

Room Temperature Ionic-Liquid Electrochemical Gas Sensor Array System for Real-Time Mine Safety Monitoring

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Abstract—This paper presents a real-time, electrochemical gas sensor array system featuring room temperature ionic-liquid interfaces and targeting safety monitoring in underground mines. A prototype system was constructed using a custom ionic-liquid sensor array, a custom multi-mode electrochemical sensor readout board, and a commercial low power microcontroller board. Gas sensors for multiple mine gases were implemented in a 2 by 2 miniaturized array. A novel resource-sharing circuit tailored to our gas sensor array was utilized to significantly decrease power, cost and size while implementing two electrochemical detection modes. The system achieves 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.

Keywords—electrochemical gas sensor array; mine safety

I. INTRODUCTION

The recent escalation in worldwide demand for mined resources, coupled with the rising cost of these resources, has fueled a resurgence of mining operations. This is especially true for energy resources, where the mounting price of oil has sparked a revival of the coal mining industry. However, despite continued safety improvements and increased regulations, underground mines remain a very dangerous work environment because mine workers lack effective real-time protection from multiple potential hazards including explosive and toxic gases like CH₄ and SO₂[1]. To effectively protect all miners throughout the vast underground environment, individuals portable/wearable devices are desperately needed. Such devices should be small size, low power, low cost, easily maintained, and able to detect multiple gas concentrations in the presence of multiple interferences.

Existing commercial mine multiple gas detectors are not suitable for broad individual use due to their high cost (over \$1000), large size and/or large power consumption. In addition, frequent maintenance required by some of these sensors raises their operating cost and lowers their feasibility. A wireless mine gas monitoring system was developed[2], but it can only monitor one gas. A portable gas detection system was built for real-time monitoring[3], but it can not measure all dangerous mine gases. A single-chip gas recognition system has been reported[4], but this device cannot measure gas concentrations. As a result, a new portable/wearable system is urgently needed to measure the concentrations of multiple explosive and toxic gases.

To meet this demand, we have developed an intelligent electrochemical gas analysis system (iEGAS) that can measure multiple mine gases in real time with high sensitivity and good selectivity while providing low power consumption and maintenance free operation. iEGAS features room temperature ionic-liquid (RTIL) interfaces embedded in an electrochemical sensor array, a multi-mode electrochemical instrumentation board (MEIB) that enables orthogonal sensing modes, and embedded sensor array signal processing algorithms to improve selectivity and predict multi-gas concentration in real time. Our team has previously reported RTIL-based electrochemical gas sensors that demonstrate high sensitivity and rapid response to methane and oxygen[5, 6]. This paper reports our latest system design progress with this new gas sensor technology.

II. GAS SENSOR ARRAY SYSTEM DESIGN

A. System Design Methodology

A gas sensor array system consists of four design layers: gas sensor layer, instrumentation electronics layer, sensor array processing algorithm layer and system control layer. The gas sensor layer transduces multiple target gas concentrations into electrical signals. The instrumentation electronics layer produces detection-mode dependent stimulus signals and converts gas sensor response signals to a recordable voltage or current. The array processing layer runs algorithms designed to identify species and quantify concentrations of target gases within a gas mixture. The system control layer stores system configurations, manages communication, and controls the system to enable automatic operation.

To maximize the system performance, a systematic design methodology must be employed across all of the design layers and funneled through a filter of application-critical performance attributes. This design methodology is illustrated in Fig. 1 along with targeted performance goals for a real-time portable multi-gas monitoring device.

B. Gas Sensor Technologies

Within the gas sensor array layer, a technology is needed that can simultaneously achieve small size, low cost, low maintenance, high sensitivity, high specificity, fast response, and low power consumption. The sensor technology choice must also consider the instrumentation electronics, which must adhere to the same requirements as the sensor. In prior

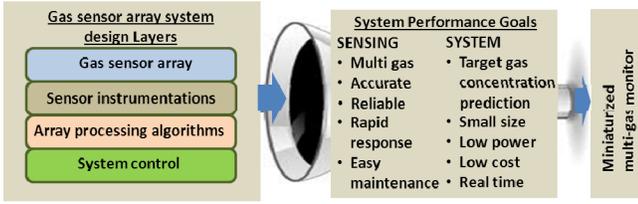


Fig. 1: All functional layers of sensor system need to be funneled through a performance goals filter to generate a system platform with maximum performance.

work [6, 7] we demonstrated that, among the many available gas sensor technologies, RTIL-based electrochemical (EC) sensors were the best option for our real-time portable multi-gas system. EC sensors and instrumentation electronics achieve good selectivity, low power consumption, low cost and wide dynamic range. With properties such as negligible vapor pressure, wide potential windows, high conductivity and high thermal stability, RTILs offer a promising electrolyte for robust EC gas sensors that can operate in extreme conditions and require low maintenance. In addition, RTILs function at room temperature and thus greatly reduce power demands by eliminating the need to heat the sensor. Furthermore, RTIL-based EC sensors have been demonstrated to measure many combustible and toxic gases for human health and safety. Therefore, RTIL-based EC gas sensors technology was chosen in our system for multi-gas measurement.

