

# Room Temperature Ionic Liquid Electrochemical Gas Sensor for Rapid Oxygen Detection with Transient Double Potential Amperometry\*

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**Abstract**—Gas monitoring is of great interest due to the critical role gases play in human health and the severe threats they can exhibit to occupational safety. Intense study has been conducted to implement gas sensors with high sensitivity, reliability and long lifetime. Room temperature ionic liquid (RTIL) based electrochemical sensors demonstrate many properties advantageous to these goals. This paper presents a microfabricated gas sensor with an RTIL electrolyte and gold electrode that was characterized for oxygen detection in air. In order to implement fast detection, a porous polytetrafluoroethylene substrate was utilized to increase gas permeability and decrease response time. Furthermore, a transient double potential amperometry (DPA) method was used for electrochemical analysis to greatly reduce measurement time and reverse reaction byproducts that could cause drift. Preliminary results indicate that the RTIL-based electrochemical gas sensor with transient DPA exhibits good sensitivity, linearity and reliability that is promising for practical real-world applications.

**Keywords**—gas sensor; double potential amperometry, room temperature ionic liquid; oxygen detection.

## I. INTRODUCTION

Gas detection in air has been of great interest in recent years due to the significant role gases play in human health and environmental monitoring. Many studies have shown the association between airborne pollutants and mortality caused by respiratory and cardiovascular disease [1]. Oxygen, though nontoxic and inflammable, is essential for human life, a prime factor in explosion risk, and a key parameter in many environmental studies. Hence, a reliable gas sensing technology, particularly one that is miniaturized, low power and low cost, is of great interest for highly distributed and real time deployment.

A great number of approaches have been investigated for gas detection. Metal oxide semiconductor (MOS) gas sensor is one of the most widely studied gas sensors using MOS as the gas sensing material [2]. Unfortunately, in order to implement high sensitivity, a heated filament is generally utilized to increase gas molecule adsorption and promote redox reaction for gas sensing [3]. This heating procedure consequently requires more cost, more power consumption and complicated configurations. Optical sensors have been shown to achieve high sensitivity,

selectivity and low response time with long lifetime in gas sensing. However, their applications are limited due to poor miniaturization and relatively high cost [4]. Compared to other approaches, electrochemical gas sensor provides good sensitivity, selectivity, miniaturization and low power consumption. However, the electrolyte in an electrochemical cell traditionally requires frequent maintenance due to the liquid evaporation. To overcome this barrier, room temperature ionic liquid (RTIL) has been used as the electrolyte due to its high thermal stability, negligible vapor pressure and large working potential window [5]. The downside of RTIL electrolytes is slow gas diffusion and long response time due to high RTIL viscosity [6]. To overcome this limitation, in prior work, we have demonstrated an RTIL gas sensor using a porous polytetrafluoroethylene (PTFE) sensor substrate that gases can easily flow through to decrease the response time [5].

In this paper we present the microfabrication process for the next generation of PTFE-substrate RTIL-electrolyte miniaturized gas sensor. Moreover, instead of conventional constant potential amperometry (CPA), a transient double potential amperometry (DPA) technique is introduced for oxygen sensing utilizing the reversible reaction of oxygen. Using transient currents and reversible reactions, this method was found to provide good repeatability in oxygen sensing with greatly decreased measurement time. Section II presents the gas sensor structure and microfabrication process. Section III mainly describes the transient DPA measurement methodology, and section IV, presents oxygen sensor test results to validate the methodology.

## II. SENSOR DESIGN AND MICROFABRICATION

Porous PTFE offers excellent thermal and chemical stability as well as good permeability in gas sensing. Herein, we used a microporous PTFE (POREX, USA) with 4 $\mu$ m pore size and 35% porosity as the substrate for microfabrication. Gold was utilized as the electrode material due to its good performance in oxygen sensing. To improve adhesion between the gold electrode and the substrate, a titanium adhesion layer was included. Fig. 1 shows the schematic of the microfabricated sensor for oxygen sensing. Three electrodes, working electrode (WE), reference electrode (RE) and counter electrode (CE) were patterned on the porous PTFE substrate. The WE and CE were

Research supported by National Institutes of Health under NIEHS grant R01ES022302.

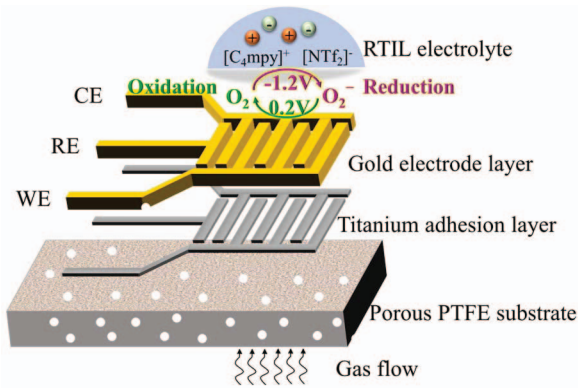


Figure 1. The schematic of the gas sensor for oxygen sensing

designed to be interdigitated with a finger size of  $1.8\text{mm} \times 100\mu\text{m}$  and a gap between fingers of  $250\mu\text{m}$ .  $[\text{C}_4\text{mpy}][\text{NTf}_2]$  was chosen as the RTIL electrolyte due to its good sensitivity and selectivity in oxygen sensing [7]. The RTIL was directly coated on the sensor surface for convenient electrochemical test. A gas inlet was placed on the backside of porous PTFE substrate to permit rapid gas diffusion.

