Title: Ionic Liquid Gas Sensors for Detection of Flammable Gases in Workplace

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Table of Contents

Final Report Abstract

Sensors for flammable gas detection are essential in occupational health and safety to prevent fire or explosion in gas facilities and underground mining. Among the flammable gas analytes, methane is one of the most important to detect. Methane is the major constituent of natural gas that is one of the most abundant US energy resources. Its use is being expanded to meet the rising energy needs in industry, homes, and truck transportation over the next decade. Methane is also the constituent of landfill and mine gases that is likely to pose the greatest explosion hazard. Except for reactions with chlorine or oxygen, methane is mostly chemically inert and is odorless and colorless. Moreover, the physical adsorption of methane on solid materials is typically very weak and as a result, methane is typically detected by heated catalytic bead [pellister], heated metal oxides [HMOx], or non-dispersive infrared instruments [NDIR], each having its own limitations. Additionally, the cost and the power required for many methane sensors precludes them from widespread deployment in mines, industrial installments, fence-lines or pipelines, homes, or wherever methane/natural gas is used.

Over a three year period of time, we investigated the Ionic Liquids (ILs) as new sensing materials for new methane sensors using real-time, portable, low cost orthogonal Electrochemical (EC) and Quartz Crystal Microbalance (QCM) transducers for readout. Having negligible vapor pressure at ambient conditions, high thermal stability in air, and high conductivity, ILs are well suited for use as coatings in QCM based methane sensor development and as electrolytes in Electrochemical based methane sensor development. Specific Aims of this study were: 1. Develop, Characterize and Optimize Ionic Liquid Chemical Interface Immobilization to Form Robust, Thin Rigid Film. 2. Evaluate and Validate the IL Sensor Array for Methane Detection. 3. Develop IL Electrochemical Sensors for Methane Detection. 4. Refine the Sensor to Increase Stability; Heighten Sensitivity and Selectivity for Real World Applications. Our studies involve basic research of methane adsorptions in a variety of IL coatings for QCM based methane sensor development as well as the basic research of methane electrochemical oxidation in various ILs for electrochemical methane sensor development. Our studies also involve the characterization of the methane EC and QCM sensors at real world conditions (water interferences and at various temperatures).

We have completed the investigation of the task specific ILs and their surface immobilization on solid supports as a replacement of conventional recognition elements for QCM methane sensors. We have revealed two new mechanisms of methane electrochemical oxidation in ILs at anaerobic and aerobic conditions. The feasibility of integrated EC and QCM methane sensors to detect methane at real world conditions has also been investigated. The knowledge gained from these investigations prove that the self-organized phases with aggregated non-polar and charged domains of ILs are the choice of sensing materials for EC and QCM based methane sensors which form the foundation to develop commercial methane sensors for mine safety application using the results obtained from this study.

Final Progress Report

Significant Findings: The goal of this project is to develop ionic liquid (IL) based methane sensors using Electrochemical and Quartz Crystal Microbalance (QCM) transducers so that the methane EQCM sensors are suitable for the real time, portable, low cost detection and quantification of methane at workplace. The significant findings are summarized below:

Aim 1 & 2. IL Based QCM Methane Sensors

1. We have validated that IL thin films perform well as QCM sensor coatings. IL thin films provide additional control over selectivity and sensitivity for analytes in gas phase by suppressing conventional solvation and solvolysis phenomena, and by providing media capable to dissolve a vast range of molecules, especially the toxic, flammable, and/or reactive organic gases such as methane.
2. We have demonstrated for the first time that the IL based QCM sensors can be used for high temperature gas sensing. There is an excellent reversibility for adsorption-desorption processes, requiring no experimental manipulation for sensor recycling and regeneration.
3. We have shown that conductive polymer (CPs) with tunable porosity and charge states can be used for the rational development of IL/CP composites to increase the sensitivity, selectivity and response time for QCM based IL sensors. Using polyvinyl ferrocene (PVF) as a model CP, we confirmed that the QCM array with the highest sensitive IL immobilized in four PVF films made at different conditions provides better discrimination of the analytes than that with highest sensitive PVF film immobilized with four different ILs. These results establish the fact that a diverse set of CP redox states allows rational development of IL/CP composite based QCM sensor array to analyze complex gas mixtures utilizing porous structure of CP and diverse intermolecular interactions among CP, IL, and gas analytes.
4. We have tested that Monolithic Quartz Crystal Microbalance (MQCM) in which an array of QCM electrodes is fabricated on a monolithic quartz wafer is effective for miniaturized methane QCM sensor array. With proper design, each QCM in the MQCM behaves like an independent oscillator that responds to mass and/or circumstance's viscosity change. This result proves that the single-chip, monolithic QCM is a feasible technology for miniaturized, highly sensitive gas sensor system that can lead to substantial reductions in cost, time and sample volumes for detection of multi-analytes.

Aim. 3. IL Electrochemical Sensors for Methane Detection.

5. We have proven that ILs are ideal solvents and electrolytes for development of electrochemical gas sensors. We have systematically investigated the IL-electrode interfacial electrochemistry with and without the presence of analyte gases and successfully applied the fundamental understanding to develop IL based electrochemical gas sensors for oxygen and methane detection.
6. We have carried out systematic characterization to understand methane oxidation in various ILs with unique structures and properties in aerobic and anaerobic conditions. Methane oxidation is thermodynamically feasible but the kinetics is very slow. We hypothesize that certain ILs can form a catalytic surface at electrode-electrolyte interface for methane oxidation. Additionally, we hypothesize that ILs can be explored as a reactive media for controlled activation of C-H bond of methane. We have validated both these hypotheses and investigated two new mechanisms of methane oxidation in ILs at aerobic and anaerobic conditions using spectroscopic methods in combination with electrochemical methods.

