Materials Research Bulletin 47 (2012) 3160–3169

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Structural studies of alkoxysilyl-functionalised ionic liquid and its application in a hybrid electrochromic device

M. Čolović, A. Šurca Vuk *, M. Hajzeri, B. Orel

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 21 February 2012
Accepted 10 August 2012
Available online 23 August 2012

Keywords:
A. Nanostructures
B. Sol–gel chemistry
C. Infrared spectroscopy
D. Electrochemical properties
D. Ionic conductivity

ABSTRACT

A new sol–gel polymerisable ionic liquid 1-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-(3-(trimethoxysilyl)propylimidazolium iodide was synthesised with the aim of preparing an I^-/I_3^- redox electrolyte. The processes of hydrolysis and condensation were followed first in acidic and basic conditions using ATR IR and ^{29}Si NMR spectroscopy. The IR bands at 1100 and 1126 cm^{-1}, together with the prevailing T^3 signal, showed that more branched silsesquioxane structures formed under basic catalysis. The formation of silsesquioxane structures was also followed *in situ* using two FT-IR techniques, *i.e.*, transmission and reflection–absorption mode. The conductivity of the basically catalysed electrolyte initially reached 4.3×10^{-3} S/cm but stabilised at 1.2×10^{-4} S/cm after condensation. The presence of I_3^- species was proven by the appearance of $\nu_s(I_3^-)$ mode at 111 cm^{-1} in micro Raman spectra and 295 and 370 nm peaks in UV–vis absorption spectra. Finally, the electrolyte was applied in a hybrid electrochromic device that displayed persistent colouring/bleaching during 4240 cycles tested.

1. Introduction

In the last decade, dialkylimidazole iodide ionic liquids have been recognised as suitable candidates for the preparation of redox electrolytes for dye-sensitised photoelectrochemical solar cells (DSPEC) [1–3] and also hybrid electrochromic devices (HEC in Fig. 1) [4–6] due to their non-volatile character, and many recent works have been devoted to study of their physico- and electrochemical properties [7–10]. Because dialkylimidazole based ionic liquids are liquids, cells require tight sealing in order to prevent their leakage. One way to avoid perfect sealing of the cells is to make the electrolytes solid. Solidification of ionic liquids has been done in the past by their incorporation in various polymer matrices [11,12] or confinement within inorganic gels produced from tetraalkoxysilanes or simple trialkoxysilanes [13], the addition of nanoparticles [14] or small-weight gelators [15] or their functionalisation with various polymerisable groups [12,16]. The latter approach includes the use of trialkoxysilyl functionalised imidazole-based ionic liquids [17–19], which after hydrolysis condense to visco-elastic solids characterised with organic–inorganic (silica) network serving as a host for various ions (I_3^-/I^-, Li^+, protons, etc.) [20,21]. The inorganic (silica) phase of such composite materials provides mechanical and thermal strength, while the variety of organic moieties impart to the corresponding bi-phasic material different optical, electrical, chemical, biochemical or magnetic properties [22].

In order to exploit versatility of the organic–inorganic (silica) hybrid materials, we have recently synthesised the ionic liquid 1-methyl-3-[3-(trimethoxysilyl)propyl]imidazolium iodide ($MTMSPIm^+I^-$), which, after hydrolysis and condensation, formed material with a quasi solid-state consistency stemming from the condensation of silanol groups to various ladder and cube-like silsesquioxanes [17–19]. The conductivity of aged material was 1.1×10^{-4} S/cm and has been attributed to diffusion of I^- ions supported by the charge exchange reactions with I_3^- (Grotthus effect) [1–3]. The efficiency of DSPEC employing the corresponding I_3^-/I^- electrolytes was 3.3–3.7%, which justifies further investigation of similar organic–inorganic (silica) hybrid materials.