Among the many EC detection methods, two modes are highly useful for RTIL-based gas sensors. Amperometry mode measures the DC current generated by redox reaction of the target gas in the RTIL electrolyte at an electrode under a fixed or variable potential. Electrochemical impedance spectroscopy (EIS) mode measures AC impedance changes in the double-layer capacitance and the charge-transfer conductance. The sensitivity of an amperometric gas sensor is proportional to its electrochemically active surface and drift over the time. EIS mode can monitor for changes in the active electrode area independent of gas concentrations. Therefore, EIS permits self-monitoring of the sensor's stability and automated calibration for drift mechanisms. For sensors that demonstrate responses to both methods, EIS also provides an orthogonal detection mode to improve reliability.

C. EC Gas Sensor Array Design

The main obstacle to response time in existing RTIL-based EC gas sensors is the slow diffusion of target gases from the RTIL surface to the electrodes [8-10]. To solve this problem, we designed a planar-electrode-on-permeable-membrane (PEoPM) structure that bypasses the slow diffusion of gas across the RTIL. As illustrated in Fig. 2, the electrodes are fabricated directly on a gas-permeable membrane, allowing gas to reach the electrodes/RTIL interface through the permeable membrane, where diffusion is much faster than in the RTIL. To miniaturize the gas sensor, a microfabrication process described in [11] was used to construct the electrodes.

Experiments have shown that the sensitivity and selectivity of the RTIL-EC gas sensor to a specific gas can be

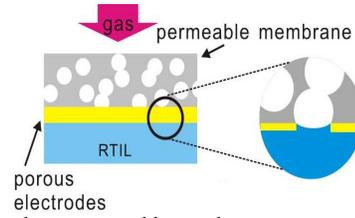


Fig. 2 Electrodes-on-permeable-membrane structure: response time is improved due to fast gas diffusion in the permeable membrane.

optimized by setting a specific DC bias voltage on the sensor. A three-electrode EC cell structure was utilized to maximize the DC bias accuracy on each gas sensor. Experiments also showed that the RTIL based EC sensor requires a long settling time to stabilize the interface after the DC bias is applied or changed. Thus, to create an array of sensors tailored to specific gas targets, each element of the array was biased to different target-specific voltage and held at that potential constantly.

D. Instrumentation Electronics Design

High-resolution instrumentation electronics are needed to maximize the sensitivity of the miniaturized EC sensors. To support the goals of a portable/wearable system, the instrumentation electronics should have low power consumption, small size and low cost. Lock-in techniques can achieve high resolution with low-cost components and small component count [12]. Small component count further decreases the total power consumption, size and cost.

A schematic of the instrumentation electronics developed for four gas detection channels is illustrated in Fig. 3. To minimize interference between the different sensor array elements, four independent potentiostats are provided to control the bias voltage at four independent reference electrode (RE). Similarly, four independent DC bias voltages, V_{dc} , are applied to four separate working electrodes (WEs) to establish independent WE-to-RE biasing potentials. The potentiostats are kept on to maintain sensor bias voltages constantly.

To decrease power consumption, size and cost, a novel resource-sharing instrumentation architecture was developed to share hardware components not only among all the gas sensor array elements but also between different EC detection modes. All of the EC sensor cells share one signal generator (SigGen) that provides detection-mode dependent

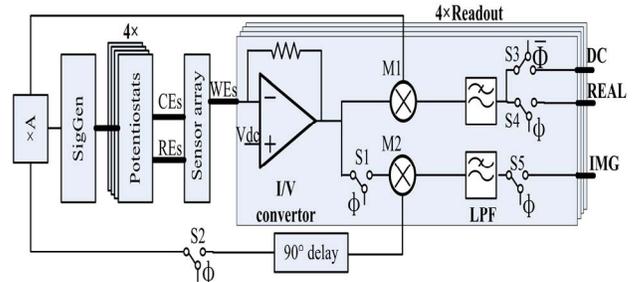


Fig.3 Instrumentation electronics for 4 gas detection channels. In EIS mode, $\Phi=1$. In amperometry mode, $\Phi=0$. LPF is low pass filter. REAL and IMG are sensor impedance's real part and imaginary part output, respectively. DC is amperometry mode output.

stimulus. Current-to-voltage (I/V) converters and low pass filters (LPFs) are shared between amperometry mode and EIS mode and controlled by the switch signal Φ .

