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**MICROFABRICATED
ELECTROCHEMICAL SENSOR FOR
CHEMICAL WARFARE AGENTS:
SMALLER IS BETTER (PREPRINT)**



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and Mark A. Shannon**

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14. ABSTRACT For the last decade, interest in the organophosphate (OP) chemical warfare agents (CWA) sensor has multiplied, especially after the tragic terrorist attack with sarin in Tokyo in 1995. The requirements for OP CWA sensors include: portability - small and light enough to be carried by a person; vapor detection - sample is gas phase, rather than liquid or solid phase; sensitivity - the vapor concentration of the target molecule is in the ppb or below; selectivity (reliability) - minimum false positives. Conventional methods for the detection of gas-phase OP CWA are gas chromatography/mass spectroscopy (GC/MS) and ion mobility spectrometry (IMS). GC/MS is in most cases not suitable for portable applications. IMS has a lower selectivity because the intrinsic detection mechanism of IMS is not based on the chemical nature of the target molecule. The objectives of this work are 1) to study the oxime-based electrochemical sensor in a beaker cell and 2) to fabricate a micro-scale gas-liquid interface so that the oxime-based sensor can be miniaturized into a small-sized device.					
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MICROFABRICATED ELECTROCHEMICAL SENSOR FOR CHEMICAL WARFARE AGENTS: SMALLER IS BETTER

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Abstract: A novel type of gas chemical sensor is fabricated by combining microfabrication techniques and electrochemical transducer. The microchannel sensor we built is composed of liquid/gas microchannels separated by a nanoporous membrane. When oxime chemistry is adapted into the microchannel sensor, it gives response of hundreds of mV to trace vapor (10 ppb) of chemical warfare agent simulants within ~10 sec. Double microchannel design further reduces potential drift and simplifies the sensor setup.

Keywords: electrochemical gas sensor, chemical warfare agent, multiphase microreactor

1. INTRODUCTION

For the last decade, interest in the organophosphate (OP) chemical warfare agents (CWA) sensor has multiplied, especially after the tragic terrorist attack with sarin in Tokyo in 1995. The requirements for OP CWA sensors include:

- Portability – small and light enough to be carried by a person
- Vapor detection – sample is gas phase, rather than liquid or solid phase.
- Sensitivity – the vapor concentration of the target molecule is in the ppb or below
- Selectivity (reliability) – minimum false positives

Conventional methods for the detection of gas-phase OP CWA are gas chromatography/mass spectroscopy (GC/MS) and ion mobility spectrometry (IMS).[1] GC/MS is in most cases not suitable for portable applications. IMS has a lower selectivity because the intrinsic detection mechanism of IMS is not based on the chemical nature of the target molecule.

The objectives of this work are 1) to study the oxime-based electrochemical sensor in a beaker cell and 2) to fabricate a micro-scale gas-liquid interface so that the oxime-based sensor can be miniaturized into a small-sized device. Compared to the macro-scale beaker cell, the microfabricated sensor exhibits the miniaturization advantages, such as faster response, reduced reagent consumption, and enhanced portability.

2. RESULTS AND DISCUSSION

Fig. 1 shows the mechanism of the reaction of keto-oximes with OP compounds. [2, 3] The keto-oximes hydrolyze OP CWA and its simulants. It is proposed that the oximate anion reacts with sarin into an intermediate phosphonylated oxime. The intermediate then reacts rapidly with hydroxide ion to produce an equivalent amount of cyanide ion. The produced cyanide can be detected with a potentiometry electrode. [4]

Fig. 2 shows the typical response of the oxime-based electrochemical OP sensor. Initially the electrode potential of cyanide selective electrode (CN ISE) is stable at about -70 mV. When 50 μ M acetic anhydride (AA), which is a good

simulant to test the oxime chemistry, is added to the cell at $t = 0$ s, the electrode potential decreases rapidly and reaches the final value of -230 mV after about 1 min.

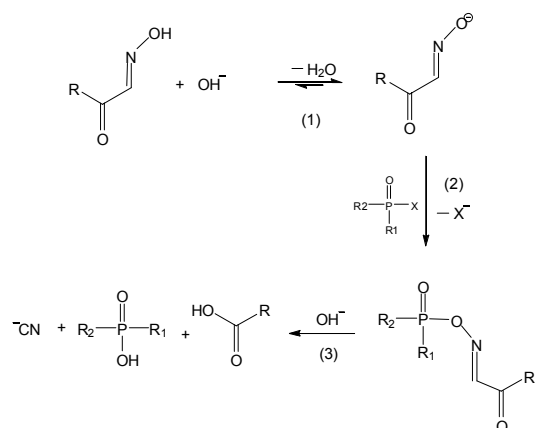


Figure 1. Mechanism of reaction between monoketo-oxime and organophosphate compound

