A MEMS PHOSPHONATE SENSOR

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ABSTRACT

The objective of this paper is to report the modeling and optimization of a new MEMS- based phosphonate sensor that utilizes a porous membrane between a gas and a liquid stream to allow operation at low liquid and high gas flow rates. Previous work from our laboratory has demonstrated that phosphonate molecules can be detected with such a device, but the sensitivity was insufficient for certain applications (e.g. detection of pesticides in foodstuffs). In this paper COMSOL simulations and design of experiments were used to optimize the device. We find that both the simulation and the experiment show that i) the size and hydrophilicity of the pores in the membranes and ii) the liquid channel height make the most difference to the sensor response. For example, we calculate that the response increases by 80 mV/mm as the channel depth decreases and the experiments show a 296 mV/mm change for decreased channel depths. Also, by optimizing the geometry the sensitivity of the device could be enhanced. The optimized device can detect 10^9 molecules with good signal to noise.

INTRODUCTION

A multiphase microchemical system, by definition, contains processes occurring at an interface of two or more phases (gas, liquid, solid)[1]. The design and fabrication of a gas-liquid interface is especially difficult because, unlike solid-gas or solid-liquid interfaces, both media are fluidic and hard to control. There are two main strategies for the fabrication of micro-channel gas-liquid interfaces: 1) gas-liquid segmented flow [2-8] and 2) gas-liquid parallel flow [9-12]. Gas-liquid segmented flow was used by Jensen to take advantage of the shortened liquid diffusion distances in order to resolve fast transient responses in cell signaling networks [4]. Previously published research reported by Kobayashi et al used a gas-liquid parallel flow regime to perform hydrogenation of benzalacetone on a palladium catalyst [10]. In order to create gas-liquid parallel flow, Kobayashi *et al* functionalized the channel walls into hydrophilic and hydrophobic regions. The liquid then flows near the hydrophilic walls, while the gas stays in the hydrophobic regions.

Recently we reported on a sensor that utilizes a micro-scale gas-liquid interface to create a multiphase micro-reactor for selective vapor detection [13, 14]. Our previous work studied the use of liquid acetylcholinesterase biochemistry and oxime chemistry to selectively detect trace amounts of phosphonate vapor. From these micro-reactors it was determined that the mass-transport of vapor molecules across the gas-liquid interface is rapid enough that the micro-reactor design can be used as a viable, rapid-response phosphonate detector. The results also show that specific liquid chemistry provides the sensitivity and selectivity needed to lower the detection limit and detection time when compared with previous methods. Before such a sensor can be developed into a reproducible device, however, there is a need to study the effect of various geometric reactor parameters on response and to more accurately understand the underlying transport phenomena in the system.

EXPERIMENTAL METHODS

Fabrication of Micro-channel Sensor

The assembly of the micro-channel sensor involves three steps: 1) fabrication of micro-channels, 2) deposition of the electrode onto a nanoporous membrane, and 3) assembly of the gas and liquid micro-channels and the nanoporous membrane. The micro-channels were machined into a small polycarbonate block. To coat the membrane with an electrode material, track-etch polycarbonate membranes of various pore size (thickness 10 μ m; SPI) are sputtered with a 40-nm thick layer of gold on the side of the liquid micro-channel. Some track-etch membranes are purchased with a hydrophilic poly(vinyl pyrrolidone) (PVP) coating. The gas micro-channel is made to overlap the liquid micro-channel. The membrane is sandwiched between the two polycarbonate micro-channels and the assembly is clamped using 5 screws. A picture of the final assembly is found in Figure 1A.

A)

B)

Figure 1: A) Cross-sectional view of the phosphonate sensor. The upper channel is the liquid micro-channel (0.25 mm wide by 0.1 mm deep). The lower channel is the vapor micro-channel (0.25 mm wide by 0.1 mm deep). The two micro-channels are separated by a nanoporous polycarbonate membrane (0.006 mm thick). The lower micro-channel was distorted during cutting. B) Schematic of silicon design. Oxime solution enters the liquid microchannel and is separated from the gas by a hydrophobic membrane.