Aim. 4. Refine EC and QCM Sensor for Real World Applications

7. Despite having many beneficial attributes, ILs pose a number of challenges for sensor development, among which, the water interference is one that can drastically alter their physicochemical properties (e.g., viscosity, conductivity, and diffusivity), consequently affecting sensor responses. We have shown that by selecting hydrophobic IL-coatings, the potential interference of water can be minimized or avoided. For the electrochemical processes, proton donation from water could modify the redox

mechanisms (e.g., O_2 to superoxide) and affect the electrochemical signals. By selecting those redox processes where protons have no influence for quantification, we can address water interference. Furthermore, the interplay between water and the target analytes was tested to calibrate the water interference. Finally, innovative sensor designs and setups were tested to minimize the water interference for IL based electrochemical gas sensors.

8. Temperature fluctuations can cause errors through variations in viscosity and conductivity of IL based EC and QCM sensors. By selecting an AT-cut crystal with a crystallographic orientation that has a zero slope (turnover) at a given temperature, the effect of temperature on QCM based sensors is minimized and avoided. High temperatures reduce the mass signal but it increases the rate of mass transport of the analyte and enhances the electrochemical signals. IL-thermal stability 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 combined EC and QCM approach can facilitate the calibration of water influence and temperature fluctuation to obtain accurate detection of the analytes in real world conditions.

Translation of Findings: Through the development of IL based EC and QCM methane sensors in this project, we have made a significant contribution on overall sensor science and occupational safety. The sensor technologies investigated in this project can not only be applied for work place safety (avoiding mine explosions) and public security (avoiding terrorism threats), with potential of saving thousands of human lives, but can also be extended to various biosensor applications for point of care diagnostics (for treatment and circumvention of diseases) and hospital environmental safety (for preventing hospital contamination). Specifically, the detection capability of methane using IL materials is based on creative and innovative concepts, and a profound understanding can lead to multi-sensitivity and multi-dynamic-range functionality of integrated EQCM sensors for gas detections in mine safety where sample concentrations and detection range is quite variable. A complete sensor system can also be constituted on the basis of the EQCM sensor technology thus allowing real time multi-sample analysis.

Outcomes/Impact: Methane is a potential hazard in mines. Methane can ignite and explode between its Lower and Upper Explosive Limits (LEL & UEL) that are 5% and 15% by volume, respectively. Robust methane sensors that can stand the hash pre- and post- explosion environment require innovative new sensing materials that are thermally stable and can be integrated with small, low cost and low power transducer (i.e., EC and/or QCM) so that a potentially wearable methane sensor can be made for accurate detection of methane in the concentration range of interests in mines.

1] **Technological Impact**: This project allows significant understanding of EC and QCM sensor approach using IL sensing materials and has laid the foundation for a new technological capability of EC and QCM sensor arrays for multidimensional gas sensing in a miniaturized and integrated format. The EC and QCM methane sensors are low power and can be further miniaturized to be low cost. They can interface with modern wireless monitoring technologies for wearable and distributed methane sensors for mine safety.

2] **Commercial Impact**: This project provides new methane sensors with patented and sustainable performance and cost advantages over existing ones. Further senor research can potentially lead to new patents for the technology transfer and commercialization to result in various business ventures producing job opportunities, thus promoting the economic and human development in the United States

3] **Social/Economic Impact**: improved emission control, safety and personal protection.

4] **Educational Impact**: During this project, several students and postdocs have participated in this interdisciplinary sensor research which provided them the basic research training and opened their minds of entrepreneurial opportunities. The communication skills, responsibility, and civil awareness, they have learned during this project will make them better global citizens.

Scientific Report

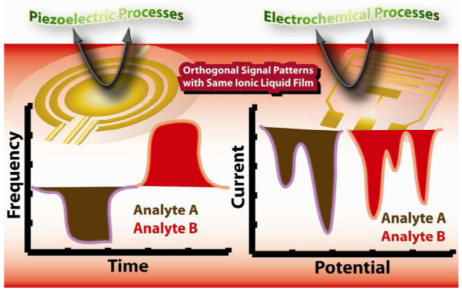

Figure 1: A schematic EQCM sensor in which orthogonal signals are shown to be obtained for the detection of two different analytes.

Ionic liquids (IL) are burgeoning in many scientific disciplines including analytical chemistry because of their robust and eco-friendly nature that is tunable to desired physiochemical dimensions so as to generate selective interaction mechanisms. Despite the availability of quality reviews in synthesis, engineering, energy sector, and electrochemistry, IL research in sensing is relatively new. Their equal usefulness in both piezoelectric and electrochemical (EC) formats with orthogonality to provide chemo- and regio-selectivity through functionalized ionics allow our lab to bridge the IL sensing materials [Rehman & Zeng, 2012] with low cost, low power EC and QCM transducers for the rational design and selection of ILs and their composites suited to be the recognition elements in EC and QCM sensing platforms to provide multidimensional solutions for detection of methane (Fig.1). There are four specific Aims: (1) Develop, characterize and optimize IL chemical interface immobilization to form robust thin rigid films; (2) Evaluate and validate the IL QCM sensor array for methane detection; (3) Develop IL electrochemical sensors for methane detection; (4) Refine the sensor to increase stability, heighten sensitivity and selectivity for real world applications. Here we will summarize the significant results obtained in this project.

