CREATING A GAS-LIQUID INTERFACE IN A MICROCHANNEL USING POROUS POLYDIMETHYLSILOXANE (PDMS)

Xiang Ren^{1*}, Miao Yu¹, Hongseok (Moses) Noh¹, and Jack G. Zhou¹

¹Drexel University, Philadelphia, Pennsylvania, USA

ABSTRACT

In order to realize gas-liquid interface in microchannel, porous polydimethylsiloxane (PDMS) was fabricated and assembled with microchannels. Carbon dioxide absorption was used to demonstrate the effect of the gas-liquid interface. The carbon dioxide absorption was determined by pH color indicator and Matlab image processing method. The results demonstrated that the carbon dioxide was able to pass through the porous PDMS and be dissolved into the fluid with little water leakage and evaporation.

INTRODUCTION

There is an increasing need for creating a gas-liquid interface in lab-on-a-chip community. Devices for cell culture [1, 2], recreation of organ models [3], and cell-based sensing [4] often require certain gas compositions in the microfluidic environment (e.g. a lung-on-a-chip device demand an accurate gas-liquid interface to simulate the functional unit of the organs [5]). Another example is an artificial photosynthesis system for energy harvesting that requires constant supply of carbon dioxide (CO₂) [6, 7]; at the same time, an artificial photosynthesis system requires for little water evaporation as a chemical reaction unit without keeping living cells inside. Currently, creating a gas-liquid interface in microfluidic channels remains challenging. This paper reports a novel way of creating a gas-liquid interface using porous PDMS. Porous PDMS provides enough contact between gas and liquid media while effectively preventing water leakage and evaporation due to its hydrophobic property [8]. To study the feasibility of porous PDMS as interface media, carbon dioxide absorption was analyzed. The experimental results indicated that our gas-liquid interface made with porous PDMS could allow CO₂ penetration while preventing water leakage and evaporation.

GAS-LIQUID INTERFACE

Device Structure

To study the performance of porous PDMS as a gas-liquid interface media, we separated the two microchannels by a porous PDMS layer (Figure 1). CO₂, which can be dissolved in water, was selected to test the performance of our gas-liquid interface. The porous PDMS (see below for its fabrication) was "locked" in to solid PDMS layers as shown in Figure 1. Extra solid PDMS surrounding the porous PDMS was necessary for this purpose and it was permanently bonded to the middle layer PDMS after plasma treatment.

Figure 1: Cross-sectional view of the device constructed to test the gas-liquid interface created by porous PDMS.

CO₂ was introduced into the lower layer of the microchannel. CO₂ molecules penetrated through the porous PDMS layer, and then continuously diffused into the fluid in the upper channel. A pH sensitive pigment was added in the fluid to monitor the color change during the CO₂ absorption process.

Porous PDMS

Porous PDMS was fabricated by sugar leaching technique where sugar cubes were used as sacrificial materials (Figure 1) [9, 10]. The sugar particles in sugar cubes were connected together; therefore, the created porous PDMS had interconnected micro pores after the removal of sugar.

A mixture of PDMS pre-polymer (Sylgard[®] 184 silicone elastomer, Dow Corning) and curing agent (Sylgard[®] 184 silicone elastomer curing agent, Dow Corning) were mixed at 10:1 mass ratio and degassed in vacuum. Sugar cubes (15×15×10 mm³) were then immersed in the mixture with a depth of 3 mm in a vacuum container for 1 hour allowing the sugar cubes fully filled with PDMS by capillary effect. The PDMS with sugar cube was then cured in an oven at 60°C for 24 hours. The cured PDMS-sugar cubes were cut into a cylindrical disc shape (diameter = 3 mm, height = 2 mm) and washed in 50°C water to remove the sugar followed by air dry. As shown in Figure 2b, the surface of porous PDMS was still hydrophobic.

Figure 2: (a) Picture of porous PDMS; (b) Porous PDMS's hydrophobic property; (c) Optical microscope image of porous PDMS.

Two main properties that characterize porous structures are porosity and average pore size. The average pore size could be roughly observed by the optical microscope image of the cross-section of the porous PDMS (Figure 2c), which was around 150~200 μm. The porosity was defined as the empty space volume over the total volume of a material. By measuring the mass of a certain block of porous PDMS, we could calculate the existing PDMS volume (the pure PDMS's density is 0.965×10³ kg/m³). The PDMS block's volume was measured by the out profile's dimensions. We measured 20 different porous PDMS samples to reduce the errors. The porosity of the porous PDMS was calculated as 69.8±0.2%.

Microchannel Fabrication

The porous PDMS was then sealed inside PDMS channels

manufactured by stereolithographically defined molds (Figure 3). The PDMS microchannels served as gas channel and liquid channel (Figure 4).

Figure 3: Stereolithography mold for PDMS microchannels.

