

New Innovations in Ionic Liquid-based Miniaturised Amperometric Gas Sensors

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Abstract:

Gas detection is an essential part of everyday life; for some applications, using sensors for toxic and hazardous gases can literally mean the difference between life and death. In this mini-review, recent progress in amperometric gas sensing using miniaturised electrodes and devices is described. The focus is on the use of non-volatile room temperature ionic liquids (RTILs) as electrolytes, which possess inherent advantages such as wide electrochemical windows, high thermal and chemical stability, intrinsic conductivity and good solvating properties. Various different gases, electrodes and RTILs have been investigated in the strive towards new materials for improved gas sensors. The most recent developments using porous membrane electrodes, planar devices (e.g. screen-printed, thin-film, microarray and interdigitated electrodes), and the modification of these surfaces for improved sensitivity are described. RTILs have great potential to be used as electrolytes in amperometric gas sensors, with improved lifespan of the sensor in hot/dry environments and allowing miniaturisation of devices. However, it is clear that more understanding of their long-term operation and utility in real environments (e.g. background air, varying temperatures and humidity levels) is needed before their realisation in successful commercial devices.

Keywords:

Gas sensing; amperometric; ionic liquids; miniaturised devices; voltammetry; chronoamperometry; Clark cell

Introduction

Gas detection is important in a wide range of fields, as highlighted in Figure 1a [1]. Many of these applications rely on the accurate determination and quantification of gases in the environment around the sensor. Among the various techniques employed for gas detection, the amperometric principle – the notion that gas concentration can be correlated with current – is popular due its high sensitivity, high selectivity, low-cost, wide detection range, and low power requirements [2]. The first amperometric gas sensor (AGS) was introduced by Leyland Clark and colleagues in 1953 [3], and many modern commercially-available AGSs are still based on variations of this design [2, 4]. Amperometric gas sensors typically comprise of a handheld battery-powered device (Figure 1b) housing one or more packaged sensor devices (e.g. Figure 1c). The user simply presses a button that applies a potential bias (depending on the target gas), and the current is converted into a quantitative display on the sensor. A schematic of the interior of a typical AGS is shown in Figure 1d, comprising of three electrodes (working, counter and reference) placed in contact through an electrolyte (usually a water/sulfuric acid mixture). These devices are extremely popular for many applications, but the lifetimes of these sensors are limited by the evaporation of the solvent, making them unsuitable for long term deployment in very hot and dry conditions. Therefore, there has been a drive towards low-volatility materials such as room temperature ionic liquids (RTILs), as replacement solvents.

