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Ionic Liquids as Green Solvents and Electrolytes for Robust Chemical Sensor Development

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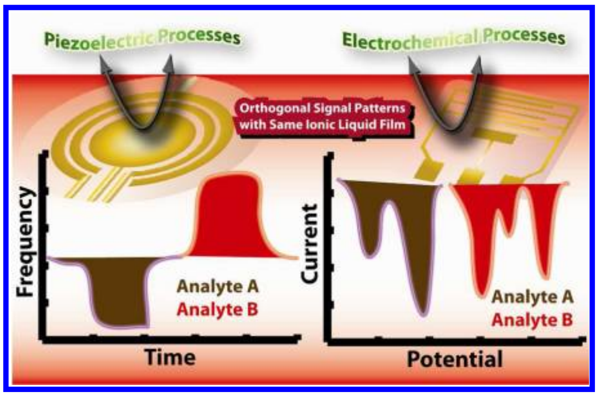

Ionic liquids (ILs) exhibit complex behavior. Their simultaneous dual nature as solvents and electrolytes supports the existence of structurally tunable cations and anions, which could provide the basis of a novel sensing technology. However, the elucidation of the physiochemical properties of ILs and their connections with the interaction and redox mechanisms of the target analytes requires concerted data acquired from techniques including spectroscopic investigations, thermodynamic and solvation models, and molecular simulations. Our laboratory is using these techniques for the rational design and selection of ILs and their composites that could serve as the recognition elements in various sensing platforms. ILs show equal utility in both piezoelectric and electrochemical formats through functionalized ionics that provide orthogonal chemo- and regioselectivity.

In this Account, we summarize recent developments in and applications of task-specific ILs and their surface immobilization on solid supports. Such materials can serve as a replacement for conventional recognition elements and electrolytic media in piezoelectric and electrochemical sensing approaches, and we place a special focus on our contributions to these fields. ILs take advantage of both the physical and chemical forces of interaction and can incorporate various gas analytes. Exploiting these features, we have designed piezoelectric sensors and sensor arrays for high-temperature applications. Vibrational spectroscopy of these ILs reveals that hydrogen bonding and dipole–dipole interactions are typically responsible for the observed sensing profiles, but the polarization and cavity formation effect as an analyte approaches the recognition matrix can also cause selective discrimination.

IL piezoelectric sensors can have low sensitivity and reproducibility. To address these issues, we designed IL/conducting polymer host systems that tune existing molecular templates with highly selective structure specific interactions. We can also modulate the IL microenvironment so that ILs act as filler molecules to optimize host template cavity size, shape, and functionality. When used as non-volatile and tunable electrolytes, ILs show great potential for the development of both amperometric and electrochemical double layer capacitance sensors for the detection of oxygen and explosives. We also designed and tested a two dimensional electrode chip that enabled simultaneous monitoring of both piezoelectric and electrochemical signals. This device imparted additional selectivity and overcame the limitations of the typical sensing protocol. The integrated piezoelectric and electrochemical sensing approach allows the measure of the charge to mass ratio under a dynamic regime. The electrogravimetric dynamic relationship allows for further discrimination between and accurate quantification of the interfacial transfer of different species. In summary, although new systematic and mechanistic studies of ILs are needed, we show that the self-organized phases of the aggregated non-polar and charged domains of ILs are useful sensing materials for electrochemical and quartz crystal microbalance transducers.

Introduction: Ionic Liquid as *Green* Sensing Entity

Sensors are miniaturized analytical devices, gathering qualitative and quantitative information about targets of interest, thus providing readable signals through different transducers. Typically, a chemically or biologically derived recognition element is combined with an electrical, an optical, or a chemical transducer, exploring various known

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TABLE 1. Physical Properties and Solvation Descriptors for Different Compounds

	physical properties (room temperature)			Abraham's solvation descriptors[a]				
liquid phase	vapor pressure	viscosity (cP)	conductivity (S/m)	*e*	*s*	*a*	*b*	*v*
water	23.8	0.862	5.5×10^{-6}	0.82	2.74	3.9	4.81	−0.21
methanol	127.2	0.544	7×10^{-6}	−0.22	1.17	3.7	1.43	0.769
ethylene glycol	0.06	18	1.07×10^{-4}	0.217	1.427	4.474	2.687	0.568
[BMIm][BF_4]	0	154	0.35	0.56	2.82	3.27	0.48	0.5
[BMPy][NTf_2]	0	63	0.22	0	1.688	2.083	0.159	0.677
[BMIm][PF_6]	0	371	0.146	0	1.914	1.887	0	0.620
[BMIm][OTf]	0	90	0.37	0.399	2.03	3.49	0.681	0.647
tetrabutylammonium triflate				0	1.579	2.135	0	0.416

[a] System coefficients of LSER: *e*, tendency to interact through π and n electron pairs; *s*, tendency to interact with dipolar and polarizable solutes; *a*, and *b*, the hydrogen-bond basicity and hydrogen-bond acidity, respectively; *v*, combination of exoergic dispersion forces and endoergic cavity factors.

chemical or biological interactions quantitatively related to chemical or biomolecular analyte properties in order to achieve good precision, accuracy, and reliability. A variety of recognition elements have been studied depending upon task specificity, among which inorganic materials are cost-effective and robust but have little functionality to provide specificity while organic and biomaterials possess such functionalities but are less stable and more expensive. The choice of recognition element crucially depends upon its immobilization ability, mostly onto solid supports, in order to facilitate miniaturization and sustainable performance. This upholds the recognition elements and their immobilization as major considerations in sensor science.

