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Methods and approach of utilizing ionic liquids as gas sensing materials

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Abstract

Gas monitoring is of increasing significance for a broad range of applications in environment and civil infrastructure, climate and energy, health and safety, industry and commerce. Even though there are many gas detection devices and systems available, the increasing needs for better detection technology that not only satisfy the high analytical standards but also meet the additional device requirements (e.g., robust that can survive in the field conditions, low cost, small, smart, more mobile) demand continuous efforts in developing new methods and approaches for gas detection. Ionic Liquids (ILs) have attracted a tremendous interest as potential sensing materials for gas sensor development. Being composed entirely of ions and with a broad structural and functional diversity i.e., bifunctional (organic/inorganic), biphasic (solid/liquid), and biproperty (solvent/electrolyte) materials, they have the complementing attributes and the required variability to allow a systematic design process across many sensing components to enhance sensing capability especially for miniaturized sensor system implementation. The emphasis of this review is to describe molecular design and control of IL interface materials to provide selective and reproducible response and to synergistically integrate IL sensing materials with low cost and low power electrochemical, piezoelectric/QCM and optical transducers to address many gas detection challenges (e.g., sensitivity, selectivity, reproducibility, speed, stability, $cost, sensor miniaturization, and robustness). We further show examples to justify the importance of understanding the mechanisms and principles of physiochemical and electrochemical reactions in ILs and then link those concepts to develop new sensing methods and approaches. By doing this, we hope to stimulate further research towards fundamental understanding of the sensing mechanisms and new sensor system development and integration using simple sensing designs and flexible sensor structures both in terms of scientific operation and user interface that can be miniaturized and interfaced with modern wireless monitoring technologies to achieve specifications heretofore unavailable in the current markets for the next generation of gas sensor applications.

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1. Introduction

Monitoring the concentrations of different gases and gathering detailed chemical information about local environments is critical for a host of applications, both in industrial world and in our daily lives.[1-4] Typically, these measurements are needed for monitoring health and safety hazards[5-11] (e.g., detection of toxic and explosive gases), process controls[12-14] (e.g., industrial combustion processes), environmental monitoring[15, 16] (e.g., automobiles and in-home air quality), or forensics and medical diagnostics[17-19] (e.g., breath analysis for disease detection). For all these scenarios, in order to have any practical value, the desired chemical information needs to be acquired on-site and real-time without having delays associated with transferring samples to centralized laboratories. Moreover, as continuous monitoring is an essential requirement, the concerns of cost-effectiveness and user-friendliness hinder the use of high-tech analytical instruments (e.g., GC-MS) for such applications. This situation has attracted an appreciable number of research and development activities into the field of gas sensors[3, 20-23] with demands of reliability and robustness of the proposed systems. As a result of these explorations, many implementable sensors[24] for gases such as CO_2, O_2, water vapors, and VOCs are already available. However, these sensors are particularly useful for detections in controlled environments with relatively fewer interfering species. For more diverse and dynamic environments (e.g., an airport security checkpoint with multitude of vapors in the air), we need much more precise and reliable gas sensors in order to meet the always emerging requirements in such complex environments.

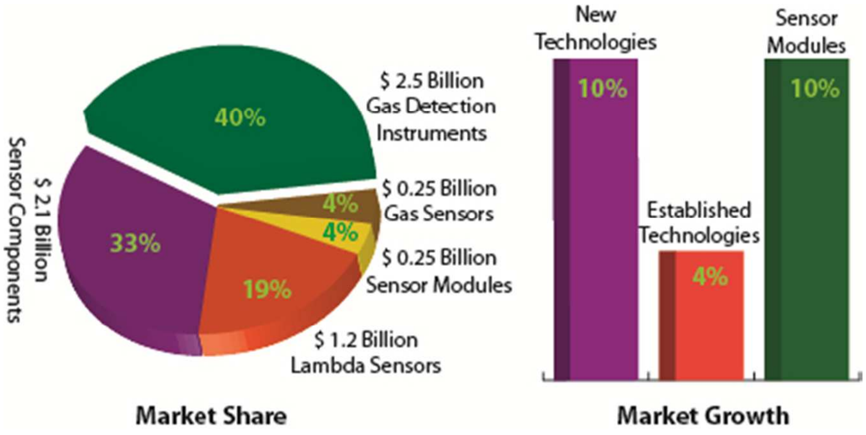

Figure 1: Fragmentation of the gas sensing market in terms of generated revenue and the expected growth for different technologies

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In context of this distinctively increasing demand for time-efficiently monitoring various gaseous components, the gas sensing market is expanding into a number of areas related to human healthcare and environment, the security and sustainable economy. However, the technology priorities have remained associated with the cost and reliability, which should be the salient features of any prototype development activity. The estimated gas sensing market is \$6.3 billion with a 10% growth rate for new technologies. The major share of this market is focused on the development of gas sensing instruments and the new or improved gas sensors as indicated in Figure 1. A lesser growth rate in existing technologies (i.e., 4%) is representative of the challenges that this market is facing in terms of operation in complex backgrounds, the ability to identify abnormal variations, and most importantly, the stability of the sensing materials. Moreover, the revenue generated by portable instruments is 70.2% which continue to increase in comparison to fixed ones having revenue of 29.8%. Hence, the motivation of the present research directions is to move towards the sensors which have the potential to offer advantages over existing sensors for volume, cost, compactness, power consumption and responsiveness, and thus have the potential to open up new application areas, displacing existing technologies or creating new markets. The feasibility of displacing existing sensor devices and systems, however, depends on the balance between investment costs and performance or functionality gains.

1.1 The Analytical Challenge:

As described earlier, there is a broad diversity in the analytical needs in terms of species and concentrations of the gaseous analytes in different environmental conditions. Our environment is inherently made up of gases which are roughly 78% N_2, 21% O_2, and 1% other trace gases including CO_2. The detection and monitoring of these gases is important for many environmental standardization issues. Additionally, the anthropogenic processes have led to multitude modifications to this natural combination, and the new compositions can have detrimental effects on the overall quality of the resulting atmosphere. The most important alteration sources for such adverse effects include: i) industrial processes generating toxic gases such as NO_x, CO, CO_2, SO_2, NH_3, and phosphene; ii) domestic and household emissions of VOCs, e.g., acetone, benzene, methanol, phenol, methylene chloride, chloroform; iii) greenhouse gases coming both from natural (e.g., wetlands, termites, and the oceans) and human sources (e.g., landfills,

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livestock farming, as well as the production, transportation and use of fossil fuels for energy) causing methane and CO_2 emissions; and iv) chemical warfare agents like mustard gas, and other volatile explosives. Moreover, there is an additional need of monitoring localized gas environments for medical diagnostic and personal safety purposes. This diversity of needs and the associated challenges have been precisely summarized in Table 1. Besides this diversity in the variety of analytes, for many of these applications, the measurements have to cover a broad range of their regulated exposure limits spanning several orders of concentration magnitudes while that being different for different analytes. This diversity in both the type and the concentrations of the target analytes is crucial for any further implementable actions. Further complicating the situation are the chemical and physical interference parameters, the most abundant and most detrimental of which for sensor performance is the humidity and temperature. At room temperature and at 100 % relative humidity (RH), water concentration is ~30000 ppm which implies that a 100 ppm detection capability of a sensor has to overcome 300 times of humidity overload in terms of interference.[25] Many other chemical interferents such as industrial solvents and household vaporizable chemicals further add to that interference-overload on the sensing capability of gas sensors.[26] Therefore the system must have the ability to withstand all these detection challenges, besides satisfying the analytical requirements of the sensor performance in terms of sensitivity, selectivity, stability, reproducibility, response time, and the cost. In order to address the requirements of the enhanced analytical performance, a logical direction could be the development of new and smart materials in which the mechanisms of detection are supportive towards more and more specificity. However, these materials still need to be generic in terms of their applications, for being utilizable in multi-analyte detections, and multi-transduction modes.

Table 1: Summary of different areas of gas sensing with the target gases in each area and the related challenges for sensor devices

Area of Application	Sensing Categories	Gas Targets	Market Barriers
Atmospheric Gases	Environmental standardization	CO_2, O_2, CO, N_2	Long term operation, interference issues
Greenhouse Gases	Health and Safety Standards for environment and workplace	CO_2, CH_4	Multi-sensor technology required for long term operation, and tackle interference issues
Industrial Safety & Industrial Process	Flammable gas leaks	HCs (CH_4)	Low concentrations, reliability and stability demands

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Control	Toxic gases	VOCs, SO_2, NO_X	Specificity
	Energy fuel	H_2	Selectivity
	Asphyxiates and oxygen	O_2, CO_2, N_2, He	Energy costs due to continuous operation
	Food quality and storage	Amines, ethylene, alcohols, food aromas	Matrix complexity
	Bioreactors and landfill	O_2, NH_3, CO_2, CH_4, H_2, VOCs, acetate vapors	Multi-sensor technology required
Domestic & Household Emissions	Cabin air quality	CO, VOCs	Cost, lack of awareness
	Exhaust gases	HCs, O_2, CO, CO_2, NO_X	Extreme environment workability, cost
	BTEX	Benzene, toluene, ethylbenzene, xylene	Versatile detection demands for each target
	Outdoor emissions	CO_2, NO_X	Cost and size
	Indoor air quality	O_3, NO_X, Formaldehyde, Cleaning solvents	Long term operation, Reliability
	Refrigerants and intensive farming	NH_3, CFCs	Cost, difficult temperature environment
	Asthma in home	O_3, NO_X, bio particulates	No scheme available for bio particles, cost and prevalence
	Nuisance odors	VOCs, CH_4	Reliability and stability
Homeland Security	Explosives, Chemical and biological attack	TATP, HMTD, Nitro-explosives, bio hazardous chemicals	Small size and efficient sampling required, selectivity to avoid false alarms
Medical Diagnostics & Personal Safety	Domestic CO	CO, O_2	Cost, self-validation
	Fire and flammables	CH_4, NO_X, SO_X, ethylene, acetylene, HCl, Cl_2	Identification of targets
	Breath and gut analysis	CO_2, VOC (e.g., Ethane)	Lack of comprehensive studies for marker specificity

1.2 Goals and Scope of This Review

Due to the challenges described above, the gas sensing technologies focusing on sensing materials, sensing mechanisms, sensing transducers, and sensing devices is a hot topic, thereby producing several reviews of the subject every year. These reviews particularly cover the sensing designs,[27] integration into miniaturizable and wirelesss sensing platforms,[4] and the diversity in sensing materials (e.g., polymers, nanomaterials, metal oxides).[3, 23, 28, 29] Sensing materials are very important since the choices of sensing materials often determine the sensing mechanisms, transducers and the ultimate design of the sensing devices. Ionic liquids (ILs) are one of the interesting materials that attracted significant recent research in many fields of science, and

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particularly in the sensor science because of their diversified nature. We have recently reviewed their overall sensing capabilities as well as their implementation for robust chemical sensor developments.[30] Despite these efforts, we believe that there is a need to comprehensively review the mechanistic understanding of these new materials that can lead to new gas sensing principles and protocols. Thus, this review is covering i) the analytical needs of gas sensing technologies; ii) gas sensing transducers and protocols when IL is used as a component for sensing; iii) the sensing mechanisms based on IL materials with particular emphasis on methodologies that provide selective and reproducible response without the use of arrays; and iv) finally commenting on orthogonal sensing based on the multi-transducers with multiple response mechanisms. With this discussion of the subject matter, the goal is to stimulate the research that can link the principles and mechanisms of sensing using ILs. Essentially, the approach should be the proper combination of sensor components (i.e., sensing material, transducer, and signal generation/processing). Furthermore, the sensing criteria have to be carefully devised to include target concentration ranges, interferences, physical parameters, and sensor reliability. Another goal is to highlight the achievements in the field, to demonstrate possible applications, and to critically analyze the non-satisfactory performance and possible solutions.

