CO_2 SELECTIVE CERAMIC MEMBRANE FOR WATER-GAS-SHIFT REACTION WITH CONCOMITANT RECOVERY OF CO_2

Quarterly Report
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ABSTRACT

For the purpose of process simulation and economic analysis of the proposed CO_2 selective membrane process, we began to generate the equilibrium and rate data at the operating condition interested to our applications. In the last quarter we presented the results obtained at 200°C. In this quarter, we have concentrated on the experiments at 250ºC and CO_2 pressure of 0 to 1 bar. In this report we present the equilibrium isotherm and the mathematical treatment using the commonly accepted Langmuir equation. The data fit the Langmuir isotherm well and will be used for future adsorber and membrane reactor modeling. In addition, unsupported hydrotalcite membranes have been successfully synthesized on the silicon wafer with micro-channels. The membrane developed in this quarter ranges 2 to 5 μm in thickness. No visible cracks or defects were observed. Performance characterization of these membranes will begin in the next quarter. Since the interference from substrate in the characterization of the supported membrane is no longer existent, it is hoped that the hydrotalcite membrane thus formed can be optimized for its CO_2 selectivity and performance with the aid of the morphological and performance characterization.

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Introduction

In this quarter we have generated adsorption isotherms at 250°C as a continuation of the adsorption isotherm study reported in the last quarter. These adsorption isotherm data will be used for our mathematical simulation for using hydrotalcite as an adsorber and as a membrane reactor. In parallel, we have performed additional hydrotalcite membrane synthesis. In the past, our synthesis was focused on the deposition of hydrotalcite on our existing porous ceramic membranes with pore size ranging from 0.2μm to 40Å. Although the hydrotalcite membrane grew well on the inner surface of these tubular membranes as support, a defect free membrane was not obtained. As part of the defect minimization effort, it is essential for us to characterize defects, such as locations, dimensions, morphology, etc. Since the hydrotalcite membrane thus prepared contributed insignificantly to the overall weight of the membrane and support, the characterization result is usually masked by the support property. To overcome this difficulty, in this quarter, we initiated an innovative synthesis approach, i.e., depositing the hydrotalcite membrane on the micro-channel of silicon wafers. Once the hydrotalcite membrane is formed, the silicon support underneath the hydrotalcite membrane could be removed. Thus, an unsupported hydrotalcite membrane can be prepared. This method allows us characterize hydrotalcite membranes without the interference of the bulk support property. In this report, we present the results on membrane synthesis results via this approach. In the next quarter, we will begin the membrane performance characterization.

Executive Summary

For the purpose of process simulation and economic analysis of the proposed CO_2 selective membrane process, we have generated the equilibrium and rate data at the operating condition interested to our applications in the last quarter. We presented the results obtained at 200°C In this quarter, we have concentrated on the experiments at 250ºC and CO_2 pressure of 0 to 1 bar. In this report we present the equilibrium isotherm and the mathematical treatment using the commonly accepted Langmuir equation. The data fit the Langmuir well and will be used for future adsorber and membrane reactor modeling. In addition, an unsupported hydrotalcite membrane has been successfully synthesized on the silicon wafer with micro-channels. The membrane developed in this quarter ranges from 2 to 5 μm in thickness. No visible cracks or defects were observed. Performance characterization of these membranes will begin in the next quarter. Since the interference from substrate in the characterization of the supported membrane is no longer existent, it is hoped that the hydrotalcite membrane thus formed can be optimized for its CO_2 selectivity and performance with the aid of the morphological and performance characterization.

Experimental

1. Silicon wafer used for the membrane synthesis is presented in Figures 8 to 10. The dimension of the wafer is presented in Figure 8. The channel width ranges from 400

to 1000μm with the depth of 70μm. The top view of the micro-channel is shown in Figure 9. SEM photomicrograph of the top view of the micro channel is presented Figure 11. SEM photomicrograph of the cross section of the wafer with the micro-channel is shown in Figure 10. Finally the top surface structure of the silicon wafer is presented in Figure 11.

2. The hydrotalcite membrane was synthesized with the protocol we developed previously for the hydrotalcite powder. In this case, the precursor solution was dropped into the channel, which was then aged for a certain time, e.g., 12 hours. Subsequently the membrane was dried at 110°C to complete the synthesis. The SEM examination was performed for morphological characterization. The cross section of the hydrotalcite membrane and its top view are presented in Figures 13 and 14 respectively.

