

# Electrode modified with ionic liquid covalently bonded to silicate matrix for accumulation of electroactive anions

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## Abstract

A thin silicate film containing imidazolium cationic groups surface was obtained by sol–gel processing of ionic liquid – 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium bis(trifluoromethyl-sulfonyl)imide together with tetramethyl orthosilicate on the indium tin oxide electrode. The formation of silicate film was confirmed by FTIR spectroscopy. This electrode when immersed into aqueous solution act as a sponge for  $\text{Fe}(\text{CN})_6^{3-}$  dissolved in aqueous solution. The corresponding voltammetric peak current is by almost two orders of magnitude larger than for electrode covered by ionic liquid precursor only. The repelling of  $\text{Ru}(\text{NH}_3)_6^{3+}$  cations by this electrode is also demonstrated.

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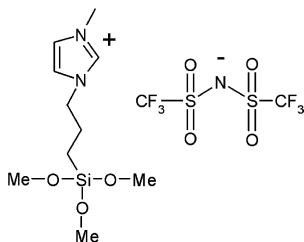
## 1. Introduction

In last few years number of studies reporting electrochemical behaviour of RTIL deposits on different electrode supports appeared in literature [1–10]. These systems were used to study various electrochemical processes like ion transfer across RTIL/aqueous solution [1–4,7,9], voltammetric behaviour of adhered organic microparticles [5,6] or efficient electrooxidation of organic substrates from aqueous solution [8]. The electrocatalytic behaviour of enzyme present in RTIL deposit on the electrode surface was also demonstrated [7]. The related bulk or film electrodes based on different forms of carbon further modified with RTIL were also reported in literature [11–17].

In most of these studies slow transport of species within RTIL phase strongly affects the electrochemical properties of the electrodes and may affect their future application. This problem was recently raised for the case of RTIL film based electrochemical gas sensor [18]. In this respect the electrodes modified by self assembled monolayers of RTIL's [19,20] represents alternative approach. Although they are effective for attraction or rectification of electroactive ions, the amount of accumulated ionic species and thereby their electrochemical response is severely limited.

Here, we propose to apply another method of immobilisation of RTIL on the electrode surface. It is based on sol–gel processing of ionic liquid consisting of cation being sol–gel precursor. The obtained mesoporous silicate surface is expected to provide large number of cationic imidazolium groups accessible from aqueous solution. Such approach was already used in catalysis. Silicate confined imidazolium cations were already used for immobilisation

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Scheme 1. The structural formula of sol-gel precursor 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium bis(trifluoromethyl sulfonyl)imide **1**.

of cationic catalyst to silicate based support [21–25]. Also similar bulk materials were tested for efficient charge transport in solar cells [26–29]. However, according to our knowledge this procedure was not applied for electrode surface modification.

As RTIL precursor, we used 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium bis(trifluoromethyl sulfonyl)imide (**1**) (see Scheme 1). RTIL composed of this cation or its triethoxysilyl analogue were used in earlier studies [21–29]. The mixture of ionic liquid **1** and tetramethoxysilane (TMOS) was sol-gel processed on the electrode surface. The modified electrode was tested in  $\text{Fe}(\text{CN})_6^{3-}$  or  $\text{Fe}(\text{CN})_6^{4-}$  aqueous solutions and compared with the electrode modified with liquid RTIL **1** just deposited on the electrode surface as a film. The penetration of the film by electroactive cations was also tested.

## 2. Experimental

### 2.1. Chemicals and materials

TMOS (99%) was from Aldrich. Methanol and acetonitrile were from Chempur. Formic acid,  $\text{K}_3\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  were from POCH.  $\text{NaClO}_4$  was from Fluka.  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  was from Strem Chemicals, Inc. ITO coated glass (resistivity  $15\text{--}30\ \Omega^{-1}\text{cm}^{-1}$ ) was obtained from Image Optics Components Ltd., Basildon, Essex, UK. Water was filtered and demineralized with an ELIX system (Millipore). Organic solvents for synthesis of RTIL **1** were purchased from Prolabo or Carlo Erba SDS. *N*-methylimidazole, (3-chloropropyl)trimethoxysilane and lithium bis(trifluoromethylsulfonyl) imide ( $\text{LiNTf}_2$ ) were obtained from Fluka or Acros Organics. All reagents were used as received.