2. Gas Sensing Attributes of Ionic Liquids

ILs have several attributes that makes them desirable for gas sensing applications. As shown in Figure 2, most ILs have organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium) whereas the anions could be inorganic (e.g., Cl^-, PF_6^-, BF_4^-), as well as organic (e.g., trifluoromethylsulfonate $[CF_3SO_3]^-$, bis(trifluoromethylsulfonyl)imide $[(CF_3SO_2)_2N]^-(NTf_2)$, trifluoroethanoate $[CF_3CO_2]^-$). Thus, they can be considered as bifunctional materials, in which both their organic and inorganic attributes can be exploited for the new sensor designs. The relatively large size of one or both ions, and low symmetry account for many unique properties of IL materials.[31] For instance, ILs have negligible vapor pressures, wide potential windows, high thermal stabilities and high viscosities. These characteristics make them stable materials for sensor design. Though, they are liquid at room temperature, yet their high viscosities enable them to be casted on solid supports to form thin, reproducible films making them behave as solid polymer like matrices. Therefore, they can be considered as biphasic materials, i.e., solid/liquid. Moreover, they show good conductivity which is desirable

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for the electrochemical processes and they have high solubility for a broad range of gases and VOCs allowing many solvating interactions of the target molecules to provide both sensitivity and selectivity. Thus, they are biproperty materials as well, acting as electrolytes and solvents at the same time. Due to such duality in phase and functions, there is a tremendous opportunity to design orthogonal sensors by integrating multimodal transduction mechanisms (e.g., Electrochemical Quartz Crystal Microbalance (EQCM) and opto-electrochemical sensors) to provide enhanced reliability and internal validations of the detection outcome. The remarkable dissolution properties for organic and inorganic substances enable analyte pre-concentration and sensitivity enhancement for the detections whereas the molecular non-covalent interactions between ILs and the analytes contribute in increasing reversibility. All these properties (e.g., melting point, dielectric constant, viscosity, polarity, water miscibility) can be further tailored by combining different cations with suitable anions. Furthermore, their miscibility with other solvents can also be controlled by the variation of cations and anions. These characteristics, thus, make them novel solvents and electrolytes, holding a great promise in many studies of gas sensing.

The use of ILs in different analytical applications is, however, determined by their intrinsic properties as well as the environmental circumstances of the targeted application. Water interference is most important of these environmental factors[32] that can drastically alter the physicochemical properties (e.g., viscosity, conductivity, and diffusivity) of ILs, consequently affecting sensor responses. It has been shown that an increased water content of IL leads to a decrease in viscosity.[33, 34] Viscosity values are related to conductivity since a decrease in viscosity enhances the mass transport of analyte to the electrode surface.[35] A decrease in viscosity and subsequent increase in conductivity may appear to be advantageous. However, an increase in water content results in narrowing the electrochemical window of an IL.[32, 34] The narrowing of the electrochemical window occurs for both the cathodic and anodic limits which is likely due to water electrolysis.[36] With this perspective, studies have been carried out to examine which ILs have the greatest water uptake and hydrophobic anions that are immiscible with water have been identified.[37] By selection of these hydrophobic IL coatings, the potential interference of water can be avoided. For the electrochemical processes, proton donation from water could modify the redox mechanisms (e.g., O_2 to superoxide) and affect the peak currents and the peak positions. Selecting those redox processes for quantification where protons have no influence

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will be simplest to address water interference. Furthermore, the interplay between water and redox analytes can be used to calibrate the water interference. Alternatively, the trace amounts of water present in ILs enables some beneficial aqueous redox reactions of some gaseous analytes to occur at controlled rates which are being explored in our lab to develop new IL based gas sensors. In this way, water is transforming from its status of interfering species to a valuable reactant, and thus IL based gas sensing is moving towards the goal of real world sensing.

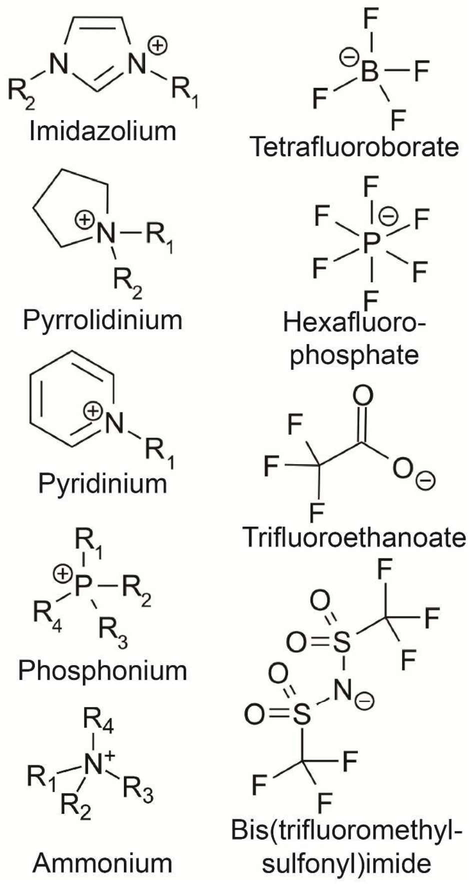

Figure 2: Names and structures of most commonly employed cations and anions for different IL applications.

One important feature of ILs is that the combinations of a variety of cations and anions provide an enormous number of ILs along with the possibility of facile custom synthesis. It is estimated that there could be up to 10^{18} ILs available.[38] Thus there is a large pool of possible ILs, from which ILs can be designed or selected for specific applications. Additionally, ILs are excellent solvents allowing them to be incorporated into conventional gas sensing matrixes, such as polymers, biopolymers, sol-gels, carbon nano-tubes (CNTs), metal nanoparticles,[39-41] to form

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stable composite materials. These composite materials amalgamate multifunctional properties of both constituents involved in preparing the composites. For example, an IL/CNT based composite, with highly electro-active nano-tubes and liquid electrolyte can be utilized for a wide variety of electrochemical gas sensing applications.

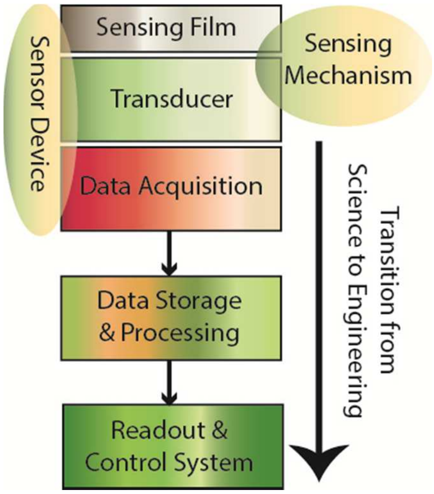

Figure 3: System layers of a typical gas sensing device showing a transition from the science to engineering protocols.

3. Gas Sensor Designs and Developments

A gas sensor is defined as a miniaturized analytical device that can quantitatively determine the concentration of a family of gases or a specific gas in a given environment. The sensor typically relies on one or more sensing mechanisms to produce a signal that detects the presence and/or concentration of the target gas. The sensor system typically refers to the device that integrates the sensor detection with associated electronics and readout devices (e.g., transducers) allowing user to directly obtain the information on the analyte. As depicted in Figure 3, a typical gas sensor is comprised of three major components, i) a transducer that converts the presence of a gas analyte to some form of readable signal; ii) a sensing film which is usually deposited onto the transducer allowing the detection and quantification of the gas analyte through a specific interaction mechanism; and iii) signal processors and readout devices (e.g., data acquisition, lodging, & processing unit) that can convert the sensor's raw signal to usable information. Many amperometric gas sensors also use a permselective membrane in the sensor design. The membrane is located in the closest proximity to the working electrode having the property of being highly permeable to the gas analyte but not to the other interfering electro active species.

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Numerous research activities have been devoted to the data processing part of the sensor system.[42, 43] Besides, the engineering aspects of remote sensing[44] and the energy harvesting processes[45, 46] for the automated sensor system also attract significant attention from scientists and engineers. Sensor calibration is another important area of research. But to keep the chemistry focus of this review article, we will concentrate on the first two components, i.e., the transducer and the sensing material with sensing/interaction mechanisms. The transducer can be a separate component or the sensing material by itself can act as the transducer. However, this is the component that has to detect the change in the local micro-environment (at the interface or in the bulk of the sensing film) as a result of change in target concentrations in the macro-environment of the sensor system. Thus, it deserves the central position in the development of any sensor application. On the other hand, the material component of the sensor most often takes up the responsibility of providing required sensitivity, selectivity, speed and reproducibility. Therefore, this area of sensor research has been explored the most. In the following sections, the mechanisms of the use of different transducers (methods) and the designs of different sensing material/interaction mechanisms have been described in particular relation to IL based gas sensing.

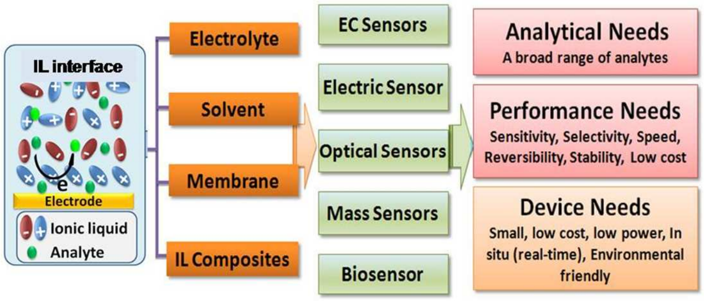

Figure 4: The demonstration of IL interface and the links between its multiphasic characters for various transducers and sensor developments thereby addressing numerous challenges.

4. Transducers for IL Based Gas Sensing

ILs' unique bifunctional (organic/inorganic), biphasic (solid/liquid), and biproperty (solvent/electrolyte) nature enables a broad range of sensing transducers being employed for IL based gas sensing. Among them, electrochemical transducers, thickness shear mode (TSM) resonators (i.e., quartz crystal microbalance (QCM)), surface acoustic wave (SAW) resonators, and optical transducers are the most explored. The rationalization behind the choice of

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transducers is directly related to the distinctive properties of ILs as shown in Figure 4. The dissolution power, the weaker Van der Waal interactions with the analyte and solid/liquid biphases of ILs are supportive towards the adsorption or dissolution of analytes on/into the ILs thin films and can be utilized for acoustic transducers. The bifunctionality of ILs as solvent/electrolyte leverages the design of membrane free electrochemical sensors. On the other hand, the ease of incorporating task specific functions and solubility for both organic and inorganic compounds enables a wide range of optical sensing approaches to be designed and implemented. The selection and relative performance of the transducers for any particular detection application require the synergistic coupling of the intrinsic properties of the specific transducer (e.g., transducing or response mechanisms) with the chemical and/or physical properties of the sensing material which often determines the sensitivity, stability and dynamic range of response under the variations of detection environment. Finally, the sensor fabrication, sensor manufacturing processes, and readout are also important to be integrated with the overall sensor engineering process.

4.1 Electrochemical Transducers

The common electrochemical methods including potentiometry, voltammetry and impedance spectroscopy have all been demonstrated for IL based sensor development. Among them voltammetry based on the measurement of redox current and impedance spectroscopy based on the measurement of the impedance/capacitance at the electrode/electrolyte interface are especially suitable for the IL based gas sensor development. Both methods require the use of the electrolytes. Notably, a majority of the electrochemical gas sensors developed to date employ aqueous-based electrolytes. Another type of electrolyte is the non-aqueous electrolyte (e.g., salts that could be dissolved in organic solvents such as lithium perchlorate, organic compounds with charged ion center such as tetra-*n*-butylammonium perchlorate, or polyelectrolytes such as perfluorosulfonate[47, 48] and Nafion ionomers).[49, 50] In contrast to the battery research, such as Li ion battery, which can be designed as a completely closed system, the electrochemical sensor cell cannot be completely sealed and it needs to be accessible to the ambient environment to detect the gaseous molecules. Aqueous electrolytes and most traditional non-aqueous electrolytes suffer from solvent volatility leading to exhaustion of solvent in the electrochemical cells. Because of their non-volatility and much higher ionic conductivity, ILs have the ability to replace almost, if

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not all, conventional electrolytes in many types of electrochemical sensors.[1, 30, 51-53] IL based electrochemical sensors[7, 30, 52-56,57] are also well suited for miniaturization and can be fabricated with very low cost. Different from the adsorption based transducers such as a surface acoustic wave devices, arrays of amperomertic and impedance transducers allow a secondary perturbation (e.g., potential) that enhances selectivity and increases analytical information content without increasing the number of physical sensor elements. However, the challenge is still the same, to achieve better sensing performance parameters, i.e., sensitivity, selectivity, reproducibility, response time, and cost. Among these parameters, the cost is often taken care of by employing the low cost, low power transducers and by miniaturization. Sensitivity and selectivity are extremely important, however, these are mostly dealt with at the material selection and design stage of the development. A significant number of successful sensors in the lab phase fail to be implemented in real world because of the reproducibility issues, and thus, the reproducibility has to be treated as most important parameter in any sensor development. Response time is critical too, in order to have appropriate action in real time. In the following, we will discuss different IL sensing approaches addressing these challenges.

4.1.1 IL Gas Sensing based on Voltammetry

Voltammetry is an electrochemical method that enables qualitative and quantitative information about the analytes to be obtained by the measurement of the current as a function of applied potential. When current is monitored at a fixed potential, the method is often called amperometry. In experiments where IRs may be high, an amperometric gas sensor typically consists of working, reference and counter electrodes connected through an electrolyte (at working electrode the desired redox reaction occurs, counter electrode establishes the current path, and a reference electrode provides a stable reference electrode potential).

