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

Quarterly Report
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ABSTRACT

In this quarter, we have focused on the completion of the loose ends of the experimental study. A series of CO_2-affinity membranes (carbonaceous base) prepared previously were characterized and evaluated for their suitability for the proposed application The CO_2 permeance and selectivity are 0.5 to >3 m^3/m^2/hr/bar and 4 to 10 for CO_2 over nitrogen respectively. Based upon its performance dependence on temperature and pore size, we conclude that this type of CO_2 affinity membrane shows significant surface affinity to CO_2 over nitrogen even at the temperature as high as 220ºC, which is within the typical operating condition for LTS-WGS. Future study should focus on mixture separations for $CO/CO_2/H_2$ to establish the selectivity of CO_2 over CO and H_2 which are present in the WGS reaction of the coal gasifier off-gas.

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1. INTRODUCTION

In this quarter, we have focused on the completion of the loose ends of the experimental study. There are two different types of CO_2-affinity membranes have been explored throughout this project. One (Type I) is based upon the hydrotalcite based materials which have demonstrated a unique affinity to CO_2 at a high temperature in the presence of steam. The other one (Type II) is the carbonaceous microporous membrane which has demonstrated surface affinity to CO_2. In this quarterly report, we will summarize the representative performance of the Type II membranes we have prepared and/or characterized during this period.

2. EXECUTIVE SUMMARY

In this quarter, we have focused on the completion of the loose ends of the experimental study. A series of CO_2-affinity membranes (carbonaceous base) prepared previously were characterized and evaluated for their suitability for the proposed application The CO_2 permeance and selectivity are 0.5 to >3 $m^3/m^2/hr/bar$ and 4 to 10 for CO_2 over nitrogen respectively. Based upon its performance dependence on temperature and pore size, we conclude that this type of CO_2 affinity membrane shows significant surface affinity to CO_2 over nitrogen even at the temperature as high as 220ºC, which is within the typical operating condition for LTS-WGS. Pore size reduction was attempted, showing no improvement in the CO_2 affinity. Future study should focus on mixture separations for $CO/CO_2/H_2$ to establish the selectivity of CO_2 over CO and H_2 which are present in the WGS reaction of the coal gasifier off-gas.

3. EXPERIMENTAL

1. A series of Type II membranes (10”L) have been prepared using our commercial ceramic membranes as substrate. They are first deposited with selected precursors and then calcined at a selected temperature to form the desired pore size and surface properties. The single component gas permeation study was performed to measure their permeances of CO_2 and N_2 at 25, 120, 180 and in some cases 220°C.
2. The protocol developed for 10”L was employed for the preparation of the 30”L membrane to evaluate its scale up possibility. The 30”L membranes were characterized for their CO_2 and N_2 permeances at a similar temperature range.
3. One of the 10”L membranes was deposited an additional layer to evaluate the potential improvement in selectivity via pore size reduction. The additional layer was prepared and characterized following a similar protocol as above.

4. RESULTS AND DISCUSSION

1. Table 1 summarizes all the membranes prepared and characterized for this project. Their single component permeances (including He, H_2, N_2, and CO_2, and methane) at 23 to 220ºC were presented. Then ideal selectivities were calculated.
2. CO_2 permeance vs selectivity (over N_2) at 120°C for all the 10”L membranes is presented in Figure 1. In general, the overall trend for permeance vs selectivity follows the familiar inverse relationship. When the CO_2 permeance is > $3m^3/m^2$/hr/bar, the selectivity for CO_2/N_2 ranges from 2 to 4. On the other hand, when the CO_2 permeance is <0.5 m^3/m^2/hr/bar, the selectivity between 6 and 12 is obtained. In comparison with the Knudsen selectivity of 0.798, our selectivities obtained here are definitely enhanced to much beyond the Knudsen selectivity.
3. Majority of the membrane tubes were prepared with a lab scale substrate, i.e., 10”L as presented in Table 1. Four 30” long tubes were prepared following the same protocol as the 10”L tubes. The permeance and selectivity obtained from the 30” L are in line

with the trend established by the 10" tubes. Thus, the scale-up from the lab scale (10"L) to the full scale of 30"L appears acceptable.