Figure 1B shows a schematic of a Si based phosphonate sensor. The sensor is composed of three parts: Si/SiO₂ pore layer, liquid microchannel, and gas microchannel. The middle layer is the 6x6 circular straight Si pore with about 100 microns diameter. An SOI (silicon on insulator) wafer is etched using KOH wet etch and ICP-DRIE process leaving a membrane. After cleaning in a piranha solution, the Si pore surface is made hydrophobic with FDTs (perfluorodecyltrichlorosilane) in an MVD (molecular vapor

deposition) process. The Si pore is filled with photoresist and sputtered with 40-nm gold layer so that only the top surface of the Si pore is coated with gold. After removing the photoresist with organic solvent, liquid and gas microchannels are attached to the Si pore layer.

Testing of Micro-channel Sensor

The testing set-up of the oxime sensor is taken from our previous work by Oh et al [14]. The oxime solution is passed along the liquid micro-channel using a manually-operated syringe. During electrochemical measurements, the liquid in the micro-channel remains stagnant. The vapor sample is introduced into the gas micro-channel using a syringe pump containing the diluted chemical sample at the flow rate of 1 mL/min. The open-circuit potential between the working electrode and the reference electrode is measured as the output signal from the micro-channel sensor.

NUMERICAL SIMULATION

A numerical simulation of cyanide concentration in the liquid micro-channel and phosphonate concentration in the vapor micro-channel was performed over a range of channel geometry, membrane pore size, and pore hydrophilicity using COMSOL Multiphysics 3.3 with the Chemical Engineering Module. The vapor and liquid micro-channels can be considered two-dimensional and possessing fluidics which are incompressible and low-Reynolds number. There is no flow parallel to the membrane in the liquid micro-channel and only diffusive transport perpendicular to the membrane is considered in the liquid micro-channel and through the membrane itself.

The constants used in the simulation are as follows. Air and liquid diffusion coefficients of $D_{\text{gas}} = 0.01 \text{ cm}^2/\text{sec}$ and $D_{\text{liquid}} = 1 \times 10^{-5} \text{ cm}^2/\text{sec}$ were used [15]. The diffusivity of phosphonate vapor through a hydrophobic membrane, D_m , was estimated using a model for gas diffusion in porous media [16]:

$$D_m = D_{\text{gas}} \varepsilon^{\frac{4}{3}} \quad (1)$$

where ε is the porosity of the nanoporous membrane. Porosity varies with the size of the pore in the nanoporous membrane.

RESULTS AND DISCUSSION

Numerical Simulation

Figure 2 shows simulations of how the phosphate concentration should vary perpendicularly to the membrane at a point 0.125 cm from the leading edge of a 0.0075 cm deep 0.25 cm long microchannel covered by a 0.0006 cm thick membrane with 50 nm hydrophobic pores. In this simulation, the liquid micro-channel contains 10 mM oxime solution and 1 cm³/min of gas containing 100 ppb of analyte flows in the vapor micro-channel. Notice that the analyte concentration is almost constant in the gas phase then decays exponentially into the liquid. These results suggest that most of the mass transfer resistance is in the liquid side of the membrane, since diffusivities are so much higher in the gas phase than in the liquid.

Figure 3 shows simulations results for the effect of pore size in the nanoporous membrane on sensor response for a micro-channel 0.25 mm wide, 0.1 mm deep, and 5 mm long with hydrophobic pores. Notice as pore size increases from 10 nm to 50 nm the sensor response increases in the form of cyanide ion concentration. These results show that mass-transport across the membrane increases with larger pores due to an increase in open surface area and therefore porosity of the nanoporous membrane. The larger open surface area increases the gas-liquid interface and

allows more phosphate molecules to cross into the liquid microchannel.

