Dye-sensitized solar cells with electrolyte based on a trimethoxysilane-derivatized ionic liquid

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Abstract

A trimethoxysilane derivative of propylmethylimidazolium iodide has been synthesized and presented for the first time. When mixed with iodine, it can be used as gel electrolyte in dye-sensitized solar cells offering through sol–gel condensation practically solid-state devices with satisfactory overall efficiency which was estimated at 3.2%. The specific conductivity of the gel electrolyte was increased by the addition of iodine and also with temperature. Variations to the cell performance were also examined by the addition of organic and inorganic acids to the electrolyte. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

A main component of dye-sensitized solar cells (DSSC) of the Graetzel type is the electrolyte that fills the space between the active porous nanocrystalline electrode and the counter electrode. Even though, in the vast majority of cases, the electrolyte contains the same I_3^-/I^- redox couple, the physico-chemical state of the material bearing this couple has been the subject of a large and ever-increasing number of studies [1–6]. In earlier works, the composition of the electrolyte was based on solvents capable to solubilize both iodide salts and iodine, which are the source of the I_3^-/I^- redox couple. Such solvents are, for example, acetonitrile, propylene carbonate, methoxyacetonitrile [7], etc. However, no solvent can be equally good for iodine and iodide salts (for example alkali salts) [5]. In addition, solvent volatility problems and the necessity of costly cell sealing urged for the search of alternative materials. Room temperature ionic liquids (molten salts) have several qualities as compared with other choices since they have negligible volatility and satisfactory ionic conductivity [8]. Ionic liquids are viscous materials. For this reason, ion diffusion is limited and it is expected to give lower conductivities than common solvents. However, it has been shown that a Grotthus-like mechanism owing to electron exchange between I^- and I_3^- in the redox couple endows ionic liquids with satisfactory conductivity despite the high viscosity value [8,9]. Conductivity of ionic liquid electrolytes is further improved by increasing iodine concentration. In this respect, it has been found that iodine encourages polyiodide formation thus facilitating electron-exchange-type conductivity [9]. Increasing of iodine concentration is, however, limited by strong visible light absorption by iodine itself. All these findings have established that iodide ionic liquids in combination with moderately high iodine concentration make a satisfactory electrolyte for DSSCs.

Volatility of molten salts is negligible but sealing of the cells cannot be avoided since high-temperature leaks compromise the cell efficiency. For this reason and by counting the fact that conductivity by electron exchange processes can be obtained to a satisfactory degree, many research groups have attempted to introduce gelators into the ionic liquids thus diminishing the leakage risks [2,10]. Introduction of gelators has to take into account the fact that the electrolyte must be fluid enough to penetrate into the semiconductor porous structure. The usual choice is to employ gelators that progressively increase solidification to allow time for the fluid to occupy the pores. Thus, small molecular gelators may be used [2] or polymerization can be carried out in situ [10]. We have opted for this last possibility but we adopted a completely different chemical concept of gelation [5,6]. We use alkylimidazole iodides derivatized with alkoxysilane groups. Thus by hydrolysis or, generally, solvolysis procedures we get gels through the sol–

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gel process. This type of electrolytes, i.e. electrolytes synthesized through the sol–gel process, have helped us fabricate high-performance DSSCs [5,6,11]. Employment of silicate modified imidazolium iodides is been done for the first time and the results are encouraging.

2. Experimental

All reagents were from Aldrich unless otherwise indicated. Cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II), abbreviated $RuL_2(NCS)_2$, was provided by Solaronix SA (Switzerland). SnO_2:F transparent conductive electrodes (8 Ω/square) were purchased from Hartford Glass Co., USA.

2.1. Synthesis of 1-methyl-3-[3-(trimethoxy-λ^4-silyl)propyl]-1H-imidazolium iodide (TMS-PMII; for the abbreviation we adopted PMII, i.e. propylmethylimidazolium iodide, with addition of TMS which stands for trimethoxysilane)

39 g (0.134 mol) 3-iodopropyltrimethoxysilane (ABCR) was added to a solution of 11 g (0.134 mol) 1-methylimidazole in 100 ml of 1,1,1-trichloroethane (Fluka). The mixture was refluxed for 12 h. Ionic liquid was decanted from the hot solution in a separatory funnel, washed twice with 100 ml of diethylether (Merck) and dried under reduced pressure. 46.05 g (92%) of TMS-PMII was thus obtained. The procedure is schematically shown in Scheme 1.