A gas-permeable membrane is located proximal to the working electrode. The gas analyte passes through the membrane, and is detected at the working electrode-electrolyte interface. For amperometric sensor, it is not necessary to use a conventional three-electrode system if the currents encountered are in the nA range or less. Amperometry can be used to detect those gas species that can undergo redox transitions at the working electrode/electrolyte interface in an electrochemical cell. Most commercially available amperometric sensors for gas detections (e.g., O_2, CO, SO_2, H_2S, NO_2, and Cl_2) currently employ conventional solvents (e.g., H_2SO_4/H_2O

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mixtures, or organic solvents such as acetonitrile or propylene carbonate) that cannot survive drastic temperature changes or extremely dry or humid conditions. The “lifetime” of a sensor is often determined by how quickly the electrolyte dries up and the solvent often has to be replaced every few days/weeks in the most extreme conditions. Another often overlooked problem is the reference electrode. In aqueous system, Ag/AgCl reference electrode is often used but a number of species in aqueous sample can dissolve the AgCl deposit off the electrode by forming soluble Ag(I) complexes. In ILs, quasi-reference electrode such as Ag or Pt wire is often used. They are stable in ILs and they are shown to maintain stable reference electrode potential avoiding the problems with traditional reference electrodes (e.g., Ag/AgCl, Hg_2Cl_2/Hg). ILs possess negligible volatility and high chemical stability, making them desired electrolytic media in robust gas sensors for potential application in more extreme operating conditions (e.g., up to 300 °C), with little possibility of solvent evaporation or degradation. These unique properties of ILs, combined with the intrinsic conductivity (no need for supporting electrolyte), wide potential windows (to investigate compounds that are not possible for amperometric detection otherwise due to the absence of redox activity in conventional electrolytes) and in some cases, increased gas solubility in ILs, makes them ideal electrolyte media to develop gas sensors. Typically, the redox reaction occurring at electrode/electrolyte interface such as $\text{Ox} + \text{ne}^{-} \rightarrow \text{Red}$, involve three major steps: i) mass transport step (diffusion, diffusion-convection, migration of Ox from the bulk solution to the electrode surface); ii) heterogeneous electron transfer (charge transfer) step at the electrode surface; iii) chemical reactions preceding or following the electron transfer. These could be homogeneous processes (e.g., chemical reactions in solution) or heterogeneous processes on the electrode surface (e.g., adsorption and desorption, nucleation, crystal growth, surface diffusion). ILs as sensing materials could affect all of these steps. Additionally, for sensor developments, where ILs are used as both electrolytes and solvents, there is a requirement that analyte need to be soluble in the ILs and ILs can facilitate redox mechanisms that are desirable for sensors. It is also important that a steady state current can be obtained at a constant analyte condition. Since the magnitude of the current is often limited by the inherent sluggishness of one or more reactions called rate limiting steps, it is very important to understand the electrode/electrolyte interfacial processes and understanding these processes will enable the selection of the electrode potential, current density, solvent, supporting electrolyte, solution pH, temperature, deliberate modification of electrode surface or addition of other reagents etc. to

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meet the requirements of a specific gas sensor application. Furthermore, for an electrochemical gas sensor to work in real world conditions and for miniaturized electrochemical gas sensor, it will be important to consider the overall reactions in an electrochemical cell and to determine the rate limiting steps for the entire electrochemical cell reactions including counter electrode.

4.1.2 Simplicity of Redox Reactions in ILs for Gas Sensing

The preferred mechanisms for sensing are reversible and simple redox reactions which allow simple sensor designs and enhance the reproducibility of the sensor performance. ILs have been shown to enable many reactions to be simple and reversible, which otherwise were complicated in conventional electrolytes. Oxygen reduction reaction (ORR) is a classical example in this regard and has been studied by many different groups.[58-63] In ILs, ORR is a one electron reversible reduction process ($O_2 + e^- \rightarrow O_2^{\bullet -}$) instead of a complicated four electron reduction process in aqueous electrolyte ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$). Because of the simple and reversible one electron reduction of oxygen to form superoxide radical which is stable in several ILs, this reaction was demonstrated for a robust oxygen gas sensor development.[53] Compared with a conventional Clark cell design based on an aqueous supporting electrolyte for the oxygen detection, the IL based sensor achieved substantial improvements in performance and stability. A limit of detection for oxygen as low as 0.05 Vol %, linearity over an oxygen partial pressure between 0% and 20%, and a steady-state response time of 2 min was demonstrated, with a stable analytical response shown over the examined period of 90 days with no obvious fouling of the electrode surface.

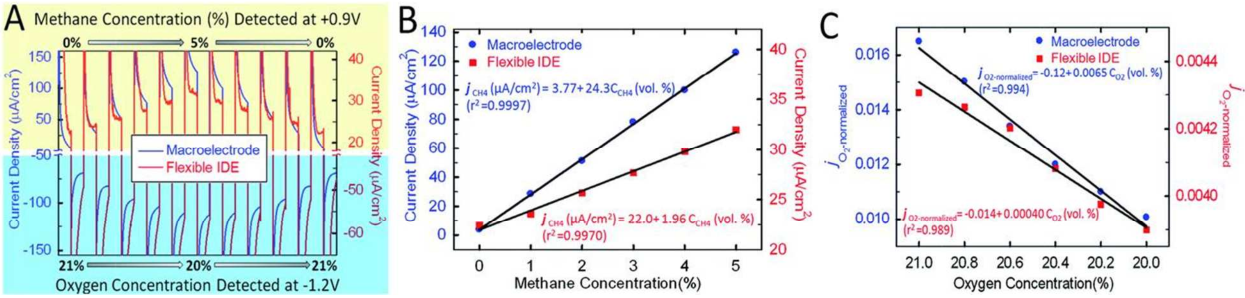

Figure 5: Response data of an IL sensor capable of detecting both oxygen and methane at two different bias potentials thereby showing a unique electrochemistry for IL systems. The data are shown for (A) the real time response by varying the conditions, (B) the calibration curves for methane using microelectrode and IDE, and (C) the calibration curves for oxygen using microelectrode and IDE. (Ref[64])

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4.1.3 New Redox Reactions in ILs for Gas Sensing

Although, IL electrolytes provide partial selectivity, the primary selectivity of an IL based voltammetric sensor comes from the redox properties of analyte observed at the interface wherein the electrical current generated by the electron transfer reactions of an analyte at an electrode at a specific potential.[2] It is known that many species have similar redox potentials in aqueous electrolyte and it is difficult to have absolute selectivity for analyte detection using amperometric sensors. The unique properties of ILs enable many new electrode reactions to occur which can be explored to enhance the selectivity of IL based electrochemical sensors. For example, we have shown a unique redox chemistry that occurs only at an IL-electrode interface and can be exploited to enhance sensor performance, especially the sensitivity and selectivity.[64] At a platinum electrode in NTf_2-based ILs, methane is detected due to electro-oxidation process. Figure 5 shows the amperometric response of a methane sensor in IL $[C_4mpy][NTf_2]$. Methane can be oxidized in $[C_4mpy][NTf_2]$ at potential of ~0.9V and oxygen can be reduced to form superoxide radical at -1.2V. Both analytes can be selectively quantified by alternating the bias potential between 0.9 V to -1.2V. Furthermore, the electro-oxidation of methane produces CO which can be oxidized to CO_2 by superoxide radical when the oxygen reduction is included. The in situ generated CO_2 arising from methane oxidation was shown to provide an excellent internal standard for quantification of the electrochemical oxygen sensor signal. As methane concentration is increased, the oxygen concentration decreases. Thus, the simultaneous quantification of both methane and oxygen in real time strengthens the reliability of the measurements by cross-validation of two co-existing ambient gases within a single sample matrix and allows for the elimination of several types of random and systematic errors in the detection. Thus, in place of a sensor array, a single sensor can be employed for real time measurements. We have also validated this IL-based methane sensor employing both conventional solid macroelectrodes and flexible microfabricated electrodes using single- and double-potential step chronoamperometry with good sensing attributes such as high sensitivity, complete reversibility, long term stability (less than 0.3% potential shift over 90 days), rapid response and strong selectivity (selectivity coefficient ~0.01% for CO_2, NO, NO_2, SO_2).

In another report,[65] much facile redox reactions have been identified for NO_X for developing IL based electrochemical sensors. The oxidation of NO_2 occurred at less positive potentials in $[C_4mim][NTf_2]$ and $[C_4mpy][NTf_2]$ coated sensors than in conventional solvents. At the same

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time, the oxidation of NO occurs, roughly to the same degree as NO_2, and at almost the same anodic potential as NO_2. Moreover, there was no significant difference between peak potentials for NO_2 and NO. These preliminary results obtained with this sensor proved that the oxidation of NO_2 and NO occurs at very close potentials, thus allowing effective NO_X determination with a single sensor. Contrarily, other atmospheric components able to act as possible interfering species (CO, H_2S, and SO_2) were found to undergo oxidation only at much more positive potentials. Therefore, the sensor was able to detect NO_X in wide concentration range with reproducible and quantitative signals and a detection limit of 0.96 ppb v/v while having good selectivity. The reported IL NO_X sensor is also suitable for measurements at reduced pressure and fairly high temperatures.

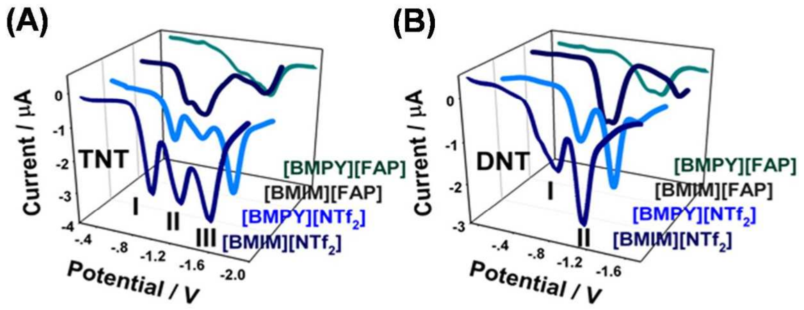

Figure 6: Square wave voltammetric response of 0.1mM of TNT and DNT in four different ILs showing a multistep reaction from which the most reproducible and interference free peak can be chosen for the quantification purposes. (Ref[66])

4.1.4 Multistep Redox Reactions in IL for Gas Sensing

Typically analytes with multi-step redox mechanisms are not desirable for electrochemical sensor development due to the difficulties for quantifications based on more complex sensor methodology. However, the unique redox chemistry in ILs provides new possibility for electrochemical sensor development taking advantage of the redox reactions that have multiple step mechanisms. In such cases, the step that is most reversible is normally chosen for quantification purposes. This strategy, sometimes, can be used to eliminate the interference as well. For instance, an array of four IL-coated glassy carbon electrodes was characterized for the voltammetric detection of dinitrotoluene (DNT) and trinitrotoluene (TNT), and a correlation (with 100% classification accuracy) between the redox properties and the physiochemical parameters of the species involved was revealed (Fig. 6).[66] Here the interference from humidity

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was eliminated by calibrating with a redox process that does not involve proton, and thus a selective response that is quantitative was obtained. The redox peak based on the redox reaction without the proton transfer thus had the most reversible character providing more accurate quantification. Gas phase analysis showed strong redox signals for TNT and DNT and demonstrated that ILs serve as a pre-concentrator to improve sensitivity of very low vapor pressure analytes. In another report,[67] the electrochemical behavior of highly toxic methylamine gas in several ILs has been investigated on a Pt microelectrode using CV. A broad oxidation wave at approximately 3.0 V, two reduction peaks, and another oxidation peak were observed indicating a complicated mechanism with ammonia as a likely byproduct. The linear plots of oxidation currents vs concentration, however, suggest that methylamine has a high solubility in ILs, thus generating a possibility to be detected using these media.

