



Use of an electrochemical room temperature ionic liquid-based microprobe for measurements in gaseous atmospheres

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ABSTRACT

A simple electrochemical microprobe (EMP) is proposed for the detection of analytes in gaseous atmospheres. The EMP consists of two platinum fibres of 25 and 300 μm in diameter encased into a theta glass pipette to form an electrochemical cell in a two-electrode configuration. Ion conductivity between the two electrodes is ensured by a thin film of the room temperature ionic liquid (RTIL), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, which is applied onto the EMP tip surface by a simple dip-coating procedure. The ionic liquid-coated microprobe (RTIL-EMP) was preliminarily investigated by using ferrocene as an electroactive species to ascertain the mass transport properties of the analytes that influence the voltammetric responses as well as the stability and reproducibility of the RTIL-EMP in the gas phase. The performance of the RTIL-EMP to gas analysis was afterward evaluated by using oxygen as electroactive species. The RTIL-EMP was exposed to different synthetic O_2/N_2 (v/v) mixtures and current responses were recorded as a function of O_2 concentration, using either cyclic voltammetry (CV) or chronoamperometry (CA). Regression analysis of the experimental current against % O_2 was linear over the range 0–100% with correlation coefficient and sensitivity of, respectively, 0.996 and 0.29 nA/(v/v) % O_2 in CV and 0.998 and 0.27 nA/(v/v) % O_2 in CA measurements. Long term stability, reproducibility of the RTIL-EMP recovery of the RTIL film layers to the initial conditions and effects of humidity on the current responses were investigated in detail.

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1. Introduction

Electrochemical techniques and sensors for the detection of a great variety of substances have been extensively employed due to their high sensitivity, low cost, ease operation and good portability [1]. However, conventional electroanalytical devices, based on amperometric responses, cannot be directly applied to gaseous samples. To overcome this drawback, gas-permeable membrane electrodes have been developed, in which gaseous analytes can permeate the membrane and, after dissolution in an internal electrolyte, can diffuse to the working electrode surface [2–4]. Their performance is however conditioned by these slow steps because they cause lowering of sensitivity and lengthening of response time.

Remarkable benefits have been introduced by the use of gas sensors based on moist ion-exchange membranes, as solid polymer

electrolytes (SPEs), in which the steps due to permeation and diffusion in solution are avoided [5–13]. Unfortunately, SPEs require the presence of an internal electrolyte, whose solvent can evaporate and cannot survive drastic temperature changes.

The past few years have seen the proposal of several gas electrochemical devices based on room temperature ionic liquids (RTILs) which act simultaneously as electrolytes and solvents [14–26]. RTILs offer quite attractive physical properties since they are characterized by negligible vapour pressure, wide electrochemical windows, good thermal stability, inherent electrical conductivity, and tunability [27–29]. Due to the relatively high viscosity of RTILs, mass transport of redox species is usually much slower than in traditional aqueous or non aqueous electrolytes. Diffusion coefficients in RTILs are typically two or three orders of magnitude lower than those in conventional electrolytes [29]. This circumstance is unprofitable in electroanalytical measurements because slow diffusion coefficients lead to small current signals. However, the use of RTILs can still provide prominent advantages if they are placed as thin films directly onto an electrode sur-

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face. Various electrode surfaces have been suggested for RTILs membrane-free gas sensors, most of them are based on macrodisc electrodes [14–17,24–26,30,31] assembled in either conventional three-electrode electrochemical cells [14–17,24–26] or screen printed [30,31]. A few examples of RTIL-gas sensors based on microelectrodes have also been reported in the literature [21–23]. In particular, platinum microdiscs [23], disposable microband electrodes [21], and arrays of recessed gold microdisc electrodes fabricated on a silicon chip by a standard photolithographic procedure [22] have been proposed. The use of microelectrodes coupled with RTILs provides the advantages of enhanced current densities, high faradic to capacitive current ratio and low ohmic drop [32,33].

Here, we propose an alternative membrane-free microsensor for gas analysis based on a RTIL-coated microelectrode integrated with a pseudo reference electrode. The microcell is fabricated by using two Pt fibres of 25 μm and 300 μm in diameter, which are encased into a theta glass pipette to provide a two-disc electrodes tip. The tip end is coated by a thin film of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTF₂], which ensures ionic conductivity between the two electrodes. [BMIM][NTF₂] has been chosen as, at 20 °C, it displays a viscosity value equal to 50 mPa s [29], which allows keeping diffusivity of electroactive specie to acceptable low values, while allowing a good adhesion and stability of the film onto the tip surface. The performance of the microcell is firstly investigated in bulk RTIL containing ferrocene as model electrochemical probe for gaining general information on mass transport characteristics of the electroactive species. Secondly, it is applied to the detection of oxygen in gas phases. Overall, in this work we show that the proposed microcell can easily be assembled, the RTIL film can be quickly restored to its initial conditions for multiple measurements, and it can be used for continuous measurements even for several days in real world conditions.