Aim 1. Develop, Characterize and Optimize Ionic Liquid Chemical Interface Immobilization to Form Robust, Thin Rigid Film.

IL/CP Composite Thin Film Prior to this grant's activities, we were optimizing the IL chemical interface with conductive polymer (CP) substrate to enhance the sensitivity, selectivity and response time as required for different gas detection for QCM sensing platform. [Jin, Yu et al. 2008] The effectiveness of most thin film based sorption sensors such as QCM 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. 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. CPs and polyelectrolytes are good choice of template materials to make IL-composite films.

Methane has a very low molecular weight, and hence, higher sensitivity methane sensing using QCM mass sensing transducers requires abundant total absorption/partition into the sensing films. PAn was selected to make IL/CP composites in order to demonstrate this approach. [Yu, Jin et al. 2008] PAn films including the doped and undoped ones were tested for the analytical response with [EMIm][CS]. UV-vis and Fourier Transform Infra-Red (FTIR) spectroscopy was used to indicate that the anion of BMICS, camphorsulfonate, could form hydrogen bonds with the "nitrogen" sites of protic acid doped PAn. These hydrogen bonds align the camphorsulfonate anions in a comblike manner along the PAn backbone and therefore enhance the long-range π-orbital conjugation of PAn as shown in figure 2. 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}). Methane molecules absorbed into the PAn/BMICS may sit in the "space" between the aligned anions and cations of BMICS. 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 for methane. By measuring the methane absorption in PAn/BMICS at a temperature range of 25-65 °C, the entropy and enthalpy of dissolution were obtained following the van't Hoff equation. They are 30.1 J/mol.K and 8.7 kJ/mol respectively, which are relatively higher than those in pure BMICS and in PAn only. These thermodynamic parameters further support that the absorbed methane molecules might exist in PAn/BMICS in a relatively ordered manner. Molecular mechanics simulation results also agreed with the spectroscopic and thermodynamic results.

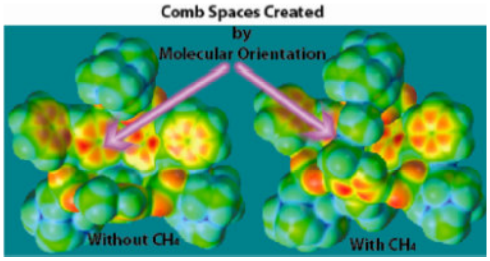

Figure 2: Molecular mechanics simulation of polymer backbone ordering to incorporate methane molecules

IL/CP Composite Thin Film QCM Array Within this project, we continued the development of IL chemical interface with a number of significant findings. For example, the effects of CP oxidation states and structures on the design and development of IL/CP composite films for gas sensing are systematically characterized. Four different polyvinyl ferrocene (PVF) films synthesized by varying the conditioning potential (0.7 vs. 0.0 V) and the electrolyte (0.1M $NaClO_4$ vs. 0.1M tetrabutyl ammonium perchlorate in methylene chloride) are tested for their gas-sensing properties (e.g., sensitivity, selectivity, response time, linearity, and dynamic range against various gas analytes such as dichloromethane, ethanol, natural gas, methane, formaldehyde, and benzene) utilizing the quartz crystal microbalance (QCM) and ATR-FT-IR. [Hou, Rehman et al. 2011] The best available film is further studied as a substrate for the immobilization of various ILs that enhanced both the sensitivity and selectivity. This whole strategy is depicted in figure 3. Furthermore, two arrays, each comprising four sensors with the following scheme: 1) highest sensitive PVF film immobilized with four different ILs, 2) highest sensitive IL immobilized in four different PVF films are developed and characterized for their ability in classification of the four target analytes by using linear discriminant analysis. The array (2) showed higher detection accuracy than array (1) in discriminating the analytes. This study establishes the fact that a diverse set of PVF redox states allows rational development of PVF/IL composite based sensor array to analyze complex gas mixtures utilizing structural differences of CPs and extent of intermolecular interactions among CP, IL and analytes.

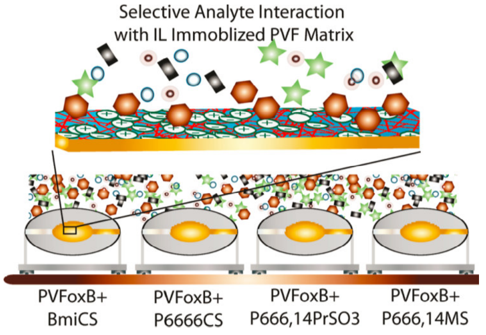

Figure 3: Demonstration of selective analyte interactions with an array of CP/IL composite films

Optimizing IL/CP Composite Film Electrochemical redox cycling of CP film such as PVF film in electrolytes with bigger size of counter ions results in the dramatic alteration in polymer film properties, typically accompanied by loss of redox activity, exemplified in this case by reduced redox currents of PVF associated with repeated exposure to glycylglycylglycine peptide (GGG). Our study shows that ILs can be used to fine tune the structure of CPs for the doping and undoping of larger counter ions by the potential control.[Tang, Baker et al. 2010] The similarity of the structure of ILs plays important roles in the effectiveness of the tuning of the CP properties. [C_4mpy][Tf_2N] and [C_5mpy][Tf_2N] can effectively tune the electro-oxidatively coated PVF to be compatible with GGG^- doping/undoping. Our studies also substantiate that both the cation and the anion of the IL must be considered as both play important roles in appropriately conditioning the PVF polymer films. [Tang & Zeng, 2008] Indeed, ILs with structures and properties highly divergent from the target GGG- failed to properly condition PVF to a compatible state. With a large range of selection of ILs, a certain ionic liquid can be identified for the purpose of tuning CP structures for the optimum transport of a specific molecule. The ease of this method shows great promise for its use in various applications of CPs as well as ILs for various sensing needs.

