Title: Autonomous Electrochemical Gas Detection Microsystem for Mine Safety

Investigators:

Andrew Mason (contact PI), Department of Electrical Engineering and computer science, Michigan State University, East Lansing, MI 48824, E-mail: mason@msu.edu

Xiangqun Zeng (partner PI), Chemistry Department, SEB 231, Oakland University, Rochester, MI 48309, E-mail: zeng@oakland.edu.

Rong Jin, (co-investigator), Department of Electrical Engineering and computer science, Michigan State Univ. East Lansing, MI 48824, E-mail: rongjin@msu.edu

Institution to which award was made: Michigan State University,

Award Number: 1R01OH009644-01A1

Start & End Dates: Sept.1, 2010- August 31, 2015

Program area: Mine Safety

Table of Contents

Final Report Abstract

A project titled, “Autonomous Electrochemical Gas Detection Microsystem for Mine Safety” was recently completed by Drs. Andrew Mason (mason@msu.edu), Xiangqun Zen, and Rong Jin. Despite continued safety improvements and increased regulations, underground mines remain a very dangerous work environment, as evident from gas explosions and numerous reports of worker injury in mines. Although many handheld portable gas sensors have been developed, none of them meet the challenging set of cost/utility/capability requirements that prevent the pervasive use of personal, continuous-use hazardous gas monitors in the real-world mine environments. The overarching goal of our project is to develop the technologies and techniques that enable a gas monitoring system which can be widely deployed with mine workers to monitor personal exposures to gaseous hazards, autonomously, in real time, over extended periods and in real world conditions. Within the aims of this grant, we establish ionic liquid (IL) electrochemical gas sensors as a promising new technology with many significant advantages over current existing commercial gas sensors and gas analyzers. By combining the unique physical and chemical properties of IL electrolytes (negligible vapor pressure, high chemical, thermal and electrochemical stabilities), a novel microfabricated electrode structure, and integrated electronics for electrochemical instrumentation, we demonstrated that a miniaturized sensor IL gas sensor system was feasible with performance specifications heretofore unavailable with existing gas sensor. Sensors for explosive and flammable methane gas and hazardous permanent gases including sulfur dioxide and nitrogen dioxide were developed and characterized. In an underground mine environment, lack of a safe level of oxygen can be as dangerous as hazardous gases, and thus our IL technology was also used to implement a miniaturized oxygen sensor. Techniques for maximizing sensor response time were explored and a novel sensor structure was developed to provide rapid response to changing environmental conditions. The long term stability of the sensors was studied and methods for sensor drift calibration were developed. Overall, this R01 project allowed us to establish the basic principles and technical pathways to achieve our goal of an autonomous electrochemical gas detection microsystem for mine safety. Beyond the successes of this project for individual gases, a key finding of our research was that multi-gas measurement in real world gas mixtures and real world environmental conditions (including sensor drift, interference of other gases, and variations due to temperature and humidity) will require further development focused on a comprehensive “sensor array” approach to overcome challenges inherent to mixed gas sensing.

Final Progress Report (Part 1)

Significant Findings:

Our goal in this project was to develop a new gas sensor technology that is distinctively poised to meet the requirements for gas monitoring in mine safety applications. The project was organized into three specific Aims: Aim 1: Develop and characterize a miniaturized electrochemical sensor array for detection and quantification of multiple mine gases; Aim 2: Design and optimize compact electrochemical instrumentation electronics and intelligent algorithms for autonomous operation; Aim 3: Integrate and characterize a model multi-gas electrochemical microsystem for mine safety monitoring and hazardous condition prediction. Within this NIOSH R01 grant, we achieved most of the objectives of these three Aims to establish ionic liquid electrochemical gas sensors as a technology that can overcome many challenges faced by other types of gas sensors for mine safety monitoring. Several significant findings are briefly summarized below.