In EIS mode, Φ is 1 and all switches except S3 are closed. SigGen generates a 1Hz, 20mV_{pp} sine wave signal to stimulate the gas sensors. This stimulus signal is amplified by A and then inputted to mixer M1 and M2 as reference signals for the lock-in technique. Two LPFs are used to extract the real (REAL) and imaginary (IMG) portions of gas sensor's complex impedance. REAL and IMG can be readily recalculated into impedance amplitude ($|Z|$) and phase angle (θ).

In amperometry mode, Φ is 0 and all switches except S3 are open. SigGen provides a fix DC voltage. Mixer M1 functions as second gain stage to provide a gain of A . Out-of-band noise is removed by LPF to improve readout resolution.

Although several switches are used in this resource-sharing circuit, they are low cost, take very small area and consume almost no power. Furthermore, the switch control signal Φ can readily be generated by system control layer. Table I shows that the resource-sharing instrumentation architecture reduces total components count from $10N$ to $(5N+3)$ for N gas detection channels. As a result, power, cost and size are significantly decreased.

E. System Control and Sensor Array Processing Layer Design

The system control and array processing algorithms layers can be combined and implemented within a microcontroller (μ C). The μ C receives commands from a graphic user interface (GUI) on a PC or smartphone wirelessly or through a USB port. It controls system operation modes, processes sensor array data, generates alerts and sends data back to the GUI. For the iEGAS prototype, the system operation parameters include sensor scan rate, output storage rate, and output reporting rate.

A sensor array processing algorithm is included within the iEGAS design concept to enable identification and quantification of individual gas concentrations within a mixed-gas environment using sensors without perfect selectivity. Our team is developing gas sensor array processing algorithms based on regression models, and initial analysis shows that regression tree algorithm achieves the best figure of merit for iEGAS-like systems [13].

III. SYSTEM IMPLEMENTATION

The PEOPM sensor array was fabricated following the procedure in [11]. To properly separate the electrochemical cells, O-rings were used to confine the RTIL within individual sensor regions. The O-rings and PEOPM sheets were tightly clamped between two rigid boards containing a hole for gas to enter the electrochemical cell. Printed circuit boards (PCB) were used for the lid and substrate because they are mechanically rigid and facilitate wire routing. The RTIL [C4mpy][NTf2] was dropped into each sensor reservoir to create 200 μ m-thick sensing layer. Fig. 4 shows

Table I. Components count of instrumentation electronics

	SigGen	gain stage	90° delay	mixer	LPF	I/V	Total count
a	N	2N	N	2N	3N	N	10N
b	1	1	1	2N	2N	N	5N+3

N: total number of gas detection channels.

a: without resource-sharing.; b: with resource-sharing.

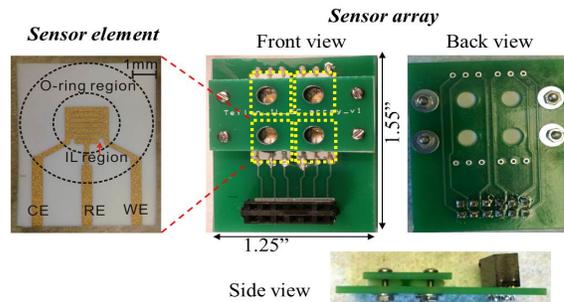


Fig. 4. Miniaturized 2x2 array of PEOPM sensors. Interdigitated electrodes for EC sensors are shown.

the 2x2 PEOPM sensor array that occupies 1.55" x 1.25" including the connector for interface with the MEIB.

A MEIB was constructed using low-power commercial chips in surface mount package to minimize size. An ultra-low-power MSP430 Launchpad (Texas Instruments, TX) μ C board was utilized to control system operation and run array processing algorithms. A prototype iEGAS integrating these components was implemented to demonstrate a small and light-weight device for personal safety monitoring, as shown in Fig. 5.

IV. RESULTS

To characterize the PEOPM sensor array, it was placed within a multi-gas flow control chamber and connected to a VersaSTAT (Princeton Applied Research, TN) EC instrument. EIS measurements were performed for two example gases of interest to mine safety, CH₄ (methane) and O₂. The resulting calibration curves are shown in Fig. 6.