Aim 2. Evaluate and Validate the IL Sensor Array for Methane Detection.

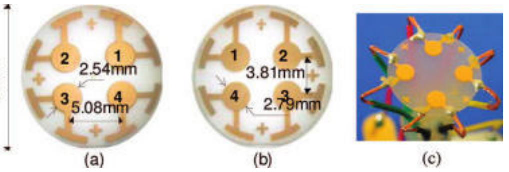

Figure 4: Photos of asymmetric MQCM array, front side (a), backside (b) the symmetric MQCM array with connection leads(c)

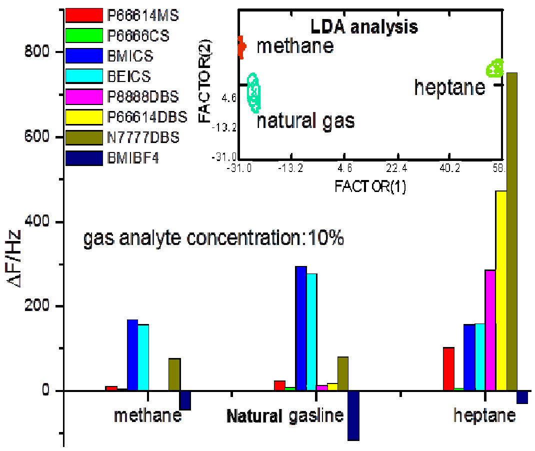

Figure 5: An eight sensor IL array for the detection of methane, natural gas, and heptane

Monolithic Quartz Crystal Microbalance (MQCM) We had demonstrated that Multichannel MQCM, [Jin, Huang et al. 2008] in which an array of electrodes is fabricated on a monolithic quartz wafer, is a very attractive approach for miniaturization using Micro-Electro-Mechanical Systems (MEMS) technology for high throughput chemical sensor systems. The monolithic QCM sensor array chip was fabricated using a simple, straightforward method. Four pairs of QCM electrodes on a single AT-cut 10 MHz quartz plate were fabricated in both symmetric and asymmetric designs. (Figure 4) Their resonance and sensing properties were thoroughly characterized and compared with a single regular QCM under the same conditions by using parallel multichannel QCM instruments. It is confirmed that each QCM in the MQCM behaves like an independent oscillator that responds to mass and/or viscosity change. Various factors that may affect the MQCM performance, such as the fabrication design, the numbers of oscillated electrodes in one MQCM, and the concentration of target analytes, were studied. The MQCM electrodes were selectively coated with an assortment of sensing films (ILs – [BMI][CS], [BMI][BF_4]) and CP (PVF). Their application capabilities for classification and detection of Volatile Organic Compounds (VOCs, i.e., ethanol, CH_2Cl_2, hexane) and water were studied. Our results showed that the single-chip, multichannel QCM is a feasible and promising technology for a miniaturized, highly sensitive multi-analysis system that can lead to substantial reductions in cost, analysis time, and sample volume. This kind of sensor array coated with different ILs can very efficiently discriminate between methane, natural gas, and a larger alkane as shown in figure 5.

IL-Analyte Interaction Models In all these studies, besides implementing the ILs and IL composite materials for the gas sensor and sensor arrays, we systematically investigated the mechanisms of molecular interactions between IL or IL/CP composite and the analyte. The understanding of the physico-chemical properties of the IL and IL/CP films as well as their interaction models with the analytes are important to allow us to rationally design the IL and IL/CP sensor interfaces. For these purpose, FTIR, *in situ* FTIR, AFM and other spectroscopic techniques were used to measure the actual changes when the IL thin films were interacting with different target molecules. This study allows us to efficiently explore the underlying mechanistic parameters and possibly guide for targeted synthesis of particularly featured ILs for the IL sensor array development. What are the design factors responsible for selective detections by these green IL 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. We have evaluated these physical parameters by considering both thermodynamic and solvation models. [Rehman, Hamilton et al. 2011] The underlying mechanism behind the specific sensory response was explored by (i) studying mass loading and viscoelasticity effects of the sensing layers, predominantly through variation in damping impedance, the combination of which determines the sensitivity; (ii) creation of a solvation model based on Abraham's solvation descriptors which reveals the fact that polarizability and lipophilicity are the main factors influencing the dissolution of gas analytes into the RTILs; and (iii) determination of enthalpy and entropy values for the studied interactions and comparison via a simulation model, which is also effective for pattern discrimination, in order to establish a foundation for the analytical scientist as well as inspiration for synthetic pathways and innovative research into next-generation sensory approaches. 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 6. 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; and imidazolium can have strong 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.