4. The permeances and selectivities at 180 to 220°C were presented in Figure 2. This temperature range is the usual temperature range for the LTS-WGS we proposed. Due to the number of data points at these temperatures were much fewer than those of the 120ºC shown in Figure 1, the permeance vs selectivity trend was not well defined. However, the permeance and selectivity fell within the range of 0.5 to 2.5 $m^3/m^2/hr/bar$ and 4 to 8, respectively. In comparison with the data obtained at a lower temperature, i.e., 120°C, the selectivity at the higher temperature is somewhat lower than that at the lower temperature.
5. Figures 3a to 3c show the effect of temperature on the CO_2 permeance from 120 to 180°C. It appears that CO_2 permeance decreases along with the temperature increase. For Figure 3a and 3b, about 50% reduction of the CO_2 permeance was observed along with the temperature increase in this range. The CO_2 permeance reduction ratio for Figure 3c, however, is <<50%. The helium permeance decreases in Figure 3b while increases in Figure 3c, so is the trend for the hydrogen permeance. It is possible that the majority of the pore size in Figure 3a and 3b are larger than those in Figure 3c; thus, the helium and hydrogen permeances are somewhat influenced by the Knudsen diffusion in Figure 3b, while the helium and hydrogen permeances are dominated by activated diffusion in Figure 3c. Since the CO_2 permeance reduction vs temperature in Figure 3a and 3b is much more sever than the theoretical prediction based upon the Knudsen diffusion (i.e., 7%), it is concluded that the permeance for CO_2 is at least partially contributed by another mechanism, surface diffusion. When the pore size is small enough as shown in Figure 3c, the surface diffusion contribution decreases while the molecular sieving becomes pronounced. Even with the pore size decreases shown in Figure 3c, no improvement in CO_2 selectivity was observed. Thus, it is believed that the separation mechanism for this type of material is contributed by both surface diffusion and molecular sieving. At the temperature range interested to us, both mechanisms are likely involved.

6. Table 2 presents the permeance and selectivity for the membrane with an additional layer of deposition and calcination for the purpose of narrowing the pore size. The result indicates no improvement in selectivity although the permeance was reduced dramatically, from 1.88 to 0.035 $m^3/m^2/hr/bar$. This is consistent with the mechanisms proposed above. The pore size reduction theoretically could improve the selectivity although the difference in the kinetic diameters of CO_2 vs N_2 is very small. On the other hand, when the pore size becomes small enough, the surface diffusion contribution is diminished. Thus, the permeance is reduced dramatically while no clear sign of selectivity improvement is observed.

5. CONCLUSIONS

The Type II CO_2 affinity membranes prepared in this quarter demonstrated significant selectivity for CO_2/N_2, i.e., 4 to 10, up to 220°C, which is much beyond the Knudsen selectivity. Surface affinity of the membrane toward CO_2 was identified as the dominating mechanism at this operating temperature range. Pore size reduction was attempted, showing no improvement in the CO_2 affinity. Future study should focus on the mixture separations for $CO/CO_2/H_2$ to establish the selectivity of CO_2 over CO and H_2 which are present in the WGS reaction of the coal gasifier off-gas.

