Positively Charged Polysilsesquioxane/Iodide Ionic Liquid as a Quasi Solid-State Redox Electrolyte for Dye-Sensitized Photo Electrochemical Cells: Infrared, ^{29}Si NMR, and Electrical Studies

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A new sol-gel precursor based on 1-methyl-3-[3-(trimethoxy- λ^4 -silyl)propyl]-1*H*-imidazolium iodide (MTMSPI⁺I[−]) was synthesized and investigated as a potential novel quasi solid-state ionic liquid redox electrolyte for dye-sensitized photoelectrochemical (DSPEC) cells of the Graetzel type. MTMSPI⁺I[−] was hydrolyzed with acidified water and the reaction products of the sol-gel condensation reactions assessed with the help of ^{29}Si NMR and infrared spectroscopic techniques. Results of the time-dependent spectra analyses showed the formation of positively charged polyhedral cube-like silsesquioxane species that still contained a small amount of silanol end groups, which were removed after heating at 200 °C. After cooling, the resulting material formed is a tough, yellowish, and transparent solid, which could be reheated again and used for assembling DSPEC cells. The addition of iodine increased the specific conductivity of the hydrolyzed and nonhydrolyzed MTMSPI⁺I[−], which we attributed to the formation of triiodide ions contributed to the conductivity via the Grotthus mechanism. DSPEC cells based on a titania-dye system with MTMSPI⁺I[−] electrolyte containing iodine (0.1 M) reached an overall efficiency between 3.3–3.7%.

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1. INTRODUCTION

DSPEC cells [1, 2] are currently considered as an auxiliary source of electricity, and as potential substitutes for standard silicon PV cells, achieving an impressive 10% efficiency. However, before their commercialization, the sealing of volatile organic solvent-based electrolytes containing redox I[−]/I₃[−] couples and the long-term stability of these cells are issues that have to be solved. Therefore, p-type inorganic semiconductors [3–6], organic hole-transport materials [7–9], and polymeric materials incorporating I[−]/I₃[−] redox couples [10–14] have been considered as solid or semi-solid-state substitutes for liquid DSPEC cells. Among these materials, sol-gel-based redox electrolytes [15] have been also extensively studied in our laboratory [16, 17] enabling production of cells reaching ~ 5% efficiency.

Ionic liquids based on 1,3-dialkylimidazolium cations with iodide [18] or other anions (BF₄[−], PF₆[−], etc) [19, 20] have been considered extensively as nonvolatile substitutes for liquid electrolytes in DSPEC cells. Since ionic liquids already act as a source of iodide the addition of iodine lead to the formation of I[−]/I₃[−] redox couples enabling the

preparation of redox electrolytes [21]. Ionic liquids represent a realistic option for the fabrication of quasi solid-state redox electrolytes since the high viscosity of these ionic liquids and the related drop in the specific conductivity is compensated by the Grotthus mechanism (a relay-type mechanism), enabling the transport of charge without any net transport of mass [22, 23]. Solidification of ionic liquids was attempted by the addition of solid particles such as silica nanoparticles [24], colloidal titania, and carbon nanotubes [25], and by the incorporation of ionic liquids in polymers [26–28]. The addition of small molecular weight gelators [29, 30], as well as sol-gel precursors [16, 17] and polymeric solvent-free anionic conductors consisting of positively charged imidazolium polymeric chains and iodide [31] or polysiloxane with quaternary ammonium side groups [32, 33], seems to be effective.

We synthesized a new imidazolium iodide type ionic liquid, namely, MTMSPI⁺I[−] (Scheme 1) which, due to the trimethoxysilane group, exhibits self-assembling properties, providing polymeric ionic liquid electrolytes and imparting to the DSPEC cell (ruthenium bipyridyl dye/TiO₂-redox electrolyte-Pt counter electrode) a light-to-electricity

SCHEME 1: Synthesis of MTMSPI⁺I[−] by refluxing in 1,1,1-trichloroethane.

efficiency of about 3.3%. In this communication we focused on elucidating the structure of MTMSPI⁺I[−] showing, with the help of ²⁹Si NMR and time-dependent IR attenuated total reflection (ATR) spectroscopy, that hydrolysis and condensation reactions of alkoxy silane groups lead to the formation of positively charged polysilsesquioxane species imparting the resultant material quasi solid-state consistency.