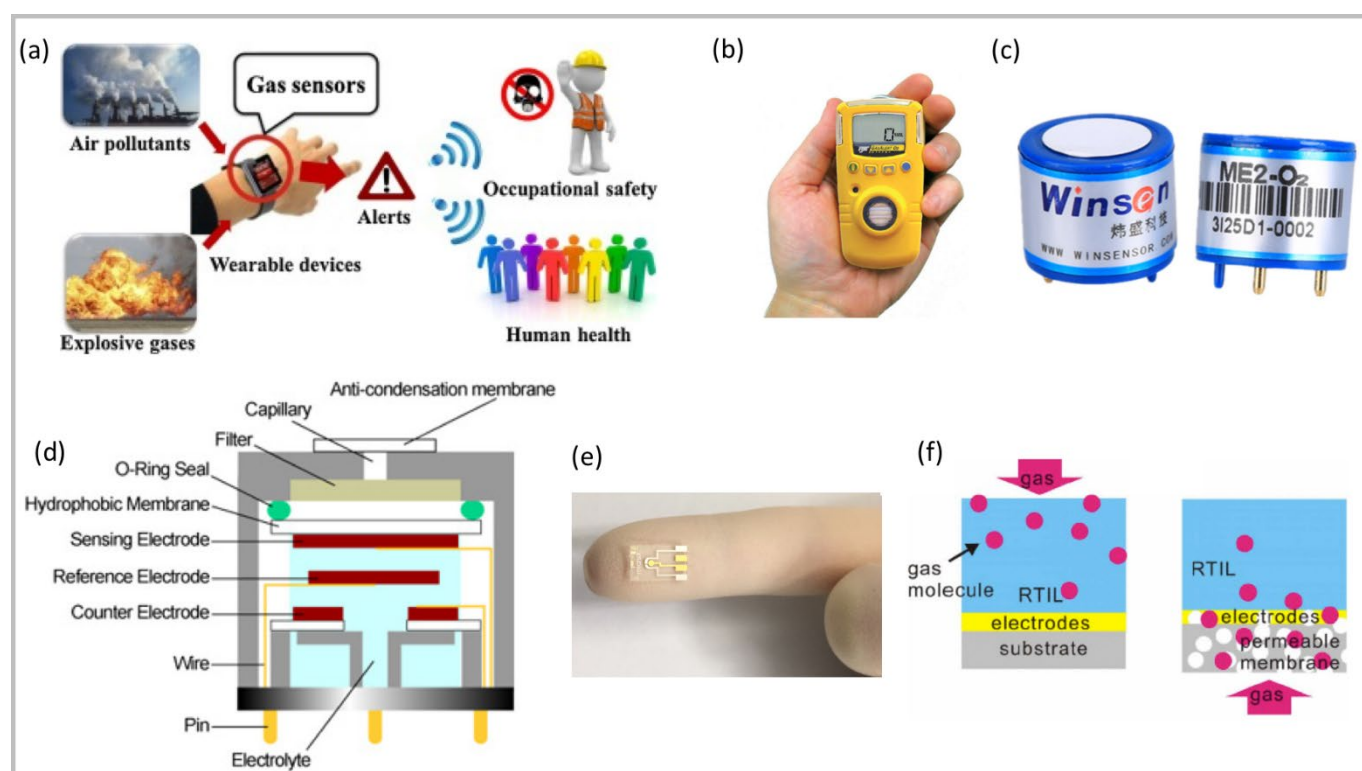


Figure 1. Overview of commercially available amperometric gas sensors and new miniaturised planar devices being used increasingly by academic researchers. (a) Applications of gas sensors deployed in wearable devices for real-time point-of-exposure gas monitoring, reproduced with permission from Elsevier from [1]. (b) Handheld device used for monitoring a single gas, from Dalton Engineering Ltd. (www.daltonengineering.co.uk). (c) Individual device(s) with gas-permeable membrane for monitoring O₂ – three pins connect to the sensing electrode (WE), RE and CE (available from Winsen, www.winsensor.com). (d) Schematic of the inside of a AGS, showing the electrodes, electrolyte, pins, seals and filter (membrane), from Membrapor www.membrapor.ch/electrochemical-gas-sensors. (e) Photo of a commercially available planar electrode device (thin-film electrode) from MicruX Technologies (www.micruxfluidic.com) showing the very small dimensions, adapted from [5] with permission from Elsevier. (f) Left: conventional sensor structure: response time is slow due to slow gas diffusion through RTIL. Right: electrodes-on-permeable-membrane structure: response time is improved due to fast gas diffusion in the permeable membrane, adapted from [6].

RTILs are salts with a melting point lower than room temperature (25°C) and have several archetypal properties such as high chemical and thermal stability, low (near zero) volatility, intrinsic conductivity, wide electrochemical window, high viscosity, high polarity, good solvation properties and tunability [7]. The reader is directed to excellent review articles describing the general properties of RTILs as electrochemical solvents [8, 9], and specifically their use in electrochemical sensors [10-14]. The concept of “membrane free” AGSs using RTILs was first introduced by Compton’s group in 2004 [15], and the same group (and others) followed-up extensively with important research in the area [2, 16, 17], particularly to determine diffusion coefficients, solubilities and reaction mechanisms of gases in RTILs.

The removal of the membrane can add additional challenges such as solvent leakage, and the high viscosity of RTILs themselves can result in slow response times; various researchers have recently been working to overcome these challenges. In this mini-review, significant progress on RTIL-based AGSs since 2016 is discussed. It is not intended to be a comprehensive review of the area – interested readers are directed to other reviews devoted to RTIL-based gas sensors [2, 18-20], and in particular, the excellent technical review article by Gebicki et al. [21] that describes mechanism types of signal generation and an analysis of literature data for RTIL-based amperometric gas sensors up to 2016. This mini-review will discuss the authors’ opinions on the future of the field and the challenges that lie ahead. A summary of the area is given in Figure 1, which compares commercially available AGS devices with miniaturised devices currently gaining attention in academic research. There appears to be a move away from conventional electrochemical devices with large volumes (e.g. several mLs) of solvent, towards miniaturized designs that require less than ~50 µL of non-volatile RTILs.

Amperometric Gas Sensing with Ionic Liquid Electrolytes

Table 1 presents an overview of various amperometric (or voltammetric) methods used to detect gases since 2016, with details on the working (sensing) electrodes, ionic liquids, electrochemical techniques, and concentration ranges studied. It is not the intention here to compare sensitivities and limits of detection – the focus will be primarily on the materials and methods used. In table 1, it is clear that a large majority of publications are focused on oxygen as an analyte gas; other gases such as hydrogen, or toxic gases such as ammonia, hydrogen chloride, sulfur dioxide, etc. are also studied. The next sections will highlight various approaches that researchers have used to incorporate RTILs in sensor devices, and innovative ways in which researchers have tried to improve their operation and overcome some of the challenges of membrane-free gas sensors.

Table 1. Overview of the most significant research on amperometric gas sensing using RTIL solvents.