Photolithograph processes were utilized to implement the sensor microfabrication. In brief, the porous PTFE was first fixed on a temporary glass substrate due to the porosity and softness of PTFE that could not be vacuum-attached to the spinner. A photoresist layer (AZ4620) of thickness  $10\mu\text{m}$  was coated on the surface of PTFE with spinning rate 2100rpm for 60s, and the glass substrate was then removed. After soft baking at  $95^\circ\text{C}$  for 5min, the photoresist was patterned through the electrode mask by UV exposure for 45s. The exposed photoresist areas were removed using AZ300 MIF developer for 4min. The metal layers were then deposited on the patterned photoresist by thermal evaporation to form 5nm titanium adhesion layer and 300nm gold electrode layer. Finally, the PTFE was immersed in acetone for more than 12 hours to pattern metal layers via lift-off. The sensor fabrication was completed by rinsing with acetone, IPA and DI water sequentially and drying in pure  $\text{N}_2$ .

The fabricated sensor is shown in Fig. 2(a) mounted on a custom PCB with a connector for convenient external electrical connection. Silver conductive epoxy was used to transfer electrode contacts and bond the device to the PCB. The gas sensor is easily tailorable to fit different shapes and sizes due to the soft substrate. The gas sensor in this study was implemented on a  $9\text{mm} \times 6\text{mm}$  piece of PTFE. The gold electrode was measured by optical microscopy; as shown in Fig. 2b, the gap

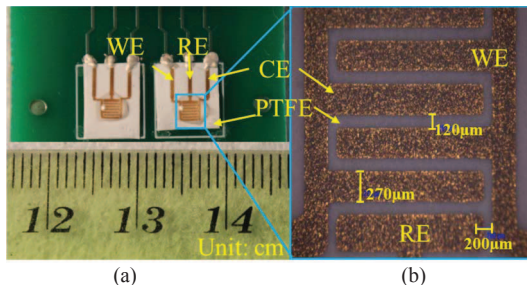


Figure 2. The packaged gas sensor (a) and photo by optical microscope (b)

between fingers is around  $120\mu\text{m}$  and the width of each finger is about  $270\mu\text{m}$ . These dimensions vary slightly from the design because the surface of porous PTFE is very rough and the photomask could not precisely overlap with the substrate.

### III. METHODOLOGY FOR OXYGEN SENSING

In electrochemistry, CPA is a classic method for gas sensing with high sensitivity and wide detection range [8]. However, this method suffers from some problems to be solved. During CPA measurement, a constant potential is continuously applied on the WE, resulting in numerous reaction products accumulating on the sensor surface. Due to the high viscosity of RTIL, these products diffuse slowly from the surface to the bulk solution, which affects the diffusion of target gases and cause current drift in subsequent measurements. Moreover, the CPA requires long time for decaying of charging current. In order to overcome this drawback, a transient DPA method was explored for oxygen sensing, in which a positive potential was intentionally applied periodically to reverse the product of oxygen reactions. The reversible reaction between oxygen and superoxide is given by



A transient current in the decaying phase can be utilized for rapid gas measurement to greatly shorten the measurement time.

Cyclic voltammetry was performed in  $\text{N}_2$  and 100% compressed air to validate the reversibility of oxygen reaction. As shown in Fig. 3, no peak was observed in  $\text{N}_2$ , denoting a clean gas background where no reactions occur. When tested in 100% compressed air, an oxygen reduction peak was observed at  $-1\text{V}$  caused by the one electron transfer reduction of oxygen. The oxidation peak at  $-0.65\text{V}$  is due to the re-oxidation of superoxide to oxygen. This oxidation peak of  $\text{O}_2^-$  also suggests that  $\text{O}_2^-$  is stable in  $[\text{C}_4\text{mpy}][\text{NTf}_2]$  and that no moisture exists in the compressed air since moisture would consume superoxide. An asymmetry of reduction peak and oxidation peak can be observed in Fig. 3 and is attributed to the diffusion rate difference of oxygen and superoxide in RTIL [9]. These cyclic voltammetry results validate that the reverse reaction of superoxide is feasible and the reaction product could be removed by applying a positive potential.

The principle of transient DPA is shown in Fig. 4. An oxidation potential  $E_O$  is first applied on the WE to oxidize reaction products.  $T_O$  indicates the time period  $E_O$  is applied.