<u>*Aim 1:*</u> *miniaturized electrochemical sensors for detection and quantification of multiple mine gases*

We have demonstrated the significant advantages of utilizing ionic liquids (ILs) as a chemically selective interface and an electrolyte in a new form of electrochemical gas sensor. IL-based sensors were shown to have a broad structural and functional diversity that enables chemically and thermally stable electrochemical sensing that solves many prevailing problems with existing gas sensor technologies. IL-based sensors were also shown to be highly suitable for miniaturization into a low cost, low power, and compact sized monitoring systems. We further demonstrated that the accuracy, selectivity and detection limits of IL sensors are suitable for the real-time monitoring of key gases in mine safety applications including CH_4 (methane), O_2, H_2, CO, NO_2, SO_2. Our investigation generated many fundamental discoveries in IL sensing chemistry, for example, a unique coupled chemical reactivity, only possible in IL electrolytes, that enables highly selective measurement of methane, an inert gas that is very difficult to measure with traditional chemical sensor methods. We also established new analytical methods, new miniaturized sensor structures and fabrication methods, and new microelectronic instrumentation platforms that are all promising for system-level implementation of our IL-EG sensors.

<u>*Aim 2:*</u> *compact electrochemical instrumentation electronics and algorithms for autonomous operation*

To enable miniaturization of a fully integrated IL sensor system, we designed and optimized a compact, multi-mode electrochemical instrumentation board (MEIB) on a printed circuit board (PCB). The ~1"x2" MEIB is a novel resource-sharing circuit tailored to our gas sensors that can significantly decrease power, cost and size while implementing multiple electrochemical measurement techniques including constant potential voltammetry, cyclic voltammetry, and impedance spectroscopy. We also began development of a CMOS microelectronics chip to perform electrochemical sensor readout. Our first version chip is a power efficient instrumentation circuit with high sensitivity and large dynamic range that combines an input digital modulation technique and a semi-synchronous incremental ΣΔ ADC structure to achieve very high power efficiency over a large dynamic range with high sensitivity. A comparison between our chip and other chronoamperometric sensor instrumentation chips shows that we have simultaneously achieved the largest dynamic range, the second best sensitivity and second best power efficiency among reported designs.

<u>*Aim 3:*</u> *model multi-gas electrochemical microsystem for mine safety monitoring*

We implemented a complete integrated system by interfacing the MEIB with an array of four IL sensors and a commercial MSP430 low power microcontroller board to form a fully functional electrochemical gas sensor system called the intelligent gas analysis system (iEGAS). iEGAS represents the final achievement of this NIOSH grant and serves as a prototype compact, low-power microsystem implementation of a real-time, multi-sensor monitoring system. The iEGAS system was tested for electrochemical performance and achieved a resolution as high as 0.01% vol in amperometry mode and 0.06% vol in impedance spectroscopy mode for oxygen as an example target gas.

Translation of Findings:

The factors important in the evaluation of a sensor device are often summarized as the five key parameters, i.e. Sensitivity, Selectivity, Speed of response, Stability, Dynamic Range. Ionic liquids are ideal sensing materials since they have negligible vapor pressure, high chemical, thermal and electrochemical stabilities and can be designed to impart new chemical properties (e.g. hydrophobic vs hydrophilic). In this grant, we focused not only on the novelty of IL sensing chemistry, which is substantial, but also on the promise of realizing new sensors with properties such as robustness, selectivity and stability that have not been possible with traditional sensing materials and methods (e.g. electronic nose and portable sensors). Briefly, we have (1) discovered IL-electrode interface can form an ordered structure that depends on the cation and anion of the IL, the properties of the gas molecules particularly their size and polarity and the applied DC potential. This unique IL-electrode interface structure was demonstrated for the sensitive, selective and reversible of sensing SO_2 and CH_4 with impedance mode; (2) developed multi-mode (voltammetric and impedance) electrochemical methods for IL-based gas sensing that allows cross validation of the analytical measurements, enhances analytical information content, and enables sensitivity improvement and automated calibration; (3) significantly increased sensor speed of response to less than 0.1 seconds via innovative sensing chemistry, sensor electrode structure and sensor data analysis methods; (4) improved fundamental understanding of the water and oxygen redox chemistry in ILs that allow new strategies to be developed utilizing water and oxygen chemistry for gas analyte detection in real world environments where the temperature and humidity can fluctuate drastically depending on the time of the day or weather conditions. These accomplishments in fundamental understanding of the target gas analyte electrochemistry and surface chemistry in ILs and new sensor chemistry and analytical methods form a strong foundation for further advancement and research of IL-EG sensors for work safety applications. At the application level, this project made a significant step forward by developing an effective electronics platform for implementing IL sensors within an autonomous system capable of the cost, utility and performance metrics needed to provide an effective solution for miner work safety monitoring that is suitable for adoption by even cost constrained mine industries.