Gas(es)	RTIL(s)	Electrode	Conc. studied	Technique(s) used	Comments	[Ref] Year
VOC in air	[C ₄ mpyrr][NTf ₂]	Clark-type sensor with polycrystalline Pt gauze.	200–3000 ppm (acetaldehyde)	CV, single, double and triple potential-step CA	Platinum gauze WE in Clark-type cell with 150 μ L RTIL used. Acetaldehyde (a VOC) could be indirectly determined by reaction with electrogenerated superoxide from reduction of oxygen in air, or trace water. Double potential-step amperometry was used after evaluation of coupled reaction mechanisms.	[22] 2016
O ₂	[C ₄ mpyrr][NTf ₂]	Clark-type sensor with polycrystalline Pt gauze.	1–20 %	CV, LTCA	Platinum gauze WE decorated with Pd nanocrystals in Clark-type cell with 150 μ L RTIL used. Presence of different facets of Pd has little effect on oxygen reduction, but significantly affects superoxide oxidation. Better sensitivity and lower LOD compared to Pt gauze.	[23] 2016
H ₂	[C ₄ mim]Cl	Pd deposited on carbon gas diffusion electrode.	1–5 %	CV, LTCA	Fuel-cell based amperometric sensor with Nafion as proton conducting electrolyte. Better adhesion of Pd when deposited from an ionic liquid. Sensor exhibited excellent sensing response despite low catalyst loading.	[24] 2017
O ₂	[C ₄ mpyrr][NTf ₂]	Clark-type sensor with polycrystalline Pt gauze.	5–20 %	Single and double potential-step CA, LTCA	Platinum gauze WE in Clark-type cell. Sensor signal drift was characterised to identify the contributing factors. Double potential step chronoamperometry used to reduce drift and extend sensor operating lifetime.	[25] 2018
H ₂	[C ₄ mim][NTf ₂], [C ₄ mpyrr][NTf ₂]	Clark-type sensor with polycrystalline Pt gauze.	0.05–1.25 %	CV, LTCA	Porous Teflon membrane in contact with Pt gauze WE. 150 μ L RTIL employed. Low concentration range studied with best results at a sampling time of 20 seconds. Electrogenerated proton diffuses quickly into the bulk RTIL, minimising signal drift. Good selectivity for H ₂ over interferent VOC gases.	[26] 2018
O ₂	[C ₄ mpyrr][NTf ₂]	Pt on porous PTFE substrate	5.25–21 %	CA, LTCA	Microfabricated WE, CE and RE (Pt//Ti) on planar porous PTFE substrate. Good sensitivity, linearity and repeatability for oxygen sensing. Methane-oxygen electrochemical coupling method used to detect methane.	[27] 2016
O ₂ (air)	[C ₄ mpyrr][NTf ₂]	Au on porous PTFE substrate	~5–20 %	CV, single and double potential-step CA, LTCA	Microfabricated WE, CE and RE (Au//Ti) on planar porous PTFE substrate. Double potential amperometry used as a favourable technique to reduce by-product accumulation.	[28] 2017
O ₂ , CH ₄ , SO ₂ , O ₃	[C ₄ mpyrr][NTf ₂]	Pt on porous PTFE substrate	5–20 % (O ₂), 2–10 % (CH ₄), 833–2500 ppm (SO ₂), 2–10 ppm (O ₃)	CA	Microfabricated WE, CE and RE (Pt//Ti) on planar porous PTFE substrate. Fast response times, with good sensitivity, linearity and repeatability. Various different gases could be detected using chronoamperometry.	[1] 2018

O ₂	[C ₂ mim][NTf ₂], [C ₄ mim][PF ₆]	SPE (graphite)	0.1–20 % and 100 %	CV, LTCA	Planar device with 2-30 μL. Six RTILs studied, with detailed analytical studies on two RTILs. Not all SPE ink formulations are compatible with RTILs for long-term electrochemical experiments. Choice of RTIL is also important for long-term experiments.	[29] 2017
O ₂	[C ₂ mim][NTf ₂], [C ₄ mpyrr][NTf ₂]	SPE (platinum)	10–100 % and 0.1–5 %	CV, LTCA	Planar device with 30 μL RTIL. Unstable behaviour towards O ₂ reduction in [C ₂ mim][NTf ₂], which improved upon mechanical polishing.	[30] 2016
NH ₃	[C ₂ mim][NTf ₂]	SPE, TFE, MATFE, microdisk (all Pt)	0.1–2 ppm and 10–100 ppm	LSV, CA	Planar devices with 2 or 8 μL RTIL. Current density for ammonia oxidation reported for planar devices and conventional electrodes. Improved sensitivity towards when recessed micro-holes were filled with Pt. Lowest LOD reported for ammonia, to date.	[31] 2016
NH ₃	[C ₂ mim][NTf ₂]	SPE, TFE, MATFE, microdisk (all Pt)	10–100 ppm	LSV, SWV, DPV	Three voltametric techniques compared – LSV, SWV and DPV. LSV gave the highest currents. Biggest difference on micron sized electrodes. 2, 8 and 25 μL RTIL used.	[32] 2018
O ₂	[C ₄ mpyrr][NTf ₂]	Interdigitated electrode	1400–4800 ppm	CV, LTCA	Miniaturised interdigitated microelectrodes detecting analytes with reversible redox activity. Product at WE1 (i.e. superoxide) is reoxidised at WE2. Can provide selectivity over gases with irreversible redox chemistry. 1 μL RTIL used on planar device.	[33] 2018
O ₂	[C ₂ mim][NTf ₂]	Pt microdisk, Pt MATFE	0.1–100 %	CV, LTCA	RTIL mechanically stabilised by PMMA to create a gel-polymer electrolyte on planar device. Low currents with MATFE/viscous GPE caused less degradation after long-term experiments compared to neat RTIL. 5 μL used on planar device.	[34] 2016
O ₂	[C ₄ mim][PF ₆], [C ₂ mim][PF ₆] and [C ₅ mim][PF ₆]	Pt interdigitated electrode	0–100 %	CV, CA, EIS	RTIL mixed with Pt-modified ordered mesoporous carbons, preventing aggregation and providing a large number of active sites for oxygen reduction. Solid/gelled materials overcame the leakage problem of RTILs. ~20 μL RTIL used on planar device.	[35] 2018
O ₂	[C ₄ mim][BF ₄]	Home-made planar electrode. Pt WE (radius 0.5 mm). Pt CE and Pt RE (0.5 mm diameter).	20–100 %	CV, CA, LTCA, EIS	RTIL combined with polymers to create robust microporous films with enhanced electrical properties. Double film (PVDF/IL and PMMA/IL) on planar substrate enhances electrochemical oxygen sensor performance. 5 × 5 mm films used.	[36] 2018
O ₂	[MOMIM][PF ₆] (thiol- functionalised RTIL)	Au microchannel electrode	5000–25000 ppm	CV, LTCA	Thiol-functionalised ionic liquid used to create microchannel arrays for robust oxygen sensing, with no flow observed when the electrode was placed in different orientations. ~1 μL RTIL used on planar device.	[37] 2016