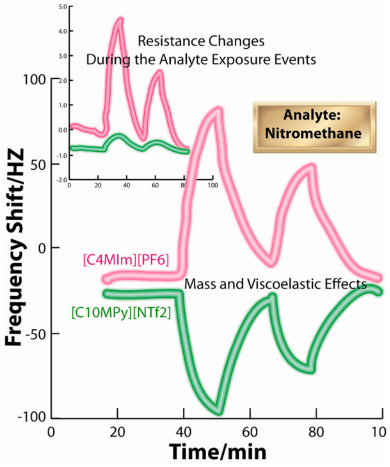

Figure 6: QCM sensor signals and associated changes in damping resistance of two ILs

Aim 3. Develop IL Electrochemical Sensors for Methane Detection

IL is a salt in the liquid state but it contains organic and bulky ions. IL has negligible vapor pressure (non-volatile), low combustibility (non-flammable), excellent thermal stability, and favorable solvating properties for dissolving a great number of polar and non-polar compounds, making them an exciting option for electrochemical electrolyte materials (Figure 7, IL replaces solvent based electrolytes). We have investigated the electrochemical properties of ILs and relative gases (methane, oxygen and carbon dioxide). The fundamental understanding was used to characterize electrochemical sensor system for methane and oxygen since their detections are important for mine safety.

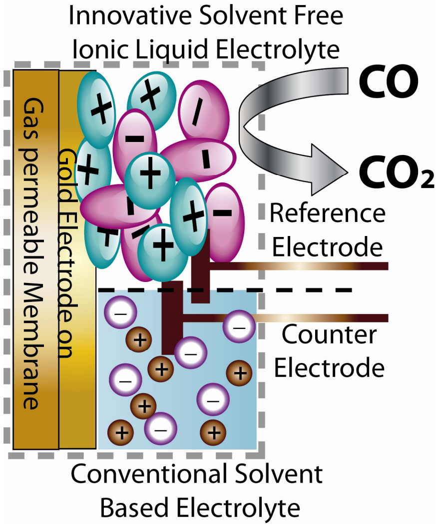

Figure 7: an electrochemical CO gas sensor. Top: solvent free electrolyte overcomes the problem of drying out of traditional solvent based electrolyte.

IL Amperometric Oxygen Sensor Increase of methane concentrations will lead to decrease of oxygen concentrations in the environment. We focus on the characterization of IL based electrochemical oxygen sensors for sensitivity, stability reversibility, selectivity, and response time so that we can optimize the electrochemical parameters of each gas sensor for sensor array including electrode materials, supporting material and electrode geometries, sensor structure , as well as the electrochemical response (e.g., potential, current etc.).

Currently electrochemical sensors based on IL with microelectrodes exhibit small limiting currents and the slow response due to the low conductivity and high viscosity of ILs, limiting their applicability in real world conditions. We have tested and characterized an easy-fabricated amperometric electrochemical sensor that measures methane and oxygen using ILs as the electrolytes and reported long-term stability and reversibility of the system. By using an innovative Clark-type sensor design based on an IL electrolyte layer immediately adjacent to a gas-permeable membrane, our sensor overcomes the limitation of high viscosity of ILs and enable observation of significant performance benefits of the non-volatile IL electrolytes for the detection of methane and oxygen. This design, consisting of a platinum gauze working electrode and incorporating IL as electrolytes, has been successfully applied for the amperometric sensing of oxygen.[Wang, Lin et al. 2011] Studying ILs comprising the bis(trifluoromethylsulfonyl)imide anion, the obtained analytical parameters were found to be strongly dependent on the choice of cation. Compared with a conventional Clark cell design based on an aqueous supporting electrolyte, the modified oxygen sensor achieves 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. 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 interface without passing through the diffusion barrier. 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. Based on these many attractive physical attributes of ILs (e.g., thermal stability beyond 150 °C), one can envision intriguing utility in nonstandard conditions and long-term online applications, as well as extension to the determination of other gases, such as methane and nitric oxide. The setup design and the results obtained in this study are shown in figure 8.

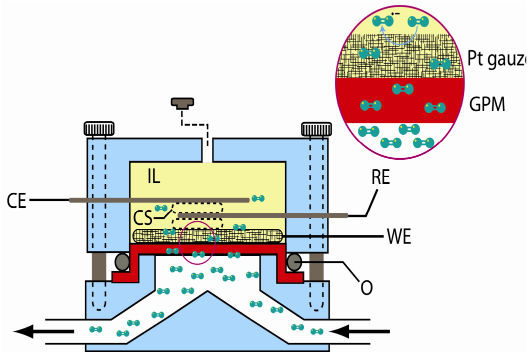

Figure 8a: Optimized configuration of electrochemical cell for oxygen detection in ILs. counter electrode (CE); cellulosic spacer (CS); gas-permeable membrane (GPM); ionic liquid (IL); O-ring (O); reference electrode (RE); working electrode (WE).

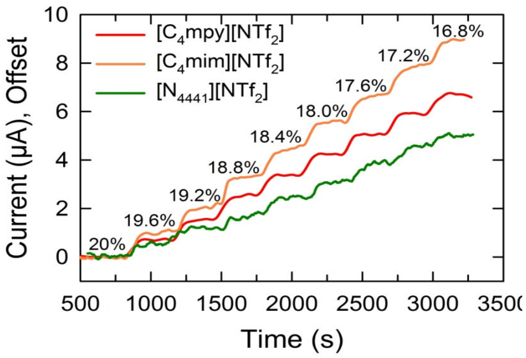

Figure 8b: Current transients recorded at −1.2 V in response to step changes in oxygen partial pressure at the membrane's outer surface for Clark-type electrodes based on three different ILs as the electrolyte. Nitrogen was used as carrier gas and the overall gas flow rate was 200 sccm.