Outcomes/Impact:

Technological Impact: This project demonstrated a unique system-level approach to gas sensing that incorporates electrochemical sensors, microelectronics instrumentation, and embedded sensor processing algorithms, to meet the requirements for multi-gas sensing capabilities and affordable system implementation. Our research in this first R01 grant has laid the foundation for multidimensional gas sensing in a miniaturized and integrated format at low power and low cost. The sensor system can be designed to interface with modern wireless monitoring technologies for wearable and distributed gas sensors for mine safety. One example of the significant impact is the demonstrated IL-based methane sensor methods detailed in two journal papers: ((i) Methane-oxygen electrochemical coupling in an ionic liquid: a robust sensor for simultaneous quantification, Analyst, in revision; (ii) Methane recognition and quantification by differential capacitance at the hydrophobic ionic liquid-electrified metal electrode interface. *Journal of the Electrochemical Society* **2013**, *160*, B83-B89) and two patents “Aerobic oxidation of Alkanes”, US 2014/0061058A1 and “Simultaneously quantifying an alkane and oxygen using a single Sensor”, US 2014/0197045A1).

Commercial Impact: This project provides new gas sensors with patented and sustainable performance and cost advantages over existing technologies. Further senor and sensor system research can potentially lead to new patents for technology transfer and commercialization, producing job opportunities and promoting economic and human development in the United States.

Social/Economic Impact: The gas sensors developed in this project are inherently suitable for improving worker safety, particularly in underground mine environments. The new sensor technology is also directly applicable to applications in improved emission control, workplace safety and personal protection.

Educational Impact: Many undergraduate and graduate students and postdocs have participated in this interdisciplinary sensor research which provided them the basic research training and exposed them to new concepts for managing and engaging in interdisciplinary and collaborative research. The communication skills, responsibility, and civil awareness they have learned during this project have made significant impact for their careers.

Final Progress Report (Part II)

Scientific Report

Summary of first cycle NIOSH grant research:

This project developed several key sensor technologies that will be integrated to form a miniaturized, wearable, instrumentation system tailored to the needs and challenges of mine safety applications with three specific aims: 1) Develop and characterize a miniaturized electrochemical sensor array for detection and quantification of multiple mine gases; 2) Design and optimize compact electrochemical instrumentation electronics and intelligent algorithms for autonomous operation; 3) Integrate and characterize a model multi-gas electrochemical microsystem for mine safety monitoring and hazardous condition prediction.

Electrochemical sensors(Bakker 2004) dominant the portable gas sensor market because they are generally fairly selective to gases and their power consumption is the lowest among all gas sensor types. However, development of reliable multi-gas electrochemical sensors capable of autonomous long-term operation remains an open challenge. Our first NIOSH R01 grant proposed to develop key sensor and instrumentation technologies that can be integrated to form a miniaturized intelligent electrochemical gas analysis system (iEGAS) tailored to the needs and challenges of mine safety applications. Innovations in the following diverse research areas were explored: 1) IL electrochemical gas sensor development for measurement of multiple mine gases, 2) low cost and high performance microsensor structures and microfabrication processes for miniaturized IL gas sensors; and 3) design of compact electrochemical instrumentation electronics and 4) integration of a compact model iEGAS system. Through these studies, (1) new redox chemistries of the selected target gas analytes were discovered in the ILs which are otherwise not possible in traditional aqueous and non-aqueous electrolytes(Rehman and Zeng 2015); (2) new sensing methods and approaches were developed based on the understanding of the sensing mechanisms in ILs(Buzzeo et al. 2004, Stetter et al. 2011, Wang et al. 2011, Rehman and Zeng 2012, 2015, Rehman et al. In review); (3) miniaturized sensor electrode designs and rapid-response sensor structures were developed for integration into an autonomous sensor system(Stetter et al. 2011, Wang et al. 2011, Rehman and Zeng 2012, Rehman et al. In review); (4) miniaturized microelectronic instrumentation circuits were developed to achieve specifications suitable for next generation electrochemical gas sensor applications(Li. et al. 2015). Below, we summarize our significant research progresses from the first grant cycle, which resulted in 17 publications (plus several in preparation), one book chapter, two invited reviews and 2 issued patents(Hou et al. , Jin et al. 2006, Jin et al. 2008, Yu et al. 2008, Yu 2009, Rehman et al. 2011, Wang et al. 2014, Xiao et al. 2015),(Li et al. 2012, Xiaoyi et al. 2012, Yang and Mason 2012, Haitao et al. 2013, Mu et al. 2013, Yuning et al. 2013, Haitao et al. 2014, Haitao et al. 2015).