We also showed through collection of specific conductivity and viscosity data that the polycondensation reactions, which brought about the formation of positively charged oligo and polyhedral silsesquioxanes, did not affect the ionic conductivity, proving the feasibility of making quasi solid-state polymeric ionic liquid electrolytes for DSPEC cells.

2. EXPERIMENTAL

2.1. Synthesis

All reagents were from Aldrich unless otherwise indicated. Cis-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), abbreviated RuL₂(NCS)₂, was provided by Solaronix SA (Switzerland). SnO₂:F transparent conductive electrodes (8 Ohm/square) were purchased from Hartford Glass Co., USA.

MTMSPI⁺I[−] was synthesized as follows: 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. The 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 MTMSPI⁺I[−] was thus obtained. The procedure is shown schematically in Scheme 1.

2.2. Measurements

IR spectra were measured on a Perkin-Elmer System 2000 equipped with Horizontal Attenuated Total Reflectance (HATR, SpectraTech) and a Silver Gate ATR cell employing a Ge (refractive index $n = 4.00$) ATR prism. It seemed, initially, that through the use of a Ge ATR crystal ATR spectra could be obtained reproducing the corresponding transmission spectra of the gels to the greatest degree. However, the moderately intense band of MeOH measured in the HATR or Silver Gate cell was red-shifted by about 10–12 cm^{−1} from the frequency of this band in transmission spectra (1033 cm^{−1}). This means that the ATR spectra of the ionic liquids characterized by

much stronger siloxane modes—even when using a Ge ATR crystal—did not accurately reproduce the vibrational spectra obtained in the transmission mode. Accordingly, the method of quantitative analysis of ATR spectra developed by Bertie and Eysell [34] was used to obtain the IR absorption spectra of the ionic liquid samples. The optical constants (refractive index, n , and absorption coefficient, k) were calculated and absorption spectra, expressed by $A = 2\pi k \tilde{\nu} d_{et}$, were constructed.

²⁹Si NMR spectra were recorded on a Varian Unity Plus 300 MHz spectrometer using a Doty CPMAS probe head. The Larmor frequency of the silicon nuclei was 60.190 MHz. Samples were spun about the magic angle at a frequency of 2 kHz. ²⁹Si chemical shifts were determined using DSS (sodium 3-(trimethylsilyl)propane-1-sulfonate) as an external standard and then expressed relative to TMS (tetramethylsilane) ($\delta = 0$ ppm).

Specific conductivity (σ in mS/cm) measurements of MTMSPI⁺I[−] in its hydrolyzed and nonhydrolyzed forms with and without added iodine were carried out in an electrochemical cell using platinum electrodes. The cell constant of the electrochemical cell was determined with 0.1 M KCl solution at 25°C. The AC impedance was measured on a SOLARTRON 1250 Frequency Response Analyser and a SOLARTRON 1286-Electrochemical Interface in the frequency range 0.1–65000 Hz. During drying and gelling MTMSPI⁺I[−] did not shrink or delaminate from the Pt electrodes.

Rheological properties of the sample were determined by a Rotational Controlled Stress Rheometer (HAAKE RheoStress RS150), equipped with a plate-and-plate sensor system (HPP 25/1 mm gap). Measurements were performed under steady shear conditions (flow curves) and under non-destructive conditions of oscillatory shear. The flow curves were carried out in the shear stress range, which depended on the viscosity of the sample. The same measurements were performed each day after the preparation until the 23rd day. All measurements were performed at a constant temperature of 20°C.

Glass transition temperatures were measured on a Mettler Toledo DSC 821^c instrument equipped with an intra-cooler, using STAR software. In and Zn standards were applied for temperature calibration and for determination of the instrument time constant. An In standard was used for calibration of the heat flow. The measurements were performed in the temperature range from −145°C to +40°C using a heating rate of 10 K/min (Table 1).