O ₂	[C ₄ mpyrr][NTf ₂]	Au microchannel electrode	500–400 ppm & 2000–5000 ppm	CV, LTCA	RTILs impregnated with magnetic nanostirrers (CoFe ₂ O ₄ nanoparticles) showed increased sensitivity towards oxygen in a rotating magnetic field (400 rpm). Response times also improved. ~1 μL RTIL used on planar device.	[38] 2017
NH ₃ , HCl	[C ₂ mim][NTf ₂], [C ₄ mpyrr][NTf ₂]	Au microchannel electrode	20–100 ppm	LSV, LTCA	Microchannel coated gold electrode with ~9 nL RTIL. Highly sensitive and fast detection of toxic gases. LODs 3.6 ppm (NH ₃) and 3.7 ppm (HCl), well below long-term exposure limits.	[39] 2018
NH ₃	[C ₂ mim][NTf ₂]	Pt MATFE, Modified MATFE	10–100 ppm	LSV, LTCA	Recessed MATFEs modified by electrodeposition of Pt ‘cauliflower’ 3D structures. Enhanced sensitivity towards ammonia oxidation (7 to 12 ×). 2 μL RTIL used on planar device.	[40] 2018
O ₂	[N _{8,2,2,2}][NTf ₂]	Pt MATFE, Modified MATFE	10–100 %	CV	MATFEs with Pt 3D structures, deposited in one-step and two steps, in the absence/presence of lead acetate to create dendritic structures with high surface areas. 16 times enhanced current. 3 μL RTIL used on planar device.	[41] 2018
H ₂	[C ₂ mim][NTf ₂]	Pt, Porous Pt, GC	10–100 %	CV, LTCA	Macroporous Pt electrode created using polystyrene spheres as a template on GC and Pt electrodes. Thin-layer characteristics in the CV with hydrogen remaining in the pores. ‘Leak detector’ application suggested. 300 μL RTIL used.	[42] 2018
H ₂	[C ₂ mim][NTf ₂]	Pt, Au and Au microchannel electrodes, both modified with Pt nanoparticles	10–100 %	CV, LTCA	Microchannel array gold electrode with ~9 nL RTIL. Hydrogen electroactivity achieved by depositing Pt nanoparticles into the channels. Thin-layer behaviour observed, and a very fast response (<2 s) to H ₂ concentration changes, due to the presence of microchannels.	[43] 2019

Note: Abbreviations are given at the end of the review.

Porous Working Electrodes Based on the Conventional Clark-Cell Design

Various groups have used home-made or commercial packaged devices based on the Clark-cell design (see Figure 1d), similar to those presently marketed to end-users. These have the significant advantage that the manufacturing process of the sensor device is well-established, all electrodes and electrolytes are well-contained, and these devices may fill the space that is already available for existing sensors. A big benefit of this design is that the gas enters the cell through a porous working electrode (Figure 1f, right), avoiding the (often slow) partitioning/diffusion of gas through a thick layer of RTIL to the electrode (Figure 1f, left), improving response times. However, drawbacks include the more complicated manufacture of the sensor, in addition to possible water adsorption into the RTIL if no membrane is present; this can cause RTIL expansion within the tightly packaged design, which can cause damage to the sensor housing and leakage under high humidity environments. There is also limited potential for miniaturisation of this design, often requiring at least 100–150 μL of RTIL solvent to connect the three electrodes, which can add to the overall cost of a sensor device due to the cost of RTILs. As a rough guide, commonly used RTILs for gas sensing applications are currently ca. 170–230 EUROS for 100 mL.