Gas Sensor Science (Aim 1):

Current electrochemical gas sensors typically are based on amperometric or impedance sensing mode consisting three components: gas permeable membrane, electrode and electrolyte. Sometimes a *scrubber* filter is installed in front of the sensor to filter out unwanted gases. For amperometric sensor, the gas of interest is oxidized or reduced at the electrode-electrolyte interface which produces a current related to the gas concentration. For impedance mode, the gas adsorbed at electrode-electrolyte interface can result in a capacitance change that can be related to the gas concentration. Fundamental investigation of molecular electrochemistry and surface chemistry of common mine gases (CH_4, CO, H_2, O_2, NO_2, SO_2) in ILs at electrode materials (Pt, Au, Carbon) were systematically performed. Amperometric and impedance sensing methods were characterized and sensor stabilities were tested (hours to days). Below, we illustrate unique IL gas sensor science using representative gases. We also summarized the findings in Table 1 to illustrate the needs of further investigation for a new 3D electrochemical sensor matrix for their applications for detection of multi-gases in real world conditions for work safety applications.

Amperometric IL gas sensors: 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 classic example in this regard.(Carter et al. 1991, Evans et al. 2004, Katayama et al. 2004, O'Toole et al. 2007, Barnes et al. 2008, Hayyan et al. 2012) In ILs, ORR is a one electron 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 one electron reduction of oxygen to form superoxide radical which is stable in IL [C_4mpy][NTf_2], this reaction was utilized for a robust oxygen gas sensor method(Wang et al. 2011). Furthermore IL electrolytes enable new electrochemistry of methane that is very difficult to be oxidized in traditional electrolytes. As shown in Fig.2, at [C_4mpy][NTf_2]-Pt electrode interface, methane can be oxidized at room temperature to form CO which can be further oxidized to CO_2 by in situ electrochemically generated superoxide radical $O_2^{\bullet-}$ via reduction of ambient O_2(Wang and Zeng 2013, Wang et al. 2014). The final oxidation product CO_2 can be directly removed from the interface by superoxide radical to form $C_2O_6^{2-}$ anion. In addition, the product CO_2 can also serve as an in-situ generated internal standard. This unique coupled redox chemistry of methane and oxygen at room temperature minimizes the Pt electrode poison due to product formation (CO and CO_2) and allows an innovative internally-referenced electrochemical method for methane and oxygen detection (**Fig. 1**) in a single sample matrix in real time with a single sensory element(Wang et al. 2014). In ambient conditions, the emission of any new gaseous species will lead to a reduction of oxygen concentration. Thus, a measure of oxygen concentration is an indicator for the emission or the presence of a new gaseous species. Thus, this new IL based amperometric methane sensor increases the accuracy of the measurements by determining two ambient gases (CH_4 and O_2) within a single sample matrix in real time. This coupled chemical reactions are made possible by the unique features of the IL milieu and have no analog in conventional (e.g., aqueous) electrolytes which enables the highly selective detection of methane and oxygen simultaneously. This methane sensor meets the analytical requirement for mine gas detection but the sensitivity needs to be further improved and the sensor life time needs to be extended for the work safety applications.

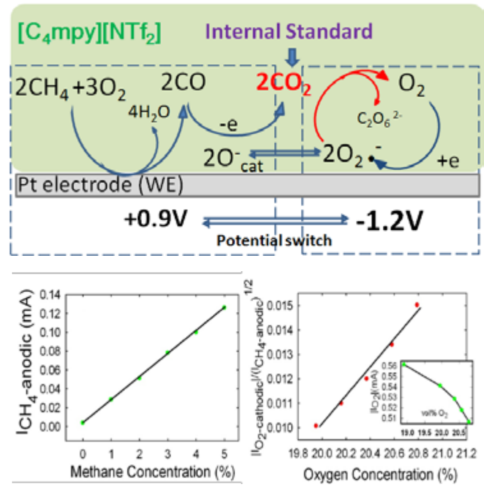

Fig. 1. (top) methane sensor principle and (bottom) CH_4 & O_2 sensor calibration curves.