TABLE 1: T_g values of nonhydrolyzed and hydrolyzed (0.1 M HCl) MTMSPI $^+I^-$.

Sample	T_g (K)	ΔC_p (J/g K)
MTMSPI $^+I^-$	208.60	0.391
Hydrolyzed MTMSPI $^+I^-$	221.48	0.412

FIGURE 1: IR transmission spectra obtained by calculations from the measured ATR spectra. Intensities were normalized to the sample thickness of 1 mm.

3. RESULTS AND DISCUSSION

3.1. Structure of hydrolyzed MTMSPI $^+I^-$ from Infrared and ^{29}Si NMR spectra

In the first step, time-dependent IR ATR spectra of hydrolyzed MTMSPI $^+I^-$ were measured (Figure 1). Inspection of the variation of the intensity of the bands over the course of ageing (0–72 h, Figure 2) confirmed that hydrolysis attained its maximum at 7–10 h, because at longer ageing times the Si-OH band ($\sim 900\text{ cm}^{-1}$) [35, 36] started to decrease in intensity. The methanol band (1028 cm^{-1}) grew in intensity corroborating the hydrolysis reactions while the Si-OMe bands ($2844, 1078, 820, 775\text{ cm}^{-1}$) decreased [37]. In this stage of ageing a shoulder band appeared in the region $1090\text{--}1110\text{ cm}^{-1}$. It shifted to higher frequencies and increased in intensity with time. The growth of this band we attributed to the formation of open cubes like $(\text{T}_7(\text{OH})_3, \text{T}_8(\text{OH})_4)$ [38], and cyclic tetramers $(\text{T}_4(\text{OH})_4)$ [39]. Isolated polyhedral species did not form because the corresponding modes appear at higher frequencies ($> 1120\text{ cm}^{-1}$) [38, 40]. The band at 1051 cm^{-1} we ascribed to one of the symmetric components of the Si-O-Si stretching mode of either linear trimers or tetramers [41, 42].

^{29}Si NMR spectra of hydrolyzed MTMSPI $^+I^-$ were in agreement with results of the IR ATR spectra analysis showing T^1 ($-49, 5\text{ ppm}$), T^2 ($-57.2, -58.5\text{ ppm}$), and T^3 ($-65.5, -67.5\text{ ppm}$) signals [43–46] in ^{29}Si NMR spectra (Figures 3a and c).

FIGURE 2: Intensity changes of the selected bands versus time of ageing.

The second stage of ageing (Figures 1 and 2) was characterized by condensation, as could be inferred from the strong T^2 (-57.1 ppm) and T^3 (-66.1 ppm) signals (Figure 3d), the slow decrease of the silanol band at $\sim 900\text{ cm}^{-1}$ and the concurrent growth of absorption above 1110 cm^{-1} . The final spectrum (72 h) showed a band at 1120 cm^{-1} , suggesting the presence of T_8 cubes [38, 40]. This band was broad and extended to the $1100\text{--}1060\text{ cm}^{-1}$ region, signaling the coexistence of the open cube-like silsesquioxanes like $\text{T}_7(\text{OH})_3$ ($1112, 1086, 1068\text{ cm}^{-1}$), $\text{T}_8(\text{OH})_4$ ($1109, 1082\text{ cm}^{-1}$), or $\text{T}_6(\text{OH})_2$ ($1108, 1089, 1060\text{ cm}^{-1}$) [38, 39]. Surprisingly, the band at 1050 cm^{-1} was still present in the spectra despite the fact that a decrease in its intensity was expected, due to the possible formation of cyclic and open cube-like species, which do not show absorption in this region. To clarify this situation, the samples were spread on silicon wafers, left exposed to ambient conditions for a few months, and then heat treated at different temperatures. The spectra were recorded in the transmission mode and are shown in Figure 4.