Ionic liquids (ILs) provide an intriguing choice with the flexibility of organics, the durability of inorganics, and the recognition ability of biomaterials. These unique properties setup a foundation to modulate future sensor devices with efficient recognition and optimized immobilization protocols. Table 1 compares IL properties with traditional salts and solvents. Being intrinsically nonvolatile, ILs can be used as environmentally benign media for a number of sensing operations,[1] whereas their unique solvation properties, as depicted by Abraham's solvation descriptors, varying with the nature of constituent ions render them ideal for selective detection strategies. The interaction abilities can be varied by judicious selection of ILs compatible with target analytes by knowing these descriptors for both of them. High conductivity, which might be correlated to the semioriented structure, and permits ions to move and interact with each other in certain directions with a variable amount of friction is ideally suited to electrochemical sensing platforms. Nondrying behavior with typical decomposition temperatures of >350 °C reduces the hazards associated with flash points and flammability. Furthermore, the tunable chemistry to generate task specific functionalities that can be transferred onto solid surfaces by forming thin layers justifies their widespread use in sensor development.

IL integration into present and future sensor schemes is not a straightforward process; rather a thorough understanding of their true capabilities and limitations as well as their physiochemical dynamics of interactions is essentially required. Our laboratory has pioneered the application of IL materials for sensor development using several different approaches (i.e., as either solvents alone or IL hybrids amenable to use in existing low cost, robust transducer formats; as electrolytes for electrochemical sensors; as solvent-cum-electrolyte for integrated electrochemical and quartz crystal microbalance (EQCM) sensing). By incorporating the desired functionality into the IL structure, we are able to generate specific molecular interactions that work synergistically to enhance the analytical performance of a sensor. Nevertheless, the chances of success, in any case, lie with the understanding of interaction forces and the underlying sensing mechanisms that dictate the overall behavior patterns. We have explored and coordinated the underlying properties of these versatile *green* materials for EQCM sensing platforms (Figure 1) that enabled us to achieve great chemical selectivity and sensitivity better than many current sensors. This Account is primarily focused on these efforts and the state of the art, which will complement some quality reviews for other IL-based applications.

Solvation-Based Sensing Protocols

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 as recognition elements. 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

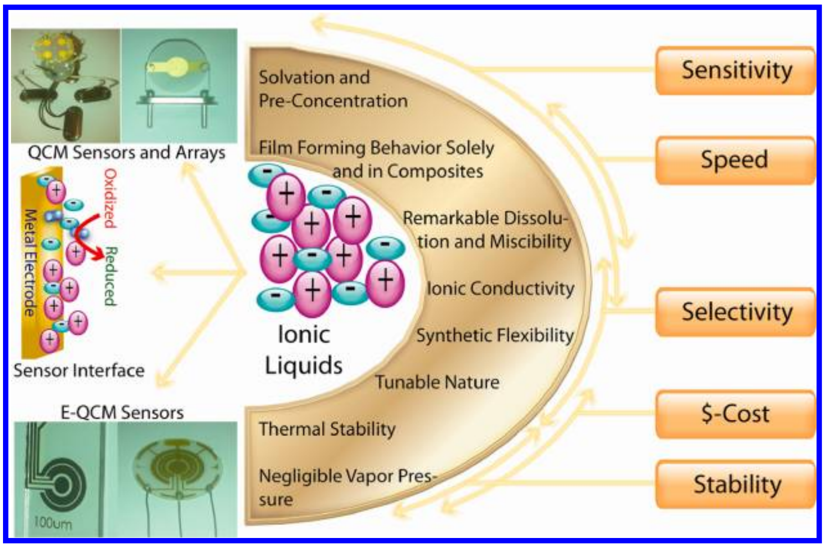

FIGURE 1. IL-properties and related sensor evaluation parameters for different sensing platforms.

these phases. Both ions of an IL can be tailored to contain independent functionalities with a specific binding motif for particular detection need. 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, which are discussed in the following sections.

Piezoelectric Sensing with Pure ILs

QCM-based sensors have been designed for some critical real-world analytes utilizing IL-solvent attributes to illustrate the scope, power, and versatility of these materials. QCM is a piezoelectric sensing transducer, the key component of which is quartz that functions for signal transduction and substrate for sensing materials (Figure 1). Applying alternating current to the gold electrodes induces mechanical oscillations modifiable by interfacial mass changes according to the Sauerbrey's equation:

$$\Delta f = -\frac{\Delta m f_0^{\,2}}{A\sqrt{\mu_q \rho_q}} \tag{1}$$

Here Δf = frequency shift, Δm = mass changes, f_0 = fundamental frequency, A = electrode area, μ_q = quartz shear modulus, and ρ_q = quartz density. This principle assumes that the foreign mass is strongly coupled to the resonator making it quite straightforward for gas/vacuum phase operations, where the added mass binds tightly to the surface, and the films are stiff and thin. However, density and viscosity strongly impact the nonrigid systems such as ILs, for which the following expressions are used:

$$\Delta f = -f_0^{\,3/2}\left(\frac{\eta_L \rho_L}{\pi \mu_q \rho_q}\right)^{1/2} \tag{2}$$

$$\delta = \left(\frac{\eta_L}{\pi f_0 \rho_L}\right)^{1/2} \tag{3}$$

Here η_L = viscosity and ρ_L = density of the liquid in contact with the crystal, while δ = decay length of the shear waves generated due to the oscillation of the quartz and is related to both the density and the viscosity. ILs form stable layers owing to their high viscosities, just like the polymer matrices. However, for being liquids, they bound firmly but not rigidly. QCM is capable of measuring the change of mass as well as the energy dissipation properties of thin films simultaneously, upon analyte adsorption/desorption or partition processes in thin films, thus providing rich information of the dynamic processes occurring during the adsorption–desorption events. The *Q* factor, which is the ratio of frequency and bandwidth, can be as high as 10^6 leading to highly stable oscillators and high accuracy in the determination of the resonance frequency.

High-Temperature Sensors and Arrays

IL films would perform well as QCM sensor interfaces and provide additional control over selectivity and sensitivity for analytes in gas phase by suppressing conventional solvation and solvolysis phenomena and by providing media capable of dissolving a vast range of molecules, especially toxic, flammable, or reactive organic gases. For the same reasons, the partition process will reach equilibrium very rapidly after the sensor is exposed to the analyte vapors. This ensures a fast response and excellent reversibility. In earlier reports, Dai et al.[2] evaluated the sensing performance of IL membranes coated on QCMs, and the sensing mechanism is explored via the viscosity changes due to solubilization of analytes. But, the real success lies in their use for high-temperature applications (e.g., exhaust gases from multiple sources), conventionally addressed by metal oxide or rubbery polymer sensors, each having inherent problems. We have demonstrated for the first time that the IL sensors show great promise for high-temperature gas sensing. For that purpose,[3] a polar IL, [P$_{14,666}$][DBS], was prepared via the alcohol-to-alkyl halide conversion method and coated onto QCM from its ethanol solution to obtain a surface loading of $17\ \mu\text{g}\cdot\text{cm}^{-2}$. 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 (Figure 2). Higher sensitivities were observed for polar compounds, which is quite obvious for this IL, being polar. As expected thermodynamically, the sensor signal decreased with increasing temperature, but still, we could achieve a 5% detection limit, 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 (*R*) showed that physiochemical parameters such as Henry's constant can be more accurately determined at higher temperatures because of the lowered viscosity contribution.

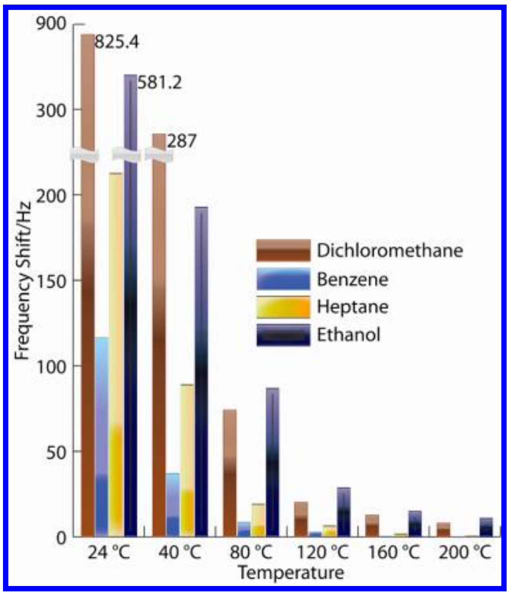

FIGURE 2. Responses shown by IL sensors from ambient to elevated temperatures.

Performance evaluation of the IL sensing at high temperatures with selectivity toward various gaseous analytes led us to design a sensor array for combustible gases[4] operable at 120 °C. The discriminative base for this type of sensing is the solute (gas)/IL interactions (e.g., hydrogen bonding, $\pi-\pi$ interactions, dipolar interactions, and ionic interactions) present in various strengths and combinations so as to dictate the IL discriminatory power toward a certain analyte. A strict criterion is generally applied to critically select the interfacial materials showing maximum diversity, possessing sufficient interactions for a range of analytes to achieve good sensitivity and adequate differences in response patterns to avoid interfering interactions. For many technical applications, the presence of halogen atoms in the imidazolium IL is a cause of concern if the hydrolytic stability of the anion is poor (e.g., choloroaluminate and hexafluorophosphate systems) or if a thermal treatment of the IL is required as in this particular case. As a result, imidazolium ILs with non-halogen anions have been selected. Other ILs selected were phosphonium or ammonium ILs with alkylsulfonate or alkylbenzenesulfonate anions. The ability to discriminate vapors depended upon the sorption isotherms, which in turn have functional dependence on the volatility of each vapor and the strength of the interactions between the vapor and the IL coatings. Specific functional groups selected in each IL maximized particular interactions. This ensured that one sensor array can identify more target analytes. The array responded linearly to all of the analytes over the full concentration range from zero to saturation both at ambient conditions and elevated temperatures with exception of only dichloromethane, which deviated from this linear behavior above 60% saturation owing to its high volatility and the resulting high mole fraction in the IL phase. The vapors were discriminated from their sorption isotherms leading to 100% classification accuracy for known concentrations that reduced to 96% for unknowns. The study was further extended to the calculation of thermodynamic parameters and FTIR analysis, which were useful in actually predicting the type of interactions involved rather than their estimation from signal patterns. The values for Henry's constant were consistent with sensitivity of various IL films and provided the basis of pattern recognition. The data for adsorption enthalpy and entropy, as calculated