3. As an alternative, to promote the adhesion of the hydrotalcite membrane on the silicon wafer, ?-Al_2O_3 thin film was coated on the wafer first. The hydrotalcite precursor solution was deposited thereon. Figures 15 and 16 present the cross section and top view of the alumina sub layer deposited on the wafer respectively. Figures 17 and 18 show the cross section and its top surface of the hydrotalcite membrane respectively.

4. The experimental aspects of the adsorption isotherm obtained in this quarter were detailed in the last quarterly report. In this quarter, we followed the same experimental protocol to perform the adsorption isotherm study at 250°C.

Results and Discussions

1. Adsorption isotherms

The adsorption isotherm at 250°C obtained from this experimental study is presented in Figure 1. The adsorption capacity appears level off at 0.23 mmole/g when the CO_2 pressure is beyond 0.3 bar. As in the previous quarterly report a typical Langmuir adsorption isotherm was selected to describe the relationship between the equilibrium solid phase loading vs. the gas phase pressure. The best fitted parameters using the Langmuir equation are presented in Figure 1. We also performed the linear curve fitting of 1/g* vs. $1/P_{co2}$ to obtain M_{CO2} and b_{CO2} as shown in Figure 2. The M_{CO2} (~0.25) this obtained is comparable to the data presented (~0.23) in Figure 1. In the last quarter, the experimental data obtained at 200°C were insufficient to fit the Langmuir isotherm well. More data were obtained for 1/P in the range of 10 to 20 in this quarter as shown in Figures 4 to 6. Unfortunately the M_{CO2} obtained here (~0.265) remains to be higher than the actual experimental data (~0.24). The curve fitting shown in Figure 6 will be adopted for our modeling effort.

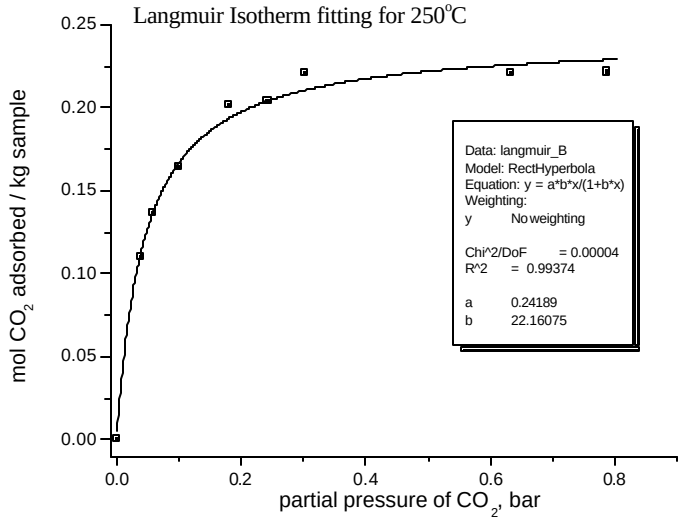


Figure 1 Equilibrium Capacity and the Best Fitted Langmuir Isotherm at 250°C.

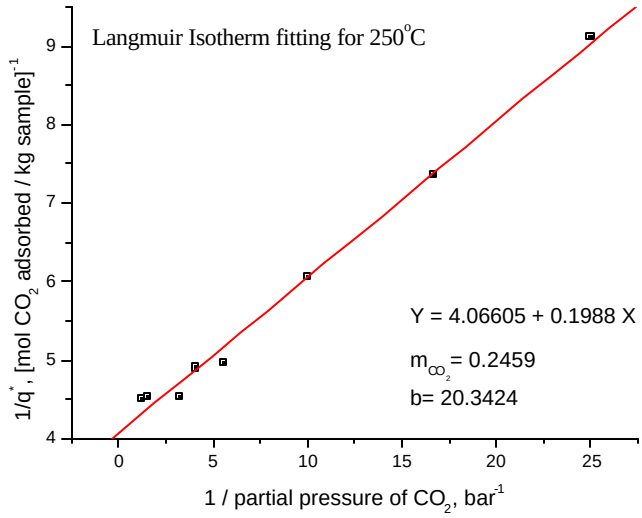
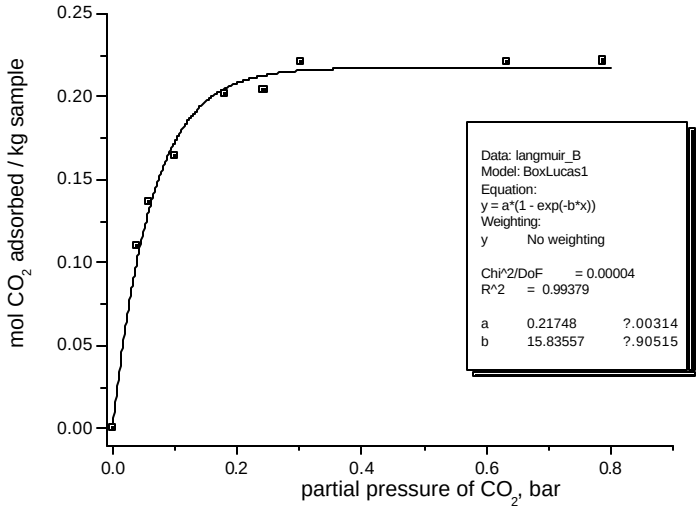