Among the various Clark-cell type designs, some highlights include the detection of oxygen [22, 23, 25] and hydrogen [24, 26] gases. Figure 2 shows a schematic of a sensor device used for detecting hydrogen gas with fast response times; hydrogen flows into the cell, where it diffuses through a gas-permeable membrane to the sensing electrode and is oxidised. Figure 2b shows the calibration graphs of current vs concentration of H₂, which show different sensitivities when the RTIL cation is changed. Figure 2c shows a real-time amperometric response (long-term chronoamperometry transient) for low concentrations of hydrogen (0.05–1.25 %) in the two RTILs, with a nitrogen purging step between each concentration change. Excellent reproducible signals are observed, with ascending and descending concentration currents almost identical. The issue of signal drift for a continuous “real-time” sensor was also discussed by the same group [25] in the context of oxygen detection.

As shown in Table 1, many of the sensing electrodes in this design are made of polycrystalline Pt gauze material, but some have been intentionally decorated with Pt nanocrystals for improved responses towards the analyte [23, 24]. In general, the porous electrode design shows great promise for gas detection with fast response times and good long-term operation, but the requirement for high volumes of RTIL and complex packaging may raise the cost of a sensing platform for use in the field.

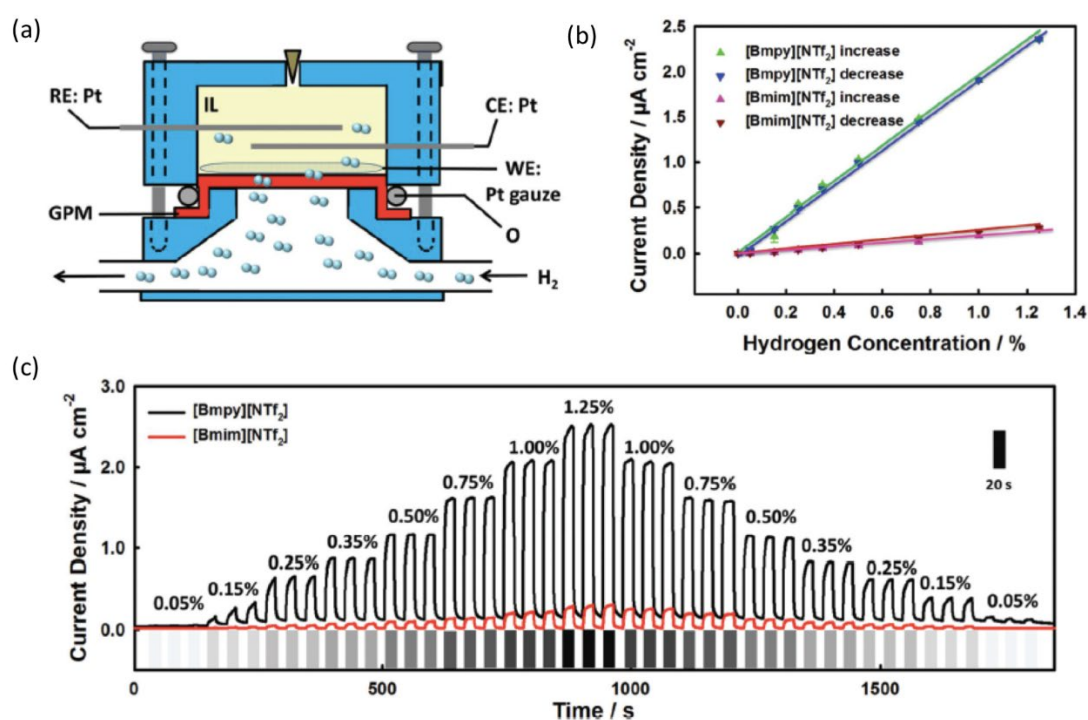


Figure 2. (a) Schematic diagram of Clark-type hydrogen sensor cell. Abbreviations are defined at the end of the review. (b) Calibration curves for concentration step up and down in two RTIL-based sensors at 20 seconds exposure time of hydrogen shown in Fig c. (c) Real-time amperometric hydrogen sensor response in two RTILs, applying a constant potential of +0.4 V vs ferrocene/ferrocenium. Hydrogen is repeatedly being introduced to the sensor with sampling time of 20 seconds and then removed by purging with nitrogen background gas for each measurement. All figures are reproduced from [26] with permission from The Royal Society of Chemistry. Here, the nomenclature [Bmpy]⁺ = [C₄mpyrr]⁺ and [Bmim]⁺ = [C₄mim]⁺.

