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Lithium Silicate Based Membranes for High Temperature CO₂ Separation

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Abstract

Processing and characterisation of a novel membrane system for CO₂ separation is detailed. The membrane was made of Lithium Orthosilicate (Li₄SiO₄), which has potential to react with CO₂ molecules reversibly at high temperature. Using the membrane, a separation factor of 5.5 was measured between CO₂ and N₂ gas molecules at a temperature of 525°C. The gas permeance value through the membrane at 525°C was around 10⁻⁸ mol/m².s.Pa. Ionic diffusion through the liquid phase electrolyte and solid phase skeleton, produced by the reaction between CO₂ and Li₄SiO₄, was suggested to assist the selective permeance of CO₂. This facilitation effect was experimentally identified by examining the variation in CO₂ flux with partial pressure. Oxygen ion conductivity through the skeleton material, Li₂SiO₃, is reportedly very high and therefore charge balance should have been achieved by O²⁻ transfer through the skeleton.

Keywords: *CO₂ separation, membrane, absorption, lithium, facilitation*

Introduction

The separation, recovery and storage/utilisation of carbon dioxide have attracted considerable attention in recent years owing to the growing problem of global warming and other health hazards [1]. High temperature processes such as the combustion of fossil fuels, especially coal and petroleum, emit a significant amount of CO₂. However, there are currently no efficient methods available for separating CO₂ from other gases at high temperature [2, 3].

The most important CO₂ removal techniques are wet absorption, dry adsorption, membrane separation and cryogenic separation. Although the present level of membrane separation technology is immature compared with the other processes, the membrane separation process is considered to be one of the least energy-demanding processes if membranes that could withstand the process temperature and conditions are available. Although membrane separation of CO₂ is reported widely [4, 5], apart from molten salt based CO₂ concentrators as reported by Winnick et al in 1982 [6], membranes that could withstand high temperatures in the order of 500-600°C are rarely reported. Furthermore, membranes such as microporous silica membranes, even if they could be processed with high CO₂ separation factors at high temperature, will definitely allow higher permeance of lighter molecules such as hydrogen making selective separation of CO₂ practically impossible from (for e.g.) membrane reactor environment where mostly H₂ and CO₂ are the conversion products. Such high temperature in situ separation of CO₂ from membrane reactor environment will increase the overall efficiency of the process and should also help in the post-process utilisation/management of CO₂. In other words, in such applications CO₂ separation membranes could be used as add-ons together with hydrogen separation membranes or even substitute the hydrogen separation process altogether.

As mentioned, inorganic membranes for high temperature separation of CO₂ are seldom reported in the literature, though inorganic membranes, primarily based on silica, for hydrogen separation are discussed widely in the literature [7, 8]. One of the present authors has also reported the processing of Si₃N₄ based membranes for hydrogen separation [9]. Recently, our group has reported the processing of Li₂ZrO₃ based materials and membranes for CO₂ separation [10, 11], a development assisted by the selective absorption of CO₂ on the membrane materials. The CO₂ absorption properties of Li₂ZrO₃ powders depended upon their particle size as well as crystalline structure [12-17]. Particles with CO₂ take-up rate as high as 5.8 mg/g.min had been obtained in our study. The total amount of CO₂ absorbed varied depending upon the morphology and crystalline structure; Li₂ZrO₃ particles with absorption capacity more than 20 % (by wt.) could be produced by several powder-processing techniques [10]. Using Li₂ZrO₃ membrane, a separation factor of 4.9 was measured between CO₂ and CH₄ gas molecules at a temperature of 600°C [11].