IL Electrochemical Methane Sensor Methane is the main constituent of natural gas. In nature, methane oxidizes to methanol at room temperature via methane monooxygenase enzymes that have iron-oxygen or copper-oxygen sites. The electrochemical oxidation of methane is thermodynamically favored, and thus attempts have been made to reproduce the reactivity of methane monooxygenase enzymes using a variety of electrochemical techniques. The direct oxidation of methane at low temperatures (e.g., from about 60°C to about 150°C) has been demonstrated with electrode systems utilizing acid electrolytes or polyelectrolytes. However, these systems exhibit extremely slow electrode kinetics at room temperature. The replication of the efficiency of nature's enzymatic oxidation of methane has proven to be challenging and difficult, especially using electrochemistry. Two representative ILs ([C_4mim][NTf_2]) and [C_4mpy][NTf_2]) were employed as electrolytes for methane oxidation at a platinum electrode and the response and electrochemical mechanism were investigated in detail using cyclic voltammetry, chronoamperometry, and infrared spectroelectrochemistry.

Methane Oxidation Mechanism We used *In situ* FT-IR to characterize methane oxidation at [C_4mpy][NTf_2]/Pt interfaces under potential control with *p*-polarized IR light. (Figure 9) The methane oxidation products in [C_4mpy][NTf_2]/Pt interface were only CO_2 and H_2O. There is also no obvious peak shifts related to the IL, which implies that, during the methane oxidation, the double layer structure at IL-Pt electrode interface maintains. Our results illustrate that the methane oxidation depends not only on oxygen concentration and the Pt electrode potential but also is governed by choice of IL. In this case, we rationalize that the more compact double layer associated with [C_4mim][NTf_2] is a hindrance to methane adsorption whereas the more loosely-packed double layer formed in [C_4mpy][NTf_2] allows for facile methane adsorption and subsequent methane oxidation. This was explained by the stronger adsorption of [C_4mim]$^+$ than that of [C_4mpy]$^+$ on the Pt electrode and the isoelectric potential points observed in multiple CV potential cycles. (Figure 10) Based on cyclic voltammetry and FTIR characterization, our proposed mechanisms for methane oxidation is shown in Scheme 1.

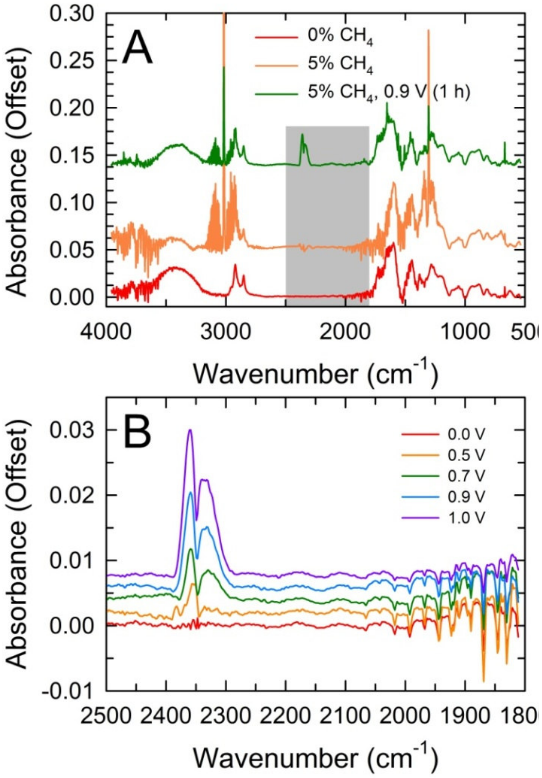

Figure 9: In situ p-type polarized FTIR reflectance spectra of (A) [C4mpy][NTf2] in air, [C4mpy][NTf2] in 5 vol.% methane in air, and [C4mpy][NTf2] in 5 vol.% methane in air after oxidation at 0.9 V for 60 mins. (B) Methane electro-oxidation after 60 mins as function of potential for 5 vol. % methane in air.

Scheme 1: Methane aerobic oxidation mechanism

(1) Pt surface activation
$\mathrm{Pt} + \frac{1}{2}\,\mathrm{O2} \Leftrightarrow \mathrm{Pt\text{-}O}_{(ads)}$
(2) Formation of interface complex
$\mathrm{Pt\text{-}O} + \mathrm{NTF2\text{-}} \Leftrightarrow \mathrm{O\text{-}Pt\text{-}NTf_2^-}_{(ads)}$
$\mathrm{O\text{-}Pt\text{-}NTf_2^-}_{(ads)} \Leftrightarrow \mathrm{O\text{-}Pt\text{-}NTf_2^{\bullet}} + e$
(3) Formation of reactive oxygen species and catalyzing oxidation of adsorbed

IL Electrochemical Methane Sensor Based on the mechanism, the [C_4mpy][NTf_2]-based electrochemical methane sensors were thoroughly characterized for analytical figures of merit, including sensitivity, selectivity, stability, and regenerability for a methane sensor. It is found that for 0–10 vol% methane, the sensitivity is 21.4μA/cm^2.%, while the sensitivity drops to 2.7 μA/cm^2.% at higher methane concentrations, illustrating that methane electro-oxidation in ILs is oxygen-concentration dependent. Figure 10 shows that methane sensor has good sensitivity in the methane detection concentration range. Figure 11a shows that it has surprisingly high selectivity. Figure 11b shows that the platinum electrode can be regenerated and long-term stability at room temperature in atmospheric conditions is sufficient. These data provide a blueprint for developing practical next-generation IL based electrochemical methane sensors that are robust, sensitive, stable, and selective.