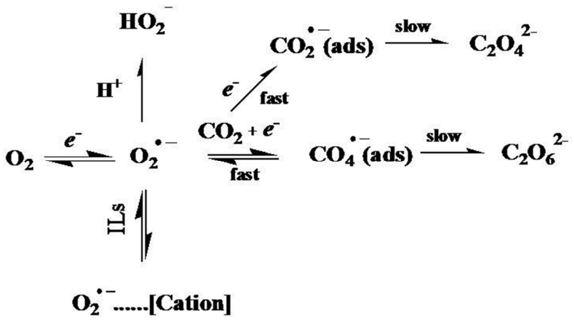

Figure 7: Mechanism of the reduction of CO_2 in the presence of oxygen using IL electrolyte which can be supportive towards IL sensor developments. (Ref[68])

The electrochemical reaction mechanisms of gases such as CO_2, H_2S, and Cl_2 have been shown to be either irreversible or a multistep reaction. For example, the electrochemical reduction of CO_2 in the IL [C_4mim][Ac] was studied on a Pt microelectrode using cyclic voltammetry. CO_2 undergoes a chemically irreversible one-electron reduction to the radical anion $CO_2^{\bullet-}$ and subsequent follow-up chemistry including interaction/complexation with the IL. The behavior was found to be irreversible due to strong absorption of CO_2 in the IL, suggesting that this system may not be suitable for real-time sensing of CO_2, however, the high solubility (>1.5 M) of CO_2 in [C_4mim][Ac] suggests a method for sequestration of the greenhouse gas. We have also used voltammetry in ILs in combination with QCM technique[68] proving that the CO_2 reduction in ILs is irreversible and forms $CO_2^{\bullet-}$ adsorbate at electrode interface. In the presence of O_2 and with increasing concentrations of CO_2, the reduction of oxygen is switched from a one electron

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process to overall two electron process, and forms adsorbed $CO_4^{\bullet -}$ intermediate species. The mechanism of the reaction thus proposed is shown in Figure 7. Such information about the mechanisms of the reaction is highly beneficial for the development of the amperometric gas sensors. However, the most important consideration in such cases is that the products of the irreversible reaction do not poison the electrode or the electrolyte.

4.1.5 Anomalous Redox Reactions in ILs

Study focusing on understanding the reaction mechanisms and comparing behavior to that in conventional electrolyte systems have shown some notable differences and anomalous behavior in some IL electrolytes.[69] It is extremely important to understand this anomalous behavior in ILs before they can be employed as direct replacements for conventional molecular solvents in sensor devices. Compton's group,[70] for example, has reported the two-electron reduction of 100% chlorine gas to chloride on a Pt microelectrode in a range of ILs ($[C_2mim][NTf_2]$, $[C_4mim][NTf_2]$, $[C_4mpy][NTf_2]$, $[C_4mim][BF_4]$, $[C_4mim][PF_6]$, $[C_4mim][OTf]$, $[N_{6,2,2,2}][NTf_2]$ and $[C_6mim][Cl]$). The behavior of the voltammetry at various scan rates was highly unusual, with limiting currents observed to decrease with increasing scan rates. This intriguing observation was assigned to a mechanism of adsorption of chlorine gas on the Pt electrode surface. The adsorbed chlorine itself cannot be reduced, but must undergo desorption before the electron transfer step. At slower scan rates with longer time scales, there is more desorption resulting in more surface available to chlorine for electron-transfer reaction, thereby resulting in higher currents at slower scan rates. The large voltammetric currents observed suggest that Cl_2 has a very high solubility (1-10 M) in ILs, making these solvents attractive for the purposes of Cl_2 gas sensor development. The authors did not report the effect of varying concentrations of Cl_2 on the current response, but this seems like the next logical step especially given the unusual adsorption mechanism. If the current scales linearly with concentration, ILs may prove to be a useful medium for robust Cl_2 gas sensing.

In a similar way, some notable differences were observed for the oxidation of toluene diisocyanate (2,4-TDI) in IL which occurred at less anodic potential than that in traditional acetonitrile based electrolytes with no side reactions.[71] In this case, the redox reaction is not that simple and reversible, yet the understanding of redox chemistry, thus revealed, and the carefully chosen measurement conditions allowed the development of a robust amperometric sensor for

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2,4-TDI detection. This was done by selecting a hydrophobic IL [C_4mpy][NTf_2] and by restricting the potential window to only include the oxidation processes. In this way, this sensor is made capable to avoid the two most ubiquitous interferents of the ambient conditions i.e., humidity and oxygen thereby enhancing the sensor performance and reliability for real world applications. 2,4-TDI detection was performed in both liquid and gas phases with detection limits of 9.32 ppm and 2.65 ppm respectively. These values are comparable to the safety standards set by NIOSH. The sensor so developed has a quick response time with good sensitivity and selectivity, and can be miniaturized for smart sensor protocols.

4.1.6 ILs as Sensitivity Enhancement Component

The distinctive characteristics of analyte redox properties in ILs was also demonstrated as sensitivity enhancing component of the amperometric sensor for the detection of ammonia by Ji et al.[72] They observed that the electrochemical oxidation of ammonia in propylene carbonate was indirect, enabling the measurement of 10-100 ppm by measuring the peak current of the reaction between ammonia and hydroquinone, as a function of ammonia concentration, giving a sensitivity 1.29×10^{-7} A/ppm and LOD of 5 ppm. On the other hand, the oxidation of ammonia has been shown to be direct in several ILs, suggesting that ammonia is initially oxidized to nitrogen, and protons, which are transferred to an ammonia molecule, forming NH_4^+ via the protonation of the anion(s). NH_4^+ was then reduced at the electrode surface, forming hydrogen gas, which is then oxidized. In all the ILs studied, the cyclic voltammetry shows a broad oxidative peak, with two cathodic peaks and one anodic peak following the oxidation. The two cathodic peaks were identified as: i) the reduction of the protonated anion(s), and ii) the reduction of NH_4^+. The resultant anodic peak is likely the oxidation of bulk hydrogen. Thus the analytical ability of this work has been established showing that the limit of detection was about ten times better than that in propylene carbonate. Moreover, it is highlighted that ILs not only provide direct redox mechanism for detection, but also appear to enhance sensitivity and other analytical performance parameters by implementing these mechanisms.

4.1.7 Innovations in IL based Electrochemical Gas Sensor Designs

ILs have higher viscosity than most aqueous or non-aqueous electrolytes which can result in slow response time due to the slow mass transport processes in an electrochemical cell.

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Furthermore, the high viscosity of ILs often result in ion-pair formation which can result in slow and less reproducible response.[20] This process can limit their direct use in practical sensors because of the longer response times and lower sensitivity. Recent advances in amperometric gas sensors involving ILs has been reviewed by Rogers et al[69] which describes the electrochemistry of various gases including O_2, CO_2, H_2, NH_3, H_2S, SO_2, and NO_2 in ILs indicating that the viscosity can be the most important limiting factor in the sensor development. One approach to surpass this barrier is to employ thin IL layers, thus overcoming the slow diffusion often associated with viscous ILs. This may result in shorter response times, on the order of minutes or seconds, which is satisfactory for most gas sensor device requirements. Another approach to increase response speed and to circumvent the high viscosity of ILs is to explore new electrochemical sensor structures. We introduced a novel macro-electrochemical cell with a porous PTFE Teflon membrane (**Fig. 8A**) with desired wettability of ILs that facilitates diffusional transport through the pores and provides two levels of selectivity.[53] Analytes entering from the back side were able to quickly reach the electrode/electrolyte interface without passing through the IL diffusion barrier, reducing the response time to mere seconds.[53] To further reduce the response time, we designed planar electrode (**Fig. 9**) with a structure joining the gas, liquid and solid phase at the site of the electrode. It features micro-fabricated porous gold electrode on porous PTFE thin film and an IL thin layer of [C_4mpy][NTf_2]) as electrolyte. The [C_4mpy][NTf_2] has high contact angle on the PTFE membrane so that the pores (typical diameter 10 μm) are slightly wetted by IL but it has low contact angle on Au and wets well on Au, allowing fast transport of gases to the electrode-electrolyte interface. Additionally, the variation of the IL structures can be used to fine tune the sensor sensitivity. Figure 8B shows the current responses for three NTf_2-based ILs and illustrates a strong dependence of the signals on the choice of cation, for this particular application. High sensitivity, complete reversibility, long term stability (less than 0.3% potential shift over 90 days), rapid response and strong selectivity (selectivity coefficient ~0.01% for CO_2, NO, NO_2, SO_2) of this IL oxygen sensor were also the benefits for this new sensor design. As discussed in later sections, microelectrodes fabricated on a silicon chip can be another important advancement in circumventing the viscosity effect shown by Compton's group.[56] The use of small (micron-sized) working electrodes can minimize any iR/Ohmic drop limitations that are often associated with voltammetry in highly resistive ILs on larger electrodes (larger currents). To improve current density and to overcome iR/Ohmic drop at

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the interface, a common attribute in viscous and resistive ILs, small sized working electrodes and eventually "lab-on-a-chip" type systems are being investigated.[21, 73, 74]

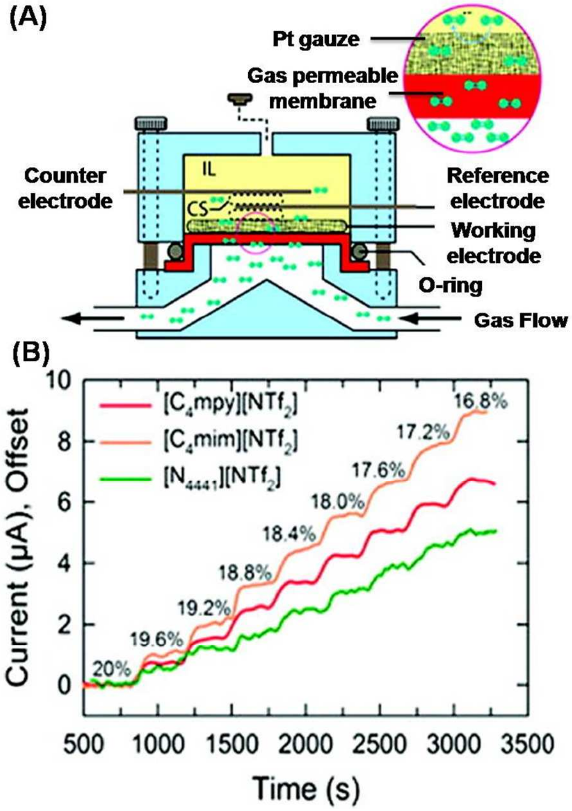

Figure 8: (A) The backflow sensor design allowing gas molecules to directly reach the interface without passing through viscosity barrier. (B) The concentration dependent electrochemical response for the oxygen with three different IL systems (Ref[53]).

4.1.8 Innovations in Electrode Designs for IL Gas Sensing

ILs provide new opportunities not only for electrochemical sensor design but also for miniaturization by innovations in electrode geometry and electrode substrate flexibility. Micro-fabrication technologies, particularly thin film deposition of microelectrodes and formation of micro-fluidic channels, have been widely applied to analytical systems.[75, 76] Electrode arrays, both macro- and micro-scale, are now commonly fabricated using thin film metal deposition and photolithography.[5, 77-79] For example, Figure 9 shows an interdigited electrode (IDE) fabricated using thin film deposition of both platinum and gold on porous Teflon that were used to obtain the sensor data for the measurement of oxygen concentrations.[64] These miniaturized sensors yield similar sensitivity to results shown before for the oxygen detection.[53] As fabrication of

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these electrodes relies on photolithography, the size and geometry of the electrode can easily be varied to meet the needs of the sensor interfaces, and different electrode configurations can be utilized within the same array to improve analytical performance.

The IL-based methane sensor discussed earlier was also characterized by these microelecrodes and compared using both conventional solid macroelectrode and flexible planar microfabricated electrode shown in Figure 9A. Both single- and double-potential step chronoamperometry experiments were performed. As shown in Figure 5, the flexible IDE electrode provided equally quantitative results but with relatively lower sensitivity. This is likely due to the vapor deposited platinum having less catalytic activity than the solid platinum electrode. In both sensor configurations, we were able to obtain reversible signals with long term stability (less than 0.3% potential shift over 90 days), rapid response, and good selectivity (selectivity coefficient ~0.01% for CO_2, NO, NO_2, SO_2).

