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Characterisation and application of carbon film electrodes in room temperature ionic liquid media

Rasa Pauliukaite [a], Andrew P. Doherty [b], Kevin D. Murnaghan [b], Christopher M.A. Brett [a,*]

[a] *Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-535 Coimbra, Portugal*
[b] *The School of Chemistry and Chemical Engineering, Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast, N.I. BT5AG, UK*

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Abstract

Carbon film electrodes have been characterised in the room temperature ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ($BmimNTF_2$), 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide, ($BpyrNTF_2$) and 1-butyl-3-methylimidazolium nitrate ($BmimNO_3$), by cyclic voltammetry and electrochemical impedance spectroscopy. The electrochemical behaviour of the ionic liquids depended on both cation and anion of these electrolytes. Oxygen reduction is clearly visible at carbon film electrodes – after oxygen removal the potential window was wider, that of $BpyrNTF_2$ being the widest. These room temperature ionic liquids were used in the electrochemical investigation of two ferrocene derivatives, benzoyl- and acetyl-ferrocene, that are both insoluble in water and cannot be investigated in aqueous solutions. They were also applied in the investigation of two sensor and biosensor mediators, copper hexacyanoferrate and poly(neutral red), with a view to using ionic liquids as electrolytes in electrochemical sensing and biosensing systems.

Keywords: Room temperature ionic liquids; 1-Butyl-3-methylimidazolium bistriflimide; 1-Butyl-1-methylpyrrolidinium bistriflimide; 1-Butyl-3-methylimidazolium nitrate; Ferrocenes; Copper hexacyanoferrate; Poly(neutral red)

1. Introduction

Room temperature ionic liquids (RTIL) are usually organic or mixed organic–inorganic salts with a melting point lower than 100 °C. RTILs are frequently used as clean reaction media for organic synthesis [1,2]. Nevertheless, in the last few years they have become more attractive in other fields such as catalysis [1], in basic electrochemical studies of organic compounds and inorganic compounds [3–12], formation of metal nanostructures [13], analytical chemistry [14] including sensors [15–18], bioanalytical chemistry [2,19–25], and for electrochemical biosensors [26].

Application of RTILs in electrochemistry is increasing because, being inherently conducting, such systems do not require additional supporting electrolyte salt [27]. However, RTILs exhibit much higher viscosities than molecular solvents, which is caused principally by the large cationic size/asymmetry and strong inter-ionic van der Waals interactions. As a result, mass transport (diffusion) within RTILs is suppressed relative to conventional solvents [3]. Moreover, concentration-dependent diffusion has been reported: different slopes of the current dependence on concentration for ferrocene oxidation were found for low and high concentrations in 1-butyl-3-methylimidazolium bistriflimide [5,28]. The potential window in RTILs depends not only on the electrode substrate material but also on their composition and the presence of impurities (e.g. H_2O) [3,29].

Carbon film electrodes fabricated from carbon film electrical resistors have been investigated for electrochemical applications since 2001 [30]. These electrodes have been characterised [30,31] and successfully used in electroanalytical [32–36] and bioelectroanalytical studies [37–42]. These

* Corresponding author. Tel./fax: +351 239 835 295.
E-mail address: brett@ci.uc.pt (C.M.A. Brett).

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carbon film electrodes have similar electrochemical properties to glassy carbon electrodes, especially after surface pretreatment; other advantages are their physical robustness and ease of preparation.

In this work, the electrochemical behaviour of three RTILs, 1-butyl-3-methylimidazolium bis(trifluoromethane)-sulfonimide ($BmimNTF_2$), 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide ($BpyrNTF_2$), and 1-butyl-3-methylimidazolium nitrate ($BmimNO_3$), at carbon film electrodes is reported. Their potential window at carbon film electrodes was determined using cyclic voltammetry before and after deoxygenation of the RTIL and electrochemical impedance spectroscopy measurements were performed to study the processes occurring at the electrode surface. The influence of the RTIL cation and anion is also discussed. Two ferrocene derivatives were electrochemically characterised in the RTILs, as well as carbon film electrodes modified by copper hexacyanoferrate and by poly(neutral red) prepared by in situ electropolymerisation.

2. Experimental

2.1. Chemicals and solutions

The two room temperature ionic liquids $BmimNTF_2$ and $BpyrNTF_2$ were synthesised by ion metathasis of the corresponding chloride salts with $LiNTF_2$ in acetonitrile, $BmimNO_3$ was prepared by ion metathasis of BmimCl with KNO_3 in acetonitrile. In all cases, the LiCl (or KCl) precipitate was removed by filtration and the crude IL washed ($\times 10$) with deionised water. The ionic liquids were then dissolved in acetonitrile and impurities removed with activated carbon [43]. The structure of these compounds is shown in Fig. 1.