Figure 2 Parameters obtained for Langmuir Equation via Linear Curve Fitting of 1/q vs 1/P.



$$q^*_{CO_2} = m_{CO_2}(1-\exp(-kP_{CO_2}))$$

$$m_{CO_2} = 0.21748\ [mol/kg]$$

$$k = 15.03557\ [bar^{-1}]$$

Figure 3 Adsorption Isotherm at 250°C based upon of boxLucas Equation

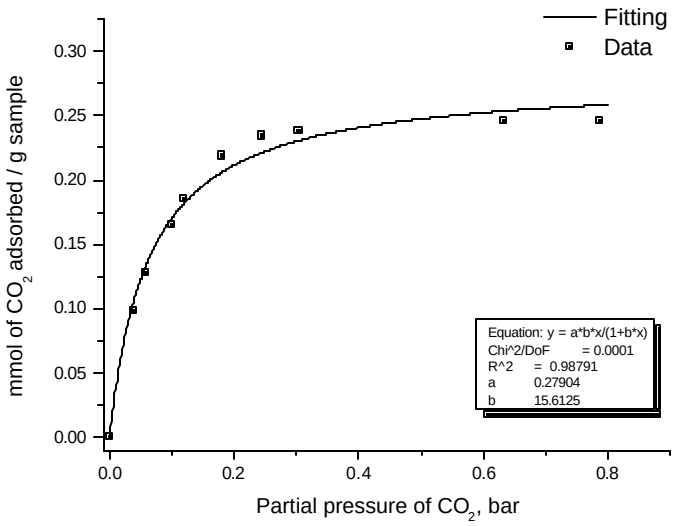


Figure 4 Equilibrium Capacity and the Best Fitted Langmuir Isotherm at 200°C.

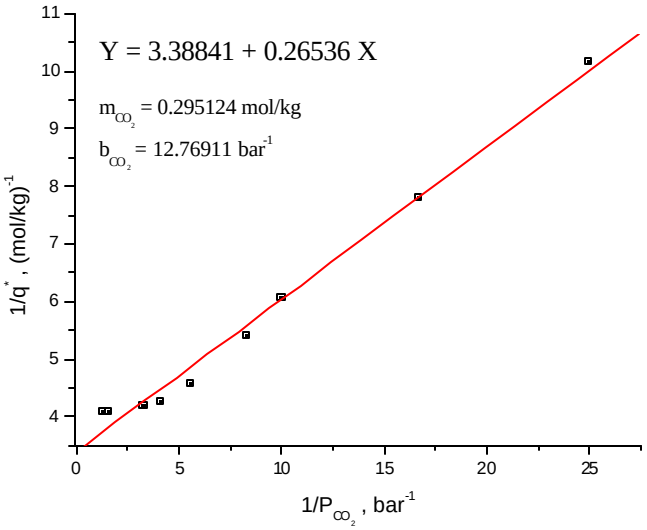
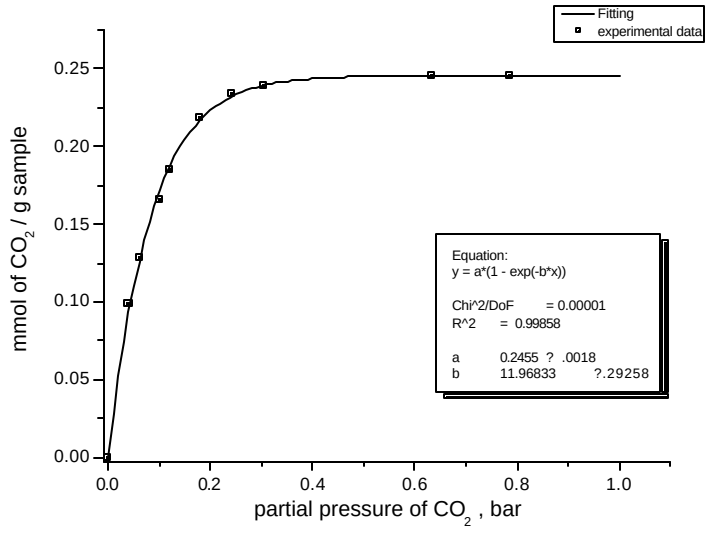