As a possible next step, the exchange of the methyl group on the imidazolium ring with a methyldiethyleneoxide one seemed reasonable, with the aim to introduce a more polar substituent. Wang et al. [11], for example, have already investigated redox electrolytes in which imidazolium-based chloride ionic liquid was functionalised with PEO oligomers of various molecular weights (up to 750). It was found that a significant contribution of a Grotthus-type electron exchange of I^-/I_3^- led to a larger apparent diffusion coefficient of triiodides in such electrolytes [11]. In addition, the ionic conductivity increased with increasing PEO molecular weight enabling higher solubility of lithium salts (LiI), surpassing the conductivity of the commonly investigated PEO

---

* Corresponding author. Tel.: +386 01 4760 254; fax: +386 01 4760 300.
E-mail address: angela.surca.vuk@ki.si (A. Šurca Vuk).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.08.036

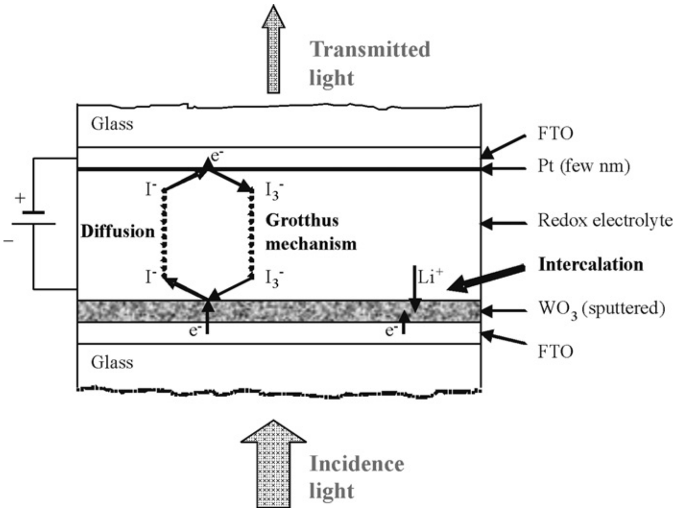

Fig. 1. Schematic representation of HEC device.

based solid polymer electrolytes, characterised with conductivity values not exceeding 10^{-7}–10^{-6} S/cm. Higher conductivity values were achieved for PEO based electrolytes with incorporated ionic liquids. For example, 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide in PEO + KI + I_2 matrix [23] gave rise to conductivity up to 8.8×10^{-5} S/cm (30 wt.% of ionic liquid). A much higher conductivity of 4.29×10^{-3} S/cm has been reported for a redox electrolyte based on silane-substituted benzimidazolium iodide [24], while the conductivity of iodide–oligosiloxane redox electrolytes produced in the reaction of 3-iodopropyltrimethoxysilane with diphenylsilanediol was not given [25].

All these studies directed us to a synthesis of single end-capped alkoxysilyl and PEO functionalised ionic liquid 1-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-(3-(trimethoxysilyl)propylimidazolium iodide (EO_2-$TMSPIm^+I^-$ in Fig. 2) and its testing as redox electrolyte in an optically switchable HEC device (Fig. 1). Usual configuration of HEC device consists of WO_3 thin film providing desired electrochromic colouring/bleaching changes in contact with I_3^-/I^- redox electrolyte, while a thin Pt layer (2 nm) acts as a catalytic layer providing fast I_3^-/I^- redox reactions [4–6]. The WO_3 film coloured ($W^{6+} + e^- \rightarrow W^{5+}$) on intercalation of the lithium ions and electrons, while deintercalation led to bleaching of the WO_3 film and, consequently, also of the HEC device.

