Comparative Study of Screen Printed Electrodes for Ammonia Gas Sensing in Ionic Liquids

Krishnan Murugappan, Junqiao Lee, Debbie S. Silvester*

Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPO Box U1987, Perth, 6845, Australia.
*E-mail:d.silvester-dean@curtin.edu.au; Fax:+61(8)92664699; Tel:+61(8)92667148

Abstract

Commercially available screen printed electrodes (SPEs) have been used for electrochemical ammonia (NH$_3$) gas sensing in the room temperature ionic liquid 1-ethyl-3-methylimidazolium bit(trifluoromethylsulfonyl)imide ([C$_2$mim][NTf$_2$]). The SPEs consist of a 4mm diameter working electrode surface (carbon, platinum or gold) with a silver reference and C/Pt/Au counter electrode. No obvious voltammetric response was observed for NH$_3$ oxidation on the carbon SPE, however, clear oxidation peaks were observed on Pt and Au. Linear calibration graphs were obtained for oxidation peak current vs. concentration in the range 240-1360ppm NH$_3$ on both Pt and Au SPEs, giving limits of detection of 50ppm and 90ppm, respectively. The voltammetry on Au was complicated by additional peaks (most likely due to water impurities in the RTIL), which leads us to suggest that Pt is the preferred electrode surface material. The conditions of the experiment were chosen to be as close to real conditions as possible (no pre-vacuuming of the RTIL and no polishing/electrochemical cleaning of the SPE surface before experiments) suggesting that Pt SPEs in conjunction with non-volatile RTILs may provide cheaper alternative sensing materials compared to those currently used in commercial amperometric gas sensing devices.

Keywords

Room temperature ionic liquids, screen printed electrode, gas sensing, ammonia oxidation, electrochemistry, voltammetry

1. Introduction

Screen printed electrodes (SPEs) are increasingly being explored as favourable sensing surfaces due to their low manufacturing costs and commercial availability [1]. To date, many experiments with SPEs have been reported in aqueous solvents [1]; but some authors have also employed non-aqueous solvents such as room temperature ionic liquids (RTILs) as electrolytes [2-4]. RTILs are favourable electrolyte media in electrochemistry, due to their intrinsic conductivity, wide electrochemical windows and low-volatility [5-7]. They also have physical properties such as high thermal stability, high viscosity and the ability to dissolve a wide range of compounds. Due to their low-volatility, RTILs have been suggested as a replacement for conventional organic solvents in membrane-free amperometric gas sensing devices [8] with the advantage that the electrolyte will not dry out and the sensor lifetime can be extremely long. However, before RTILs can be employed in commercial gas sensing devices, the electrochemical reactions and mechanisms of gases need to be fully understood. Rogers et al. [9] have reviewed much of the recent work in this area, focussing on the detection of oxygen, carbon dioxide, hydrogen, ammonia, hydrogen sulfide, sulfur dioxide and nitrogen dioxide, mainly on metallic microdisk electrode surfaces (e.g. Pt or Au) or Au microdisk electrode arrays. The behaviour of many of these gases in RTILs on screen-printed surfaces is yet to be explored. In this work, we report the electrochemical oxidation of a target gas, ammonia, in the RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) on three screen printed electrodes (carbon, platinum and gold). Although ammonia gas sensing has been reported using inkjet-printed polyaniline electrodes in aqueous solutions [10], this is believed to be the first report using commercially available SPEs and/or non-aqueous/RTIL solvents. The analytical utility is studied on Pt and Au surfaces, and these results will be used to suggest if SPEs in conjunction with RTIL solvents are favourable for ammonia amperometric gas sensing.

2. Experimental

2.1 Chemicals and Gases

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C$_2$mim][NTf$_2$]) was synthesized by standard literature procedures [11] and was kindly donated by Professor Christopher Hardacre at Queens University Ionic Liquids Laboratory (QUILL), Belfast, UK. Ammonia gas (4.95%, nitrogen fill) was purchased from CAC gases (Auburn, NSW, Australia). N$_2$ gas (for further dilution of NH$_3$) was obtained from a gas line plumbed into the building from 99.99% purity N$_2$ cylinder. Acetonitrile (99.8% purity, for washing) was purchased from Sigma-Aldrich.