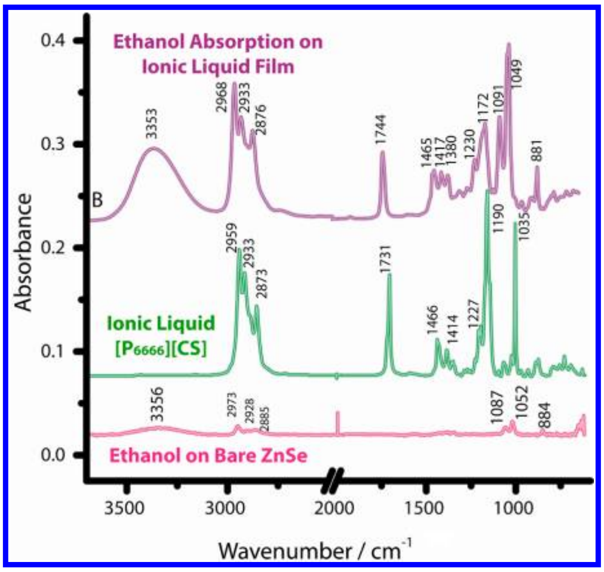

FIGURE 3. Representative example of FTIR peak shifts during VOC absorption on IL films.

from the van't Hoff equation, describes the strength of interaction forces and the degree of ordering, respectively, during the dissolution event. Thus we were able to assert that the dipole induction caused by the cations and anions has generated higher sensitivities for nonpolar analytes. IL structures (e.g., bicyclic or the substituted alkyl chains) play a significant role as well to modify the ordering of the analyte molecules inside the IL and hence to provide preferential response of one sensor over the other.

Design Interfacial Selectivity via ATR-FT-IR Characterization

The key factor in array designs is to use chemically selective interfaces which exhibit high level of chemical independence and structural order. Consequently, the information about interacting functionalities is critical for the controlled IL configuration on surfaces to generate films with greater diversity in structural and chemical properties. Elucidation of the exact nature of interactions and the reversibility of absorption–desorption phenomenon came from ATR-FT-IR experiments. For example, three types of peak shifts are observed in case of ethanol/IL exposure, the hydroxyl group of ethanol and the sulfonate and carbonyl groups of the ILs (Figure 3). It was concluded that the asymmetric vibration peak shift of the sulfonate group is caused by hydrogen bonding between hydrogen of hydroxyl and oxygen of sulfonate groups. The supporting evidence for this interpretation came from the hydroxyl peak broadening. Carbonyl peak shifts were observed for polar analytes, which implied that polar solvents can interact with camphorsulfonate anions. The blue shift of the carbonyl groups was caused by dipole–dipole interactions, while the red shift was a result of hydrogen bonding. Similar conclusions were made for all other analyte/IL combinations, which can efficiently explore the underlying mechanistic parameters and possibly guide for targeted synthesis of particularly featured ILs, yet a question remained unanswered. What are the design factors responsible for selective detections by these green materials, and how can we conceive the rational structures for any specified application beforehand? On many occasions, the dictating forces are primarily physical rather than chemical, which cannot be probed by vibrational spectroscopy. Even the hydrogen bonding and π-electron cloud effects have far less role to play. In a recent effort,[5] we have evaluated these physical parameters by considering both thermodynamic and solvation models. The range of ILs differed widely in terms of mass and viscoelastic effects, differential temperature effects, and sorption characteristics, which have drawn more general, rather multidimensional conclusions. The sensory responses happened to be defined by combination of mass loading and the viscoelastic effects demonstrable via damping resistance as shown in Figure 4. The solvation model is based upon the linear solvation energy relationship (LSER) approach where empirical data depends upon the ion structures. For example, alkyl group length and configuration can contribute toward the dispersion factor; carbonyl and sulfonate groups provide hydrogen bonding, affecting polarizability and dipolarity; imidazolium can have strong

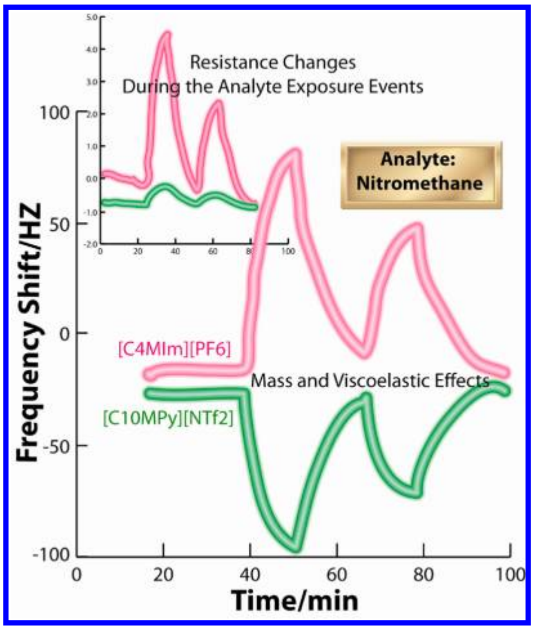

FIGURE 4. QCM sensor signals and associated changes in damping resistance for two ILs.