An important factor that influences the structure of the final sol–gel networks is the catalyst used to initiate the reactions of hydrolysis and condensation [20,21,26] and this aspect has not yet been systematically investigated for any alkoxy-functionalised ionic liquid. Various studies, however, have been made on simple tetraalkoxysilanes, in order to determine the effect of catalysts with an acid or basic character on gelation rates, the properties of formed gels and the definition of reaction mechanisms [26,27]. Pope and MacKenzie [26], for example, performed a systematic study of gelation of tetraethoxysilane (TEOS) with a series of catalysts comprising halides, inorganic (HCl, ...) and organic (AcOH) acids and an ammonia base. It was confirmed that acid catalysed hydrolysis is an electrophilic reaction with hidronium ions, while a nucleophilic substitution of hydroxyl ions for –OR groups occurred in basic catalysed hydrolysis. Moreover, the hydrolysis rate of TEOS was linearly proportional to the concentration of the inorganic acid or base [26,27]. In contrast to strong inorganic acids, AcOH gave shorter gelation times, which was surprising in view of its lower dissociation constant. The anionic substitution of the acetyl radical was proposed, leading to an ethylacetate by-product [26]. In view of the large differences in sol–gel structures obtained with acidic (more linear products) or basic (more branched products) catalysis, the newly synthesised EO_2-$TMSIm^+I^-$ was characterised from this aspect. Specifically, 0.1 M AcOH and 0.1 M LiOH were chosen as representatives of acidic and basic catalysts and profound FT-IR and ^{29}Si NMR were made to evaluate the differences in their structures. Attenuated total reflectance IR (ATR IR) spectroscopy has already been recognised as a powerful tool for the analysis of structures obtained during the course of sol–gel reactions [28,29]. Possible distortions in the experimentally measured ATR IR spectra have already been evaluated in our previous works on similar systems [18,28,29].

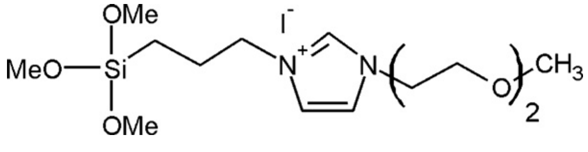

Fig. 2. The structure of a single end-capped ionic liquid 1-(2-(2-methoxyethoxy)ethoxy)ethyl)-3-(3-(trimethoxysilyl)propylimidazolium iodide (EO_2-$TMSPIm^+I^-$, for short).

The question of whether the structure of the electrolyte follows the same hydrolysis/condensation pattern as in the open air in an ATR IR attachment when encapsulated between two substrates, *i.e.*, *in situ* in the cell, remains a particular challenge. Direct *in situ* measurement of the electrolyte in either HEC [4] or DSPEC [30–32] cells is possible with the micro Raman technique but only changes in the $\nu_s(I_3^-)$ and $\nu_s(I_5^-)$ bands have usually been followed, not the structural development of the sol–gel network. Another challenging technique that can be used is FT-IR spectroscopy but in this case the HEC cell cannot be measured directly, due to the FTO glass substrates. Instead, the redox electrolyte can first be encapsulated between two silicon wafers, which partly transmit IR radiation, and the FT-IR spectra then recorded in transmission mode. A further possible approach is the use of IR reflection–absorption (IR RA) spectroscopy under near-grazing incidence angle (NGIA) conditions (80°) and P polarisation [33,34], a technique that is usually used for thin film structural measurements. In this technique, FTO is used as a reflective backside substrate, while the redox electrolyte is covered by the silicon wafer. Such an approach has already been used for *in situ* time dependent measurements of an electrolyte based on organic–inorganic hybrid bis[(N′-(3-triethoxysilylpropyl)ureido]-terminated poly(propylene glycol) 230 (PPGU 230), revealing that ethanol, ester and silylester bands remained entrapped in the electrolyte even after 63 days, although beneficially influencing the conductivity and elasticity of gels [29].

To summarise, a synthesised EO_2-$TMSPIm^+I^-$ was used for the preparation of redox electrolytes. ATR IR and ^{29}Si NMR spectroscopies were first used to analyse the structures achieved by the addition of either an acidic or basic catalyst, in order to determine the most favourable conditions for initiating reactions of hydrolysis and condensation. On the basis of these results, a redox electrolyte was then prepared with a 0.1 M LiOH catalyst and iodine to produce an I^-/I_3^- redox pair and applied in a hybrid electrochromic cell (HEC). This cell was tested for more than 4200 cycles, revealing a persistent colouring/bleaching response that was comparable to those of HEC devices prepared on the basis of organic–inorganic hybrid bis[(N′-(3-triethoxysilylpropyl)ureido]-terminated poly(propylene glycol) 4000 (PPGU 4000) [4], ionic liquid 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide [6] and silsesquioxane (POSS)-modified 1,3-alkylimidazolium iodide ionic liquid [5]. The structural properties of the EO_2-$TMSPIm^+I^-$ based electrolytes were also determined *in situ* using FT-IR transmission and FT-IR reflection absorption techniques.