IL capacitance sensor: At room temperature, ILs have high viscosity. Thus, they can be regarded as a solid and liquid interface simultaneously. It was shown that the double layer structures in ILs are highly dependent on IL physicochemical properties and the applied potential(Kornyshev 2007, Wang et al. 2013, Fedorov and Kornyshev 2014). We discovered that the [C_4mpy][NTf_2]-Au interface can sensitively and selectively measure the concentrations of CH_4 (**Fig. 2**) using electrochemical impedance spectroscopy (EIS)(Wang et al. 2013). The selectivity comes from the unique highly ordered arrangement of ions in the innermost layer of IL-electrode interface which depends on the molecule dipole moment, kinetic diameter and the IL-electrode interface structure at different electrode potentials. The high viscosity of ILs is an advantage in capacitance measurement(Ohsaka et al. 2007) due to a more ordered and compact double layer. Impedance method does not require the gas analyte to be redox active. The current signals of the amperometric sensor and the impedance signals are all related to the active area of the electrodes. Thus capacitance-based sensors provide orthogonal detection modes to amperometric sensors, also permit self-monitoring of the sensor's stability and automated calibration for drift mechanisms and improving sensor accuracy.

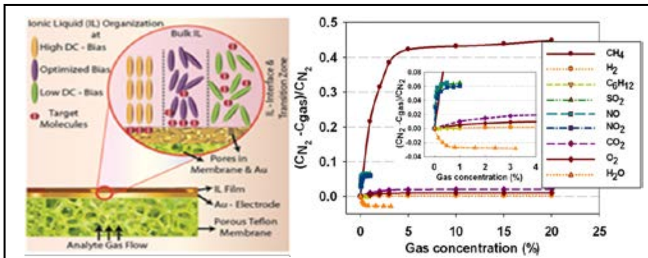

Fig. 2. Methane capacitance sensor, DC biased at -0.3V with Au electrode and [C_4mpy][NTf_2] IL.

Fast response IL sensors: Continuous hazardous gas sensing requires fast sensor response time. For example, in a sudden methane outburst, the delay due to slow sensor response can easily lead to a frictional ignition before the sensor can shut down the equipment. Gas sensors based on ILs were considered slow in response due to the low gas diffusivity in the high viscosity of IL electrolytes. To increase response speed and circumvent the high viscosity of ILs, we introduced a novel macroelectrochemical cell with a porous PTFE Teflon membrane (**Fig. 3**) with desired wettability of ILs that facilitates diffusional transport through the pores and provides two levels of

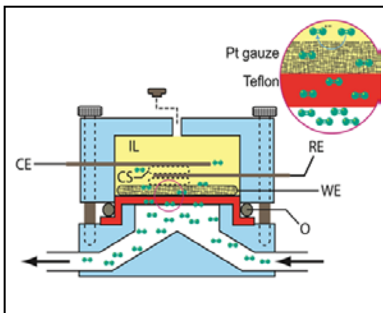

Fig. 3. Fast response macroelectrochemical cell

selectivity(Wang et al. 2011). 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. 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 EIS readout. In addition, we designed a fuel cell type gas sensor structure (not shown) which further reduces the sampling time. Finally our recent work shows that by identifying the rate of CO oxidation in IL diethylmethylammonium trifluoromethanesulfonate ([Dema-TfO]) using impedance spectroscopy to be 12.58 Hz, we demonstrated new sensor method to detect CO as fast as 0.1 second using chronoamperometry (**Fig. 4**).

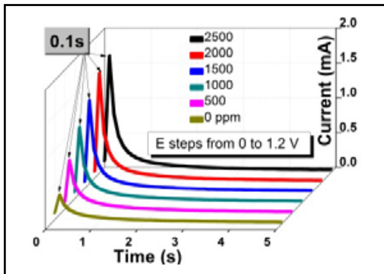

Fig. 4. Response time of IL-based electrochemical sensor under different CO concentrations with Pt gauze working and counter electrodes in [Dema-TfO].