Planar or printed electrode devices

An alternative design to the Clark-type sensor is one that allows partitioning of the gas into the liquid phase, followed by diffusion of the gas towards the electrode surface for detection, as demonstrated in Figure 1f (left). Various low-cost devices such as screen-printed electrodes (SPEs), thin-film electrodes and

interdigitated electrodes have been developed by companies and are now widely available for academic research. RTILs are ideal for use with planar electrode devices, since volumes as small as a few microlitres can be employed without any issue of solvent evaporation. The choice of electrode material is important; there are very few studies with carbon SPEs due to large capacitive currents observed with RTIL solvents [44]. However, a home-made low-cost screen-printed graphite electrode was successfully employed for low-cost oxygen detection [29], with different ionic liquids showing varying responses, and some showing degradation of the electrode after long-term biasing. Binding materials from DropSens screen-printed Pt electrodes were found to facilitate proton-abstraction by superoxide from imidazolium RTILs [30], giving rise to an irreversible oxygen reduction peak and vast potential shifting between scans. Various electrode pre-treatment methods were attempted, and it was found that mechanical polishing of the SPE could improve the long-term response, but also successfully regenerate a “fouled” electrode [30].

Electrode materials made purely of metals give much more stable responses compared to screen-printed electrodes that are complicated by the presence of binders. Thin-film electrodes (TFEs), microarray thin-film electrodes (MATFEs), and interdigitated electrodes (IDEs) have all been explored as new sensor surfaces in RTILs for the detection of ammonia [31, 32] and oxygen [33] gases. The design of a commercially-available MATFE form MicruX is shown in Figure 3a; the WE consists of 90 recessed microdisk electrodes, in close proximity with the RE and CE. This electrode design was used successfully with 2 μ L of RTIL for ammonia detection with extremely stable and reproducible results, and it produced the lowest limit of detection reported for ammonia in pure RTILs reported to date (20 ppb) due to the high current density possible from the microarray design. A platinum interdigitated electrode was used for enhanced oxygen detection, taking advantage of the electrochemical reversibility of the oxygen reduction reaction [33]. An innovative approach involved producing a product (superoxide) at WE1, which was reoxidised at WE2. This gave enhanced current signals and potentially provides selectivity over gases with irreversible redox chemistry [33].

Improving Response Times

The use of a droplet of RTIL can cause slow response times to changing gas concentrations due to the slow partitioning and diffusion time in RTILs. Therefore, several attempts have been made to facilitate the diffusion of gas analytes in RTILs. A highly efficient strategy involves the formation of thin layers of RTILs on microchannel arrays. Transport of the analyte gas (oxygen) to the electrode was aided by the inclusion of magnetic nanostirrers into the RTIL with faster response times and improved current density [38]. This electrode design was later used (but without the nanostirrers) to detect the toxic gases ammonia and hydrogen chloride [39] in RTILs, with stable and fast responses at low ppm concentrations, well below the long-term exposure limits. Planar devices have also been used with a porous PTFE substrate [1, 27, 28], onto which metallic electrodes (gold or platinum) were microfabricated into a small area. This design combines the benefits of fast response times, miniaturisation, low-cost, and small volumes of RTILs. The

authors successfully detected multiple pollutants with better sensitivity, linearity, and repeatability compared to the Clark-cell predecessor [1, 27], with response times as low as 4 s for oxygen [28]. These devices show great promise for deployment as wearable devices for real-time point-of-exposure gas monitoring.

Mechanical Stabilisation of the Electrolyte

Using planar devices with droplets of ionic liquids introduces the issue of solvent flow or leakage when the sensor is tilted, shaken or agitated. As a result, various attempts have been made to mechanically stabilise the RTIL solvent on the electrode with the goal to create “spill-less” devices. One method is to mix RTILs with polymers to create gelled materials that do not flow [45]. Not only does the polymer aid in stabilisation of the RTIL on the surface, it also allows the possibility to spin-coat thin layers onto planar substrates without the formation of discontinuous droplets that occurs with many pure RTILs [16]. This reduces response times due to the small diffusion distance to the electrode surface. For example, a drop-casted film (50:50 mass ratio) of [C₂mim][NTf₂] and poly(methyl methacrylate) (PMMA) was used with a microarray thin-film electrode device for oxygen detection [34]. Lower currents were observed due to the viscous gel-polymer mixture, however, better long-term behaviour even at very high concentrations of oxygen (>60 % vol.) was achieved, where traditional sensors often struggle to function. In addition to the improved sensing performance, by replacing 50 mass % of the RTIL electrolyte with a cheaper common polymer (PMMA) results in a significant for cost reduction for materials in the sensor device. Zhang et al. [36] proposed an oxygen sensor using a “double layer ionic liquid film”, created by combining a PMMA/[C₄mim][BF₄] film with a PVDF/[C₄mim][BF₄] film. Good linearity was observed between current and oxygen concentration and the authors suggested that the synergism of different polymers also enhances the electrochemical oxygen sensor performance.

An alternative and highly innovative approach for a “spill-less” gas sensor was proposed by Gondosiswanto et al. [37], who used thiol-functionalised ionic liquids bound to a gold electrode surface through sulfur-gold interactions to produce thin-layer microchannel arrays. The electrode was tested for its response to oxygen reduction in various orientations (upright, upside down, sideways) and showed good stability and reproducibility, combined with fast response times due to the thin layer of RTIL employed.