2.2 Electrochemical Experiments

All electrochemical experiments were preformed using a μ-Autolab type-III potentiostat (Eco Chemie, Netherlands) interfaced to a PC with NOVA software. A three-electrode cell was employed, with the working, counter and reference electrodes of the screen-printed electrodes (SPE) connected directly to the potentiostat via soldered wires. The SPEs from DropSens (Oviedo, Spain) consisted of a C, Pt or Au working surface (4mm diameter), Ag quasi-reference electrode and C/Pt/Au counter electrode (see www.dropsens.com). The SPEs were used "as-is" with no polishing, activation or electrochemical cleaning of the working electrode surface before experiments, as this did not show any improved response (peak shape/current) for the ammonia oxidation peak. This also better represents the conditions required for real sensors where activation/cleaning steps may not be feasible. The SPE was housed in a modified version of a glass cell designed for investigating microsamples of ionic liquids under a controlled atmosphere [12]. ~8μL of the RTIL was drop-cast onto the SPE, the minimum volume required to fully cover the three electrode surfaces, before being placed in the air-tight cell. The cell was then purged with N$_2$ gas to remove impurities naturally present in the RTIL (e.g. oxygen, water). When the baseline was stable (after ~90 minutes), ammonia gas was introduced into one arm of

the cell. The gas was allowed to diffuse into the RTIL until equilibrium was obtained (typically after 10 minutes). An outlet gas line (PTFE tube) led from the other arm of the cell into a fume cupboard. All experiments were carried out at a temperature of 295±2 K.

2.3. Gas Mixing System

NH_3 (4.95%, nitrogen fill) was diluted with N_2 gas using a gas-mixing system, which consisted of two PTFE tubes from two flow-meters (one from the ammonia cylinder and one from the N_2 line) connecting via a Swagelok T-joint. The mixed gas was then passed through an additional gas mixing segment that constricts air-flow comprising of two mirroring tapered glass-needles, inserted into a short piece of PTFE tubing for support, to create gas turbulence and ensure adequate mixing. The relative flow rates of the two flow meters were then used to calculate the % concentrations of NH_3 being introduced into the cell.

3. Results and Discussion

The RTIL chosen in this work ($[C_2mim][NTf_2]$) has a wide electrochemical window (>4.5V), high intrinsic conductivity, and is also one of the least viscous RTILs available. This RTIL was employed in all experiments described throughout this work.

3.1 Cyclic Voltammetry for Ammonia oxidation in an RTIL on three SPE surfaces

Figure 1 shows cyclic voltammograms at $100mVs^{-1}$ for the oxidation of 0.136% (1360ppm) ammonia on carbon, platinum and gold SPE surfaces using the RTIL $[C_2mim][NTf_2]$ as the electrolyte (response in the absence of ammonia=dotted line). On carbon (Figure 1a), there is a much larger capacitive current most likely due to the large and rough surface of the carbon deposit. Additionally, there is no obvious oxidation peak for ammonia visible at this concentration and therefore is not a favourable

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sensing surface. However, clear and sharp oxidation peaks for ammonia were observed on both Pt and Au surfaces (Figure 1b and 1c) and the blanks were relatively flat with low background charging currents. The voltammetry on Pt (Figure 1b) shows the ammonia oxidation peak (I), followed by two reduction peaks, (II) and (III), and a corresponding second oxidation peak (IV) on the reverse sweep. These peaks are similar to those observed on Pt microdisk electrodes [12, 13] and are assigned to the following reactions:

Peak (I) $$NH_3(g) + 3A^- \rightarrow \frac{1}{2}N_2(g) + 3HA + 3e^- \qquad (1)$$
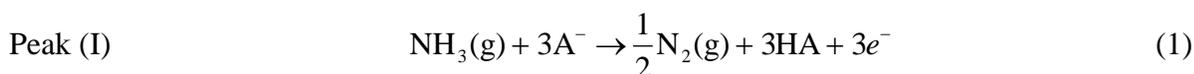
where $A^- = $ RTIL anion ($[NTf_2]^-$). HA can then transfer its proton to an ammonia molecule in the following equilibrium reaction:

$$HA + NH_3(g) \leftrightarrow NH_4^+ + A^- \qquad (2)$$

Two reduction processes occur: the reduction of HA (eqn 3) and the reduction of NH_4^+ (eqn 4) followed by oxidation of the adsorbed protons on the reverse sweep (Peak (IV)).