<u>Summary</u>: **Table 1** summarizes the key analytical parameters obtained using electrochemical cell shown in Fig.3. The redox reaction of methane results in product formation which is shown to lead to sensor baseline drift when the sensor is tested in an extended period which will require further research to develop calibration methods to address this issue. Hydrogen sensor shows excellent stability and reversibility but the H_2, SO_2 and NO_2 sensor sensitivity and selectivity will need to be tested in much low concentration range and in the integrated sensor devices since all components of the sensors (e.g. gas permeable membrane, electrode and electrolyte interface properties, electrode geometry and sensor structure) contribute in determining the overall analytical characteristics of a sensor device. Initial testing of the sensor methods in the planar electrodes were described in the next section. Further characterization and understanding the fundamental sensor science and sensor methods will be carried out in a new continuous R01 proposal since they are critical for the intelligent design, selection and integration of effective sensing components for a 3D electrochemical sensor matrix for detecting multiple mine gases in real world conditions.

Table 1. IL-EG sensor characteristics summary

Gas	Electrode/Electrolyte	Potential	Redox mechanism	Sensitivity	Method
CH_4	Pt/[C_4mpy][NTf_2]	+0.9 V	$CH_4 + O_2 \overset{Ox}{\rightleftarrows} CO_2 + H_2O$	2.2 nA/ppm	EIS/Amperometry
O_2	Au/[C_4mpy][NTf_2]	-1.2 V	$O_2 + e^- \overset{Red}{\rightleftarrows} O_2^{\bullet -}$	6.4 nA/ppm	Amperometry
H_2	Pt/[C_4mpy][NTf_2]	+0.4 V	$H_2 - 2e^- \overset{Ox}{\rightleftarrows} 2H^+$	9.1 nA/ppm	Amperometry
CO	Pt/[Dema][TfO]	+1.2 V	$Pt\text{-}CO + Pt\text{-}OH \overset{Ox}{\rightleftarrows} CO_2 + H^+ + Pt$	33 nA/ppm	Amperometry
SO_2	Au/[C_4mpy][NTf_2]	-1.5 V	$SO_2 + e^- \overset{Red}{\rightleftarrows} SO_2^{\bullet -}$	9.9 nA/ppm	EIS/Amperometry
NO_2	Pt/[Bmim][NTf_2]	-0.5 V	$NO_2 + e^- \overset{Red}{\rightleftarrows} NO_2^-$	13.7 nA/ppm	EIS/Amperometry

Microsensor Structure & Fabrication (Aims 1 and 2):

The goal of this task was to develop and characterize a miniaturized electrochemical sensor suitable for measuring gas concentrations within a small/wearable system. Thus, the main task was to significantly reduce the size of our macro-scale sensor discussed above using inexpensive and robust batch-fabrication processes without sacrificing performance. Building on the back-side gas exposure approach described above, we developed the *planar-electrode-on-permeable-membrane* (PEoPM) structure shown in **Fig. 5**. In the PEoPM structure, POREX® porous PTFE with 35% porosity and 4-micro pore size was chosen as the permeable membrane due to its excellent inertness and hydrophobic response to IL electrolytes. Because porous PTFE is soft and has high surface roughness, traditional lithography processes for defining patterns is severely complicated and deposition of thin-film metal electrodes is challenging. Through rigorous experimental study, we have established new process techniques to overcome these challenges(Mu et al. 2013) and fabricate the miniaturized thin film patterns shown in **Fig. 5**. The final fabrication process (**Fig.**