Electrode Surface Modification for Enhanced Analytical Responses

In addition to changing the ionic liquid material, the underlying electrode surface can also be altered to provide enhanced functionality. This has been exploited, for example, in the formation of highly porous electrodes using a polystyrene sphere template [42], where the sensitivity towards hydrogen oxidation was greatly increased by the presence of the pores to which the gas had a strong affinity. A potential application is a ‘leak-detector’ for low concentrations of hydrogen gas [42], that could trigger an alarm at concentrations well below explosive levels (<4 % vol. H₂ in air).

Further modifications to electrode designs were investigated for enhanced sensitivity towards gases. For example, MATFEs were modified with 3D ‘cauliflower’ [40] and dendritic platinum growths [41] (see Figure 3b) to produce arrays of 90 high-surface area electrodes that had massively enhanced surface areas compared to the unmodified microarrays. Increased current density was observed for ammonia oxidation [40] due to the improved diffusion characteristics that come about by filling of the pores (see Figure 3c). The highest sensitivity for oxygen reduction (Figure 3d) was achieved when dendritic growths were grown from the pores in the presence of a structure directing agent, lead acetate, during a two-step Pt deposition process [41]. In both cases, less than 3 μL of RTIL was required for the gas sensing experiments. These studies demonstrate that low-cost commercially available devices can be successfully modified for improved analytical responses, with 9 times and 16 times sensitivity enhancements for ammonia [40] and oxygen [41], respectively.

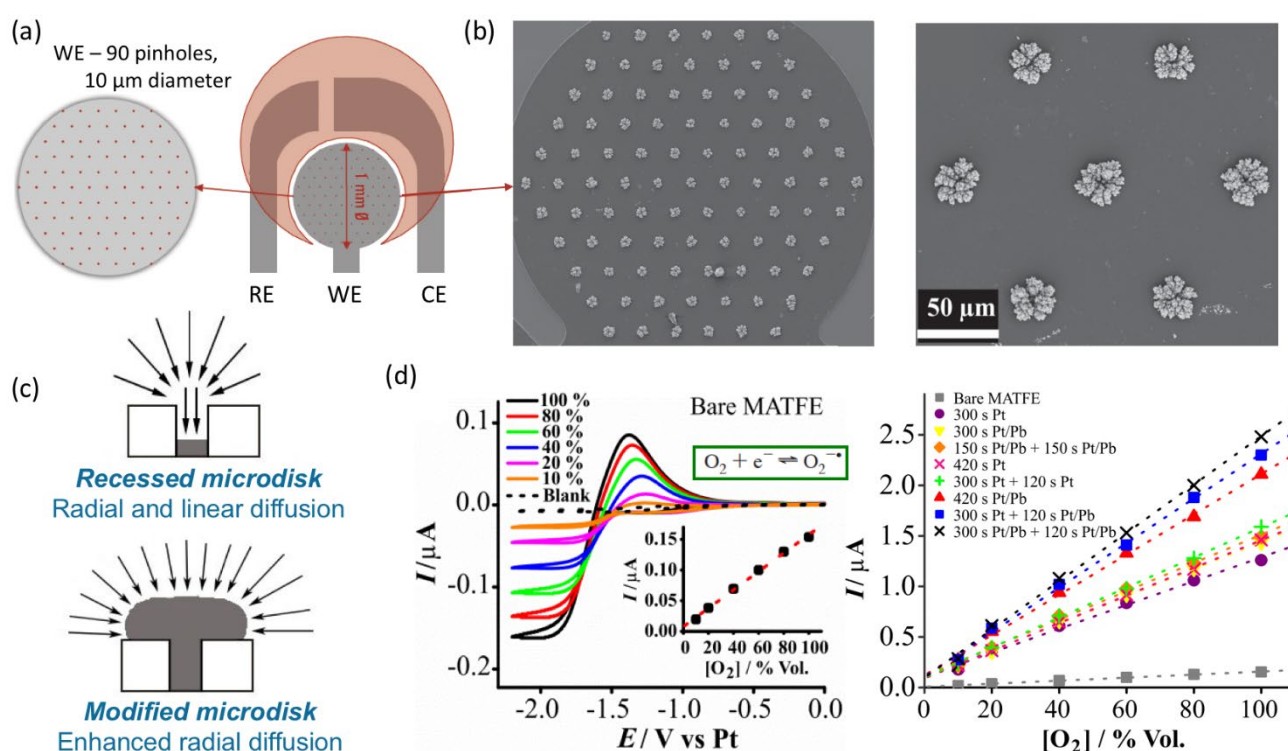


Figure 3. (a) Schematic of a micro-array thin film electrode (MATFE) from MicruX (www.micruxfluidic.com) with 90 recessed electrodes, each 10 μm in diameter, in close proximity to the counter and reference electrodes. (b) SEM images of a MATFE modified with Pt 3D dendritic structures by deposition from a Pt plating bath solution (20 mM $\text{H}_2\text{PtCl}_6/0.5$ M H_2SO_4 in the presence of 2 mM lead acetate, one-step holding the potential at -0.2 V vs Ag/AgCl for 300 s). (c) Expected diffusion patterns to the unmodified MATFE with a recessed microdisk, compared to a modified macrodisk with 3D Pt structures. (d) Cyclic voltammetry for the reduction of 10–100 % vol. O_2 on the unmodified MATFE and (inset) the corresponding calibration graph. Figure to the right is a comparison of O_2 calibration graphs on MATFEs modified with the different structures formed by varying the deposition parameters (see [41] for full details), compared to the unmodified array (grey squares). Figures b and d are modified from [41].