The spectra recorded at room temperature revealed the absence of the methanol band and the presence of well-developed bands at $1129, 1092, \text{ and } 1049\text{ cm}^{-1}$. The silanol band at $\sim 900\text{ cm}^{-1}$ was also noted, indicating that complete condensation was not attained even after several weeks. However, this band disappeared in the spectra of samples heated at 150°C and 200°C . As expected, the strongest siloxane stretching mode, shifted to 1135 cm^{-1} , grew in intensity and the shoulder band at 1092 cm^{-1} , attributed to the partially hydrolyzed open cube-like species $(\text{T}_7(\text{OH})_3 \text{ and } \text{T}_8(\text{OH})_4)$ [38, 39], disappeared. This indicated the condensation between partially hydrolyzed open cube-like species to cube-like condensation products. The ^{29}Si NMR spectra confirmed the formation of products containing only trisiloxane bonds (Figure 4, inset), characterized with a single T^3 signal at -68.0 ppm [43]. Because there were no uncondensed

FIGURE 3: ^{29}Si NMR spectra of nonhydrolyzed a and hydrolyzed MTMSPI $^+\text{I}^-$ in various stages of ageing: b: 2–3 h (initial), c: 1 day, d: 1 week, and e: 2 weeks.

FIGURE 4: IR transmission spectra of hydrolyzed MTMSPI $^+\text{I}^-$ aged 4 months and then was heat treated at various temperatures. Inset: ^{29}Si NMR spectrum of heat-treated (200°C) sample.

silanol groups in the sample heat treated at 150–200°C, as inferred from IR and ^{29}Si NMR spectra (Figure 4), the ladder species must be terminated by some arrangement similar to T_8 – T_{12} cage molecules. The structure as illustrated in Figure 5 was corroborated by the fact that the main bands at 1138 and 1049 cm^{-1} did not match either the spectra of cube-like [38–40, 47, 48] or ladder polymers [49, 50] perfectly, but contained the features of both.

The transformation of redox electrolyte from liquid to quasi solid-state is a relatively slow process which can be accelerated using heat treatment. Consecutive viscosity measurements of hydrolyzed MTMSPI $^+\text{I}^-$ sol exposed to ambient conditions during 23 days of ageing showed that its viscosity increased from a few mPas to 40000 Pas. However, it still behaves as Newtonian liquid, indicating that the nature of the interactions between the species (positively charged silsesquioxanes and iodide) present in the sols remained unchanged despite the growth of the silsesquioxane species.

3.2. Electrical measurements

In the first step we determined the specific conductivities (σ) of the nonhydrolyzed MTMSPI $^+\text{I}^-$ without added iodine. As shown in Figure 6, the specific conductivity of MTMSPI $^+\text{I}^-$ is of the same order of magnitude as for other 1,3-dialkylimidazoliumiodide based ionic liquids [21], but approximately 10 times lower than ionic liquids containing other anions [19]. Upon increasing the temperature to only 60°C, the specific conductivity increased nearly 3 times, reaching values similar to those of molten Bu_4NI [22] (i.e. $4.5 \cdot 10^{-3} \text{ S/cm}^{-1}$), which also did not contain triiodide ions, thus indicating a similarity with our ionic liquid.

The corresponding σ values became higher when iodine was added (Figure 7). The increase of the σ values with increasing iodine content could be easily explained for the nonhydrolyzed samples where the Lewis acid acceptor iodine, in combination with the Lewis base donor I^- , forms I_3^- . The latter ions are considered as building blocks, which easily catenate to form various polyiodides. Due to the increased content of iodine, the connectivity between I_3^- and iodine increased and since the distance between iodine and triiodide (or higher polyiodides, see below) ions was reduced, the transport of the charge carriers became easier. The Grotthuss mechanism (a relay-type mechanism), enabling the transport of charge without any net transport of mass was first stated for molten polyiodides $((\text{R}_3\text{S})\text{I}_x, (\text{R}_4\text{N})\text{I}_x)$ [22], also established for the 1,3-dialkylimidazoliumiodide ionic liquids electrolytes used in DSPEC cells [23] and justified recently with efficiency measurements of DSPEC cells employing molten and solid metal-iodide-doped trialkylsulfonium iodides and polyiodides [21].

