Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

Amperometric detection of oxygen under humid conditions: The use of a chemically reactive room temperature ionic liquid to 'trap' superoxide ions and ensure a simple one electron reduction

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A B S T R A C T

The amperometric detection of oxygen under moist (humid) conditions via Clark cell type devices using Room Temperature Ionic Liquids (RTILs) as electrochemical solvents can be complicated, because the number of electrons transferred in the electrode reaction varies between one and two as a function of the humidity. The problem is avoided through the use of phosphonium cation based ionic liquids in which the alkyl group of the phosphonium cation has acidic protons which are rapidly abstracted by superoxide ions. Thus the reduction of O_2 is to be trapped at the one electron level on the micro-electrode voltammetric timescale, allowing the amperometric detection of oxygen under humid conditions to be quantitatively viable.

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1. Introduction

Room temperature ionic liquids [1–6] offer many advantages for amperometric gas sensing using Clark Cell type devices [7] in comparison with conventional aqueous based solvents. Of particular note is the near zero volatility of many ionic liquids [8] such that the evaporative losses, which plague the use of aqueous sensors, are easily avoided to the extent that even membrane free devices have been proposed [9]. In addition, the wide potential windows available in ionic liquids open up the use of many electrochemical reactions which are obscured by solvent decomposition in aqueous media [10–13]. Further the wide liquid ranges of selected ionic liquids allows measurements at both lower and higher temperatures than those which are possible using conventional molecular solvents (water, organic solvents, etc). Additional advantages include the inherent conductivity of ionic liquids such that there is no need to add supporting electrolyte to suppress migration [14,15]. Ionic liquids also show high thermal stability to ca. 200 °C in favourable cases. Ionic liquid based solvents have been proposed for Clark-type sensors for oxygen [9,16–21], hydrogen sulphide [22–24], chlorine [25], nitrogen oxides [26–28], hydrogen [29] and other gases [30].

In the context of Clark-cell measurements using ionic liquid solvents we have previously advocated the use of micro-electrodes or their arrays as opposed to macro-electrodes for gas sensing [31]. The benefits arise partly from the much reduced currents drawn such that cells can be designed such that at steady state any gas permeable membranes used to separate the electrolyte from the gas phase shows a negligible impact on the steady-state current in contrast to classical Clark cells using macroelectrodes [32]. Further we have shown the merits of using transient current measurements using from potential step measurements at micro-electrodes. These lead to a changing diffusional region with time in which linear diffusion to the electrode precedes the convergent diffusion characterising the steady-state. Consequently the currents under the former, 'Cottrellian' conditions scale as $nD^{1/2}c$ where D is the diffusion coefficient of the target gases of interest of solubility c and n is the number of electrons transferred in the electrochemical process of interest. In contrast, the current scales with nDc under the latter steady-state conditions. Hence it is possible to extract values of D and (nc) from so-called 'Shoup and Szabo analysis' of the current-time transients [33]. This approach has been demonstrated to work very successfully for the measurement of oxygen under dry conditions [16,18,34,35].

Micro-electrodes measurements are additionally useful since they can be combined with simultaneous electrochemical measurements both of temperature and/or humidity [33,36]. Thus by combining temperature and humidity data with Shoup and Szabo

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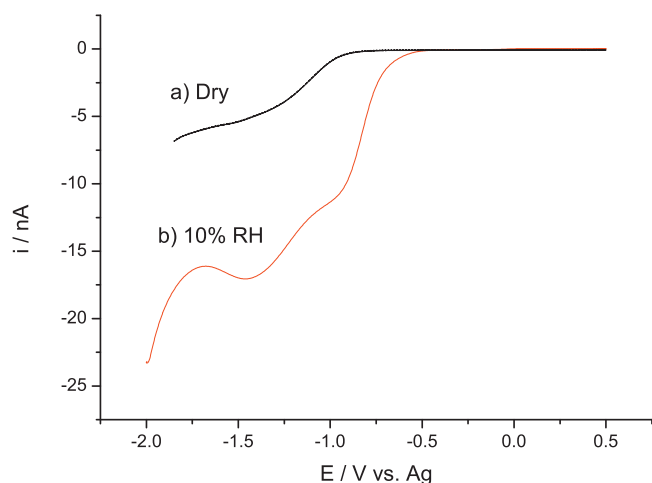
Fig. 1. Comparison of liner sweep voltammetric responses of (a) dry and (b) 10% RH O_2 in [Pmim][NTf$_2$] at a 5.4 μm Pt electrode at 298 K at a scan rate of 100 mV s^{-1}.

analysis, the latter is able to provide reliable measurements of dissolved gas concentrations which, combined with the former parameters, allows gas phase concentrations to be inferred. This approach, of course, requires that the number of electrons, n, transferred in the electrochemical reaction used to probe the dissolved gas remains constant and independent of both temperature and humidity.

One case of considerable interest where variable humidity can alter an electrode reaction is that of oxygen reduction. In dry ionic liquids a one-electron ($n = 1$) reaction to form superoxide is seen:

$$O_2 + e^- \rightleftharpoons O_2^{\bullet-} \tag{1.1}$$
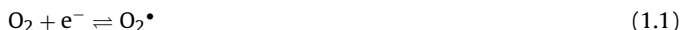
Under dry condition the superoxide is stable. However in the presence of water, protonation and further electron transfer is possible leading to the overall formation of hydrogen peroxide for which $n = 2$:

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \tag{1.2}$$

An example of this transition is shown for the reduction of O_2 in [Pmim][NTf$_2$] in Fig. 1 where linear sweep voltammetric responses are shown for both 'wet' and 'dry' solvent. The former shows an increased current and the formation of H_2O_2.