^{1}H NMR: δ(ppm)=0.55 (m, 2H), 1.82 (broad s, 2H), 3.45 (s, 9H), 3.86 (s, 3H), 4.15 (m, 2H), 7.73 (s, 1H), 7.80 (s, 1H), 9.16 (t, J=7.7, 1H).

^{13}C NMR: δ(ppm)=6.250, 24.223, 36.826, 51.063, 51.816, 123.017, 124.420, 137.400.

Microanalysis data (Hydrolyzed silane): calculated: C (25.46%), H (4.58%), N (8.48%); measured: C (25.01%), H (4.47%), N (7.49%).

2.2. Construction of titania films

3 g EtOH, 0.7 g Triton X-100, 0.6 ml AcOH and 0.36 ml Ti(OiPr)$_4$ were mixed in this order under vigorous stirring and under ambient conditions [11,12]. After 5-min stirring, an 8 Ω/square transparent conductive fluorine-doped SnO_2 (SnO_2:F) glass slide, previously cleaned by sonication in ethanol, was dipped in the sol, giving a uniform, transparent film. The film was then calcined at 550 °C. The procedure was repeated 10 times. The thus obtained TiO_2 film was optically transparent, as can be seen by the absorption spectrum of Fig. 1. The thickness of these films is about 2 μM [11].
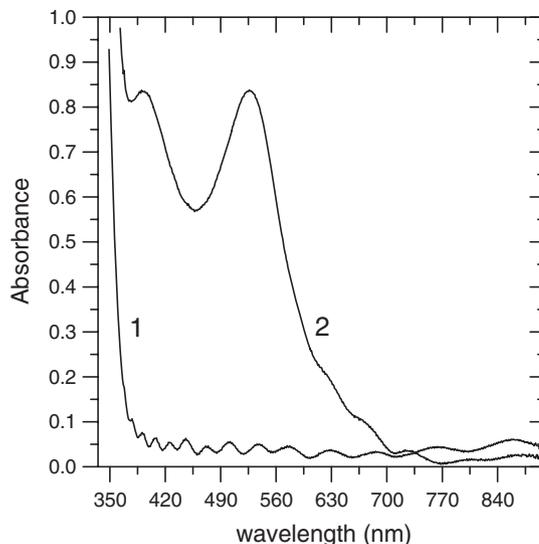

Fig. 1. Absorption spectrum of the titania film without (1) and with adsorbed RuL_2(NSC)$_2$ (2). The oscillating part of the titania spectrum is due to interference fringes.

2.3. Preparation of the electrolyte

TMS-PMII was mixed with various quantities of I_2. Optimal results were obtained with 10% wt of iodine. This mixture was exposed to ambient humidity being continuously stirred for 24 h and then it was applied for the construction of DSSCs. Alternative electrolytes were obtained by adding either 0.1 M HCl or 4% wt AcOH. These mixtures gel faster but the waiting time before application was again 24 h.

2.4. Construction of dye-sensitized solar cells

When the TiO_2 film was taken out of the furnace and while it was still warm, it was dipped into a 1 mM ethanolic solution of $RuL_2(NCS)_2$, and was left there overnight. Then the dye-coated electrode was copiously washed with ethanol and dried in a stream of N_2. The counter electrode was a slightly platinized SnO_2:F transparent conductive glass slide. Platinum was thermally evaporated in a vacuum chamber. It formed a very thin layer (<100 nm) that very slightly affected electrode transparency. Finally, a drop of the above-described electrolyte was applied on the TiO_2/$RuL_2(NCS)_2$ electrode and then the counter electrode was placed on the top and the two were squeezed together by hand. Si–O–Si and Ti–O–Si bonds developing inside the gel and at the interface between the gel and the electrodes act as a gluing material holding the whole structure together, thus making a practically solid-state cell.
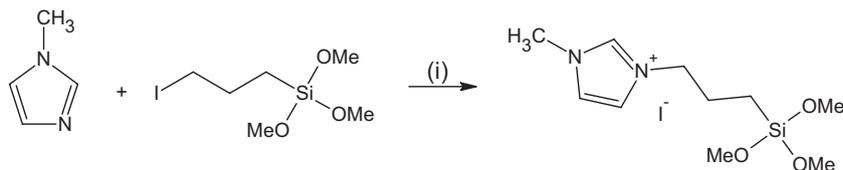
Scheme 1. Synthesis of TMS-PMII by refluxing in 1,1,1-trichloroethane.