Figure 5 Parameters obtained for Langmuir Equation at 200°C via Linear Curve Fitting of $1/q^*$ vs 1/P.

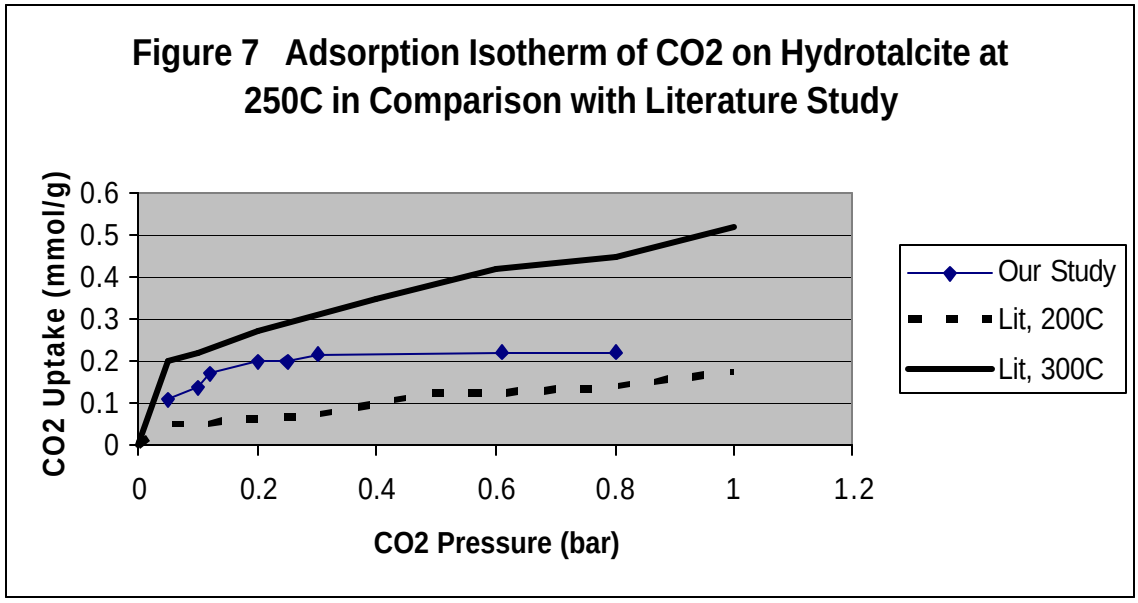


$$q^{*}_{CO_2} = m_{CO_2}(1-\exp(-kP_{CO_2}))$$

$$m_{CO_2} = 0.2455\ [mol/kg]$$

$$k = 11.96833\ [bar^{-1}]$$

Figure 6 Adsorption Isotherm at 200°C based upon of boxLucas Equation



Literature data at 200 and 300°C were presented along with our result in Figure 7. According to Figure 7, our adsorption capacity reaches the maximum at a rather lower pressure, i.e., ~0.25 bar, at 250°C than those reported in the literature. However, the adsorption isotherm from our study is consistent with the literature published data at 200 and 300°C [Ref. 1 to 3].

2. Hydrotalcite Membranes without Alumina Sublayer

The hydrotalcite membrane without the alumina sublayer is presented in Figures 13 and 14. The cross sectional view of the membrane shown in Figure 13 indicates that the membrane thickness in the range of 2-3 μm has been successfully prepared. The crystal size in the submicron range was observed. More importantly, no major defects or cracks were recognized. However, some intercrystal voids were observed on the top view of this membrane shown in Figure 13. Whether these voids penetrate throughout the entire membrane thickness resulting in defects is unknown to us presently. The performance study to be conducted in the next quarter will answer this question.