Hydrolyzed MTMSPI $^+\text{I}^-$, aged 24 h, exhibited similar temperature dependence (Figure 6), but the corresponding specific conductivities were found to be dependent on the ageing of hydrolyzed samples (Figure 8). During the first three days of ageing σ dropped severely to $\sim 0.1 \text{ mS/cm}$ but was stable thereafter. The same was found for samples containing iodine, showing similar dependence of the specific conductivity with duration of ageing (Figure 8). This made the establishment of correlations between the effects of the added iodine on the σ values of the hydrolyzed MTMSPI $^+\text{I}^-$ difficult and hence this was not investigated in detail.

The most plausible explanation for the observed variations of the σ values for hydrolyzed MTMSPI $^+\text{I}^-$ with or without added iodine was that acidified water used for

FIGURE 5: Probable structure of the positively charged polysilsesquioxane species constituting heat-treated (200°C) hydrolyzed $\text{MTMSPI}^+\text{I}^-$.

FIGURE 6: Changes of the specific conductivity of nonhydrolyzed (closed squares) and hydrolyzed (0.1 M HCl) $\text{MTMSPI}^+\text{I}^-$ aged 24 h (closed circles).

FIGURE 7: Influence of added iodine on the specific conductivity of nonhydrolyzed $\text{MTMSPI}^+\text{I}^-$.

hydrolysis contributed to the observed effect. MeOH and water, which were produced due to the condensation reaction could also affect the σ values. The stabilization of the σ values observed for the hydrolyzed $\text{MTMSPI}^+\text{I}^-$ after long ageing times was attributed to the fact that the samples still contained certain amount of nonreacted silanol groups as inferred from IR spectra measurements.

The stability of the specific conductivity for hydrolyzed $\text{MTMSPI}^+\text{I}^-$ was demonstrated from measurements of the light-to-electricity conversion efficiency of DSPEC cells prepared with nonhydrolyzed and hydrolyzed $\text{MTMSPI}^+\text{I}^-$ containing iodine (0.5 M I_2) [51]. An unsealed DSPEC cell made from nanocrystalline TiO_2 soaked in ruthenium bipyridyl dye in contact with a thin Pt layer counterelectrode, with hydrolyzed $\text{MTMSPI}^+\text{I}^-$ electrolyte, showed nearly the same efficiency of about 3.3–3.7% over 6 weeks.

Hydrolyzed $\text{MTMSPI}^+\text{I}^-$ heat treated at $150\text{--}200^{\circ}\text{C}$ transformed to a viscous liquid, as shown in Figure 5, to which was added iodine, providing a redox electrolyte. After cooling to ambient temperature the sticky liquid solidified to a tough, amber-colored, and transparent material, which could be reversibly heated and cooled, changing from a tough to a viscous material, which adhered perfectly to glass. The preparation of the DSPEC cells with heat-treated $\text{MTMSPI}^+\text{I}^-$ containing iodine is planned in the future and results will be published elsewhere.

4. CONCLUSIONS

In summary, we have demonstrated a new sol-gel precursor that could be considered as a potential novel quasi solid-state ionic liquid redox electrolyte for dye-sensitized

FIGURE 8: Changes of the specific conductivity of hydrolyzed (0.1 M HCl) MTMSPI⁺I⁻ (closed squares, solid line) and hydrolyzed MTMSPI⁺I⁻ + 0.5 M I₂ (closed circles, dotted line) with the duration of ageing. σ value of the MTMSPI⁺I⁻ + 0.5 M I₂ heat treated at 200 °C (closed triangle).

photoelectrochemical (DSPEC) cells of the Graetzel type. With the help of ²⁹Si NMR and infrared spectroscopic techniques we showed that the condensation of hydrolyzed MTMSPI⁺I⁻ led to positively charged polyhedral cube-like silsesquioxane species characterized with certain amount of silanol end groups. Heating at 200 °C removed the silanol groups and ionic species consisting of ladder-like polymers terminated with cube-like species were formed. From the viscosity measurements, which confirmed the Newtonian behavior of hydrolyzed MTMSPI⁺I⁻, we concluded that the final product is still an ionic liquid although it showed quasi solid-state consistency.

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