Bibliography:

None

Acronyoms :

LTS:	**Low temperature shift**
WGS:	**Water gas shift**

Table 1 Summary of Type II CO_2 Affinity Membranes and their Performance Characterization

Sample ID	Temp [c]	Press [psi]	Permeance $[m^3/m^2/hr/bar]$ He	H_2	N_2	CO_2	CH_4	Ideal Selectivity He/N_2	H_2/N_2	CO_2/N_2	N_2/CH_4
10" CO2 Affinity Membraens											
NN-01-2	**23**	30	2.051	3.846	0.748	4.011		2.7	5.1	5.4	
	120	30	1.765	4.198	0.330	2.239		5.3	12.7	6.8	
NN-02&03	**120**	20	1.231	2.816	0.080	0.846		15.3	35.1	10.6	
	180	20	1.483	3.039	0.097	0.633		15.2	31.2	6.5	
NN-06-03	**180**	20	1.203	2.753	0.140	0.730	0.098	8.6	19.6	5.2	1.4
	120	20		2.939	0.155	1.216			19.0	7.8	
NN-10-03	**120**	20	0.541	1.373	0.081	0.432	0.059	6.7	16.9	5.3	1.4
	180	20	0.585	1.227	0.064	0.254		9.1	19.1	4.0	1.4
NN-14	**120**	30	2.804	5.529	0.998	3.152		2.8	5.5	3.2	
NN-15	**120**	20	1.171	1.866	0.083	0.595	0.089	14.2	22.6	7.2	0.9
NN-47	**120**	20	3.429	7.344	0.276	1.880	0.157	12.4	26.6	6.8	1.8
NN-66	**120**	20	2.420	6.362	0.188	1.578	0.092	12.9	33.9	8.4	2.0
NN-71	**120**	20	0.707	1.804	0.037	0.418		19.2	48.9	11.3	
NN-80	**120**	20	2.868	7.464	0.494	3.585	0.523	5.8	15.1	7.3	0.9
	180	20	3.215	7.285	0.470	2.315	0.458	6.8	15.5	4.9	1.0
	120	30	2.010	4.646	0.185	1.655	0.169	10.9	25.2	9.0	1.1
NN-81	**120**	20	2.642	6.129	0.289	2.048		9.1	21.2	7.1	
NN-82	**120**	20	1.654	4.349	0.234	1.726	0.112	7.1	18.6	7.4	2.1
NN-94	**120**	20	1.819	4.250	0.335	2.110	0.355	5.4	12.7	6.3	0.9
	120	20	1.545	3.462	0.191	1.288	0.173	8.1	18.1	6.7	1.1
30" Length CO2 Affinity Membranes											
NN-27	**120**	20	1.370	3.106	0.445	2.229		3.1	7.0	5.0	
NN-29	**120**	20	1.643	4.650	0.304	1.994	0.200	5.4	15.3	6.6	1.5
	220	20	2.015	4.544	0.299	1.222	0.215	6.7	15.2	4.1	1.4
NN-30	**120**	20	0.990	2.956	0.176	1.360		5.6	16.8	7.7	
	220	20	0.879	2.082	0.103	0.821		8.5	20.1	7.9	
NN-49	**120**	20	2.136		0.632	3.354		3.4		5.3	

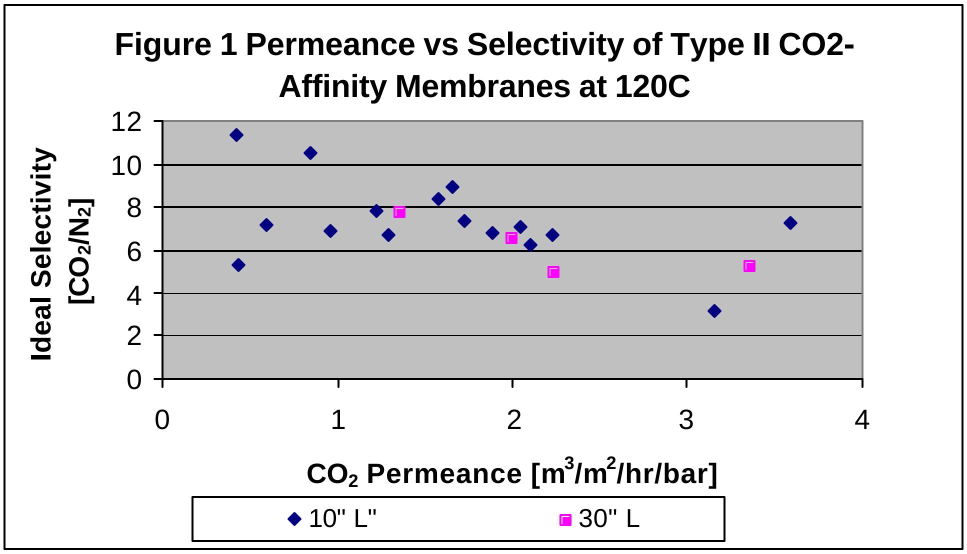
Figure 1 Permeance vs Selectivity of Type II CO2-Affinity Membranes at 120C
Ideal Selectivity [CO2/N2]
12
10
8
6
4
2
0
0
1
2
3
4
CO2 Permeance [m3/m2/hr/bar]
10" L"
30" L