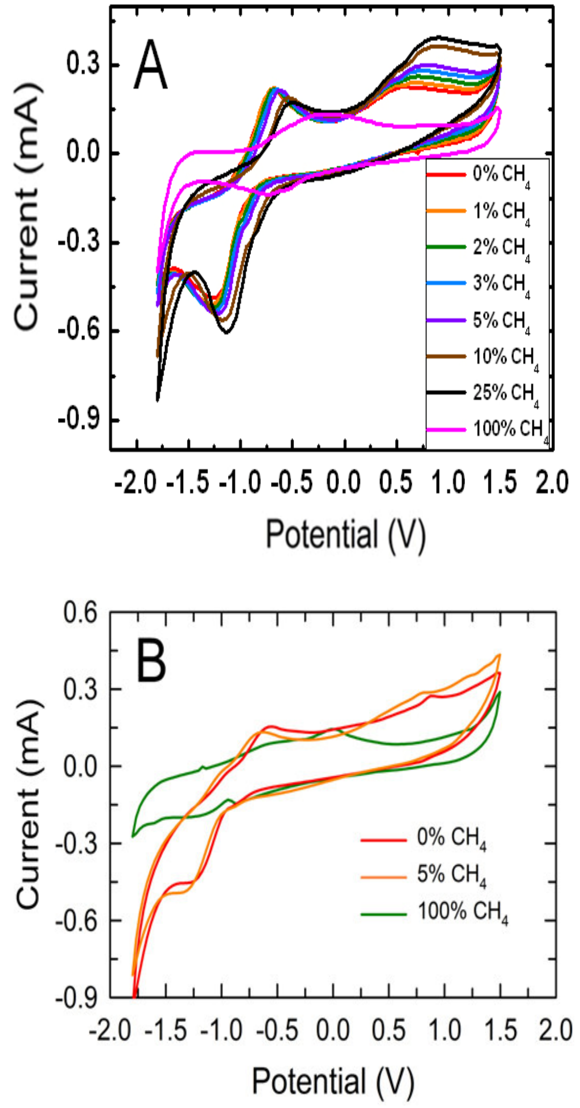

Figure 10: Cyclic voltammograms (500 mV s^{-1} scan rate) of different methane concentrations in (A) [C_4mpy][NTf_2] and (B) [C_4mim][NTf_2]. The balance of the carrier gas is air. All voltammograms shown were recorded on the 6th scanning cycle.

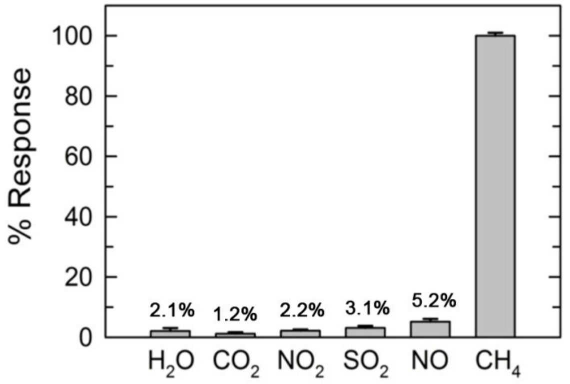

Figure 11a: Peak current response of sensor to non-target gases present at 1.0 vol% in an air stream relative to 1.0 vol% methane in air based on the potential-step method. The number appearing over each bar denotes the selectivity coefficient for methane over a given gas, based on the respective i_p ratio.

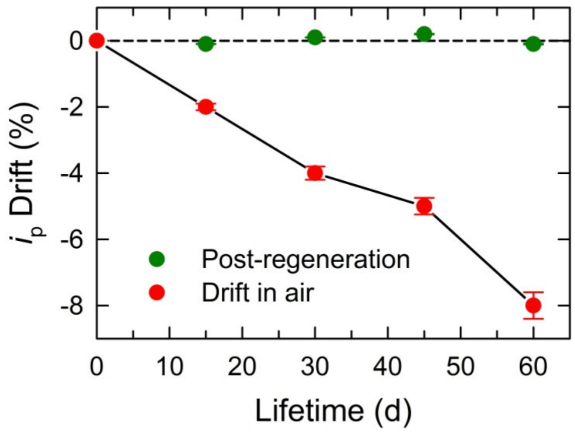

Figure 11b: Dependence of the 5% methane response over time. (a) in air; (b) after regeneration by potential programming.

Aim 4. Refine the Sensor to Increase Stability; Heighten Sensitivity and Selectivity for Real World Applications.

In order to improve the sensor's analytical performance parameters mentioned in this aim to make them prevail in real world detections, a multidimensional approach is followed in our lab. This includes (1) to integrate orthogonal transduction platforms e.g., EQCM; (2) IL/CP material selection and design to magnify the sensitivity, selectivity, and stability of QCM sensor array; and (3) to understand the fundamental interfacial chemistry between IL and analyte using in situ techniques e.g., in situ FTIR characterization, AFM, [Singh & Zeng, 2011] and EQCM and using that knowledge to enhance the real world feasibility of these EC and QCM sensors.