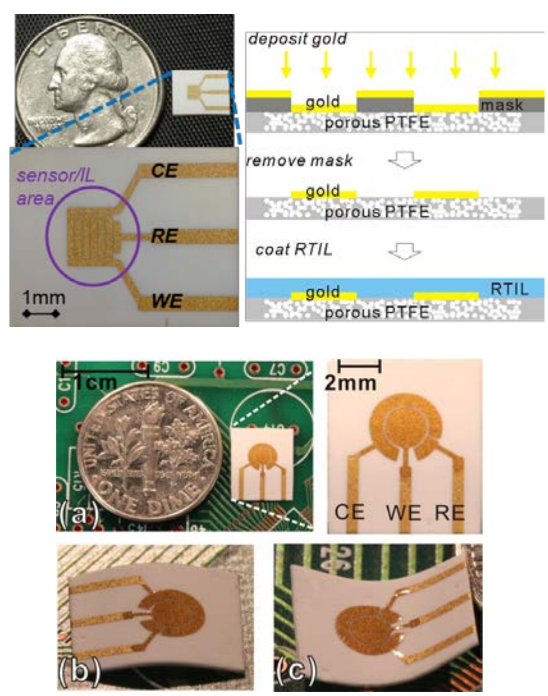

Fig. 5. Miniaturized PEoPM structure for inexpensive, robust, rapid-response IL gas sensors. (top) Interdigitated electrodes version and fabrication sequence. (bottom) Disk electrode version on flexible thin-PTFE substrate.

5 (top-right)) deposits a 10nm/300nm thin film of Ti/Pt or Ti/Au through a 10um mask of AZ4620 photoresist using a lift-off technique. This process has been employed to construct electrochemical sensors on the order of 1mm in diameter. Both concentric disk and interdigitated electrode geometries have been produced. IL films were immobilized using a method that exploits the different wetting properties of the PTFE substrate and the metal electrodes provides homogeneous and strong IL coating with superior stability. The miniaturized thin-film electrode IL-EG sensors have been tested to confirm electrochemical functionality. For example, **Fig. 6** shows a PEoPM sensor responding nearly 3x faster to SO_2 through the porous PTFE than requiring gas to diffuse through the membrane. **Fig. 6** also shows accurate response of PEoPM sensors to varying concentrations of O_2. The sensor has also been successfully used to measure CH_4 concentrations (Fig.3). By employing standard microelectronics fabrication processes, this miniaturized thin-film IL-EG sensor structure ensures reproducible and cost effective batch production and permits rapid design modification for further development to be incorporated into a sensor matrix system.

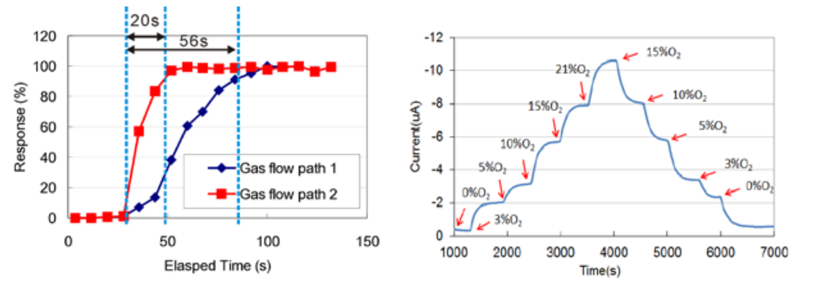

Fig. 6. (left) Transient response of RTIL-PEoPM sensor to 250ppm SO_2, with gas flow either through the IL membrane (path 1) or through the porous substrate (path 2). Path 1 has a 56s full scale response while the new rapid-response structure that reduces response time to 20s. (right) O_2 response from IL sensor with PEoPM electrode structure.

Electrochemical Instrumentation (Aims 2 and 3):
Sensor readout electronics & system integration: To enable miniaturization of a fully integrated IL-EG sensor system, we designed and optimized a compact, multi-mode electrochemical instrumentation board (MEIB) on a printed circuit board (PCB). The ~1"x2" MEIB is a novel resource-sharing circuit tailored to our gas sensors that can significantly decrease power, cost and size while implementing multiple electrochemical measurement techniques including constant potential voltammetry, cyclic voltammetry, and impedance spectroscopy. Once the analog performance of the MEIB was verified, we implemented a complete integrated system by interfacing the MEIB with an array of four PEoPM IL-EG sensors and a commercial MSP430 low power microcontroller board to form a fully functional electrochemical gas sensor system called the intelligent gas analysis system (iEGAS), shown in **Fig. 7**. iEGAS represents the final achievement of our prior NIOSH grant and serves as a prototype compact, low-power microsystem implementation of a real-time, multi-sensor monitoring system. The iEGAS system was tested for electrochemical performance and achieved a resolution as high as 0.01% vol in amperometry mode and 0.06% vol in impedance spectroscopy mode for oxygen as an example target gas.