Benzoyl- and acetyl-ferrocene were obtained from Sigma (Germany) while the neutral red monomer was purchased from Aldrich (Germany). $CuCl_2{\cdot}2H_2O$, $K_3Fe(CN)_6$ and KNO_3 were obtained from Merck (Germany); KCl was purchased from Fluka (Switzerland). Milli-Q nanopure deionised water (resistivity $\geqslant 18\ M\Omega\ cm$) was used for the preparation of aqueous solutions.

2.2. Electrode preparation

Electrodes were made from carbon film resistors ($2.0 \pm 0.1\ \Omega$ resistance) as described previously [30,31]. The resistors were fabricated from ceramic cylinders of external diameter 1.5 mm and length 6.0 mm by pyrolytic deposition of a thin carbon film. One of the tight fitting metal caps, joined to thin conducting wire, was removed from one end of the resistor and the second one was sheathed in – plastic tubing, adhered with epoxy resin. In this way, the exposed electrode geometric area was $\sim 0.20\ cm^{-2}$.

Copper hexacyanoferrate (CuHCF) was chemically deposited by immersing the electrodes for 50 min in an aqueous solution containing 10 mM $CuCl_2$, 10 mM $K_3Fe(CN)_6$, and 100 mM KCl. After this, the electrodes were dried in a hot air stream for 3 min and left for 24 h to stabilise.

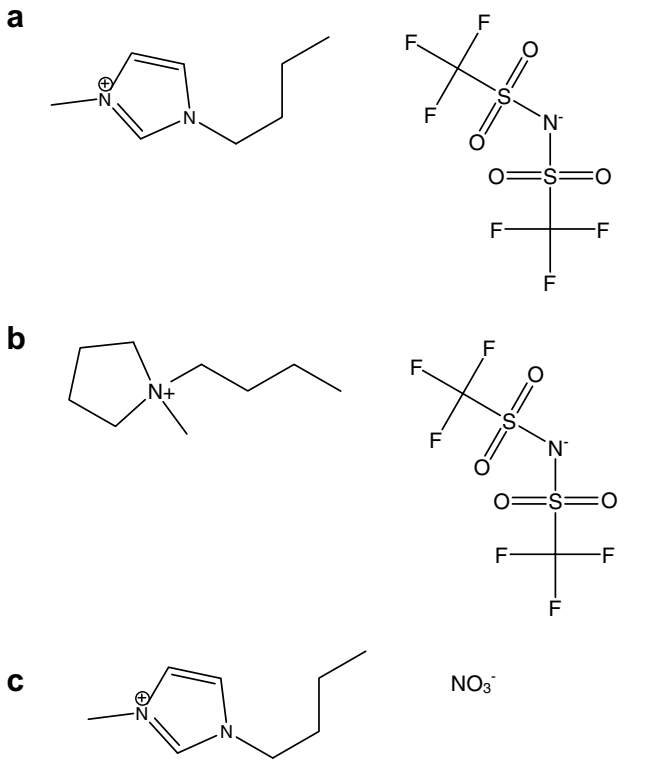

Fig. 1. Structure of ionic liquids used: (a) 1-butyl-3-methylimidazolium bistriflimide ($BmimNTF_2$); (b), 1-butyl-1-methylpyrrolidinium bistriflimide ($BpyrNTF_2$); (c) 1-butyl-3-methylimidazolium nitrate ($BmimNO_3$).

Poly(neutral red) (PNR) was deposited by electrochemical polymerisation from a 3 mM solution of its monomer (neutral red) in all three RTILs by cycling the applied potential (20 cycles at $10\ mV\ s^{-1}$) from -1.3 to $+0.8$ V (in $BmimNTF_2$), from -1.0 to $+0.75$ V (in $BpyrNTF_2$), and from -1.0 to $+1.0$ V (in $BmimNO_3$) vs. solid-state Ag/AgCl reference. In the first three cycles, the positive potential limit was extended by a further 0.3 V in order to produce radicals to initiate polymerisation. The electropolymerisation procedure in aqueous solutions is described elsewhere [44]. After preparation, PNR-coated electrodes were left in air to dry and stabilise for 24 h.

2.3. Methods and instruments

The three-electrode electrochemical cell of volume 300 μL contained a carbon film working electrode, a platinum wire as counter electrode and a silver wire covered with silver chloride as solid-state pseudo reference electrode ($Ag/AgCl_{ss}$); all measurements are given versus this electrode. Measurements were performed using a computer-controlled μ-Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Eco Chemie, The