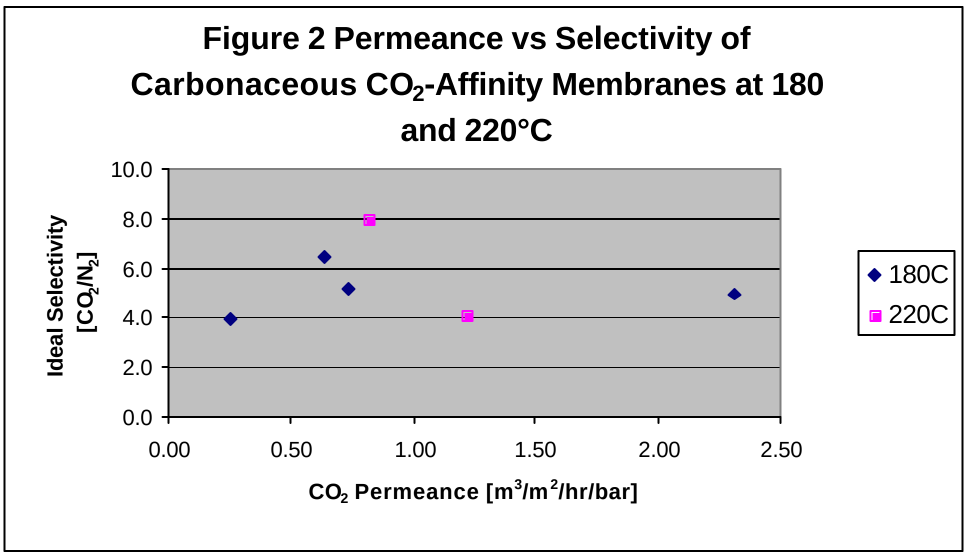
Figure 2 Permeance vs Selectivity of Carbonaceous CO2-Affinity Membranes at 180 and 220°C
Ideal Selectivity [CO2/N2]
10.0
8.0
6.0
4.0
2.0
0.0
0.00
0.50
1.00
1.50
2.00
2.50
CO2 Permeance [m3/m2/hr/bar]
180C
220C

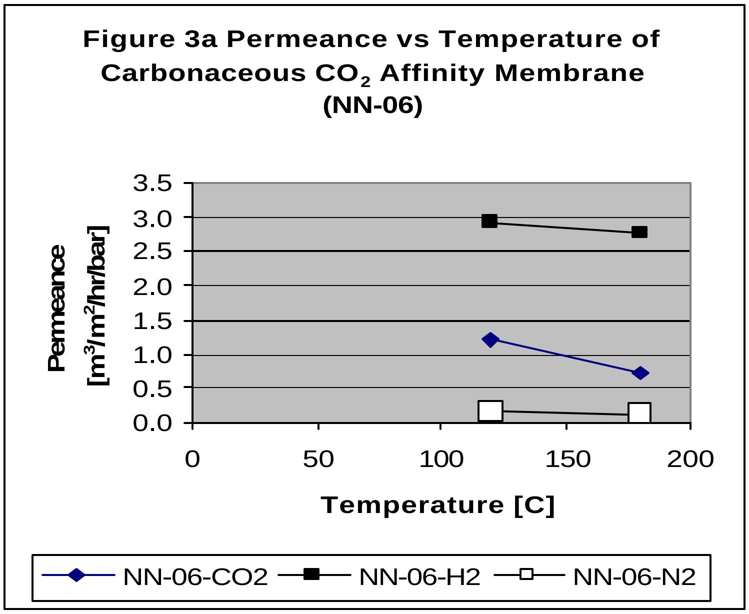
Figure 3a Permeance vs Temperature of Carbonaceous CO2 Affinity Membrane (NN-06)
Permeance [m3/m2/hr/bar]
Temperature [C]
NN-06-CO2
NN-06-H2
NN-06-N2