3. Hydrotalcite Membranes with Alumina Sublayer

Figures 15 and 17 exhibit the cross section of the alumina sublayer and the HT membrane deposited thereon respectively. Based upon Figure 17, the thickness of the HT and alumina membrane is in the range of 5 μm. The alumina sublayer in the range of 1 μm was estimated. The hydrotalcite crystals, similar to what observed in the membrane without the sublayer, are uniform with the dimension in the submicron range. Further, there is no clear separation between the hydrotalcite membrane and the alumina sublayer. Since alumina is one of the two major components in the hydrotalcite we prepared here, it is expected that the alumina sublayer was blended into the hydrotalcite membrane nicely. Figures 16 and 18 show the micro-crystal structure of the top surface of the alumina sublayer and hydrotalcite membrane respectively. The crystal size in this membrane appears much smaller than that observed in the hydrotalcite membrane without the sublayer. Since no clear difference in the morphology of this membrane vs the one without the alumina sublayer, it is hoped that the performance characterization to be performed in the next quarter will determine whether any advantages exist for the use of the alumina sublayer.

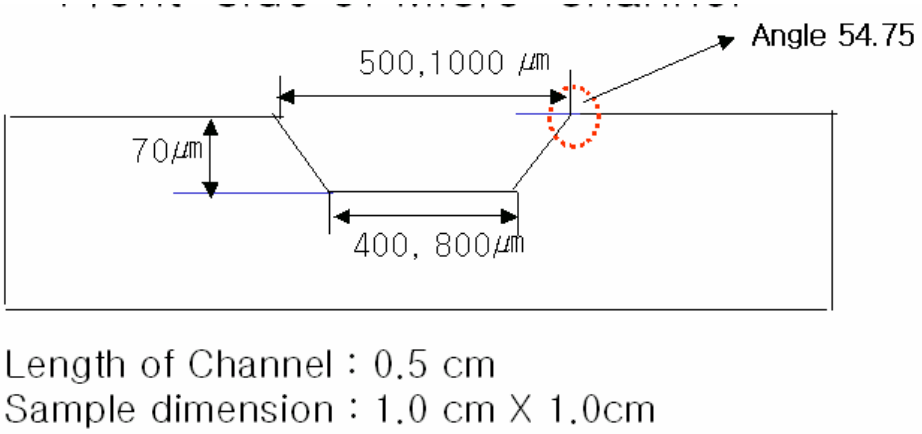


Figure 8 Dimension of Micro-Channel used for Hydrotalcite Membrane Synthesis (Cross-Section View)

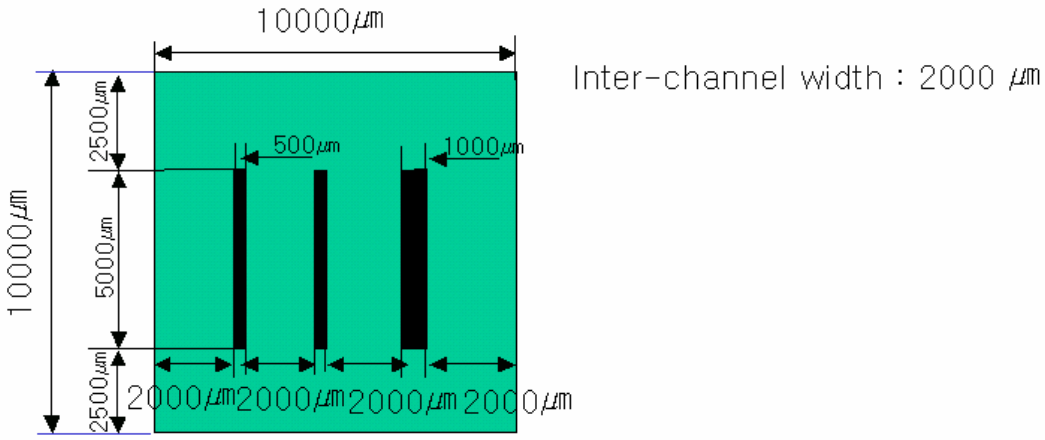


Figure 9 Dimension of Micro-Channel used for Hydrotalcite Membrane Synthesis (Top Surface View)