Summary and Perspectives

The variety of studies over the last few years demonstrate the continued interest in RTIL-based AGSs. Since their initial suggestion as membrane-free electrolytes ca. 15 years ago, many studies have been performed with these materials as electrolytes, yet it is surprising that there are no commercially available AGS devices adopting RTILs. Despite their obvious advantages of low-volatility, high thermal stability, wide electrochemical windows, and good solvating properties, the additional challenges of RTILs that come

about by removal of the membrane have yet to be overcome. The most obvious issue is the sensitivity of RTILs to water [46, 47], since water is known to change RTIL viscosity and influence reaction outcomes; this requires more detailed understanding of the effect of ambient moisture and air on reaction mechanisms and current responses. Although self-calibrating “intelligent sensors” can adjust to changes in the sensing environment, this may not be possible if the outcome of the electrochemical reaction is altered. Innovative ways to address this issue could be the use of more hydrophobic materials – either the RTIL itself, or for example, by mixing with a polymer possessing highly hydrophobic functionalities. The choice of RTIL is already known to be important – e.g. both imidazolium [48] and even phosphonium [49] cations are known to undergo proton abstraction in the presence of strong bases such as superoxide.

It has been demonstrated that RTILs can be successfully employed with traditional Clark-type cells while retaining fast response times, but the drawback to this design is the use of relatively large (~150 μL) volumes of solvent and complicated sensor design, adding to the overall cost. Miniaturised planar electrodes with very small volumes (e.g. 1–5 μL) can reduce cost – both in terms of the sensor device manufacturing and electrolyte amount needed; while response times can be improved by employing thin electrolyte layers. However, the build-up of electrogenerated products may be significant, especially if very thin layers are employed. In this case, the use of innovative techniques, such as double potential step chronoamperometry [28] to selected reactions could effectively extend the sensor lifetime by reducing the build-up of undesired products.

Another consideration for RTIL-based AGSs is the common use of a quasi-reference electrode, which has been shown to shift the potential of a bare Pt-TFE surface by ~200 mV and ~800 mV upon the introduction of 20 % vol. O_2 and 1 % H_2 gas, respectively [50]. With such large potential shifts occurring when gas is introduced, the development of a reference electrode surface insensitive to atmospheric changes would be highly desired. A novel reference electrode was recently developed, comprising of a Pt-TFE coated with a common battery material (lithium iron phosphate) [50] that avoided the large reference potential shifts seen at the bare Pt surface, but the behaviour of this material in the presence of strong bases or dissolved water is still unknown.

Overall, it is clear that RTILs show tremendous promise as electrolytes in AGSs, and the tunability in their structure allows for tailoring the response towards different intended applications. Both sensitivity and selectivity could be improved by the judicious choice of RTIL ions, electrode materials, and electrochemical methods. It would be exciting to see RTIL-based gas sensors become widely available as low-cost, mass-producible devices available to everyone (e.g. to monitor air quality) in the same way as the highly successful blood glucose sensor.

Declaration of Interest

None

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Abbreviations

[C ₂ mim][PF ₆]	1-ethyl-3-methylimidazolium hexafluorophosphate
[C ₂ mim][NTf ₂]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₄ mpyrr][NTf ₂]	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[N _{8,2,2,2}][NTf ₂]	triethyloctylammonium bis(trifluoromethylsulfonyl)imide
[C ₄ mim][Cl]	1-butyl-3-methylimidazolium tetrafluoroborate
[C ₄ mim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[C ₄ mim][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[C ₄ mim][NTf ₂]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₅ mim][PF ₆]	1-pentyl-3-methylimidazolium hexafluorophosphate
[MOMIM][PF ₆]	1-[8-mercaptooctyl]-3-methylimidazolium hexafluorophosphate
Ag/AgCl	Silver/Silver chloride
AGS	Amperometric gas sensor
CA	Chronoamperometry
CE	Counter electrode
CV	Cyclic voltammetry
GC	Glassy carbon
GPM	Gas-permeable membrane
IL	Ionic liquid
LOD	Limit of detection
LSV	Linear sweep voltammetry
LTCA	Long-term chronoamperometry
O	O-ring
RE	Reference electrode
RTIL	Room temperature ionic liquid
PMMA	Poly(methyl methacrylate)
ppm	Parts-per-million
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
rpm	Revolutions per minute
SEM	Scanning electron microscopy
SPE	Screen-printed electrode
SWV	Square wave voltammetry
TFE	Thin-film electrode
VOC	Volatile organic compound
WE	Working electrode

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- Paper of special interest
- Paper of outstanding interest.

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