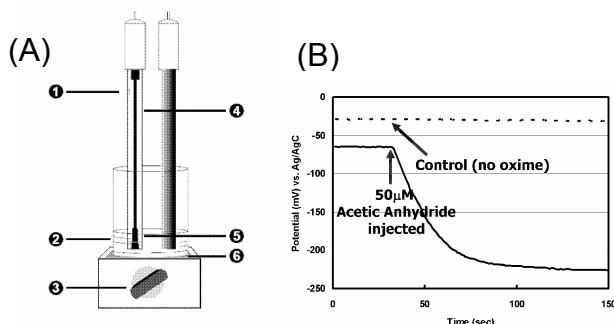


Figure 2 (A) A beaker cell with a cyanide-sensitive electrode (CN ISE) in oxime solution (B) Electrode potential response of CN ISE in 5mM 1-phenyl-1,2,3-butanetrione 2-oxime (PBO) + 25mM borate buffer (pH=10). Straight: 50 μM acetic anhydride injected at $t = 0$ s. Dashed: control experiment. 50 μM acetic anhydride injected at $t = 0$ s into blank 25mM borate buffer (pH=10) in the absence of oxime

We created a multi-phase microchemical reactor that implements a micro-scale gas-liquid interface, using a dual microchannel/membrane design. (Fig. 3) A hydrophobic nanoporous membrane is sandwiched between the liquid microchannel and the gas microchannel. A thin layer of electrode material is coated on the membrane or inside the microchannel so that electrochemical responses can be measured from the electrode.

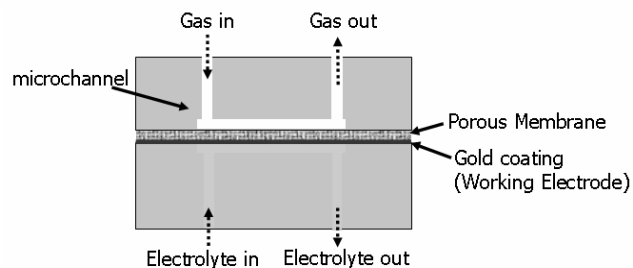


Figure 3. Schematics of the microchannel sensor

Fig. 4 demonstrates that the dual microchannel/membrane design can be used as a fast and sensitive gas sensor. The liquid microchannel contains the oxime solution and the gas channel passes a trace (10ppb) acetic anhydride vapor. The acetic anhydride dissolves into the liquid microchannel, reacts with the oxime, and produces cyanide anion, which gives the electrochemical response. The mass transfer of the gas molecules into the liquid microchannels is efficient, thus leading to a fast potential response of the electrode. (approximately 10 seconds) The liquid volume inside the microchannel is small (ca. 500nL) such that the reaction product (cyanide ion) is concentrated inside the microchannel, enhancing the magnitude of the potential response.

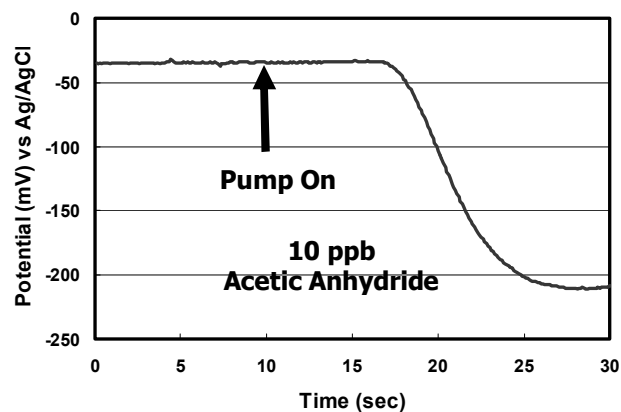


Figure 4. Electrode potential response of the microchannel sensor. Liquid channel contains in 5mM PBO + 25mM borate buffer (pH=10). 10 ppb acetic anhydride vapor is passed along the gas channel at 10mL/min.

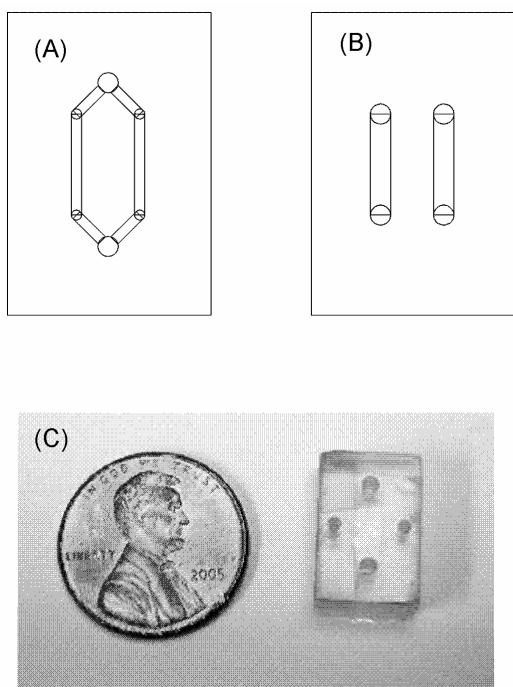


Figure 5. Double microchannel design. (A) Liquid microchannel. (width = $500\ \mu\text{m}$; depth = $100\ \mu\text{m}$) (B) Gas microchannel. (width = $1000\ \mu\text{m}$; depth = $100\ \mu\text{m}$) (C) An optical microscope image of the assembled microchannel sensor.