Figure 4 shows the effect of channel depth on sensor response from the COMSOL simulation for a micro-channel 0.25 mm wide and 1 cm long with 50 nm hydrophobic pores. Notice as the channel depth decreases from 0.2 to 0.05 mm the sensor response increases in the form of increased cyanide concentration. The increase in response may be due to a build up of cyanide ions or phosphate molecules near the gas-liquid interface caused by a smaller amount of liquid in reduced channel depths.

Figure 2: Simulation results for concentration profile of phosphonate concentration along channel depth

Figure 3: Simulation results for the effect of pore size of the nanoporous membrane on sensor response. The micro-channel dimensions and analyte concentration were the same as the experimental set-up. The simulation results also show that with an increase in pore size from 10 nm to 50 nm there is an increase in sensor response in the form of an increase in cyanide ion concentration. These results indicate that the mass transfer through the pore is faster with larger pores, leading to a faster response.

Experimental Results

After study of the statistical analysis of the COMSOL simulation, a design of experiments was completed. From the simulation results it was noted that varying channel length and channel width did not have a large effect on sensor response while varying channel depth, pore size, and pore hydrophilicity greatly affected response (channel width was varied in our two-dimensional simulation by varying the superficial velocity). Testing of the oxime microreactor focused on changing channel geometry, pore size, and membrane coatings to determine the effect of each on sensor response.

Figure 5 shows experimental results for the effect of the pore size in the nanoporous membrane on sensor response for a liquid microchannel 0.25 mm wide, 0.10 mm deep. Notice that as the pore size increases from 10 nm to 50 nm the response of the sensor also increases from 11 mV to 60 mV (Pore sizes above 50 nm could not be tested due to flooding of the oxime solution into the vapor micro-channel). These results show that mass-transport across the membrane increases with larger pores due to an increase in open surface area and therefore porosity of the nanoporous membrane. The larger open surface area increases the gas-liquid interface and allows more phosphate molecules to cross into the liquid microchannel.

Figure 4: Simulation results for the effect of channel depth on cyanide ion concentration for a micro-channel that is 0.25 mm wide and 1 cm long. The liquid micro-channel contains 10 mM oxime solution in borate buffer (pH=10) with 100 ppb analyte gas at a flow rate of 1 cm³/min in the vapor micro-channel. As the channel depth decreases from 0.05 mm to 0.1 mm the cyanide ion concentration increases. This result may be due to an increased build-up of cyanide ions at the electrode surface for smaller channel depths.

Figure 5: Experimental results for the effect of pore size of the nanoporous membrane on sensor response. The liquid micro-channel (250 μ m wide x 100 μ m deep x 0.5 cm long) contains 10 mM oxime solution in borate buffer (pH=10) with 100 ppb analyte gas at a flow rate of 1 cm³/min in the vapor micro-channel. As the pore size increases from 10 nm to 50 nm the response of the sensor also increases from 11 mV to 60 mV.

The effect of channel depth on sensor response is shown in Figure 6. Notice that as the channel depth decreases from 0.05 mm to 0.2 mm the sensor response increases, for all channel widths. These results may be due to an increased build-up of cyanide ions or phosphate molecules at the electrode surface for smaller channel depths.

The effect of vapor residence time on the microreactor was also studied. Figure 7 shows that a longer residence time does not affect sensor response experimentally.

Comparison of Simulation and Experiment

A comparison of the statistical analysis of numerical simulation and experimental data is shown in Table 1. Notice in both experimental results and numerical simulations, varying the channel length and channel width had little to no effect on sensor response. Experiments show that the effect of channel width is only seen at widths less than 0.025 mm and at small channel depths. This result may be caused by entrance effects into the gas micro-channel that are not accounted for in our two-dimensional simulation. Conversely, channel depth has a large effect on sensor response. These results show that one rate-limiting step for phosphonate diffusion is perpendicular to the nanoporous membrane, and depth of the micro-channel is an important factor in sensor design.