π-interactions. But for the IL array selected, the major contributing forces were determined to be the polarization and cavity forming effects. Additionally, the thermodynamic parameters calculated from the sorption isotherms were compared with ones obtained through simulation model. Finally, an array was structured based on these observations in order to differentiate different explosive gases and even their mixtures with a classification accuracy of 92%, which could be improved to 100% when the thermodynamic parameters were used for classification.

Enhanced Sensing Performance with IL Composites

The effectiveness of most thin film based sorption 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. Nonrigidity 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. In one such example, ILs are trapped as nanodroplets into the cylindrical cavities of solid alumina matrix, thus avoiding liquid wetting and softness.[6] 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,[7] 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) was selected to provide this dimensionality. Four different oxidation states of PAN including the doped and undoped ones are tested for the analytical response with [EMIm][CS], which can form hydrogen bonds through the sulfonate group. 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 up to the maximum achievable surface coverage of 14.8 ± 1.7 nmol cm^{-2}. The interference from air components such as O_2 and CO_2 was very low and the detection limit of 0.02% was much lower than the explosion limits, that is, 5% for methane. UV−vis and FT-IR results confirmed[8] 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 (Figure 5). 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.

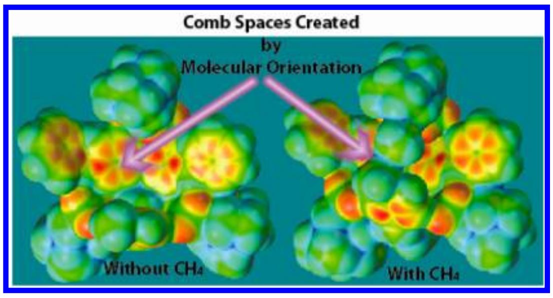

FIGURE 5. Molecular mechanics simulation of polymer backbone ordering to incorporate methane molecules.

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. To have experimental evidence, four different polyvinyl ferrocene (PVF) films[9] with varied doping levels (from metallic to semiconducting) were synthesized by changing the conditioning potentials and solvents. Differences in response pattern for these PVF films indicated that chemical selectivity can be provided by varying the oxidation states. PVF (oxidized) prepared by electrochemical cycling in $NaClO_4$ solution provided the best results. It is quite likely that conditioning in $NaClO_4$ and ClO_4^- doping as counterion have promoted the PVF film structure to be adapted toward adsorption of targets by surface area and structure enhancements. This best responding film was then immobilized with various ILs to generate an array of sensors, which caused some definite peak shifts in FTIR spectra

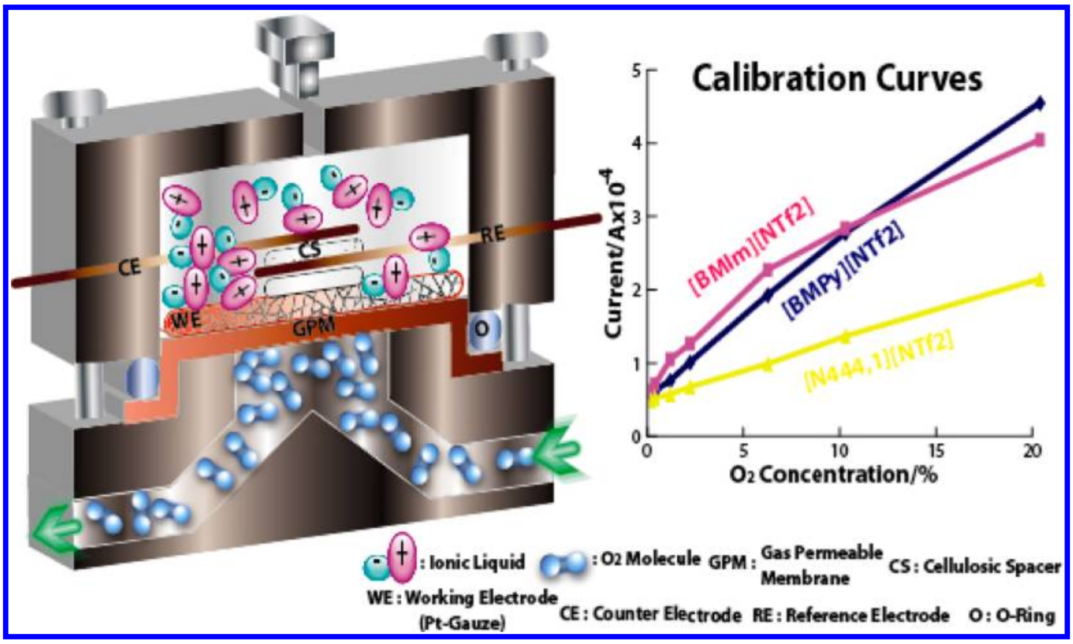

FIGURE 6. Optimized configuration of electrochemical cell for oxygen detection in ILs.

owing to the specific interactions between particular PVF/IL composite. With the introduction of target gases, peak shifts were observed for the involved interactions that helped to explain the difference in analytical performances of various analytes. Two different sensor arrays were constituted, one including the sensors having the most responsive PVF film in combination with different ILs and the other including the sensors having the most responsive IL in combination with different PVF films. We intended to determine the major component of the system responsible for discrimination, and the results favored the latter one. ILs contributed more toward sensitivity by fast solvation of target analytes while the base substrate, that is, PVF, provided the desired selectivity by variable structures. Electrodes modified by immobilization of single species (CP or polyelectrolyte) are widely acknowledged, and we believe that using appropriately chosen pairs of immobilized species can produce unique surfaces with valuable chemical properties (e.g., controlled porosity, orientation, and tunable thickness). The simplicity of this strategy enables systematic IL-hybrid design to "tailor" new or existing CP materials that can exhibit structure and electronic features for enhanced selectivity and sensitivity.