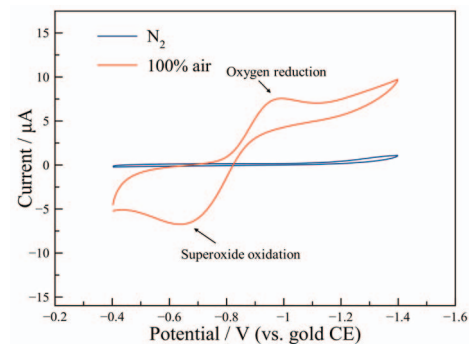


Figure 3. Cyclic voltammetry test of microfabricated gas sensor in  $\text{N}_2$  and 100% compressed air.

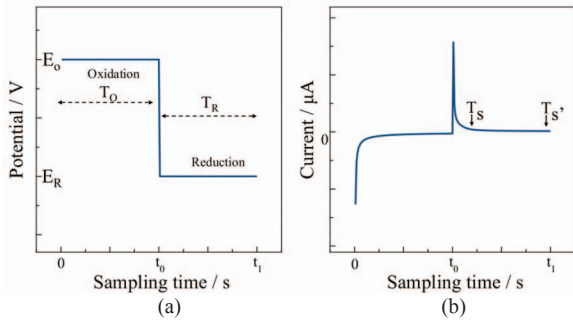


Figure 4. Principle of transient DPA for oxygen detection: (a) the potential vs. time applied on WE; (b) the current response vs. time of WE.  $E_O$ , oxidation potential;  $E_R$ , reduction potential;  $T_O$ , oxidation time;  $T_R$ , reduction time;  $T_S$  and  $T_{S'}$  sampling time after oxidation for oxygen analysis.

Afterward, a reduction potential  $E_R$  is applied for a period of  $T_R$  to implement oxygen reduction. The current response is recorded in both periods and the reduction current is recorded for oxygen analysis. The distinct difference of this method to other work [10] is that a transient current at  $T_S$  is used for gas sensing instead of a stable current at  $T_{S'}$ . In this study, the parameters were set as follows:  $E_O=0.2V$ ,  $E_R=-1.2V$ ,  $T_O=2s$ ,  $T_R=2s$ , and  $T_S$  was studied varying from 0s to 2s.

#### IV. RESULTS AND DISCUSSIONS

In order to validate the function of the microfabricated sensor and the feasibility of transient DPA, the sensor was tested in different air concentrations. To ensure consistent working conditions of gas flow equipment, the lowest concentration was set to 0.1% air instead of pure  $N_2$ . Nine repetitive tests were conducted in each concentration to preliminarily study repeatability of the sensor. The averaged current response in repetitive tests is shown in Fig. 5 at different concentrations. The reduction current decreases very fast due to the exponential decay of charging current. Even though the current is in a decaying phase, the transient current presents a gradient response to different concentrations. Data analysis was

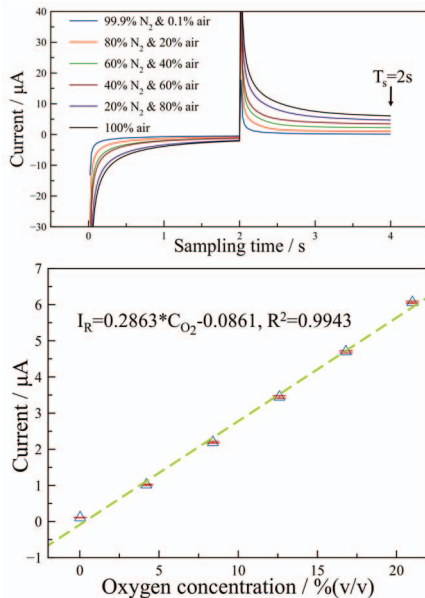


Figure 5. (top) Current response of the gas sensor in different air/oxygen concentrations; (bottom) Calibration curve for oxygen measurement.

performed using MATLAB to measure sensitivity, linearity and repeatability. As  $T_S$  varied from 0s to 2s, sensitivity was found to slowly decrease, but the linearity and repeatability were found to significantly increase. After the exponential decay of charge current, faradic current generated by oxygen reduction dominates and improves the linearity and repeatability. Since charging current is regarded as noise to faradic current in electrochemical analysis, longer decay time also enhances the signal to noise ratio and decreases the limit of detection. (LOD). As a compromise, currents at  $T_S=2s$  were chosen for oxygen calibration.

Assuming that 100% compressed air is equivalent to 21% oxygen, the calibration curve shown in Fig. 5 was generated. The sensitivity of the sensor, defined as the slope of calibration equation, is  $0.2863\mu A/[\%O_2]$  with a linearity of 0.9943. The standard deviation of nine repetitive tests is shown as error bars in each concentration. The largest standard deviation of  $0.010675\mu A$  was observed at 60% air, indicating a resolution of 0.037% for oxygen measurement. The relative standard deviation (RSD) in all tests is below 5%, denoting good repeatability of this gas sensor using transient DPA.

#### CONCLUSION

This paper introduced an RTIL-based microfabricated gas sensor for oxygen measurement using transient double potential amperometry. The feasibility of this new method was validated with good sensitivity, linearity and repeatability. Significantly, this method could reverse the reaction products and greatly shorten the measurement time to 4s. This sensor, together with transient DPA could potentially be implemented in wearable microsystems for real-world gas monitoring.

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