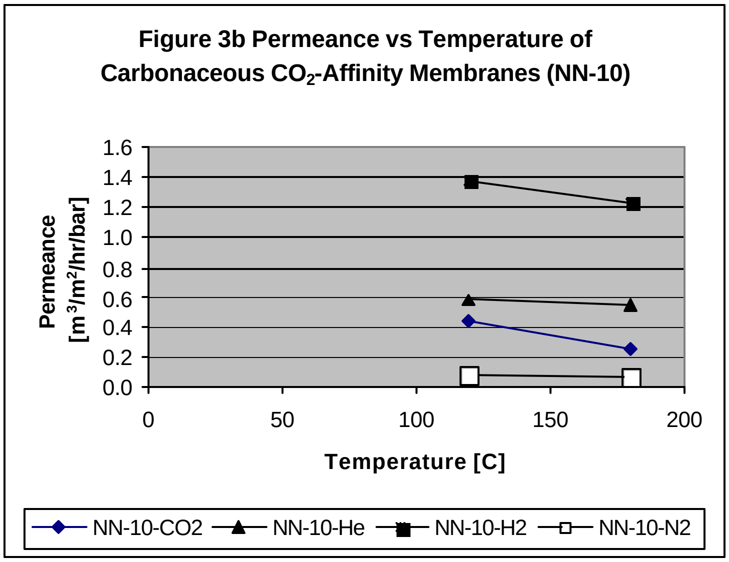
Figure 3b Permeance vs Temperature of Carbonaceous CO2-Affinity Membranes (NN-10)
Permeance [m3/m2/hr/bar]
Temperature [C]
NN-10-CO2
NN-10-He
NN-10-H2
NN-10-N2

Figure 3c Permeance vs Temperature of Carbonaceous CO_2 Affinity Membrane (NN-02)

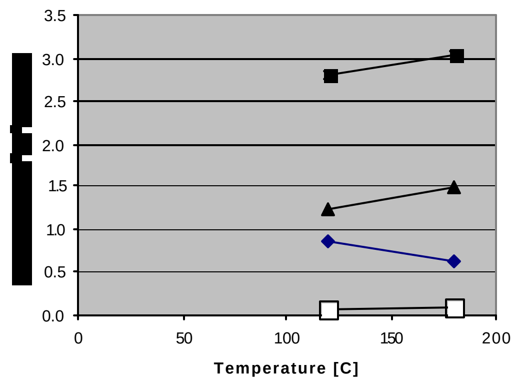

Table 2 Effect of Additional Layer Deposition on Performance of Type II CO_2 Affinity Membrane

Sample ID	Notes	Temp [c]	Press [psi]	Permeance He	[m^3/m^2/hr/bar] H_2	N_2	CO_2	CH_4	He/N_2	H_2/N_2	CO_2/N_2	N_2/CH_4
NN-47		**120**	20	3.429	7.344	0.276	1.880	0.157	12.4	26.6	6.8	1.8
	additonal deposition and firing	**120**	20	0.665	0.965	0.044	0.035	0.044	15.2	22.0	0.8	1.0