Electrochemical Sensors Based on IL Electrolytes

ILs have a dual role of solvents and electrolytes based on their nonvolatility, and ionic conductivity for electrochemical sensor developments, supplemented by chemical/electrochemical stability and wide potential window (up to 5.5 V) to suit modern electrochemical devices. Due to their entire ionic composition, the supporting electrolyte is not required, significantly benefiting the robustness and miniaturization. Buzzeo et al[10] demonstrated a robust IL sensor without the use of membranes at the sample/electrolyte interface. Solid state oxygen sensors[11,12] using hydrophilic [EMIm][BF_4] and hydrophobic [BMIm][PF_6] ILs were shown as alternatives to both metallized gas-permeable membrane based as well as solid polymer electrolyte based gas sensors. An abundance of charge carriers and the variation of ion pairing and size controlled mobility can produce distinctive response pattern in redox analysis by diversifying the mass transport mechanism and the dynamics of ion–ion and ion–solvent interactions. Efforts to incorporate ILs into different electrode systems to achieve the goals of chemosensing and biosensing have undergone extensive research;[13] however, high viscosity and low conductivity have limited their direct utilization by presenting some problems of response time[10] and irreversible redox activity. The diffusion coefficient of gases in ILs is few orders of magnitude smaller than that in regular solvents as per Stokes–Einstein relation retarding the response time. To overcome this problem, we developed[14] an electrochemical cell similar to the Clark type with IL coated onto a platinum gauze electrode for the amperometric sensing of oxygen with a detection limit as low as 0.05%. In our system, two levels of selectivity were achieved by using a porous Teflon and IL selectivity. The analyte flow was directed from the base, opposite to the electrolyte, which allowed it to directly reach the electrode/electrolyte

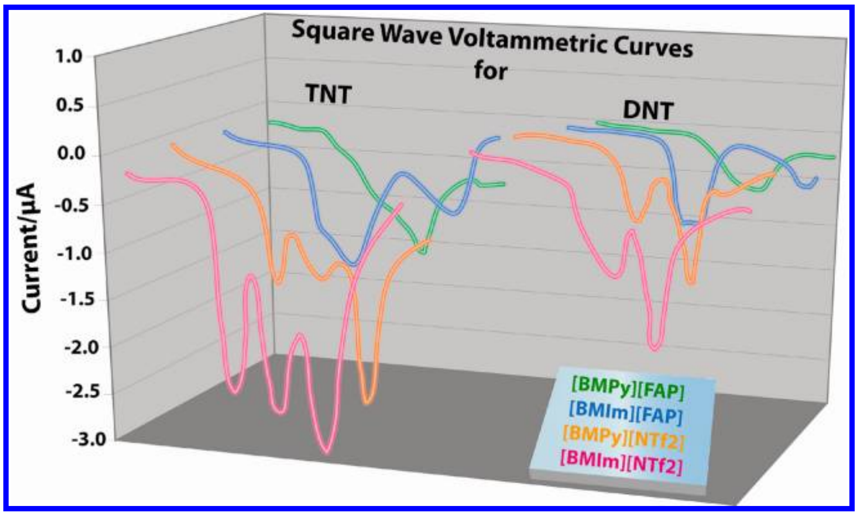

FIGURE 7. Amperometric signals to furnish selectivity among different analytes.

interface without passing through the diffusion barrier (Figure 6). Typical sensor evaluations and interference analysis were performed in the presence of major atmospheric gases (e.g., NO, H_2O, CO_2, SO_2, NO_2). The displayed level of interference was appreciably small in most cases except water where the selectivity coefficients were in the order of 10^{-2}. However, this can be compensated by employing more hydrophobic ILs as could be seen in case of $[N_{444,1}][NTf_2]$, which showed least interference to water. The redox mechanism of oxygen to superoxide in different ILs is shown to be influenced by variations in IL–electrode interface structure and properties. We have demonstrated that the IL adsorption depend upon the double layer arrangement of constituent ions (microstructure) at the interface, both of which depend upon the applied DC bias potential. By adjustment of the IL structure (i.e., $[BMPy][NTf_2]$) and applied DC potential at -0.3 V, the IL double layer structure was tuned into an electrochemical capacitor that can be modulated to interact with specific molecular species, methane in this case, following a Langmuir adsorption model. We have illustrated that the methane oxidation depends not only on oxygen concentration and the Pt-electrode potential but also on choice of IL. A methane amperometric sensor using $[BMPy][NTf_2]$ was thoroughly characterized for analytical figures of merit, showing sensitivity of 13.7 μA/% for 0–10% methane concentration, which dropped to 1.73 μA/% at higher methane concentrations, illustrating that methane electro-oxidation in ILs is oxygen concentration dependent.