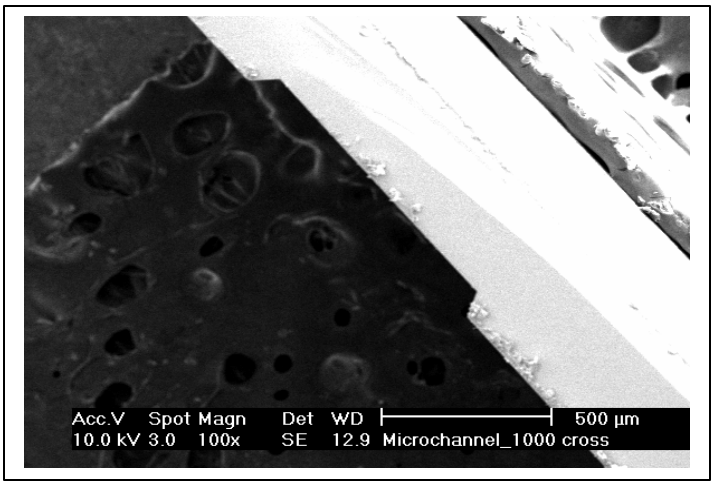


Figure 10 SEM Photomicrograph of Micro-Channel used for Hydrotalcite Membrane Synthesis (Cross Sectional View)

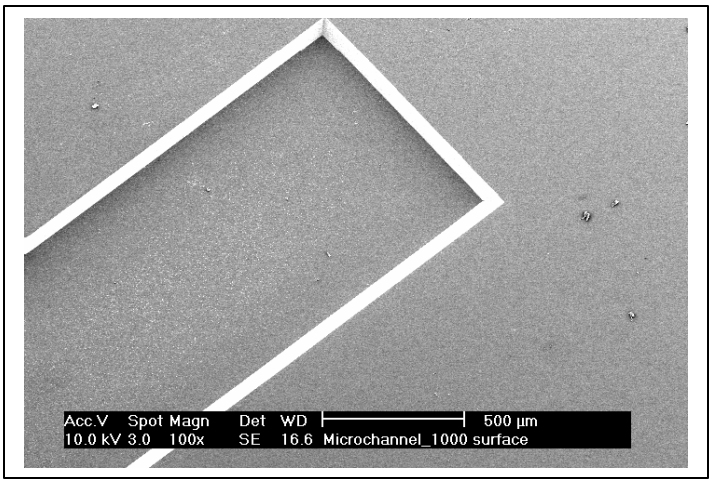


Figure 11 SEM Photomicrograph of Micro-Channel used for Hydrotalcite Membrane Synthesis (Top Surface View)