Moreover for sufficiently 'wet' conditions, this reaction might take place on the time scale of micro-electrode voltammetry/chronoamperometry, thus complicating the 'Shoup and Szabo analysis' proposed above. In the present paper, we show how this problem can be overcome and the reduction can be 'trapped' at the one electron only stage by the use of an ionic liquid, which reacts very quickly with superoxide preventing its further reaction to hydrogen peroxide, not least since the ionic liquid is present in very high concentration relative to dissolved water resulting from ambient humidity. In particular, we use a phosphonium cation based ionic liquid using long chain alkyl groups as shown in Fig. 2.

It is known that the protons alpha to the phosphonium cation are acidic and are rapidly abstracted by superoxide ions [37]. Thus the use of [P$_{14,6,6,6}$][NTf$_2$] for the reaction of O_2 aimed at gas sensing enables the latter to be stopped at the one electron stage,

$$PR_4^+ + O_2^{\bullet-} \rightleftharpoons HO_2^{\bullet} + ylide \tag{1.3}$$
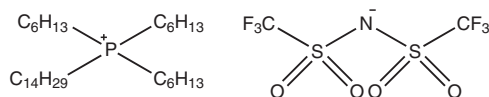
Fig. 2. Structure of [P$_{14,6,6,6}$][NTf$_2$].

and the quantitative analysis of O_2 via micro-electrode 'Shoup and Szabo analysis' to be facilitated.

2. Experimental

2.1. Chemicals

Ferrocene (Fe(C$_5$H$_5$)$_2$, Aldrich, 98%), decamethylferrocene (Fe(C$_{10}$H$_{15}$)$_2$, Fluka, 95%), tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%) and acetonitrile (MeCN, Fischer Scientific, dried and distilled, 99%) were used as received without further purification. Tri-hexyltetradecylphosphonium bis(trifluoro-methylsulfonyl)imide ([P$_{14,6,6,6}$][NTf$_2$], see Fig. 2) and 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide were kindly donated by Queen's University, Belfast.

2.2. Instruments

All electrochemical experiments were performed using an Autolab (Eco Chimie, Utrecht, The Netherlands). Solutions were in housed in a sealed glass vial [17], with a three electrode arrangement consisting of a platinum microdisc electrode as a working electrode, two silver wires as a counter electrode and a pseudo reference electrode, respectively. The platinum microdisc electrode was polished on soft lapping pads (Kemet Ltd., UK) using alumina powder (Buehler, IL) of sizes 1.0, 0.3 and 0.05 μm. The electrode radius (5.4 μm) was calibrated electrochemically by analysing the steady state voltammetry of a 2.0 mM ferrocene in acetonitrile containing 0.1 M TBAP, using a diffusion coefficient for ferrocene of 2.30×10^{-9} m^2 s^{-1} at 298 K [38]. [P$_{14,6,6,6}$][NTf$_2$] was put under vacuum to remove any impurities (e.g. water and organic solvents) before addition of oxygen into [P$_{14,6,6,6}$][NTf$_2$]. For experiments carried out in dry conditions, [P$_{14,6,6,6}$][NTf$_2$] was saturated with oxygen by passing dry oxygen (99.5%, BOC, Guildford, Surry) through for more than 30 min and confirmed by cyclic voltammetry. To minimise the possible influences of humidity for experiments in dry conditions, the gases were pre-dried using a drying column composed of 4 Å molecular sieves.

The humidified oxygen was realised via the following method: the inlet line of the gas is divided into two lines, with one connected to a drying column and another to a Dreschel bottle containing deionised water. These two lines then merge into a common outlet line, which allows the gas to flow into the vial. The humidity is controlled by the flow metres in the dry and wet line, respectively (see Fig. 3). The drying column consists of 4 Å molecular sieves. Before the electrochemical measurements, gas was run for at least 1 h to ensure steady-state conditions were fully established. The values of humidity were recorded using an ADC-16 pico-logger (Honeywell, UK). The humidity is described using the relative humidity equation below [39]:

$$RH\,(\%) = \frac{e_w}{e_w^*} \times 100 \tag{2.1}$$

where e$_w$ is the partial pressure of water vapour (H$_2$O) in the mixture and e$_w^*$ is the saturated vapor pressure of water at a prescribed temperature. The variation of humidity during an experiment was no more than 3% RH. Different RHs were achieved by tuning the flow rates of the dry column and a wet column. The flow rates corresponding to each RH are shown in Table 1. Water content was tested using Karl–Fischer Titrator (Mettler-Toledo Ltd, Beaumont Leys Leicester). 100 μL of [P$_{14,6,6,6}$][NTf$_2$] exposed to 36% RH O_2 for 3 h gave a concentration of H$_2$O of 6.7 mM (12 μg). A longer time was needed to reach O_2 saturation at higher RH. Therefore humidified O_2 was purged into [P$_{14,6,6,6}$][NTf$_2$] for at least 1 h before carrying any analysis to ensure the saturation was reached.