### 2.2. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium bis(trifluoromethyl sulfonyl)imide

At first 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride (**2**) was synthesized by the reaction of one equivalent of *N*-methylimidazole with two equivalents of (3-chloropropyl)trimethoxysilane at  $90\ ^\circ\text{C}$  for 48 h [30,31]. The reaction mixture was cooled down to room temperature and the organic upper phase was separated from the yellow ionic liquid phase. Then product **2** was washed thoroughly with  $\text{Et}_2\text{O}$  and residual ether was

removed under vacuum. Finally **2** was lyophilised for 12 h, then kept under vacuum over  $\text{P}_2\text{O}_5$ . Its structure was confirmed by the  $^1\text{H}$  NMR data (200 MHz,  $\text{CDCl}_3$ ).  $\delta$  (ppm): 0.6 (m,  $\text{CH}_2\text{Si}$ ); 2.0 (m,  $\text{CH}_2\text{CH}_2\text{N}$ ); 3.6 (s,  $\text{OCH}_3$ ); 4.1 (s,  $\text{CH}_3\text{N}$ ); 4.3 (t,  $^3J = 7.3\ \text{Hz}$ ,  $\text{CH}_2\text{N}$ ); 7.4 (m,  $\text{H}_{\text{Im}}$ ); 7.5 (m,  $\text{H}_{\text{Im}}$ ); 10.5 (s,  $\text{H}_2$ ).

An equimolar amount of  $\text{LiNTf}_2$  was added to a solution of **2** in dry acetone and the mixture was left under stirring for five days at room temperature. After concentrating under vacuum the solid was solubilized in  $\text{CH}_2\text{Cl}_2$ , dried, filtered over a celite/sand bed and washed with water till  $\text{AgNO}_3$  test was negative. Organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtrated and solvent was removed under vacuum. Orange **1** was lyophilised, then dried under vacuum over  $\text{P}_2\text{O}_5$ . The resulting viscous fluid was kept under argon. The  $^1\text{H}$  NMR data were as follows: (200 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 0.6 (m,  $\text{CH}_2\text{Si}$ ); 2.0 (m,  $\text{CH}_2\text{CH}_2\text{N}$ ); 3.6 (s,  $\text{OCH}_3$ ); 4.0 (s,  $\text{CH}_3\text{N}$ ); 4.2 (t,  $^3J = 7.4\ \text{Hz}$ ,  $\text{CH}_2\text{N}$ ); 7.3 (m,  $\text{H}_{\text{Im}}$ ); 8.8 (s,  $\text{H}_2$ ).

### 2.3. Electrode modification

The ITO electrodes were cleaned with ethanol, then with deionized water and finally with hot redistilled water. The electrode surface was defined by masking off an area of  $0.2\ \text{cm}^2$  with scotch tape. The electric contact was assured by using a piece of copper tape.

The sol precursor was obtained by mixing 0.3209 g of **1**,  $196\ \mu\text{l}$  of TMOS and  $370\ \mu\text{l}$  of formic acid as a catalyst. The mixture was sonicated for 10 min. Then the stock sol was diluted with methanol at 1:10 volume ratio. For electrode modification,  $5\ \mu\text{l}$  of diluted stock sol was deposited onto the electrode surface. The modified electrodes were left for drying for at least 12 h at room temperature to let the silicate film form.

To obtain the unconfined ionic liquid modified electrode, solution of 0.0428 g **1** in 1 ml of acetonitrile was prepared. For the electrode modification,  $5\ \mu\text{l}$  of this solution was deposited onto the electrode surface and left for solvent evaporation.

### 2.4. Instrumentation and cell

Cyclic voltammetry was done with Autolab (Eco Chemie) electrochemical system in a conventional three electrode cell with dedicated software. Modified ITO, platinum wire ( $d = 0.5\ \text{mm}$ ) and  $\text{Ag}/\text{AgCl}/\text{KCl}$  sat. were used as the working, counter and reference electrode respectively. All experiments were carried out at  $22 \pm 2\ ^\circ\text{C}$ .

FTIR and FTIRRAS spectra were measured with FTIR 8400 Shimadzu spectrometer. FTIR spectrum of the liquid gel precursor was recorded as thin liquid film between KRS-5 plates. The reflectance spectrum of ionic liquid modified silicate film was obtained using the variable angle reflectance accessory model 500 from SpectraTech Inc at  $80^\circ$  incidence angle.

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