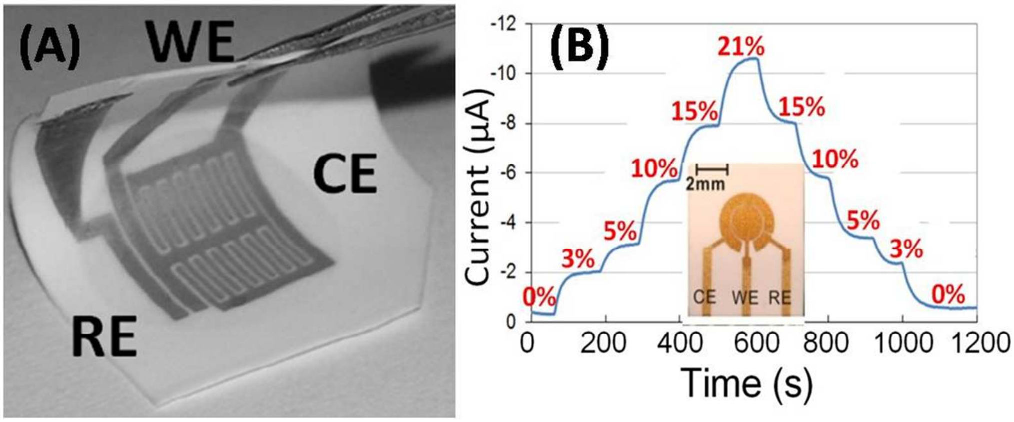

Figure 9: (A) Image of a flexible Pt-interdigited electrode (IDE) made on a Teflon gas permeable membrane via micro-fabrication techniques; (B) Amperometric sensing of oxygen using micro-fabricated concentric ring disk Au-electrode (shown in the inset) on porous Teflon. (Ref[64])

4.2 Impedance Based Gas Sensing Approaches

Although the voltammetric approaches can be used for reproducible sensor developments, but still in many cases, it is not easy to establish a reversible or feasible reaction mechanism for the target analyte detection. The products from the redox reactions often generate changes at electrode interfaces which can reduce the sensor lifetime. Electrochemical impedance spectroscopy (EIS) involves the application of a sinusoidal electrochemical perturbation (potential or current) over a wide range of frequencies, allowing the measurement of impedance

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changes in the forms of double-layer capacitance and the charge-transfer conductance that originate from the change of polarization of IL-electrode interface. EIS is an alternative approach to promote reversible sensing mechanisms since there is no redox reaction, thereby making no product, thus avoiding any fouling or poisoning of the electrode or the electrolyte. This mechanism is non-invasive as well, providing better reversibility for sensing which has led to long sensor life times. Thus EIS-based sensors not only provide orthogonal detection modes to amperometric sensors, but they also permit self-monitoring of the sensor's stability and automated calibration for drift mechanisms. At room temperature, ILs have high viscosity. Consequently, the diffusion and conductivity of ions is normally lower in ILs than in aqueous electrolyte solutions. Thus, they can be regarded as a solid and liquid interface simultaneously, making them ideally suited for applications that require a thin or intensely concentrated layer of ionic charge, such as capacitance sensor development. Compared with molten salts at room temperature, the ions comprised of ILs are often large, flexible, highly polarizable, and chemically complex with a number of interionic forces (such as dispersion forces, dipole-dipole interactions, hydrogen bonding, and pi-stacking forces) in addition to coulombic forces present. Additionally adsorption of anions and/or cations is likely to happen at the interfaces with ILs. Varying the applied potential can result in the rearrangement of adsorbed ions which allows the modification of the IL double layer capacitance. When exposed to an analyte especially small gaseous molecules, the molecular interaction events that occur at the IL interface can lead to polarization reaction at interface via redox reaction, as well as binding or dissolution of the analyte in ILs. For example, the analyte can displace or rearrange the IL order in the double layer to a new orientation. Removing analyte allows the IL double layer to return to its original orientation. Based on these principles, an innovative capacitance sensor has been demonstrated for methane detection[8] measuring the change of the surface charge at IL-electrified metal interfaces. The adsorption of anions and/or cations is likely to happen at the interfaces whereas the specific adsorption depends upon the chemistry of the ions and applied potential. The IL $[C_4mpy][NTf_2]$, which has double layer structure favoring small gas molecule adsorption, can sensitively and selectively measure concentrations of CH_4 (Fig. 10) using EIS with a -0.3V DC bias. Figure 10 also clearly shows that the sensor returns to its baseline value when the analyte is removed, demonstrating the reaction is fully reversible with less than 0.1% drift. The selectivity comes from the unique highly ordered arrangement of ions in the innermost layer of IL-electrode

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interface which is potential dependent. The degree of ordered structure at IL-electrode interface can be tuned by the applied bias (e.g. -0.3V for CH_4) and by the unique molecular structure of the IL ions. The high viscosity of ILs that is usually considered a limitation to practical electrochemical applications due to slow rate of mass transport is an advantage in capacitance[80] measurement due to a more ordered and concentrated double layer. The response time experimentally measured is often the sum of gas sampling time related to the test set-up and sensor response time. The overall response times t_{90} of NO_2, CH_4 and SO_2 were only 5.1s, 6.4s and 23.6s respectively when tested using electrochemical impedance spectroscopy (EIS).

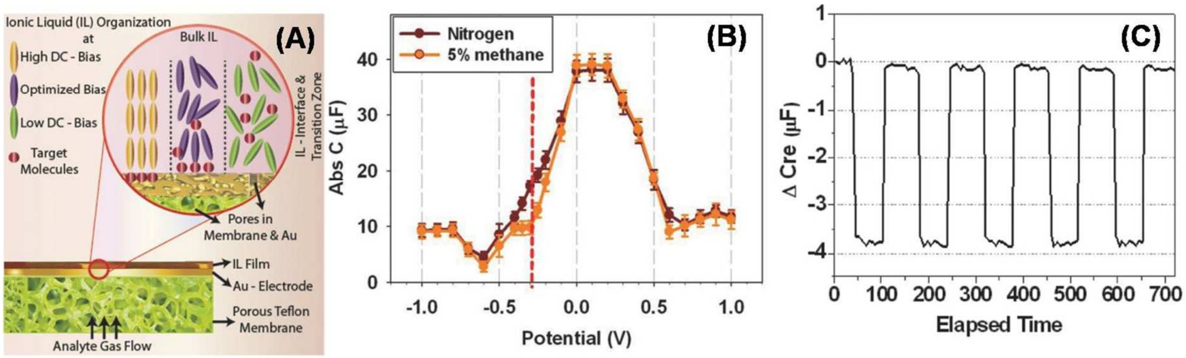

Figure 10: (A) Schematic diagram of IL-electrified interface sensor response mechanism indicating that an optimized bias potential is required for the gases to absorb at the interface. (B) The capacitance-potential curves for the exposure of nitrogen or 5% methane at a frequency of 1 Hz and carefully chosen potential range (−0.8 V to 0.8 V) where no Faradaic processes are there for the gases tested. The response of the two gases is exactly similar except at a specific optimized DC bias (-0.3 V in this case) where the absorption of methane occurs. (C) Capacitance measured over five cycles of alternate exposure to 5% methane and nitrogen (as the baseline gas) indicating that the response is fully reversible. (Ref[8])

4.3 Electrochemical Gas Sensing Approaches Based on Disposable Devices

Even if there is an unavailability of simple and reversible redox reaction, or the mechanism is too complex to identify one quantification parameter, or the reaction products are present which can hinder the reproducible use of the developed sensor, as might be the case with above detailed methods, the IL materials still present an opportunity to design electrochemical gas sensors on disposable platforms due to the possibility of low cost production of ILs at mass scale. Although this opportunity is not usually conceived for solving the above problems, rather, for a more critical need, to implement the electrochemical sensors for much more remote areas and third world countries where the availability of even the simplest technical equipment is scarce and the end users are limited in their experience. Moreover, such sensors can be cost efficient as well by

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using the inexpensive materials (e.g., paper) in fabrication as shown in Figure 11. ILs are also stable and relatively low cost when they are being mass produced. One of the first examples in this regard is a sensitive and fast-responding membrane free amperometric gas sensor consisting of a small filter paper foil soaked with an IL, with three electrodes screen printed on it with carbon ink.[21] By carefully controlling the preparation procedure, a very close contact between the IL and the carbon electrode is achieved, allowing gaseous analytes to undergo charge transfer just as soon as they reach the electrode. Thus, the adverse effect on recorded currents of slow steps such as analyte diffusion and dissolution in a solvent is avoided. To evaluate the performance of this device, 1-butanethiol vapors were adopted as the model analyte. The results obtained were quite remarkable for a disposable sensor (detection limit: 0.5 μM; dynamic range: 2–200 μM, both referring to solution concentrations; correlation coefficient: 0.998; repeatability: ±7% RSD; and long-term stability: 9%). A similar strategy is utilized by this group for the detection of acidic vapors such as phenol as model analytes,[74] but with a shift towards task specificity in the IL selection. This time, the inexpensive paper support was soaked by an acetate anion based IL, thus having a basic character. The results obtained showed that the detection of these acidic analytes can be done at significantly lowered oxidation potential which otherwise are quite high for the selected targets. In this way, overlap with the medium discharge is avoided, and the possible adverse effects of interfering species are minimized. The sensor performance was also comparable to the previous report by the same group. Toniolo et al[81] also reported a paper supported amperometric sniffer for monitoring volatile amines (VAs) released from fish samples, in order to gain indication of their state of turning spoiled. The performance of this sensor was preliminarily tested on synthetic samples of trimethylamine (TMA), dimethylamine (DMA), methylamine (MA) and ammonia (i.e. the main species responsible for the typical flavor of spoiled fish), detecting only TMA, DMA and MA without interference from NH_3 whose oxidation occurred beyond the solvent discharge. This detection of the sole TMA, DMA and MA as a whole turned out to be well suited for the rapid assessment of fish spoilage, since during storage the release enhancement for these amines is largely predominant over that of NH_3. This approach was then applied to the detection of VAs released from real fish samples with a substantially satisfactory agreement of data obtained by routinely adapted approaches.

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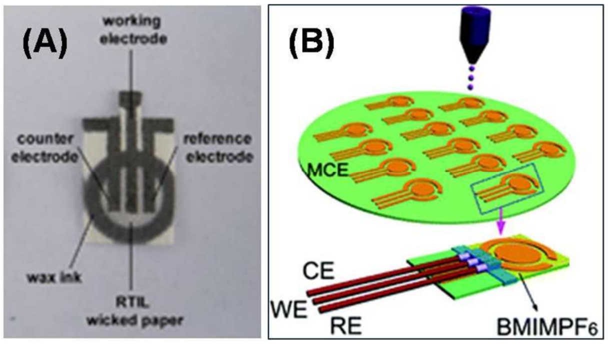

Figure 11: A couple of examples using IL systems and disposable electrodes made on; (A) filter paper by screen printing with carbon ink (Ref[74]) and (B) cellulose membrane by inkjet printing of gold nanoparticles. (Ref[73])

Another step towards the disposable sensors is to utilize commercially available electrodes and sensors which can be cost effective by the batch production technologies. This has been done by Gebicki et al[82] for the detection of VOCs using different ILs as the electrolyte (e.g., $[C_4mim][N(CN)_2]$, $[C_8mim][BF_4]$, $[C_4mim][NTf_2]$). The sensors implemented for this study were designed by DropSens Company in Spain in the form of stripes with the electrodes screen printed on a ceramic substrate. The working and counter electrodes were made of deposited gold layer, whereas the reference electrode was made of deposited silver layer. The presented prototype for measurement of benzaldehyde, methyl benzoate and acetophenone in argon atmosphere was characterized by the sensitivity from 71 to 191 nA/ppm, whereas the limit of detection of these analytes was at the level of 1.4–5.7 ppm (v/v). However, these parameters again depended on the analyte measured as well as on the electrolyte employed, confirming the previously obtained results. The developed prototype was also shown to have good reproducible character as the sensor was operated for 2 months yielding relative standard deviation below 8%. This indicates that even the commercial sensors can be employed for obtaining an enhanced performance if stable and reproducible redox chemistry has been identified and IL materials are utilized. In order to do the mass production of such sensors, a simple approach of inkjet printing of gold nanoparticle (GNP) patterns with the self-catalytic growth of these patterns into conducting layers on cellulose membranes has been introduced[73] and presented for electrochemical sensing of oxygen using IL electrolytes. By using this approach, hundreds of self-designed gold arrays can be fabricated in hours using an inexpensive inkjet printer. The resulting paper-based gold electrode arrays had several unique properties as thin-film sensor platforms. The porous nature of these new electrodes also allowed the addition of electrolytes

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and analytes from the back side of cellulose membrane and controllably produced large three-phase electrolyte/electrode/gas interfaces at the front side of the electrode. The sensor looked like a piece of paper but possessed high sensitivity for O_2 in a linear range from 0.054 to 0.177 v/v %, along with a low detection limit of 0.0075% and a short response time of less than 10 s, foreseeing its promising applications in developing cost-effective and environment friendly paper based electrochemical gas sensors.

4.4 IL Modified Electrodes

Although, the use of ILs as electrolytes and solvents can be performance enhancing factor for the electrochemical gas sensors development based on voltammetric and impedance readout in terms of selectivity and reproducibility, yet another new direction in using the IL materials as sensing interfaces is by employing them as a component for developing modified electrodes, and in many innovative ways to produce good responses for analyte detection in real-world samples. Surface modified electrodes are electrodes with deliberately immobilized materials so that the electrodes display the chemical, biological and other properties of the immobilized molecules. The properties of the surface modified electrodes are closely associated with the physical and chemical properties of immobilized molecules as well as the immobilization processes on the substrate electrodes. ILs are good solvents to be miscible with many other materials and they are not volatile allowing many new composites materials to be made. Task specificity of ILs renders high selectivity, if employed in the modification. Many of the sensing performance parameters are enhanced up to certain extents, even if the ILs are used only as an inert solvent. The low melting points and low tendency to crystallize, realized by combination of large, usually asymmetric cation and smaller anion, make ILs good candidates for this modification that can lead to really a diverse set of applications in sensing field. These modifications can be done in many different ways; however, the choice of modification is entirely based on the application requirements.