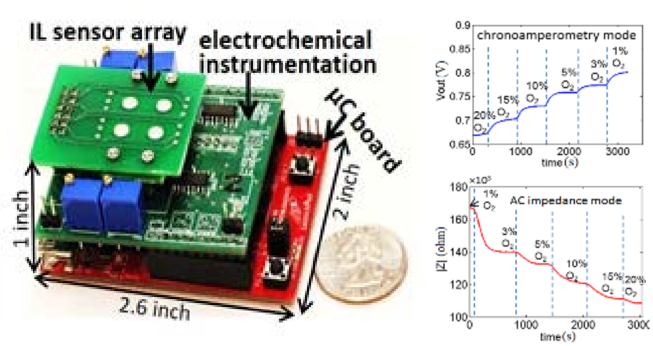

Fig. 7. (left) Compact integrated gas sensor microsystem with IL-based electrochemical sensor array, custom instrumentation electronics, and system management microcontroller. (right) MEIB outputs for sensor array with O_2 concentration from 1% to 20% using (top) chronoamperometry mode and (bottom) AC impedance mode.

We also began development of a CMOS microelectronics chip to perform electrochemical sensor readout. Our first version chip(Haitao et al. 2015) is a power efficient instrumentation circuit with high sensitivity and large dynamic range that combines an input digital modulation technique and a semi-synchronous incremental ΣΔ ADC structure to achieve very high power efficiency over a large dynamic range with high sensitivity. The instrumentation chip was implemented in 0.5µm CMOS technology within an active area of 0.157mm^2, allowing many readout channels within a small chip area. Measurement results demonstrate that 164dB cross-scale dynamic range and 100 fA sensitivity are achieved by the chip will maintaining high power efficiency. A comparison between our chip and other chronoamperometric sensor instrumentation chips shows that we have simultaneously achieved the largest dynamic range, the second best sensitivity and second best power efficiency among reported designs.

Sensor analysis algorithms: Due to selectivity limits, an *array* of gas sensor is often preferred for gas mixture concentration estimation. Several pattern recognition techniques have been used to process gas signals for this purpose. However, most of these techniques are implemented offline in a host computer, not real-time within the sensor system. There is no consensus as to which techniques are the most appropriate for use in a real-time and low power gas sensor system. We performed a thorough analysis on gas sensor array signal processing techniques suitable for implementation within a resource constrained microcontroller. Some of the techniques are only used for gas recognition of individual unknown gases are thus incapable of analyzing gas mixtures and hence concentration estimation. Some of them can provide gas mixture concentration estimation but are beyond the resource constraints of the microcontroller. We found that regression methods are the only feasible technique for establishing a relationship between sensor outputs and gas concentration such that gas concentration is a function of sensor outputs. Different regression methods were implemented in an MSP430 microcontroller with integer point operation. Their computation complexity was evaluated by measuring time to compute the algorithm in a microcontroller. The concentration estimation accuracy of regression methods was evaluated as the number of sensors varied in a sensor array. A metric was also developed to select different number of sensors for improvement of estimation accuracy. By comparing the product of the compute time and the concentration estimation error, the regression tree method and the linear model tree method demonstrated the best performance for a low power and portable gas sensor array system.(Yang and Mason 2012, Yuning et al. 2013)

Conclusion and Future Work:

In this first phase R01 grant, we have developed what appears to be an ideal sensor technology for continuous personal health and safety monitoring in mines that overcomes many challenges plaguing other gas sensors. However, we also identified new research needs to be addressed in further work. For example, our IL sensors exhibit signal drift during long term testing and secondary sensitivities in real world gas mixtures. These are common issues among gas sensors, but by applying our interdisciplinary scientific and engineering understanding of IL sensors, we are confident that we can resolve such challenges using an innovative sensor matrix approach. We have submitted a competitive renewal R01 application with new aims to further advance this promising technology through a combination of sensor-level innovations and novel system-level solutions to advance scientific knowledge of IL sensors and develop the system components and techniques needed to shape this robust technology into an autonomous, portable, low cost system capable of measuring multiple hazardous gases continuously and in real time with pervasive benefit to the safety and health of workers and vulnerable individuals around the globe.

Publications Funded or Funded in Part by This Grant

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