The effects of the IL–electrode interfacial microenvironment on the electrochemical sensor designs were demonstrated by the detection of solid explosives with an array of electrochemical IL sensors.[15] Variations in reduction potentials of the analytes in different ILs reveal the correlation of the redox mechanism and the physiochemical properties of the involved species (i.e., ILs and target analytes). The role of different ILs in generating the sensitivity and selectivity for the redox systems was evidently proven by showing that not only do the physical parameters such as viscosity and conductivity control the reaction mechanism through mass transport and ionic movements but the chemical structures influence the reactivity by protonation and hydrogen bonding administered stabilization effects. Humidity experiments proved the hypothesis that ILs with protonation capability can facilitate the reduction of nitro functionalities to hydroxylamine groups. Gaseous analysis demonstrated the IL capability for acting as preconcentrator that was seen elsewhere[5] too, which made gas sensing more feasible than the liquids contrary to the classical systems. Being a prototype of a miniaturized, robust device, the array showed 100% classification accuracy for TNT, DNT, and their mixture without a single mismatch even for the mixture (Figure 7). Interference experiments with closely related species and temperature has validated the selective performance and enhanced feasibility under harsh real-time conditions elucidating the excellent sensory potential of this strategy.

EQCM Sensors Based on IL Solvent and Electrolyte Properties

The individual merits of piezoelectric and electrochemical sensing via ILs under their standard protocols has prompted us to fabricate their combination in the form of integrated EQCM on a single chip.[16] Electrochemical sensors are generally quite specific, but mostly require signal amplifications, whereas, QCM devices are very sensitive but lack selectivity. These critical limitations in both techniques could be overcome by putting them together where all the electrodes are on the same plane, thus allowing a two-dimensional sensing through orthogonal systems. ILs serve as the materials that can form thin stable layers for adsorption–desorption processes while possessing the required solubility, conductivity, and wettability required by the electrochemical sensor approach. The EQCM combines QCM with electrochemistry methods such as impedance and cyclic voltammetry (CV) that allow real time *in situ* mass changes in the nanogram range to be monitored during the electrochemical perturbation of the electrode solution interfaces. Simultaneous measurements can furnish additional selectivity and accuracy at a little or no power cost. Different interactions of ILs and the analyte functional groups not only increase the QCM sensor signals but also affect the redox mechanism; together they provide the needed partial specificity for pattern recognition so that the combined response can analyze the largest possible cross-interaction of analytes.[17] The validation of the approach came from the example of EQCM sensor for ethylnitrobenzene (ENB) and dinitrotoluene (DNT), the targets of choice because of terrorism threats across political borders.

Concentric ring-disk electrodes were fabricated by vapor deposition, followed by photolithography and wet etching to get the desired structures. The geometry was optimized to ascertain the stability of all the electrodes and to reduce IR-drop. CV was used to study electrode reaction mechanisms while differential pulse voltammetry and square wave voltammetry were used for quantitative analysis. The electrochemical process was found to be diffusion controlled. Reduction of nitro groups generated two peaks; the first belonged to the formation of nitro anion radical and was electrochemically reversible, whereas the second one was irreversible and was related to the protons in the solution, thus heavily affected by the presence of humidity in the system. In addition to electrochemical reversibility, the redox process was also connected to the physical process of absorption–desorption. It switched on and off with the addition and removal of analytes from the system as shown in Figure 8. In order to develop EQCM sensors and their further integration in miniaturized forms, fundamental understanding of IL–electrode interface structures and properties under potential control is essentially required. The nature of ionic interactions with the metal electrodes as well as their interfacial orientation has a functional dependence over the IL structural heterogeneity. Applied electrochemical potential can disrupt this orientation, though very subtly, affecting the fate of the reaction occurring in the IL a great deal. The structure and dynamics of the IL–electrode interface properties and the time-resolved variation in surface populations due to the electrochemically driven redox reactions (i.e., O_2 to superoxide) was characterized by EQCM. This study paves the way for designing highly specific IL-EQCM sensor systems to address the key challenges of sensitivity, selectivity, interferences, and real world operations by modifying the underlying chemistry and by exploiting the heterogeneity of chemical structures of the involved species.

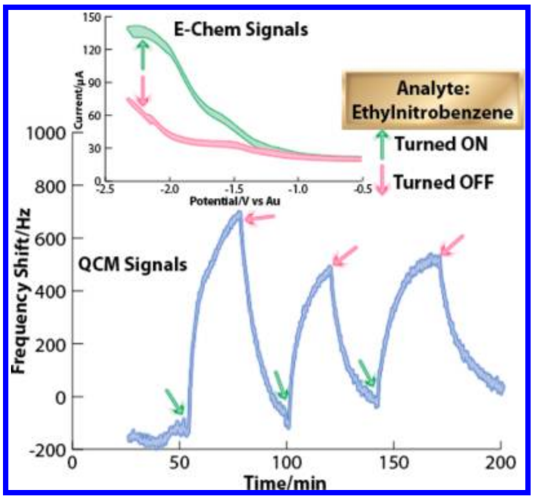

FIGURE 8. Variation of EQCM responses with analyte switching (ON/OFF).