Peak (II) $$HA + e^- \rightarrow A^- + H(ads) \qquad (3)$$

Peak (III) $$NH_4^+ + e^- \rightarrow NH_3(g) + H(ads) \qquad (4)$$
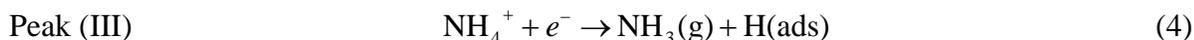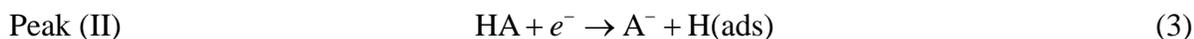
To confirm the mechanism on the SPE, the reduction of NH_4PF_6 in $[C_2mim][NTf_2]$ was also studied. In the absence of ammonia, two reduction peaks and a corresponding oxidation peak were observed for NH_4^+ (voltammetry not shown here). When ammonia was introduced into the cell and oxidised by CV, all three peaks from NH_4^+ reduction increased in current (albeit with a shift in reference potential of $\sim+0.4$ V after the introduction of NH_3 likely due to ammonia adsorption on the silver quasi-reference electrode) suggesting that they correspond to the same reactions.

On the Au SPE (Figure 1c), the voltammogram is complicated by additional peaks, which are also present in the blank scan. These are most likely due to trace water impurities in the RTIL that cannot be easily removed by purging with N_2 gas (these peaks are not present when the RTIL is purged of water impurities using a vacuum pump on a microelectrode [7]). It is noted here that voltammetric

peaks in the blank RTILs on Au SPE surfaces have been reported previously in an ethylene gas sensing paper [4]. Therefore, it appears that Pt surfaces are favoured for voltammetric sensing in RTILs under atmospheric conditions.

3.2. Peak Current vs Concentration for Ammonia Oxidation on Pt and Au SPEs

Of the 3 surfaces investigated, Pt and Au were chosen for analytical studies of ammonia due to the presence of a clear oxidation peak at 0.136% NH_3. NH_3 was systematically diluted to concentrations of 0.024, 0.049, 0.073, 0.102 and 0.136% (240-1360ppm) using a gas-mixing system. Figure 2 shows linear sweep voltammograms for ammonia oxidation on both surfaces, along with corresponding calibration graphs of current (baseline corrected) vs. concentration. A small shift in the oxidation peak potential is observed on both surfaces, probably due to the unstable potential of the Ag quasi-reference electrode. The current response is linearly proportional to concentration in this range on both surfaces (R^2=0.999 on Pt and 0.991 on Au). The currents are reproducible and the error bars represent the variations of current observed when the same experiments were performed on subsequent days and also on fresh SPE surfaces (we note here that one SPE surface can be used for several days with a reproducible current response (s.d. $\pm$ 6 %)). The error bars for concentration were estimated based on the uncertainties in the flow-meter readings. Using this sensor design, limits of detection of 50ppm (Pt) and 90ppm (Au) were obtained, comparable to 48ppm reported in [C$_2$mim][NTf$_2$] on a Pt microdisk electrode [12]. It was found that one SPE could be used for many experiments on several days without any appreciable change in the NH_3 oxidation peak current and shape; they are therefore not necessarily 'disposable' sensors.

3.3. Constant-Potential Amperometry

In order to test the ability of the sensor for "real-time" NH_3 detection, constant potential amperometry experiments were preformed on the Pt SPE. First, the cell was flushed with nitrogen until the blank voltammogram was obtained. The potential was then stepped from 0 to +1.4V and held for an extended period of time. Ammonia gas was introduced into the cell at different concentrations, while performing a nitrogen 'flushing' step between each addition to ensure that the baseline is stable. Figure 3 shows the constant-potential transient obtained on successive additions of ammonia (shown by arrows on the graph). At the beginning of the experiment, a current close to zero is observed in the absence of ammonia. When ammonia is added, the current increases to a plateau. This is repeated for different concentrations as shown in Figure 3. The response time is relatively long under these conditions (several 100s of seconds required to obtain a true plateau current), and may be improved in future experiments e.g. by employing a thinner layer of RTIL so the gas has less distance to diffuse to the electrode surface. At longer times, the current plateau begins to drop rapidly, indicating that the surface has been fouled. The last two additions of ammonia did not show the expected current response, suggesting that the surface is no longer suitable for NH_3 sensing. It is noted that fouling also occurred on the microelectrode system (results not shown) but at longer times (~25,000 seconds), suggesting that this effect may be due to the complicated ammonia oxidation mechanism rather than the screen-printed electrode itself. Although all of the techniques used in this work are viable systems for disposable electrodes, these observations suggests that continuous "real-time" measurement of NH_3 concentration may not be possible using this approach, but sensing can take place via voltammetric/chronoamperometric transients taken at specific time intervals (e.g. every 5 minutes), where stable responses were observed for several days on the same SPE surface.