EQCM Integrated Sensor An integrated sensor that combines electrochemical and piezoelectric transduction mechanisms into a single miniaturized platform was developed and validated for the detection of nitro aromatic compounds such as ethyl nitrobenzene (ENB) and dinitrotoluene as a proof of concept for the EQCM methane sensor development. An IL ([Bmim][BF_4]) was used as both the electrolyte and the sorption solvent for the two-dimensional electrochemical and piezoelectric gas sensors. [Yu, Huang et al. 2009] 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 electrochemical behaviors of these nitro compounds in [Bmim][BF_4] were studied by cyclic voltammetry, differential pulse voltammetry and square wave voltammetry, in parallel. The electrochemical properties of these compounds resembled the electrochemical reduction processes in their aprotic solutions, showing first a reversible reduction process and then subsequently an irreversible reduction processes. The redox properties of these compounds also depend on the number of nitro groups and the position of the nitro groups on the benzene ring. Square wave voltammetry was used to quantitatively analyze the ENB in [Bmim][BF_4]. Reduction peaks in the square wave voltammetric curves could be obtained when the concentrations were at ppm level. A small amount of moisture in the IL electrolyte did not significantly affect the redox behaviors. Detection of the volatile ENB vapor with this integrated EQCM chip was tested with both QCM and amperometric methods. The sensor's signal was related quantitatively to the ENB vapors adsorbed in [Bmim][BF_4] from air. Combining amperometric and QCM detection was shown to simultaneously cross-validate the detection technology, reduce false positives and false negatives, and increase the accuracy of the detection.

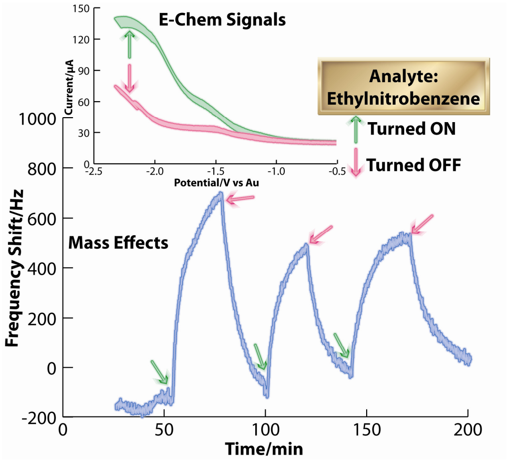

Figure 12: Variation of EQCM responses with analyte switching (ON/OFF) in an Au EQCM electrode with [Bmim][BF_4] thin film.

Water and Temperature Interference Despite having many beneficial attributes, ILs as sensing materials also face a number of challenges, among which water interference is one that can drastically alter their physicochemical properties (e.g., viscosity, conductivity, and diffusivity), consequently affecting sensor responses. We have shown that by use of CP template and by selection of hydrophobic IL coatings, the potential interference of water can be minimized or 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 8a).

Temperature fluctuations, on the other hand, can cause errors through variations in viscosity and conductivity. We have addressed the temperature effects 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.

Conclusion

This project enables us to systematically investigate IL materials for low cost, low power EC and QCM based methane sensor development. Research in our lab has proved that IL sensing materials are amenable to low power and low cost field-rugged electrochemical and QCM sensor platforms that can be tailored for reactivity toward methane and other important environmental volatile and gaseous analytes. The integrated EQCM methane sensor array that combines QCM with electrochemistry methods such as impedance and cyclic voltammetry (CV) will be the future research directions to realize the real time in situ mass changes in the nanogram range to be monitored during the adsorption and electrochemical oxidation of methane at the electrode IL 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.

Our study also shows that water is a significant interfering compound for IL based sensors for real world detections. We have tested several effective methods for calibrating and/or minimizing water interferences for the sensing signals. Currently, we are exploring ways to selectively minimize the environmental effects while making sensors. For example, the oxygen reduction in IL is stable and reversible and is sensitive to the amount of 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 water and 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.

In summary, this R21 research project allows us to demonstrate the feasibility, and establish the viability of EC and QCM methane sensor for monitoring methane in future mine safety applications. The technology has broad application which can be applied to detect many gas targets besides methane at high-temperature or real-time situations, opening up new horizons in chemical sensing. The research in this project has led to several patent applications and reached to a level of confidence appropriate for R&D in product development and commercialization.

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Manuscripts Completed:

1. Wang Z, Baker G, Stetter J, Zeng X: Analytical Performance and In Situ Infrared Spectroelectrochemical Study of an Ionic Liquid Based Electrochemical Methane Sensor, Patent filed and manuscript completed for submission.
2. Wang Z, Sevilla M, Zeng X: Anaerobic Oxidation of Methane by in situ Electrochemical Generated Precursors from an Ionic Liquid **,** Patent in preparation and manuscript completed for submission.

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2. “Devices with Surface Bound Ionic Liquids and Method of Use thereof”. Xiangqun Zeng, US Patent 7,886577B2.
3. "Ionic Liquid Thin Layer Sensor For Electrochemical and/or Piezoelectric Measurements", Xiangqun Zeng**,** Lei Yu, Yue Huang and Andrew J. Mason, US Patent No. 2009/0293590 A1,
4. Aerobic oxidation of alkane, Xiangqun Zeng, Zhe Wang, U.S. Patent Application S.N. 13,597,071. a filing date of August 28, 2012.

Material available to other investigators: The publications and other related results and materials are available to others with a material transfer agreement.