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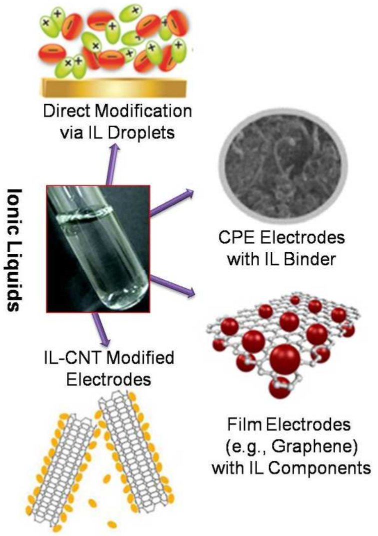

Figure 12: Schematic of most commonly employed electrode modification protocols utilizing ILs as one of the component

Among many different types of electrode modifications possible for the sensor applications, electrodes modified with IL droplets or films are the most commonly employed. In this method, electrodes are prepared by direct deposition of IL on the electrode surface[83] or from its diluted solution in volatile solvent.[84] These two procedures may provide different geometry of the deposit. Thin liquid film geometry is most important for sensors which can be enforced by surface coverage with porous Teflon membranes. The preparation of IL-modified electrode *in-situ* by adsorption of IL from aqueous solution has also been reported.[85] The appropriate selection of electrode substrate and IL is important in this case to obtain stable liquid deposit in contact with aqueous solution. Although research on IL-modified electrodes started from electrode substrate covered by droplets or liquid film, in the absence of other film components, but now the focus has been shifted to develop modified electrodes with organic or inorganic polymers, nanoparticles, nanotubes and other micro- or nano-objects as other components. Their complexity ranges from simple ones as polymer film plasticized with IL to multicomponent films. In many of these cases of direct modification, ILs, especially the imidazolium based, can also be appended to demonstrate functionalities which are related to their immobilization onto the electrodes to generate different type of modified electrodes. These functionalities include self-assemblies of IL on the electrode surface, covalent bonding of IL to the electrode surface, IL functions that can be used for preparation of IL based polymer films (PILs), and IL used for functionalization of conductive elements of the film. When the electrode is ready, the

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counterions are electrostatically attracted to positively charged functionalities and they can be exchanged after immobilization on the electrode surface. Such small modifications can be highly suitable for incorporating the desired characteristics to the electrode materials. But most importantly, the electrodes modified by any of these methods can then be utilized for various sensing applications. For example, Ng et al[86] employed a nanocomposite gel consisting of a three-dimensional graphene material and the IL [C_4mim][PF_6] for the amperometric detection of nitric oxide (NO). A linear response of current vs. concentration over the range 1-16 μM NO was observed, with a fast response time of less than 4 seconds and a low detection limit of 16 nM. The improved response of this modified electrode is attributed to the porous graphene material that has a high specific surface area and superior conductivity which generated a 3-D graphene/IL nanocomposite to provide a novel platform for sensitive NO detection. Composites of IL materials can also be used for electrode modifications. For instance, an amperometric NO sensor based on poly(eosin b)-IL composite (PEB-IL) films has been described.[87] In this work, conducting PEB was firstly electrodeposited on the surface of a glassy carbon electrode, and then a composite of [C_6mim][PF_6] and didodecyl dimethyl ammonium bromide (DDAB) was coated on the PEB film. The resulting PEB-IL composite has the advantages of fast response and high selectivity for the determination of NO. The results showed that the PEB-IL composite modified electrode exhibited an excellent anti-interference ability and a wide linear relationship over a NO concentration range of 3.6×10^{-8} to 1.3×10^{-4} mol/L with a low detection limit of 1.8×10^{-8} mol/L (S/N = 3). This sensor was successfully applied for the monitoring of NO release in rat kidney signifying its real life performance which can have potential applications in many heart and kidney related conditions.

High viscosity of ILs can also be employed to enhance the performance of the modified electrodes, for example, as binder in carbon paste electrodes which can then be used as sensing materials as well. In most cases, hydrophobic ILs are used for IL-based carbon paste electrodes (ILCPE). Contrary to classic CPEs, their binder is composed of charged species and exhibits ionic conductivity which enhances the electrochemical sensing capabilities of these modified electrodes. Typically, ILCPEs are prepared as classic CPEs by mixing or grinding of graphite particles with the IL and placing the mixture in a cavity of the polymer or glass tube. After polishing, the electrode is ready to use. The IL/graphite particles ratio has to be optimized from the point of view of not only mechanical stability but also capacitive current, resistance and

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specific electrode process and 7:3 graphite to IL ratio has become a popular composition. Imidazolium-type ILs also tend to form physical gel when grounded with SWCNTs by physical cross-linking of the nanotube bundles, mediated by local molecular ordering of ILs. Recently, ILs have been found to be efficient binders in the preparation of carbon composite/carbon paste electrodes (CPEs). They are prepared by mixing or grinding graphite particles with the IL, followed by the transfer of this mixture into a cavity of a polymer. Higher currents (both faradaic and capacitive) are often observed at ILCPEs compared to traditional CPEs, This is believed to be due to the larger electro-active area for electron transfer in the ILCPEs due to the conductive IL medium. In traditional oil-based CPEs, electron transfer can only take place at the carbon/aqueous electrolyte interface. Other reasons for the higher currents may also be explained by the changes in paste morphology, better solubility of polar analytes in the IL (compared to the binder) or the presence of additional interface where transfer across the liquid/liquid interface can occur. Due to these attributes of IL-carbon pastes, they have been employed for highly selective sensing of explosive TNT by Guo et al.[88] The IL [C_4mim][PF_6] was combined with three-dimensional graphene to make an IL-graphene paste electrode with a large surface area, low background current and pronounced mesoporosity. A linear relationship was observed between peak current using absorptive stripping voltammetry and concentration from 2 to 1000 ppb, with a low detection limit of 0.5 ppb for TNT. This performance was superior to that demonstrated by IL-CNT and IL-graphite composites.

4.5 Mass Sensing Transducers; QCM and SAW Devices for IL sensing

ILs provide unique properties required for a chemical sensor using mass sensing transducer such as QCM and SAW devices. QCM and SAW transducers are often made of quartz crystals or other piezoelectric materials with associated metal electrodes that are in contact with the sensing films. The mechanism of operation of these sensors involve analyte induced changes in the mass, viscosity, elasticity, and even the conductivity of the sensing film and the correlation of these changes with the changes in the frequency, dissipation, and damping resistance of the sensor. In contrast to electrochemical sensors, the high viscosity of ILs is beneficial for these sensors since they can be cast into thin films. Being highly volatile, solvents are seldom used as sensing elements. Contrastingly, ILs have no significant volatility, allowing chemical processes to be carried out with essentially zero emission of toxic organic solvents and enabling their utilization

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as recognition elements. In these applications, ILs behave as both solid and liquid interfaces simultaneously, thus overcoming the issues associated with interchangeable use of solid and liquid phases and the requirement of solvents to generate these phases. Depending on the physical phenomenon involved for the solvation of analytes in ILs, a coating of IL can swell, shrink, or undergo a viscosity change. The solvation in ILs is controlled by the variable contributions of adsorption-desorption and partition phenomena depending upon IL and analyte properties to furnish additional selectivity, thus opening up excellent opportunities to design different arrays of chemically selective IL films. Such characteristics make these ILs suitable for detection of analytes in gas environments via QCM, SAW, and even with MEMS transducers. The major outcome in all these cases, however, is the reversibility of gas sensing as the mechanism is absorption based and is mostly relying on weaker chemical interactions. The sensitivity and selectivity, on the other hand, has to be achieved by selection, or design of ILs, or by using the combinations of them in the form of sensor arrays.

Dai and co-workers[89] first developed a sensor for organic vapors based on QCM using ILs as sensing materials. When analytes were dissolved in an IL, the viscosity of this IL changed rapidly which generated a frequency shift of the QCM device. The response of the QCM depended on the nature of both the analyte and the IL. Some of these ILs also have strong affinities for selected chemical species. Sensor arrays comprising multiple of these sensors, each with a different IL coating, thus can not only detect target analytes but also help identify chemical speciation. In most of these cases, ILs are solely used as sensing films which interact with target analytes through ion and dipole forces, hydrogen bonding, and van der Waals interactions on various time and space scales. All these interactions depend upon variations in ionic composition and structure of ILs, thereby generating a criterion for selective incorporation and interaction of analytes. In addition, great solvation ability of ILs enables the rapid and reversible incorporation of gases, as shown in the work done by our group for detecting different explosive gases.[7] We have also shown that the very different solubilities of ILs for specific reactant gases creates a membrane-like selectively to enhance or suppress (pre-concentrate) transport of specific reactants and provided a mechanism for selectivity.[53] Using this principle, we have successfully classified four volatile organic compounds (benzene, hexane, methylene chloride and ethanol) via seven IL film-based mass sensors, where the unique selectivity of the

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ILs results from strong hydrogen bond basicity and significant capacity for dipole-type interactions with the analyte.[22, 90] A similar strategy was implemented for the detection of organic acid vapors using [C_4mim][C1] coated on QCM.[91] The experimental results indicated that the sensor showed fast response, excellent sensitivity and good reproducibility towards organic acids. There was a good linear relationship between the frequency response and the testing concentration of these organic acid vapors.

Expanding this approach to real life applications, an array of quartz crystals coated with seven different ILs is proposed for the analysis of flavors by QCM measurements.[92] The selected ILs were all containing imidazolium or phosphonium cations, differing from one another in the length and branching of alkyl groups. The array was at first applied to the analysis of 31 VOCs chosen as representative components of a wide variety of food flavors. Multivariate data analysis by using principal component analysis (PCA) led to separated clusters for these different chemical categories. To further prove the good performance of the developed electronic nose, it was applied to the analysis of headspaces from cinnamon samples belonging to different botanical varieties (Cinnamon zeylanicum and Cinnamon cassia) indicating that the responses recorded on different stocks of samples of both varieties could be fully discriminated.

4.5.1 High Temperature Mass Sensing via ILs

ILs possess high thermal stability.[93] Most ILs show typical decomposition temperatures of 350+ ^{o}C. This remarkable thermal stability has important implications in the use of ILs for high temperature sensing.[9, 94] For example, a polar IL, [$P_{14,6,6,6}$][DBS], was prepared via the alcohol-to-alkyl halide conversion method and coated onto QCM from its ethanol solution. This sensor was studied for the exposure of both polar (ethanol, dichloromethane) and nonpolar (heptane, benzene) vapors even at 200 °C showing linear response pattern and clear signals as shown in Figure 13. As expected thermodynamically, the sensor signal decreased with increasing temperature, but still, a 5% detection limit was achieved, which is encouraging because most solid surfaces are unable to adsorb vapors at temperatures that much higher than their boiling points. Additionally, there was an excellent reversibility for adsorption-desorption processes, requiring no experimental manipulation for sensor recycling. The data for the damping resistance showed that physiochemical parameters such as Henry's constant can be more accurately

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determined at higher temperatures because of the lowered viscosity of the ILs. In another study,[95] the gel beads containing ionic liquid were prepared by suspension polymerization with diameters of 100-2000 μm and were applied as hydrogen sensing materials. The sensor utilizing this material has nice flexibility and high heat endurance. The weight and shape of gel beads were maintained not only in high temperature condition but also under vacuuming condition. The resulting hydrogen micro sensor was able to detect 2% hydrogen concentration. It has high grade gas selectivity and can detect hydrogen gas in the range of explosion limit. These results indicate that IL materials can be employed for detection in harsh, otherwise unmanageable environments.