The mold for PDMS replica was made of a photo-sensitive polymer (Photosilver, EnvisionTec) using stereolithography machine (EnvisionTEC, model Perfactory, Germany; voxel resolution: 35 μm). After the mold was prepared, the standard PDMS replica molding was used to fabricate the microchannels. PDMS pre-polymer and the curing agent were mixed at a weight ratio of 10:1. The mixture was then placed in a vacuum container for 30 min to remove all the air bubbles. The degassed PDMS mixture was poured onto the mold and placed in a 60°C oven for 24 hours for the solidification of PDMS.

After fabricating the top microfluidic channel, bottom gas channel, and middle layer porous PDMS holder (porous PDMS are partially sealed inside), three layers of PDMS were permanently bonded after plasma treatment (Covance, Femto Science, South Korea).

CO₂ Measurement

Bromothymol blue solution (BBS, SigmaAldrich) was used as CO₂ absorption indicator [11]. BBS contains stable pigments that will not have any chemical reactions with either water or CO₂. The color of BBS depends on the solution's pH value: pH > 7.6 (blue); 6.0 < pH < 7.6 (green); pH < 6.0 (yellow). The microchannel inlet was connected to a syringe with BBS. The water's initial color is adjusted to blue by adding pH buffers, in order to reach the largest capacity of CO₂ absorption and the corresponding pH value change.

The color alteration of the BBS was monitored over time at different flow rates (8~30 $\mu\text{L}/\text{min}$) in addition to the static condition. However, if using the color change from blue to green to yellow to identify the pH, the data is not accurate enough to calculate the exact amount of CO₂ absorbed. Therefore, we recorded the video of the color change process, and used Matlab to analyze the pixels of the color changing region. PDMS is clear and optically transparent to any light wavelength of 240~1100 nm, which contained the BBS color change wavelength.

EXPERIMENT

In order to test the gas-liquid interface performance, the liquid with BBS was applied to one channel using a syringe pump, and CO₂ was imported to the other channel using a glass flask filled with dry ice. The flow rate of CO₂ was considered constant during the dry ice sublimation because of the significant smaller gas channel volume compared to the glass flask.

The fluid with BBS was connected to the inlet. Syringe pump (Harvard Apparatus Pump 33, Holliston, MA) was set with a flow rate from 8~30 $\mu\text{L}/\text{min}$ with a step of 2 $\mu\text{L}/\text{min}$. The whole color change was recorded by a high-resolution camera for further image processing. Therefore, a white background was placed behind the experimental device, and the lighting conditions as well as the camera were fixed during all the experiment process.

(a) Before CO₂ introduction

(b) After CO₂ introduction

(c) BBS color chart

Figure 4: BBS color alteration before and after introducing CO₂.

However, the flow rate should be moderate; otherwise, the pressure tends to increase with higher flow rate. Once the pressure reached the maximum threshold that the porous PDMS could hold, the fluid would overcome the hydrophobic resistance of the porous PDMS layer and penetrate through the layer.

RESULTS

The color images were imported into Matlab and isolated into red, green, and blue (RGB) color maps (Figure 6). By comparing the data of gray map and RGB map, the fluid's color was represented by relative intensity numbers from 0 to 255. The algorithm we used was demonstrated in Figure 5 by flow chart. The first step was changing the video into image frames. The "mov" file was changed into "avi" file, and then cut into 10 frames per second; in another word, between two images, the time step was 0.1 s. Matlab could change each color image into gray map to roughly tell the difference when the pH color changed.

Figure 5: Algorithm of the fluid's pH identification by Matlab.

In order to improve the accuracy of the image matrix's relative intensity numbers representing the pH value, we used four comparisons: gray map, red, green, and blue maps. A pre-set relative intensity threshold was established to identify the best resolution of pH value correlating with the image's relative intensity number. If a single color map could not represent pH value in some part of the pH, we could use other color maps to further divide the color into intensity numbers. For example, when the color was green or blue, the red map's data of each image pixel were almost same by the changing of time, which meant the red map data could not identify the pH value during that small period of time. Therefore, we should continue to use the green and blue map to identify the pH value during that period of time. These data were then analyzed to calculate the fluid's pH value (Figure 7) by comparing the fluid's color with standard BBS color chart (Figure 4c).

Figure 6: RGB color intensity analysis.

The data of static condition and one of the dynamic conditions (10 $\mu\text{L}/\text{min}$) were shown in this paper for clearer demonstration. The static case data indicated that CO_2 was dissolved and diffused into the liquid channel through porous PDMS; the dynamic flow case showed faster transfer of CO_2 .

Figure 7: pH value change over time in static and dynamic conditions.