2.5. Measurements

^1H NMR and ^{13}C NMR (300 MHz, internal Me_4Si) spectra were recorded using a Varian VXR-300 instrument for solutions in DMSO-d_6. Microanalyses were performed on a Perkin-Elmer CHN Analyser 2400. UV–VIS absorption measurements were made with a Cary 1E spectrophotometer. Conductivity measurements were made with a Metrohm 660 conductometer. I–V curves have been recorded by connecting the cell to an external variable resistor and by measuring the current flowing through the resistor and the corresponding voltage across the resistor. Cell dimension for these measurements was 1 cm^2. Illumination was done by an Oriel 450W Xenon lamp. Control of intensity of incident light was obtained with superposed multiple wire grids. Illumination intensity was 100 mW/cm^2, which corresponds to 1 sun at AM1.5. Outdoor experiments using natural sunlight (performed in Patras, Greece) gave similar results with simulated light of equivalent intensity.

3. Results and discussion

Synthesis of trimethoxysilane-derivatized propylmethylimidazolium iodide was carried out by a relatively simple procedure as analyzed in Experimental, schematically shown in Scheme 1 and presented for the first time. TMS-PMII is a viscous fluid with a slight orange color. It becomes deeply colored when it is mixed with iodine, as can be seen by the absorption spectra of Fig. 2. The absorption below 300 nm is due to I^- while the absorption (two peaks) above 300 nm is due to I_3^-. By progressively increasing I_2 concentration, we obtained a progressive increase of absorption at >300 nm indicating an increasing presence of polyiodide species.

This is beneficial for electrolyte conductivity, as it appears from the data of the inset of Fig. 3, and subsequently for cell efficiency, as already discussed in Introduction. However, extensive absorption by the electrolyte screens absorption of light by $RuL_2(NCS)_2$, as it is seen by comparing Curve 2 of

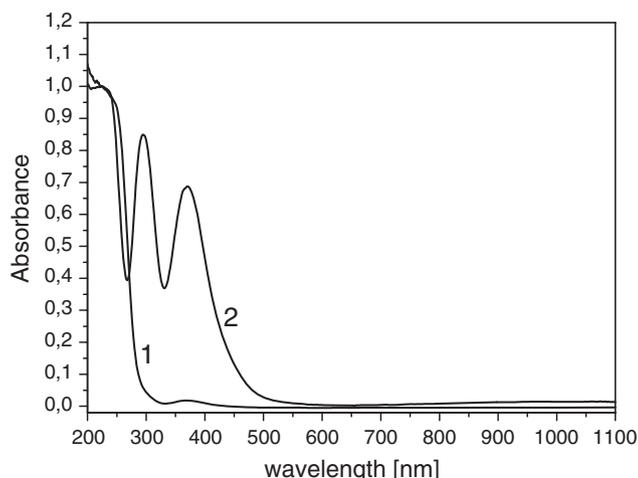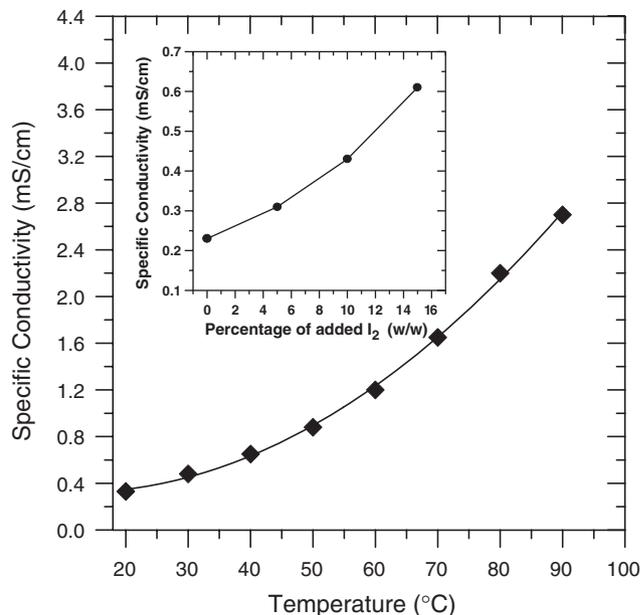Fig. 3. Variation of electrolyte conductivity vs. temperature for TMS-PMII ionic liquid mixed with 10% wt I_2 and specific conductivity of various TMS-PMII/I_2 mixtures as an inset.