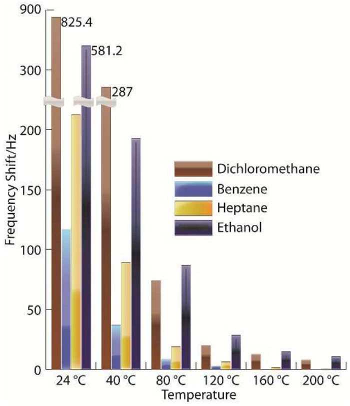

Figure 13: Responses shown by IL-sensors from ambient to elevated temperatures for different VOCs (Ref[30])

4.5.2 IL Composites for Mass Sensing Approach

For IL based mass sensors, to minimize the bulk properties (e.g., viscoelastic property) change generated signals, the sensing films on the electrodes have to be thin which are usually formed by employing the methods of electrode modification. The effectiveness of most thin film based sensors relies on high sensitivity and specificity of the detection interface. The obvious approach to increase the sensitivity of QCM sensors is to increase the thickness/amount of the sensing material. Pure ILs inherently possess certain limitations in this regard, especially for low molecular weight analytes, where sensitivity enhancement by thicker IL films can substantially influence the reproducibility through temperature-controlled variations in IL-layer thickness and the spreading out effects. Non-rigidity of thicker films makes the Sauerbrey's equation invalid in addition to slower responses, requiring a strategy to achieve higher IL-loading while maintaining the IL-film integrity. Thin films made from ILs would perform well as sensor interfaces and provide additional control over selectivity and sensitivity when interacting with analytes in gas

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phase. Most organic solvents or vapors are soluble in ILs. Therefore, the partition process will reach equilibrium very fast after the sensor is exposed to the vapors. For these situations, IL composite films are usually employed. Several approaches have been developed for fabricating IL-composite sensing films. In one such example, ILs are trapped as nanodroplets into the cylindrical cavities of solid alumina matrix, thus avoiding liquid wetting and softness.[96]Although, this matrix can hold more IL than planar gold surface, yet the detection limits were not low enough for selected analytes. Contrarily, conducting polymers (CPs) and polyelectrolytes have charges, which make them ideal template materials to make IL-composite films. The proof of the concept was provided with the example of methane,[6] a highly inflammable gas with very low molecular weight, and hence an evidential candidate for higher sensitivity in mass sensing devices requiring abundant total absorption/partition into the films. An ideal template for this purpose should be a porous and stable scaffold that can be modified to generate required surface area and wettability for IL immobilization. Polyaniline (PAN) can provide this dimensionality. Four different oxidation states of PAN including the doped and undoped ones can be tested for the analytical response with an IL e.g., [C_2mim][CS], which can form hydrogen bonds through the sulfonate group, however, the doped PAN showed the highest sensitivity being highly charged, facilitating IL wettability through electrostatic interactions, in addition to hydrogen bonding. This increased IL surface area exposed to the analyte. The IL distribution into the nanosized channels of the PAN film helped to increase the response owing to the increase of IL film coverage. UV-vis and FT-IR data in this case confirmed[97] the formation of hydrogen bonds between camphorsulfonate and the nitrogen sites of protic acid doped PAN. These bonds force the anions to align along the polymer backbone in a comb like manner so as to enhance the long-range π-orbital conjugation. The interacting methane molecules can fit into these comb spaces and thus an enhanced sensitivity was observed. The enthalpy and entropy of the dissolution were shown to be higher than those in pure IL or PAN which further supported the existence of methane inside the composite generating a more ordered structure. Molecular mechanics simulation agreed with these results as well. This example and others indicate that CPs often have fairly rigid structures with tunable porosity and charge states, which can promote the rational development of the CP/IL interface alongside the IL-controlled parameters. The chemical selectivity can be provided by varying the oxidation states of CP and ionic structure of IL.

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Besides this, many useful approaches are available for IL-composite formation both for their use in QCM sensors, as was the case with electrochemical sensing applications. The most widely used techniques include direct mixing, casting, physical adsorption, electrodeposition, layer-by-layer assemblies, and sol–gel encapsulation. Physical adsorption of the IL onto a solid support is most often used to prepare the sensing films, which is based on binding forces including ionic interactions, hydrogen bonds, van der Waals forces, hydrophobic interactions, and so on. However, the more sophisticated methods for this immobilization are electrodeposition, sol-gel encapsulation, and layer by layer assembly. In electrodeposition, a clean electrode is immersed in a bathing solution containing the supporting electroactive material and corresponding IL which are then electrochemically deposited onto the electrodes.[98, 99] Electrodeposition of metal nanoparticles onto IL/CNT is another well studied technique to prepare AuNP/IL/CNT nanocomposite based sensors.[100] In sol-gel encapsulation, an IL-silica sol is synthesized which is then mixed with different types of interesting molecules to form the films[101] whereas in layer-by-layer method, a sequential deposition of multiple layers is achieved,[102] one being the IL and the other one that is supporting material, onto the electrode surface by electrostatic, van der Waals, hydrogen bonding, and charge transfer interactions. From all these approaches, benefits and weaknesses can be identified for any of them; however, the selection is highly related to the particular application in which the approach is going to be implemented.

4.6 IL Based Optical Approaches for Gas Sensing

Although, the solvation capability of IL films play the role of interaction with the target analytes both in the electrochemical and mass sensing formats, thereby having a partition coefficient and defining the sensitivity and selectivity of the resulting sensor, yet their roles as solvating species can be best described from the examples of optical sensing. Here, ILs allow many important optical substances to be dissolved to form stabilized optical matrices.[103,104,105,106] Optical sensing mechanism probably has the highest face value for the commercial sensing as most of the times, it involves the change in some color patterns (readable by the end user without technical knowledge) after the interaction of the target with the sensing film, though, there are many sensor developments where the change in the color pattern is so minute or complex to be detected visibly, or the change involves some non-visible part of the electromagnetic spectrum thereby requiring analytical tools/instruments for detection and further analysis. Moreover, the

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use of ILs provides even more stability to the resulting optical matrix thereby enhancing the reliability and reproducibility of the sensing.

4.6.1 IL Matrices and Composites for Optical Gas Sensing

The IL-based colorimetric sensors are usually fabricated by use of color responsive dyes that are integrated into ILs and change their colors based on intermolecular interactions, such as acid-base, dipole-dipole, and π-π interactions. IL-based optoelectronic sensors have shown higher chemical selectivity and sensitivity compared to other type of sensors.[107,108,109] For instance, Oter et al. reported[110] an optical CO_2 sensor using the ILs ([C_4mim][BF_4] or [C_4mim][Br]) as the matrix with 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS). The detection of CO_2 is based on the fluorescence signal change of HPTS when pairing to CO_2. More recently, the same group reported[111] that IL modification of an ethyl cellulose matrix extended the detection range to 0–100% pCO_2. In comparison to conventional solid matrix or liquid optical sensors, which have leaching problems, short life times because of evaporation of solvents, and poisoning issues from the ambient air and interfering gases, IL based optical sensor showed much better performance due to ILs' distinctive properties and better CO_2 adsorption than polymeric materials. For these optical sensors, again, different composites of ILs have also been tested to enhance different sensing parameters. In one such report,[112] the feasibility of being able to control the selectivity of solid-state ruthenium complex based electrochemiluminescence (ECL) sensors is examined by selecting ILs with appropriate hydrophobicity in the sol-gel titania/Nafion composite film. Four different kinds of ILs with different hydrophobicity were incorporated in the sol–gel films and the sequence of the ECL intensities for different hydrophobic analytes was observed. It was found that this sequence was closely related to the sequence of the hydrophobicity of the ILs. In contrast, the observed ECL sequence for hydrophilic analytes was opposite to the sequence of the hydrophobicity of the ILs. Based on these signals, the sensor was able to give a remarkable detection limit (S/N = 3) of 0.48 nM for tripropylamine. Similar ECL sensor designs have also been reported[113] for the detection of SO_2 with remarkable outcomes in terms of sensing capabilities (e.g., ppb level detection).

4.6.2 IL Structural Diversity for Optical Sensing Approach

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IL diversity in terms of anion and cation combinations has been able to provide further selectivity in the optical protocols as well. Only by the simple counter-ion exchange of ILs, a rapid, facile, and efficient strategy was developed to create a cross-reactive sensor array with a dynamic tunable feature,[114] which can then be used to construct a florescence sensor array for the identification and classification of nitroaromatics and explosives mimics. The cross reactive array so generated had diversiform properties, such as different micro-environments, diverse molecular interactions, and distinctive physico-chemical properties for a distinct fingerprint of explosives to be obtained. It was found that the LUMO-HOMO energies, excitation and emission spectra, fluorescent lifetimes as well as the sensing capability of the synthesized IL could be significantly influenced and tuned by coupling different counter-anions, indicating that from one single IL sensor element, a large sensor element pool with rich diversities could be conceivably created by simple exchange process of counter-anions. Moreover, the reversible counter-ion exchange capability of IL also provides a plenty of room and useful means to post-modify the sensing properties of individual element for further correcting or optimizing the sensing performance of the formed sensor array. The reversible anion exchange ability further endowed the sensor array with a dynamic tunable feature as well as good controllability and practicality for real-world application. In addition to these cross reactive arrays, the specific colorimetric ILs have also been synthesized from readily available pH indicator dyes. For example, a series of 12 different chemosensory ILs were synthesized[115] by pairing anionic pH indicator dyes with trihexyl(tetradecyl)phosphonium ($[P_{6,6,6,14}]$) cation via an ion exchange reaction. The incorporation of the $[P_{6,6,6,14}]$ cation imparted hydrophobic characteristics to these ILs, and this induced hydrophobicity led to their desired low solubility in aqueous solutions, as well as eliminated the need for a specialized hydrophobic matrix/substrate for immobilization. These sensor arrays were then used to analyze pH values of aqueous solutions as well as for detection of acidic and basic vapors. Use of cotton threads as a matrix led to development of an even more flexible, low volume, and lightweight array to estimate pH and detect a variety of vapors. These wearable arrays may possibly be incorporated into bandages, sweatbands, diapers, and similar systems. Overall, these IL-based sensor arrays should provide a new research direction in the development of advanced colorimetric sensor arrays for detection and identification of a range of analytes relevant to many different applications.

4.6.3 Innovative IL Chemistries for Optical Detection

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A unique contribution that IL materials have provided to the sensor science is new and innovative chemistries of the reactions which are due to their biphasic nature and inorganic/organic characteristics. These new chemistries are not letting themselves behind in the development of new optical detection technologies. The most important and most comprehensively studied of these is the stability of superoxide radical in ILs. The same basic principle has been utilized to develop a CO_2 gas sensor.[116] It has been shown that in the absence of stable superoxide in a conventional system, the oxygen-luminol reaction was unable to produce the ECL signal in an electrolyte-free N,N-dimethylformamide (DMF) dipropylamine (DPA) co-solution. However, when CO_2 was introduced in the system, it induced the formation of carbamate IL by reacting with DPA. Because of the presence of this IL in the system, the superoxide radical become stable thereby generating an ECL signal from luminol. This system was used as a sensing mechanism for CO_2 demonstrating nice performance parameters such as high safety, high selectivity, wide linear response range, and good sensitivity. The gas sensor was found to have a linear response range from 100 ppm to 100 v/v% and a detection limit of 80 ppm. Besides showing innovative chemistries, IL are also entitled to the stability and other performance parameters which was shown in a ratiometric CO_2 sensor[111] based on the spectrophotometric signal change of bromothymol blue (BTB). Effects of ILs with different anionic and cationic parts on the sensor signal intensity were tested. For this sensor, the sensing agents were produced both in form of nanofibrous materials and continuous thin films. The nanofibers were fabricated by electrospinning technique. The ratiometric response to CO_2 was monitored at 396 nm and 640 nm. The offered sensing material can be used for quantitative determination of CO_2 in the concentration range of 0.0-100.0% pCO_2. With respect to continuous thin films, the electrospun nanofibers offered enhanced sensitivity extending to 98% relative signal change, lower detection limits and shorter response times. BTB also satisfies best the requirement of a distinguishable color change with naked eye when encapsulated in nanofibers. ILs not only provided the enhanced long-term stabilities in this system but also facilitated the fabrication of nano fibers providing an electrical conductivity in the polymer by the effect of ionic groups.

4.6.4 Photo-responsive ILs

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Another straightforward method for IL-based colorimetric sensors is the synthesis of luminescent ILs, which can be obtained by integrating photochromic cation or anion into ILs and can enable direct detection of targeted reactions. Pina et al. recently reported, for example, the successful synthesis of photochromic intrinsic ILs by using photochromic methyl orange anion,[117] which takes advantage of light response together with properties specific to ILs. Deng and coworkers also synthesized a new class of azobenzene-based ILs, which showed distinct and reversible solvent-dependent photoresponsive conductivity.[118] It is interesting to see that sometimes even same photochromic modified IL could show different properties by isomers.[119,120,121] The modification of ILs by photochromic group which will present reversible photochromic behavior,[122] and can exhibit lower melting points will be an ideal possibility for gas sensor developments.