Now that we demonstrated that the microchannel/membrane design can function as an efficient gas sensor, we moved one step forward and built a double microchannel sensor, as shown in Fig. 5. The disadvantages of the single microchannel sensor are that a separate reference electrode is required outside the sensor assembly and a potential drift is often observed when the open-circuit potential of a single electrode is measured. However, when an additional reference microchannel/electrode is incorporated in the double microchannel design, no separate reference electrode is required. Furthermore, any potential drift of the working electrode is cancelled out by the same drift of the reference electrode, dramatically reducing the overall potential drift and setting the initial output potential from the sensor assembly to close to 0.

Fig. 6 shows a stand-alone sensor package, in which the inlet and the outlet of the double microchannel sensor are connected to the liquid

source and drain, respectively. Also, the working and the reference electrodes are connected to the miniature amplifier/filter electronics.

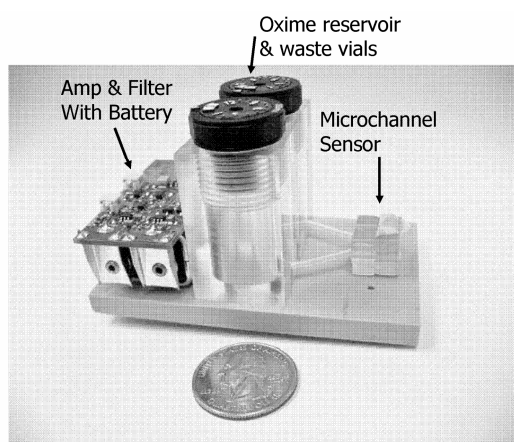


Figure 6. A photograph of the stand-alone sensor package. The package is composed of a double microchannel sensor, vials for liquid source and drain, and battery-operated miniature amplifier/filter electronics.

Fig. 7 shows the potentials response from the double microchannel sensor package. Initially, the potential output from the amplifier/filter is adjusted close to zero. At $t = 10\ \text{sec}$, $10\ \text{ppb}$ acetic anhydride vapor begins to flow along the gas microchannel. Approximately 20 sec after the onset of the gas flow, the potential increases by $\sim 500\ \text{mV}$. When the potential reaches $\sim 500\ \text{mV}$, the gas flow is stopped. A few seconds after the gas flow is stopped, the potential begins to decrease and, about 1min after the gas flow is stopped, becomes less than $100\ \text{mV}$. After the regeneration, the sensor can be used again, as shown in Fig. 7(A). Fig. 7 (B) shows the long term stability of the sensor response. The baseline of the response is measured over a period of 12 hours. The baseline of the response is quite stable and the variation range is less than $15\ \text{mV}$.

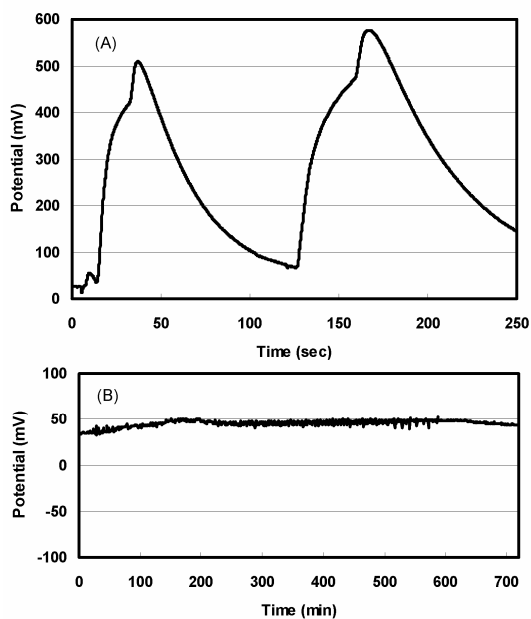


Figure 7. Potential response from the double microchannel sensor package. (A) Initially, the potential output from the amplifier/filter is adjusted close to zero. At $t = 10$ sec, 10ppb acetic anhydride vapor is introduced into the gas microchannel. When the potential response reaches ~ 500 mV, the gas flow is stopped. After regeneration, ($t = 120$ sec) the sensor can be used again, as shown in Fig. 6(A). (B) A long term stability of the sensor response. The baseline of the response is measured over a period of 12 hours. The baseline of the response is quite stable and the variation range is less than 15 mV.

3. Conclusion

A multiphase microreactor is fabricated with gas and liquid microchannels separated by a nanoporous membrane. Mass transfer of gas samples into the liquid electrolyte is fast enough that the microchannel/membrane assembly can be used as a fast and sensitive gas sensor. It was showed that, when the oxime chemistry is adapted into the microchannel sensor, the microchannel sensor gives response to the organophosphate CWA simulants. It was demonstrated that the double microchannel design has such advantages as reduced drift and incorporation of reference electrode into the assembly.

4. References

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