Fig. 1 with Curve 2 of Fig. 2, thus decreasing cell efficiency. Optimal conditions were obtained, as already said in Experimental, at 10% wt iodine. The conductivity of the material of this composition is about half a mS/cm and increases rapidly by increasing temperature, as can be seen in Fig. 3. Addition of a few drops of HCl makes the sol–gel faster than in the case of the non-acidified TMS-PMII/I_2 mixture. In that case, the conductivity values immediately after preparation were higher, despite the higher viscosity, but this is only due to some water released by hydrolysis. By heating the material so as to make water evaporate, conductivity drops below that of the non-acidified gel. It is obvious that the presence of a fluid in the gel increases ionic conductivity since it helps ion diffusion. However, this type of an electrolyte is always subject to evaporation and cell instability.
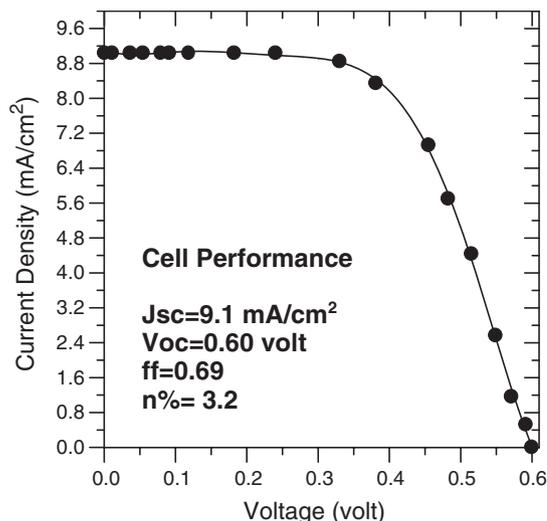

Fig. 2. Absorption spectrum of pure TMS-PMII (1) and TMS-PMII with added 10% wt iodine (2).

Fig. 4. I–V curve for DSSC containing TNS-PMII with 10% wt I_2.

Table 1
Performance data of DSSC employing electrolytes composed of TMS-PMII and 10%wt I_2 in the absence or in the presence of acids

Type of electrolyte	Open circuit voltage V_{oc} (Volt)	Short circuit current density J_{sc} (mA/cm^2)	Fill factor f	Overall efficiency (%)
No acid	0.60	9.1	0.69	3.2
0.1 M HCl	0.59	8.9	0.69	3.1
4%wt AcOH	0.59	9.4	0.69	3.3

Cells made with TMS-PMII/10% wt I_2 produced the I–V curve of Fig. 4. Similar data for electrolytes acidified by using either HCl or AcOH are presented in Table 1. The overall efficiency of these cells was comparable with the efficiency of cells using other sol–gel electrolytes [13]. The efficiency can, of course, be increased by adding a solvent [5], since in that case the gel electrolyte conductivity and, subsequently, the short-circuit current is larger. However, as already said, a solvent may evaporate and cause cell instability.

The functioning of the three cells was not affected by the presence of the acids which resulted in some variation of the short-circuit current but did not affect the cell fill factor. A slight decrease of V_{oc} was obtained by adding acid to the electrolyte. Those slight changes are without importance. We can then say that non-acidified or acidified electrolyte of the above composition makes DSSCs of satisfactory efficiency.

4. Conclusion

A propylmethylimidazolium iodide ionic liquid derivatized with a trimethoxysilane group is presented for the first time. When mixed with iodine, it acts as electrolyte applicable to DSSCs with satisfactory efficiency (>3%). The ionic liquid is condensed in situ by the sol–gel process through the silicate groups, i.e. by forming Si–O–Si–O–bonds. A solid gel is thus obtained. The formation of a solid gel is slow but it can be accelerated by adding inorganic or organic acid without loss in efficiency.

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