4.7 Task Specific Approach for IL Sensing

The interplay of physical forces and interactions between ILs and gases results in many sensor applications as described earlier, however, the most important limitations in this regard can be the sensitivity and selectivity. The improvement in sensitivity can be brought by increasing the solvation power of the ILs which has recently been proposed with the use of task specific ILs which can take up higher concentrations of simple gases, such as CO_2,SO_2, H_2 and O_2.[123, 124] Presently, this field of research is expanding because of the need of CO_2 and SO_2 capture and absorption studies for these gases.[125] Davis and co-workers have done the pioneering work in this regard to design a special task-specific IL that can capture CO_2 specifically by chemisorption.[126] The imidazolium cation in this IL contains an amine functionality, which forms a carbamate upon the addition of CO_2. In this way, a maximum CO_2 uptake of 0.5 mol per each mole of the IL was reached within 3 h. The process can be reversed by heating to 80–100 °C under vacuum which can be an important step towards detection and then regeneration of sensor by heating. The same research group used combinatorial click chemistry to generate an array of ILs[127] based on a bifunctional anion containing an amine and a sulfonate group, in combination with an ammonium cation. These ILs all had the gas capture abilities and thus can be used for sensors.

Although, the generic combinations of IL with other electrode materials as shown in case of NO sensing have proven quite useful for sensing applications,[86] yet the results are again generic in

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most cases with much less selectivity than required. Therefore, the focus is now shifting to use more task specific ILs in the case of electrode modifications as well. Lu et al[128] have shown that a task specific IL in combination with bismuth oxide (Bi_2O_3) can be used for the electrochemical detection of heavy metal oxides including cadmium oxide (CdO), copper oxide (CuO) and lead oxide (PbO). The IL contained an $[NTf_2]^-$ anion and a tetraalkylammonium cation with one carbon chain functionalized with a carboxylic acid group. The presence of the acid group allowed for solubilization of the metal oxides into the IL. The IL was coated as a thin layer onto a surface containing three indium tin oxide (ITO) printed electrodes and acted as the selective solubilization medium and electrolyte. It is envisioned that more analyte species may begin to be detected by employing newly-synthesized ILs with specific functional groups.

4.8 IL Gas Sensors with Multi-Transduction Modes

Despite the availability of such a large library of IL materials and their composites, existing and intended gas sensor applications need more sophisticated methodologies to overcome the posed complications in gas sensing. For example, a gas sensor system can be calibrated to quantitate up to three individual gases in the mixture with the interferents using the available transducers and methodologies. Starting from this calibrated state, the quality of the performance degrades due to: i) the presence of analytes and interferents above the calibrated levels; ii) temperature fluctuations; iii) contamination and poisoning of the sensor surface; iv) moisture or mechanical damage; and v) ageing of the sensing material and transducer. All these end-user factors results into poor selectivity and reversibility of the sensor responses which are often conflicting to each other. Full reversibility is only achievable by using weak interactions of the film while the selectivity/specificity comes from the stronger interactions. In order to address this problem, either the design of new sensing materials or the development of sensor arrays is the direction to look for. However, more recently, the development of multi-transducer sensor and sensor arrays is gaining importance. Examples of such hyphenated devices are shown in Figure 14 and include chemiresistor-capacitor, cantilever-capacitor-calorimeter,[129] electrochemical-QCM,[68, 130] optical-QCM,[131] FET-QCM[132], and opto-electronic sensors.[133] Even the multiparameter detections were also demonstrated within the same transduction principle (e.g., capacitance-resistance)[134, 135] and by using FET-temperature programmed sensors.[136]

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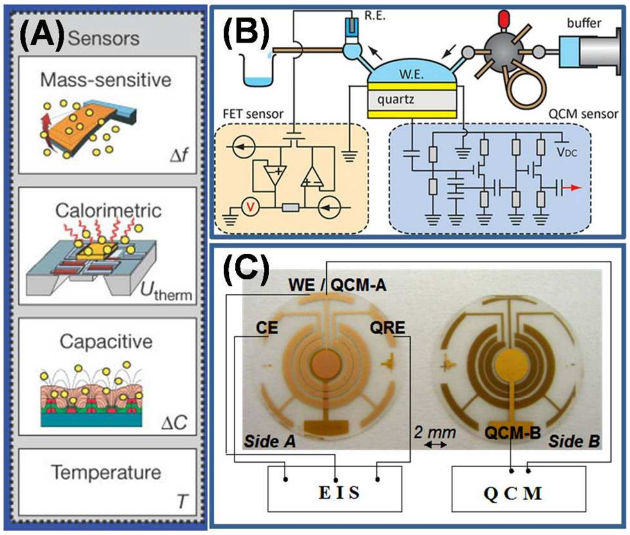

Figure 14: Examples of multimodal transduction modes for gas sensor development; (A) a single chip microsystem for smart gas sensing using mass sensitive calorimetric and capacitive measurements simultaneously, (B) a sensor design utilizing QCM and field effect transistor (FET) approach, and (C) and integrated electrochemical QCM for simultaneous EIS and mass sensing measurements. (Ref[129, 132])

A critical limitation in this regard is the sensing material that is capable of being used for the multiple transducers applied for the sensor system. The diverse nature and properties of ILs is a special gift in this regards, as it can be exploited for this multi-sensing approach. Electrochemical quartz crystal microbalance (EQCM) is a powerful analytical technique to demonstrate this potential, as IL can be used as an electrolyte and the sensing film at the same time. Figure 12 shows an integrated EQCM electrode fabricated on a monolithic quartz wafer. AT-cut quartz crystals oscillating in a shear thickness mode exhibit extraordinary high sensitivity to potential-induced changes in the mass at electrode-electrolyte interface via the change of its resonance frequency. In addition to that, the monitoring of the mechanical state of the viscoelastic coatings at quartz crystal electrode via a change in their shear storage and loss modulus is possible. Thus, its dynamic capability allows for the real-time monitoring of minute mass changes during electrochemical reactions in ILs and the accompanying viscoelastic changes.[137] Thus, a QCM used with electrochemistry methods such as EIS and CV allows real time *in-situ* mass changes in the nanogram range during the electrochemical perturbation of the electrode solution interfaces. Forzani et al[138] proposed a hybrid electrochemical-colorimetric sensing platform for the detection of explosive trinitrotoluene (TNT) vapors. A thin layer of the IL [C_4mim][PF_6] was found to selectively pre-concentrate the explosive materials and quickly transport the analytes to the electrodes. The explosive vapors were detected by electrochemical (cyclic voltammetry) and

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colorimetric (absorbance change) methods at the working electrode. The observed currents and distinct color changes provide a fingerprint for the identification and quantification of TNT. The same group later employed a conducting polymer nano-junction that was sensitive only to the reduction products of TNT and was able to discriminate from other redox-active interferents found in ambient air. The sensor simultaneously measured the current for the reduction of TNT and the resulting conductance change of the polymer (poly(ethylenedioxythiophene), PEDOT). A linear response (current vs. concentration) was observed at concentrations of 30 pM to 6 nM TNT and the sensor was capable of detecting extremely low levels of TNT within 1-2 minutes. Thus it can be shown that the IL materials are capable to bring plentiful new innovation in sensor technology by this hyphenation approach.

Concluding Remarks and Future Directions

By synergistically utilizing IL interface as well as molecular design and control of IL composites, many sensing platforms have been demonstrated enabling multiple gas detections with multiple modes detection principles, addressing many gas sensing challenges, especially the sensitivity, selectivity, and reproducibility for real world scenarios. In terms of resolution, however, these sensors are not competitive against high-end laboratory instruments (e.g., a GCxGC instrument equipped with TOF-MS can detect ~1300 volatiles in breath at signal/noise resolution of ~100. Even the field deployable and micro versions of these instruments (e.g., a cell phone sized gas analyzer can detect and quantify ~10 volatiles at ppb level) are establishing themselves in this competition due to their power requirements similar to packaged sensor systems, and due to the advances in miniaturization of these instruments. Thus, the conventional arguments of low cost, low power and small size in favor of the sensors are not so compelling. However, a number of clear advantages (e.g., the smallness which allow wearable sensors to be developed; the mobility which allow continuous measurements performed by the sensor in comparison to periodic measurements done by the instruments; the ability to design wireless sensors thereby enabling continuous tracking of gas emission, interpret sensing data in real time, and provide *in-situ* alerts and control services for a broad range of applications; low costs which allows the disposable and wireless sensors to be developed for the harsh environments by exposing only the detection part to the harsh environments and keeping the readout as well as the operating personnel protected from that environment; and the overall capability to address the

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new and emerging sensor markets utilizing so developed wearable and disposable sensors even by the non-technical users) are holding us and other proponents of gas sensor technology to continue advocating for it. However, in order to keep doing this, there is a critical need for innovative approaches and to identify and analyze the failure factors in each and every practical sensor development. For this purpose, three aspects of the sensor development should especially be focused: i) sensing materials should be developed based on new design concepts and new fabrication principles; ii) a proper selection and possibly the proper combinations of transduction principles should be favored to obtain best response parameters and to suppress the interference; and iii) signal processing should be reinforced to move towards complex signal resolutions from real life data.

Specifically for the IL sensors, many fundamental aspects of the physical chemistry and electrochemistry remain to be thoroughly explained, before they can promise to further improve the potential of their gas sensing applications. For example, the fundamental electrochemical issues such as the structure of the double layer and diffusion layer at electrode/IL interface; the speciation of solute ions such as metal ions and polymerized ions; transference numbers and how these are influenced by speciation; dielectric properties and how these merge with conduction properties as a function of frequency; surface chemistry and wetting phenomena of ILs in three-phase interface; thermodynamic quantities such as chemical potentials of solutes in ILs, and how these influence redox potentials; ion association and its effect on thermodynamic and transport properties; and interactions of ILs with solutes and interfaces should be focused. The study towards thermal stability of ILs for engineering applications should analyze the IL with thoughts on evaporation or temperatures at which evaporation kinetics are known. The temperature dependent properties and the high dependency of the results on the experimental factors need to be investigated in comparison of different conditions. Additionally ILs have been shown as promising alternative solvents in variety of applications. However, only a few processes are commercialized due to the relatively high cost of ILs. The recovery and reuse of ILs play an important role in the commercialization of processes employing ILs. The understanding of recyclability of ILs based on the available literature in various application fields is still in its infancy stage. Therefore, this aspect of the research should be focused for all practical applications.

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Another area where we are lacking in terms of IL sensor, rather all sensor systems, is field testing or actual deployment of the prototype to work. The initial experiments under controlled conditions are critical, however, without further testing under real world environments; most of the development in the field is just piling up as publications. This is why; the number of sensors deployed in the field is rather limited. In order to speed up this commercialization process, more research is required for system designs and integration thereby engaging collaborations from diverse disciplines for prototype development and field testing.

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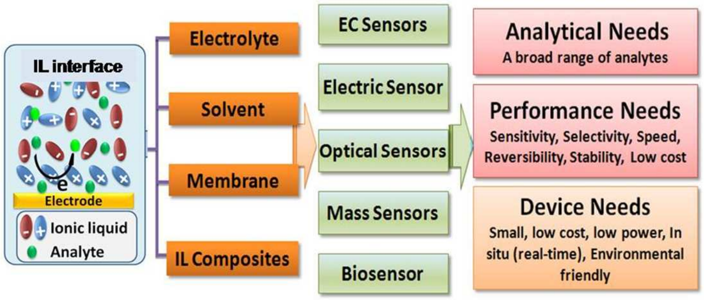
TOC Figure



Linking ionic liquid interface designs to specific device protocols to address analytical challenges of the gas sensing

Author Biographies

Abdul Rehman *received his Ph.D. in Analytical & Food chemistry (University of Vienna, Austria) under the supervision of Professor Franz Dickert. Afterwards, he worked as postdoctoral associate first in Professor Mark Meyerhoff's group (University of Michigan, Ann Arbor) researching on biocompatible polymers for in-vivo blood sensors and devices, and then in Professor Xiangqun Zeng's group (Oakland University) investigating the integration of various sensor platforms for critical real world applications. He also served as a visiting assistant professor at Oakland University and now he is joining KFUPM as a faculty. His*

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research interests include the material/interface designs for various sensing protocols, the related data analysis algorithms, and integration into prototypes and devices.

Xiangqun Zeng *received her Ph.D. in Electrochemistry and Surface chemistry (State University of New York, Buffalo) in 1997 under the supervision of Professor Stanley Bruckenstein and worked in the same lab for one year as a postdoctoral associate. She served at the University of Wisconsin, Oshkosh, as an assistant professor (1998-2001) and then moved to Oakland University where she is a full professor now. Her lab is interested in the study of fundamental and applied interfacial phenomena, particularly the design and control of molecular characters and characterizations of the dynamic reactions at electrode interfaces for chemical and biosensor applications.*

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