Environmental Interferences for IL-Based EQCM Sensors

Despite having many beneficial attributes, ILs pose a number of challenges too, among which water interference is one that can drastically alter their physicochemical properties (e.g., viscosity, conductivity, and diffusivity), consequently affecting sensor responses. By use of conductive polymer template and by selection of 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 will be simplest to address water interference. Furthermore, the interplay between water and redox analytes can be used to calibrate the water interference. Finally, the viscosity changes caused by water affect the rate of mass transport of analytes, which can be minimized using innovative setups (for example, Figure 6).

Temperature fluctuations, on the other hand, can cause errors through variations in viscosity and conductivity, which can be addressed by selecting a crystallographic orientation that has a zero slope (turnover) at a given temperature for QCM based sensors. High temperatures reduce the mass signal but it enhances the mass transport of the analyte and electrochemical signals. Thermal stability of IL allows us to regenerate the IL-sensing surface by eliminating low boiling point contaminants such as water by heating as well as to eliminate the water influence by measurement at high temperature such as 100 °C. The integrative EQCM approach can facilitate the calibration of the water influence to obtain accurate detection. Turning the problem around, we have been exploring ways to selectively minimize the environmental effects while making sensors. For example, the oxygen reduction in IL is stable and reversible and is not affected by water. A thin IL film allows oxygen concentration to be saturated. Consequently, the oxygen peak can be used to calibrate the quasi-reference electrode potential as well as serve as an internal standard for quantitation of the analytes. Both the temperature effect and the variation of electrode potential can be calibrated using oxygen redox signal and thus allowing for a high precision analysis. Similarly, the presence of water reduces the viscosity and increases the conductivity, which not only benefits the electrochemical process but also can be explored for new selective chemistry for sensing. Furthermore, taking advantage of the unique IL–electrode double layer structure, electrochemical impedance sensors based on the capacitance of double layer changes are shown to be very promising for robust electrochemical sensors in addition to being environmentally tolerant (manuscript in preparation).

Concluding Remarks

Many research groups are developing new materials and transducers for gas sensing with particular emphasis on optimizing interface properties among the gas phase, the sensitive materials, and the transducer. ILs are rapidly burgeoning to be impactful in this field and strenuous efforts have been made by our group in recent years to keep pace with that progress. In parallel, our group continued exploring the fundamental interplay of CPs and ILs so as to generate optimized sensing platforms. We were able to demonstrate that ILs with some structural similarity to the analyte could be used to reconfigure PVF for reversible doping of GGG peptide under potentiodynamic control.[18] Just like molecular imprinting, the geometry and chemical nature of both IL cations and anions should be considered for overall effectiveness of this process. The ease and generality of this technique suggest great promise for highly specific chemical sensing of relatively larger species. Electrochemical intercalation–deintercalation[19] of IL anions into a HOPG surface was studied by using electrochemical atomic force microscopy, and the morphological changes observed were used to conclude that this process is controlled by the size of intercalating anions. The applied potential has to be carefully tuned in order to achieve controlled and selective intercalation; otherwise, HOPG could be degraded to carbon nanoparticles. All these parameters, in combination, can be effective tools for preparing future electrodes for electroanalytical and sensing purposes. Furthermore, the mechanistic understanding of methane oxidation in ILs provides significant fundamental insights for oxidation of hydrocarbon in IL-based electrochemical systems, which could facilitate the development of optimal electrocatalysts for methane oxidation that can enable the use of methane as an electrochemical energy storage material for portable power applications. Different projects for commercialization of IL sensors are also underway. A monolithic QCM sensor array[20] was designed and demonstrated for its utilization for IL-based protocols already described, a significant step toward miniaturization and temperature compensations across the arrays.

In contrast to this rapid growth, the molecular basis for incorporating specific properties into the IL structure is lagging somewhat behind the application side, so the task specificity lacks a meaningful relevance. Systematic and mechanistic understanding for IL features is not fully established, which makes the IL selection for each project an ambiguous task. Long-term stability and toxicity can be a point of concern as well. Although the investigations have given quite encouraging results,[21] these studies should be expanded to be reliable. More and more challenges continue to be forthcoming with the maturity of the science; for example, the next-generation aryl alkyl ILs have a role to play in coming years. The foundation already set and rapid emergence of interest, however, makes us believe that the best is yet to come. Our goal is to develop sensors exploring robust, versatile, and green IL materials to provide autonomous, maintenance-free sensor operation with a very long lifetime by taking advantages of networked sensing and next-generation monolithic implementation.

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BIOGRAPHICAL INFORMATION

Abdul Rehman received his Ph.D. in analytical chemistry (Vienna University, Austria) under the supervision of Professor Franz Dickert. Afterwards, he remained as a postdoctoral associate in Professor Mark Meyerhoff's group working on biocompatible polymers for blood contacting sensors and devices and then moved to Professor Zeng's group. His research interests include the material/interface designs and pattern recognition algorithms for various sensing platforms and protocols.

Xiangqun Zeng received her Ph.D. in Electrochemistry/Surface chemistry (State University of New York, Buffalo) in 1997 and spent one year as a postdoctoral associate under the supervision of Professor Stanley Bruckenstein. She served at the University of Wisconsin, Oshkosh, as assistant professor (1998−2001) and then moved to Oakland University where she is a full professor now. Her research focuses are electroanalysis, surface designs, and characterization of electrode interfaces for chemical/biosensor applications.

FOOTNOTES

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The authors declare no competing financial interest.

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