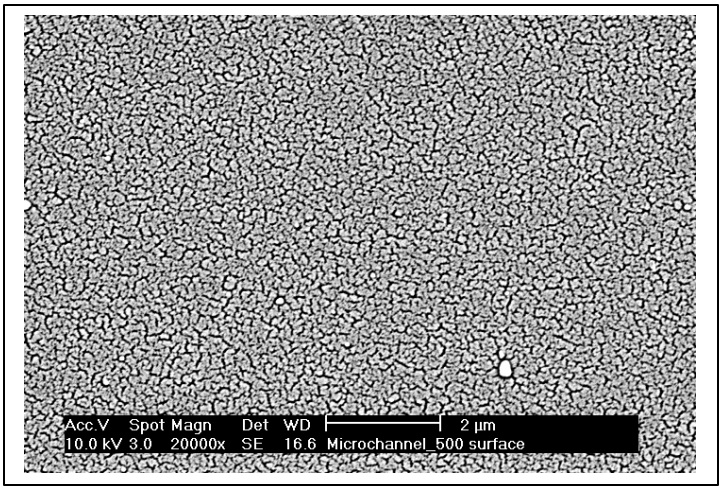


Figure 12 SEM Photomicrograph of Silicon Wafer Surface

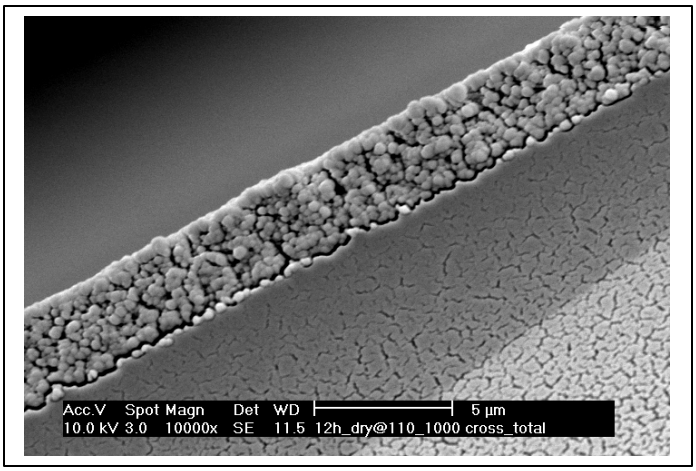


Figure 13 SEM Photomicrograph of Hydrotalcite Membrane Deposited on Micro-Channel (Cross-Section View)

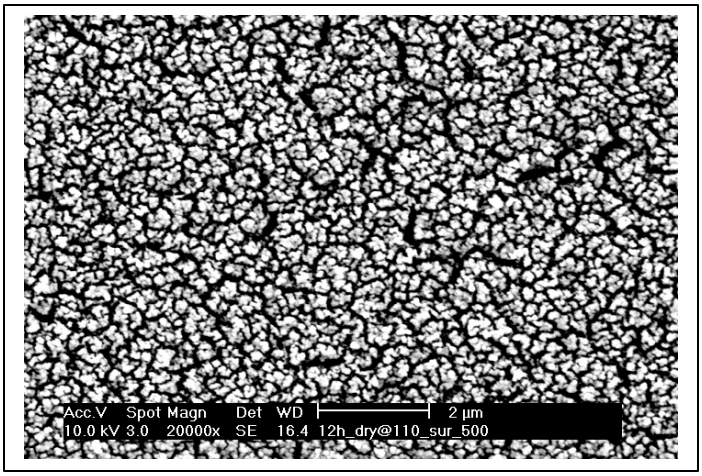


Figure 14 SEM Photomicrograph of Hydrotalcite Membrane Deposited on Micro-Channel (Top Surface View)

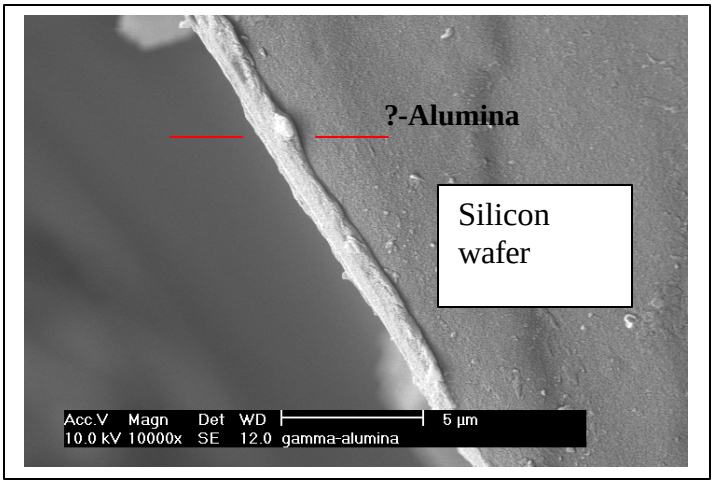


Figure 15 SEM Photomicrograph of Alumina Sublayer Deposited on Micro-Channel (Cross-Section View)

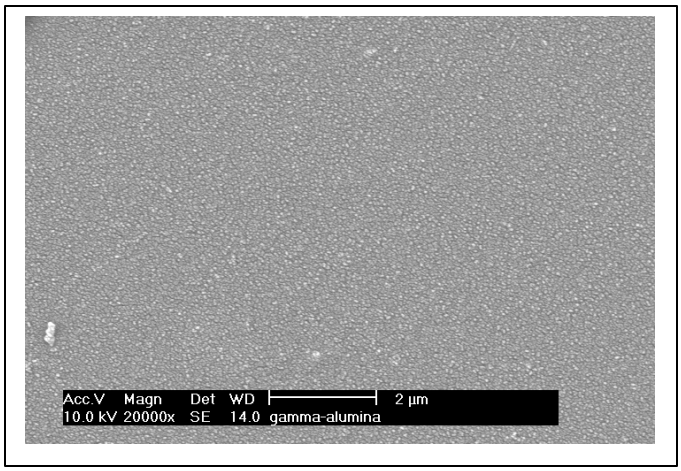


Figure 16 SEM Photomicrograph of Alumina Sublayer Deposited on Micro-Channel (Top Surface View)