2. Experimental

2.1. Chemicals

1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Merck, Darmstadt, Germany) was used as received, without further purification. Analytical-reagent grade potassium chloride, ferrocene (Fc) and potassium ferrocyanide were purchased from Sigma-Aldrich (Milan, Italy). Ultrapure grade (99.999%) oxygen, nitrogen and carbon dioxide, purchased from SIAD (Trieste, Italy), were used to prepare mixtures with controlled oxygen content by adopting two flow meters Brooks model 5850 EM (Hatfield, USA). Washing operations were always made with ultrapure water, purified by an Elgastat UHQ-PS system (Elga Lab. Water, Siershahn, Germany). Unless otherwise stated, all measurements were performed at room temperature (23 ± 1 °C).

2.2. Instrumentation

All voltammetric and amperometric measurements were performed using a 430A CHI electrochemical analyzer (CH Instruments, Austin, TX, USA) driven by the relevant 2.07 software. Unless otherwise stated, measurements for the general characterization of the microprobe were performed in a 2 mL polyethylene vial, into which 1 mL of the desired solution was introduced.

The microprobe surface was inspected by an optical microscope Leica IC50HD (Leica Microsystems GmbH, Wetzlar, Germany), equipped with an inverted optic and managed by the Leica LASEZ program. The values of relative humidity (RH) were recorded using a HMT 100 digital hygrometer (Vaisala, Vantaa, Finland). Viscosity values were obtained by using a SR5 rheometer (Rheometric Instrument, Germany). The water content in the RTIL was mea-

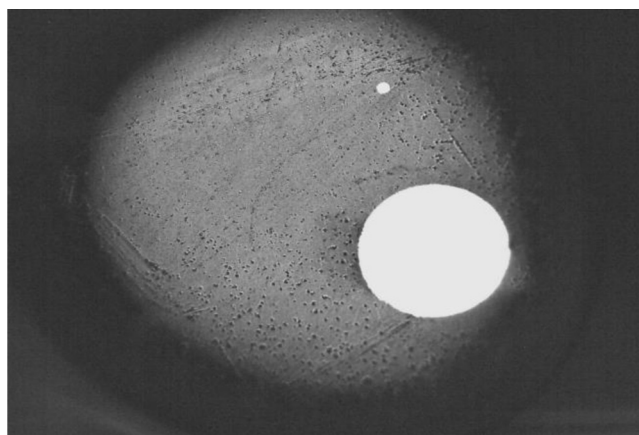


Fig. 1. Optical image of the microprobe tip surface.

sured by titration with a Karl-Fischer titrator DL 32 (Mettler-Toledo, Greifensee, Switzerland).

2.3. Microprobe fabrication and characterization

The microprobe was fabricated by sealing platinum wires of 25 and 300 μm diameters (Goodfellow, Cambridge, UK) in a theta pipette (10 cm long and 1.5 mm OD, Sutter, Instruments, CA). The platinum fibers, 20 mm long, were inserted separately into each compartment of the theta-pipette. Subsequently, the pipette tip was gently melted by means of a methane-oxygen flame, to seal platinum fibers into the glass. Then, the theta-pipette was placed, by a suitable holder within a heated (to incandescence) nickel-chromium spiral, and maintained under vacuum by continuously pumping till the platinum microfibers were completely sealed into the glass. The electrical connections with the external circuit were done by inserting two copper wires (1 mm OD) through the top ends of the theta-pipette to make a back contact with small indium flakes melted by a flame. To expose the two platinum discs to the electrolyte, the theta-pipette tip was smoothed mechanically with sandpaper of different grain size and then polished with aqueous suspensions of graded alumina powder of different size (1, 0.3 and 0.05 μm) supported on a polishing microcloth (Buehler, Düsseldorf, Germany). An optical image of the tip surface of the assembly thus produced is shown in Fig. 1.

The radii of the disc electrodes were calibrated periodically by cyclic voltammetry in a 1 mM K₄Fe(CN)₆ aqueous solution containing 0.1 M KCl as supporting electrolyte. In these measurements a conventional electrochemical cell in the three-electrode configuration was employed. Each electrode of the microprobe was investigated separately and used as the working electrode; an Ag/AgCl, KCl_{sat} and a platinum spiral were employed as reference and counter electrode, respectively. The radius of the working microdisc electrode was established from the diffusion limiting current (I_d) obtained in the CVs at low scan rates and using Eq. (1) [34]:

$$I_d = 4nFD C^b a \quad (1)$$

where n is the number of electrons, F is the Faraday constant, D is the diffusion coefficient of the electroactive species ($6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), C^b is the bulk concentration, a is the radius of the microdisc.

2.4. RTIL film formation

[BMIM][NTF₂] films without or with dissolved known amounts of Fc (5, 10, 15, 20 mM) were adhered to the tip of the microprobe

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