Table 1 also shows that residence time also has little effect on the response of the sensor. This trend is due to the saturation of the gas-liquid interface with phosphonate molecules. Most importantly, this trend shows that a rate determining step in phosphonate molecule transport occurs at the gas-liquid interface and the pore size and pore hydrophilicity of the nanoporous membrane are therefore extremely important.

Figure 6: Experimental results for the effect of channel depth on sensor response. The liquid micro-channel is 0.5 cm long and the depth and width of the channel are varied (pore size = 50 nm). The liquid micro-channel contains 10 mM oxime solution in borate buffer (pH=10) with 100 ppb analyte gas at a flow rate of 1 cm³/min in the vapor micro-channel. As the channel depth decreases from 0.05 mm to 0.2 mm the sensor response increases, for all channel widths. This result may be due to an increased build-up of cyanide ions at the electrode surface for smaller channel depths.

Accordingly, Table 1 shows that increasing pore size has the largest affect on sensor response. This result shows that increasing the surface area of the gas-liquid interface has a large impact on sensor response. Also, in our simulation results, hydrophobic pores showed higher sensor response than hydrophilic pores due to wetting of the pores with oxime solution. In our experimental analysis, however, we were not able to test hydrophilic pores due to flooding of the gas micro-channel. This is most likely caused by the slight hydrophilic nature of the polycarbonate membrane and from contact angle measurements PVP-free polycarbonate membranes sputtered with gold still wick the pores with oxime solution and provide a lower sensor response. Using a more hydrophobic membrane should prevent wetting of the membrane with oxime solution and further improve sensor response.

CONCLUSIONS

In this study a numerical simulation of a multi-phase microreactor for use as a phosphonate sensor was created. The simulation was used to design a set of experimental conditions, in order to further optimize the microreactor. The experimental results were then compared to the numerical simulation to further understand the underlying transport phenomenon. From the results, a microreactor with a 0.05 mm channel depth, 0.25 mm channel width, and 50 nm PVP-free nanoporous membranes provided the best sensor response. After the optimization of the sensor geometry the detection limit of our sensor has decreased from 10^{11} to 10^9 phosphonate molecules.

Figure 7: Experimental results for the effect of vapor residence time on sensor response. The liquid micro-channel contains 10 μ M oxime solution in borate buffer (pH=10) with 100 ppb phosphonate analyte gas at a flow rate of 1 cm^3/min in the vapor micro-channel. Vapor residence time has very little effect on the sensor response with an average potential response of 73 mV and a standard deviation of 8.5 mV. This trend is also found from simulation results.

Both experimental results and numerical simulation show that a decrease in channel depth and an increase in pore size allow for faster mass-transport and faster sensor response. Comparison of experimental results and numerical simulations also shows that the PVP-free membranes treated with gold are wetted with oxime solution and preventing the fastest possible mass-transport of vapor molecules across the nanoporous membrane.

Table 1: Comparison of experimental data to simulation results for varying geometric reactor parameters.

Geometric Parameter	Range studied	Calculated slope	Measured Slope
Residence time	0.05 to 0.5 msec	0	0.004 ± 0.26 mV/ms
Channel length	1 mm to 8 mm	0	0.5 ± 2.0 mV/mm
Channel width	0.25 to 1 mm	0	18 ± 52 mV/mm
Channel depth	0.05 to 0.25 mm	-80 mV/mm	-296 ± 90 mV/mm
Pore size	10 to 100 nm	125 ± 38 mV/ μm	1225 ± 400 mV/ μm
Pore hydrophilicity	hydrophilic to hydrophobic	38 mV/change	Hydrophilic membrane leaked

The results from this study show that future work should be done to fabricate the microreactor in silicon wafers, such as in Figure 1B. For polycarbonate machining, 0.05 mm is the lower limit of channel depth. However, by moving the sensor into a silicon wafer we can create smaller channels and may be able to

further improve sensor response. Also, by creating a porous membrane with a silicon wafer we can create a more hydrophobic membrane with larger pores.

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