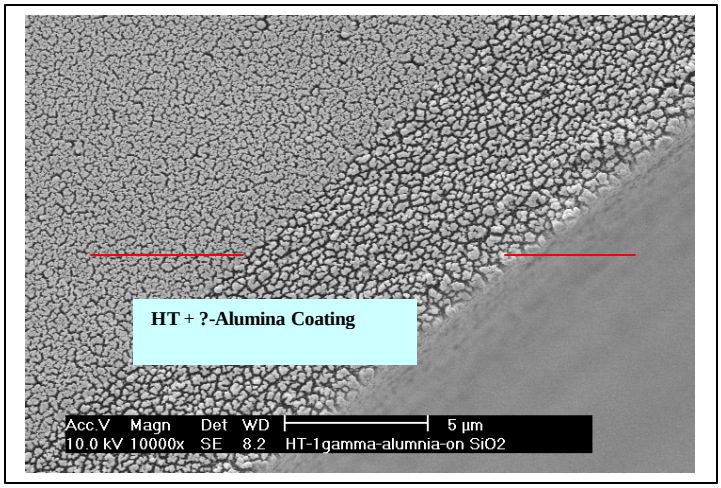


Figure 17 SEM Photomicrograph of Hydrotalcite Membrane with Alumina Sublayer Deposited on Micro-Channel (Cross-Section View)

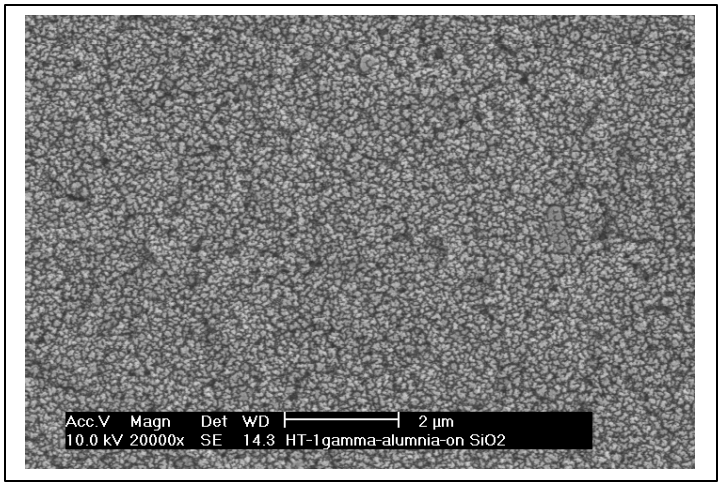


Figure 18 SEM Photomicrograph of Hydrotaclite Membrane with Alumina Sublayer Deposited on Micro-Channel (Top Surface View)

Conclusions

We have generated additional data of the thermodynamic and kinetic parameters required for future process simulation in this quarter. Besides an innovative membrane synthesis concept is introduced and some of the results from the morphological characterization are presented in this quarterly report. Key conclusions are summarized below:

- The equilibrium capacity of CO_2 on the hydrotalcite material at 250ºC and up to 1 bar was obtained. The results were fitted very well with the Langmuir equation. Additional data on the 200°C were generated in this quarter to complete the adsorption isotherm data at this temperature.
- In comparison with the literature data at 200 and 300°C, our material reaches the maximum capacity at a lower pressure, i.e., 0.25 bar, than the literature data. Our adsorption isotherm at 250°C is consistent with the literature data at 200 and 300°C.
- Synthesis of unsupported hydrotalcite membranes were attempted in this quarter. Silicon wafer with micro-channels was employed as a template for this purpose. The resultant hydrotalcite membranes appear uniform with no visible defects or cracks. The membrane in the thickness of 2 to 5 microns has been produced successfully in this quarter.

In the next quarter, we will begin to characterize the unsupported hydrotalcite membrane. Hopefully through this unsupported membrane approach, we will be able to develop a hydrotalcite membrane with minimized micro-cracks or defects.

Bibliography

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Acronyms

HT: Hydrotalcite
SEM: Scanning Electron Microscopy