DISCUSSIONS

At room temperature, CO_2 dissolves in water to form carbonic acid (H_2CO_3) that gradually changes pH value of the solution, which contains H^+ , CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} . The pH value is defined by the proton H^+ concentration in the solution; however, measuring the H^+ concentration was difficult in microfluidic environment, so we used the data for other negative ions. The hydration equilibrium constant (K_h) of CO_2 and H_2CO_3 in water (25°C) is:

$$K_h = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} = 1.70 \times 10^{-3} \quad (1)$$

where the “[]” represents the compound concentration [12].

The hydrolysis of H_2CO_3 in water follows the dissociation equation below:

and the dissociation constant (K_{a1}) of this reaction at 25°C are [12]:

$$K_{a1} = 2.5 \times 10^{-4} \text{ mol/L} \\ pK_{a1} = 3.6$$

However, when $[\text{H}_2\text{CO}_3] \ll [\text{CO}_2]$, the dissociation of H_2CO_3 in water follows:

The dissociation constant ($K_{a(app)}$) of this reaction at 25°C is:

$$K_{a(app)} = 4.6 \times 10^{-7} \text{ mol/L} \\ pK_{a(app)} = 6.3$$

The further hydrolysis of HCO_3^- is:

The dissociation constants (K_{a2}) of this reaction at 25°C are [12]:

$$K_{a2} = 4.69 \times 10^{-11} \text{ mol/L} \\ pK_{a2} = 10.329$$

Finally, the pH value can be related to the concentration of carbon-containing species by Henderson-Hasselbach equation [12],

$$pH = pK_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (5)$$

This equation was used to calculate the overall concentration of the absorbed carbon in the solution, as shown in Figure 8. The concentration of CO_2 molecule, H_2CO_3 , HCO_3^- , and CO_3^{2-} can be calculated individually. According to equation (5), the concentration of H_2CO_3 and HCO_3^- was obtained from the pH value. Based on equation (4), the concentration of CO_3^{2-} was much smaller than any other ions in the water. Because the unhydrolyzed CO_2 keep the molecule status in the water and not affecting the proton's concentration, CO_2 molecule didn't affect the pH value of the fluid. The concentration of CO_2 molecules was calculated by the hydration equilibrium constant K_h in equation (1). For example, we listed some concentrations with different pH values in Table 1.

Table 1: Absorbed CO_2 , H_2CO_3 , HCO_3^- , and CO_3^{2-} concentration (unit: mol/L) with the change of pH.

pH	$[\text{CO}_2]$	$[\text{H}_2\text{CO}_3]$	$[\text{HCO}_3^-]$	$[\text{CO}_3^{2-}]$
7.00	3.36×10^{-10}	5.71×10^{-13}	1.42×10^{-9}	7.90×10^{-13}
6.94	3.36×10^{-9}	5.71×10^{-12}	5.90×10^{-9}	1.90×10^{-12}
6.81	3.36×10^{-8}	5.71×10^{-11}	9.16×10^{-8}	3.30×10^{-11}
6.42	3.36×10^{-7}	5.71×10^{-10}	3.78×10^{-7}	4.53×10^{-11}
5.92	3.36×10^{-6}	5.71×10^{-9}	1.19×10^{-6}	5.57×10^{-11}

The overall carbon concentration was the combination of CO_2 molecule, H_2CO_3 , HCO_3^- , and CO_3^{2-} . Therefore, the overall carbon

atom that absorbed into the fluid was defined as carbon fixation rate, represented by “[C]” in Figure 8.

As observed in Figure 7 the dynamic fluid condition presented a faster CO₂ transfer compared with the static fluid condition. With the consumption of CO₂, more CO₂ molecules would be hydrolyzed into HCO₃⁻, and the equilibrium would continue to shift to create more HCO₃⁻, allowing more CO₂ molecules to diffuse into the fluid.

Figure 8: Carbon concentration in the liquid chamber.

Considering the microchannel dimensions, the average CO₂ absorption rates was 13.7 μmol/(L·min) in static condition and increased to 18.2 μmol/(L·min) under flow rate of 8~10 μL/min. We can further modify the microchannel dimensions and the inlet flow rate to increase the CO₂ absorption rate. Besides, the porosity and average pore size may also affect the CO₂ penetration rate as well as the absorption rate.

CONCLUSIONS

We developed a novel method of creating a gas-liquid interface in microchannel systems using porous PDMS and demonstrated its performance using CO₂ absorption. We believed that this gas-liquid interface method could be applied to many applications in lab-on-a-chip systems, especially in artificial photosynthesis systems, which is our ultimate target system. Such system will simulate the leaf function: absorbing CO₂ with less water evaporation.

ACKNOWLEDGEMENTS

The authors would like to thank Centralized Research Facilities in Drexel University. Travel support has been generously provided by the Transducer Research Foundation. This research project is supported by National Science Foundation CMMI-1141815 and CMMI-1300792.

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CONTACT

*Xiang Ren, tel: +1-215-808-7369; xiang.ren@drexel.edu