4. Conclusions

The voltammetry for ammonia oxidation has been studied in [C$_2$mim][NTf$_2$] on C, Pt and Au screen-printed electrodes. No obvious response was observed on carbon surfaces, however, clear and well-defined oxidation peaks were observed on Pt and Au. The calibration curves on both surfaces were linear, suggesting that this system is a viable method for NH$_3$ sensing, with Pt surfaces favoured over Au due to the lack of interfering voltammetric peaks. The use of low-cost screen-printed Pt electrode surfaces and very small (microlitre) volumes of non-volatile RTILs is a huge advantage and may significantly reduce the costs of voltammetric/amperometric ammonia gas sensing devices.

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Figure 1. Cyclic voltammograms for the oxidation of 0.136% (1360ppm) ammonia gas on (a) carbon, (b) platinum and (c) gold screen-printed electrodes in the RTIL $[C_2mim][NTf_2]$. Dotted line= response in the absence of ammonia. Scan rate $100mVs^{-1}$.
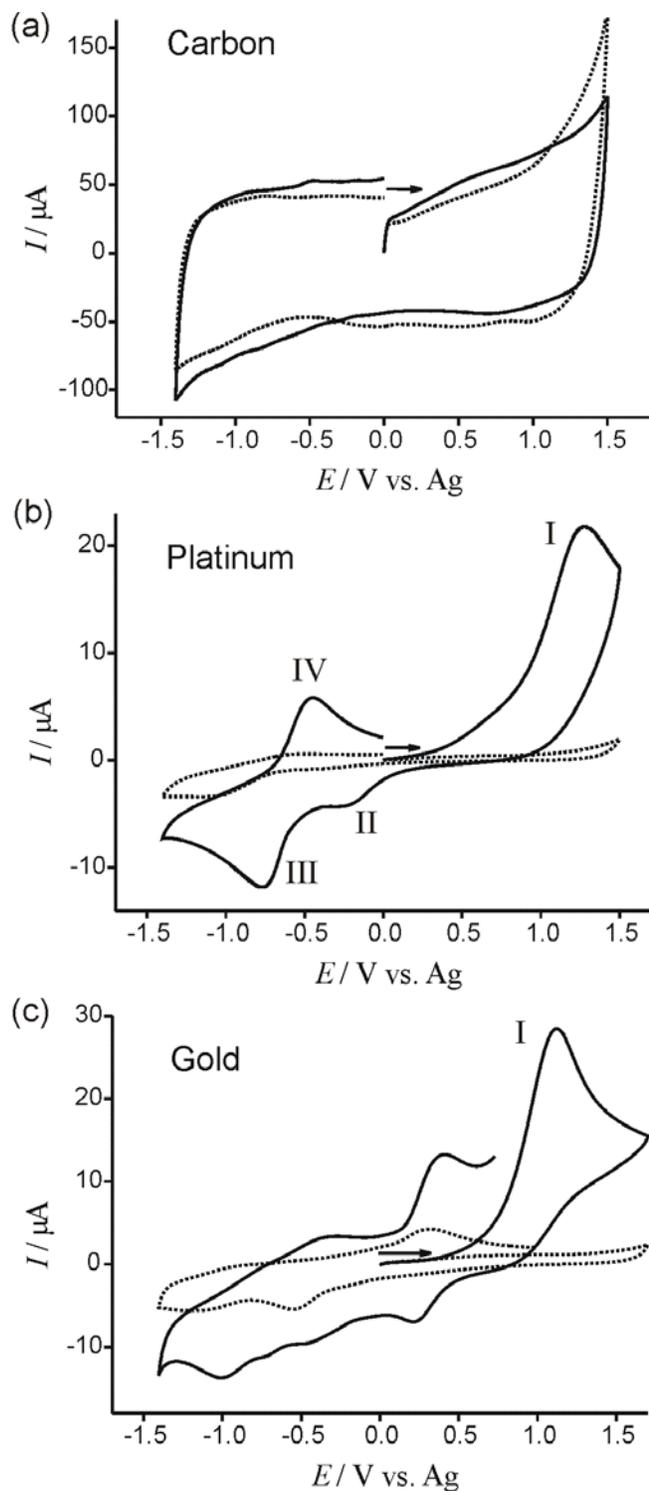
Figure 2. Linear sweep voltammograms for the oxidation of different concentrations of NH_3 in [C_2mim][NTf_2] on (a) Pt and (c) Au SPEs. Dotted line=N_2 saturated (blank) RTIL. Scan rate 100mVs^{-1}. (b) and (d) show the corresponding calibration graphs of peak current vs. % concentration NH_3.
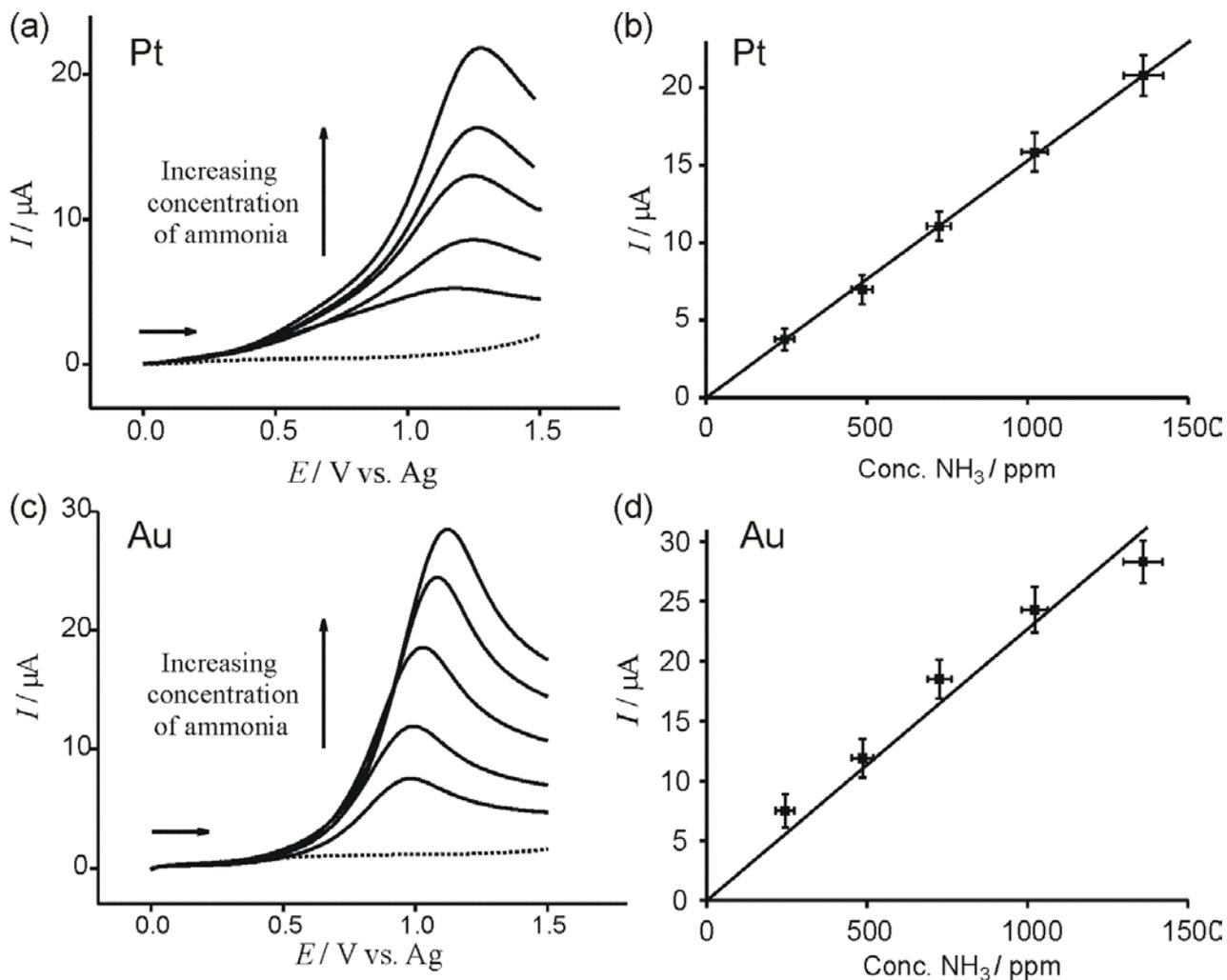
Figure 3. Constant-potential amperometry experiment obtained after holding the potential at +1.4V vs. Ag for different ammonia additions on a Pt SPE in [C$_2$mim][NTf$_2$]. The arrows correspond to the introduction of ammonia gas at different concentrations.