with a much improved *IV* profile (Fig. 2). The better performance was due to better fill factors and higher V_{oc} values, on average 40 mV higher at all light intensities. Impressive improvements in performance were also observed using the more viscous MPN-based electrolyte.

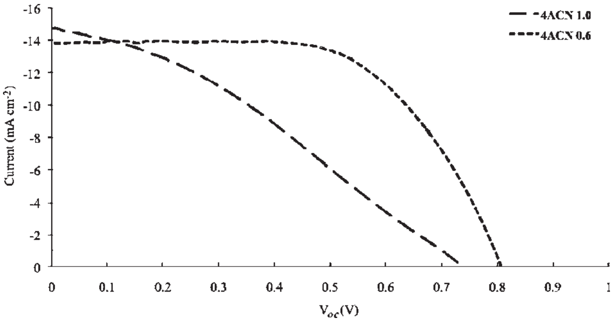

Fig. 2 Comparison of the *IV* curve measured at 1.0 sunlight for cells constructed using **4ACN 1.0** and **4ACN 0.6** as electrolytes.

Two factors could be contributing to the better performance of cells with lower organic iodide concentrations in the electrolyte. Firstly, there is better mass transport for cells constructed with 0.60 M organic iodide *cf.* 1.0 M organic iodide (note: a 1.0 M solution of **4** corresponds to 585 g L^{-1} *cf. ca.* 350 g L^{-1} at 0.60 M). At these high siloxane loadings, mass transport becomes limiting at high sunlight levels. Secondly, the addition of EMITFSI introduces the EMI cation which enhances charge screening and decreases internal resistance, leading to a higher fill factor and improved cell efficiencies.

Cells constructed using a standard organic iodide source, 1-propyl-3-methylimidazolium iodide in a 3 : 1 (v/v) acetonitrile–valeronitrile mixture, were found to have the same efficiencies at the three light intensities tested (7.7–7.9%) but, at the lowest sunlight level (0.1 Sun), these cells showed a poorer performance than the longer chained organic iodide, **4**, due to a significant decrease in short circuit currents.

To gain insight into the physical interactions of the organic iodides with the DSSC components, ATR-FTIR spectroscopy, photovoltage transient decay and impedance studies were conducted on the DSSC devices constructed using the optimised ACN-based electrolyte. ATR-IR spectroscopy was performed on the dyed titania films to ascertain whether the siloxane moieties had condensed on the titania surface forming a blocking layer. In this case, vibrations arising from Si–O–Ti bonds could not be detected in the spectra, suggesting that surface attachment had not occurred.

Photovoltage transient studies were then performed according to a literature procedure[28] to determine electron lifetime variations for different electrolytes. The lifetime of electrons injected into the titania films were measured using the fully assembled cells as a function of V_{oc}. The recombination rates obtained (Fig. 3) give a direct measure of the rate of recombination of the electron in the titania film with either the dye cation or the triiodide in the electrolyte.[29] At a V_{oc} similar to that achieved by these cells during testing, (Fig. 2, at $V = -750$ mV), the average electron lifetime for cells constructed using the undecyl analogue, **4**, was 18 ms. This value was more than twice the value of 8 ms observed for cells constructed using the propyl analogue, **3**. Longer electron lifetimes indicate slower

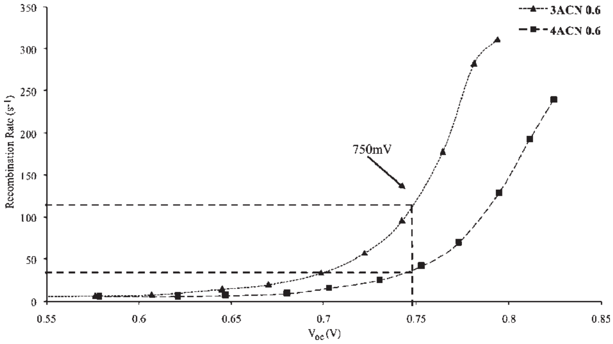

Fig. 3 Electron lifetime measurements for cells constructed using **3ACN 0.6** and **4ACN 0.6** as electrolytes.

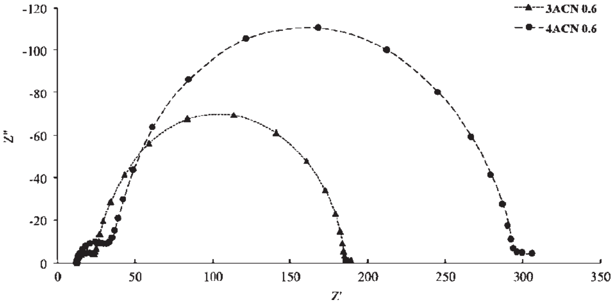

Fig. 4 Nyquist plot (at −750 mV bias in dark conditions) for cells constructed using **3ACN 0.6** and **4ACN 0.6** as electrolytes.

recombination kinetics and these parameters equate to better DSSC efficiencies and improved device performances. While the exact nature of the interaction between the organic iodide sources and the titania requires further study, the enhancement in performance correlates with a slower recombination rate for those organic iodides containing a long alkyl group in comparison to a shorter one.

Impedance spectra were measured in dark conditions at an applied potential of −750 mV, to confirm the difference in electron lifetimes for cells constructed using **4** and **3** as iodide sources. The data from these experiments, presented as a Nyquist plot in Fig. 4, provide information about the resistance of electron recombination.[30,31] The much larger real (Z') and imaginary (Z'') values (from the second semicircle) observed in the Nyquist plot, for cells prepared using **4** as the iodide source, reflect an enhanced resistance in comparison to that observed for cells constructed using **3** as the iodide source. This higher resistance leads to increased electron lifetimes for cells using **4**, supporting the results obtained from the photovoltage transient decay studies.

These results further demonstrate that the performance of DSSCs can depend on the cation present in the electrolyte and support the view that judicious structural modification of the cationic moieties can lead to improved cell performance. Investigations are being conducted to further ascertain the nature of the cation–titania interaction and to better define the effect that changing the organic nature of the cation has on the performance of the solar cell.

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