To characterize the response of the overall iEGAS system, the sensor array was connected to the custom MEIB and tested using O₂ as an example target gas. The resulting MEIB outputs in EIS and chronoamperometry mode are

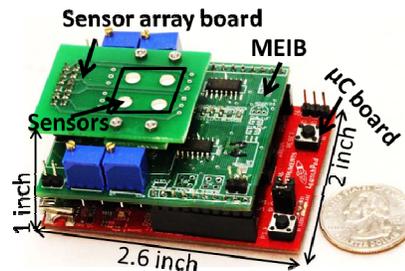


Fig. 5: A prototype iEGAS system with a 4-element RTIL electrochemical sensor array, an MEIB for electrochemical voltage bias and sensor readout, and a μ C board for system control and signal processing algorithms to predict multi-gas concentrations.

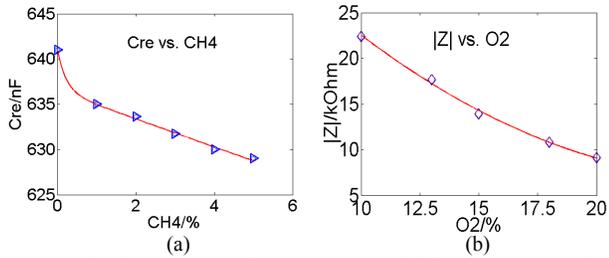


Fig. 6: Calibration curves of EIS response for RTIL electrochemical gas sensor array for (a) capacitance response to CH₄ and (b) impedance magnitude response to O₂.

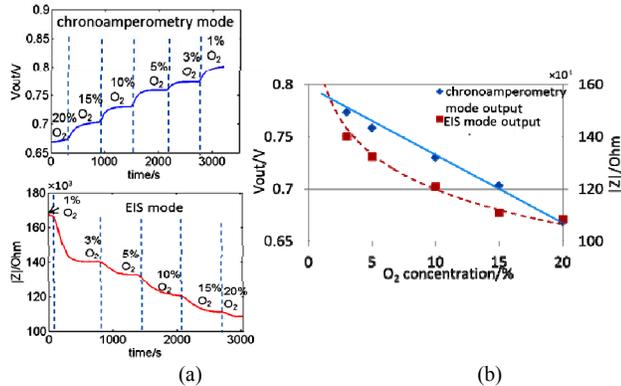


Fig. 7. (a) MEIB outputs for sensor array with O₂ concentration from 1% to 20% using (top) chronoamperometry mode and (bottom) EIS mode. (b) O₂ calibration curves for data in (a). The chronoamperometry O₂ response shows good linearity with an R-squared value of 0.98.

shown in Fig. 7 along with the corresponding calibration curves. From these test results, system and sensor performance were determined and are summarized in Table II. The iEGAS system achieves a maximum response resolution of 0.01% vol in amperometry mode and 0.06% vol in EIS mode for the O₂ example target gas. Additional gases critical to mine safety that are currently under test with the iEGAS system include CH₄, SO₂, NO_x, and CO.

V. CONCLUSION

A unique gas sensor array system featuring room temperature ionic-liquid interfaces and targeting safety monitoring in underground mines was presented in this paper. A systematic design methodology across all of the necessary system layers was employed to achieve several application-critical performance attributes. A prototype system was constructed using a custom miniaturized RTIL sensor array, a custom multi-mode electrochemical sensor instrumentation board, and a commercial low power microcontroller board. A novel resource-sharing instrumentation architecture effectively decreases power, cost and size. The iEGAS prototype system achieves system-level critical performance goals including high resolution gas measurements, demonstrating that it is a suitable platform for further miniaturization toward a wearable multi-gas mine safety monitoring system.

Table II. iEGAS system performance

System		
Dimension	2.6×2×1 inch ³	
Weight	1.6 Oz	
Power (active mode)	6mW	
Power (standby mode)	4mW	
Detection modes	Amperometry Impedance spectroscopy	
Monitored gases	CH ₄ SO ₂ NO ₂ O ₂	
O ₂ response: amperometry mode	Sensitivity: 6.5mV/% Resolution ¹ : 0.01%	
O ₂ response: EIS mode @20% O ₂	Sensitivity: 1.36kohm/% Resolution ¹ : 0.06%	
Sensor	Concentration range	Sensitivity
CH ₄	0%~5%	1.5nF/% @5%
O ₂	1%~20%	0.7kohm/% @20%

¹ resolution = system output noise divided by system sensitivity

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