In the study reported in this paper, we have used another material, Li_4SiO_4 , with enhanced ability to absorb CO_2 at high temperature [18-20]. As in the case of lithium zirconate, the absorption of CO_2 took place because of a reaction to form lithium carbonate and a solid oxide. Theoretically this reaction, if proceeds to the end, should make SiO_2 as in the reaction $\text{Li}_4\text{SiO}_4 + 2\text{CO}_2 = 2\text{Li}_2\text{CO}_3 + \text{SiO}_2$. Hence, the material should be capable of absorbing 73.5 % (by wt.) of CO_2 . However, in practice the solid product Li_2SiO_3 , which is formed as the reaction product between one mole of Li_4SiO_4 and CO_2 restricts the absorption. Hence the reaction proceeds according to the equation $\text{Li}_4\text{SiO}_4 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3$. Consequently the total amount of CO_2 absorbed is limited to 36.7 % (by wt.). Still, the amount of CO_2 that could be absorbed in Li_4SiO_4 is higher than the amount absorbable in Li_2ZrO_3 , which is only 28.7% of its weight. Moreover, the rate of absorption of CO_2 by lithium orthosilicate also was found higher than that of lithium zirconate. Hence, we have studied the possibility of membrane making using lithium orthosilicate material.

In this paper we have reported the morphology and CO_2 absorption characteristics of lithium orthosilicate powders made in our laboratory. Membranes were prepared using the powders and CO_2 separation measurements were conducted. The details of the permeance and separation measurements were also reported in this paper. The mechanism of selective separation is discussed as well.

Experimental

Li_4SiO_4 was prepared by mixing Li_2CO_3 (Wako Chemicals) with SiO_2 (99.9% pure, 0.8 μm size, High Purity Chemical Laboratory Co. LTD., Japan,) in the molar ratio 2 to 1. The mixture kept in a crucible made of 99.9% alumina was heated under air atmosphere for ten hours for sintering. Crystalline structure of the samples at heat-treatment temperatures between 700°C and 1000 °C were studied using X-ray diffraction (XRD). The morphological details of the samples were examined using Field Emission Scanning Electron Microscope (FE-SEM). Surface area values of the powder particles were determined using N_2 adsorption based BET analysis. The absorption of CO_2 was measured using Thermo Gravimetric Analysis (TGA). TGA was performed in CO_2 gas medium at a gas flow rate of 150 ml/min. For TGA

measurement, the temperature was raised from room temperature to 700 °C, at the heating rate of 100 °C/min.

Li_4SiO_4 membranes were made as follows: Porous alumina supports (thickness: 1.5 mm, pore diameter: 0.1 μm) were initially fixed on the top of dense ceramic tubes using high temperature glass seals. The surroundings, except the top surface of the alumina supports, were glass sealed. The disk was then dipped in the mixture of 700°C heat-treated lithium orthosilicate powder and poly vinyl alcohol (PVA) solution for 10 seconds and dried at 50 °C in an air-oven. These dipping and drying processes were repeated 5-10 times. The coated pellet was then heat-treated at 750 °C to sinter the membrane layer. To minimise the physical/leakage flux, we have further coated these membranes with a solution of carbonate salts (20 mol% K_2CO_3 and 80 mol% Li_2CO_3) by dipping the substrate in a carbonate solution dispersed in toluene followed by drying at room temperature.

We have measured CO_2 and N_2 separation factor and CO_2 permeance rate using CO_2/N_2 equi-molar gas mixture as feed gas. All the measurements were made at steady state conditions after prolonged exposure of the membrane to the conditions of measurements. The selectivity was calculated from the ratio of area values corresponding to feed and permeate streams of gas chromatography peaks. The permeance rate was calculated from the total gas flow rate and from the CO_2 concentration values in the feed/permeate sides obtained using the gas chromatograph.

Results and Discussions

Figure 1 show XRD charts for Li_4SiO_4 . The numbers shown in the figure correspond to heat-treatment temperatures. There are not many differences between the charts corresponding to the different heat-treatment temperatures. Peaks of the starting materials such as Li_2CO_3 and SiO_2 were not visible. The peak data confirmed the formation of lithium orthosilicate (Li_4SiO_4) crystalline phase (JCPDS 37-1472) by the processing and heat-treatment. It should be noted that the starting composition of SiO_2

and Li_2CO_3 is very important in this respect. Inadequate quantities of Li_2CO_3 will lead to the partial formation of Li_2SiO_3 -lithium metasilicate- phase.

SEM images of the powder particles are shown in Figure 2. Figures 2(a) and (b) correspond to particles sintered at 700°C and 1000°C and indicate particle sizes of $\sim 1\mu\text{m}$ and $100\mu\text{m}$ respectively. Surface area values of the corresponding powder samples were $8.36\text{ m}^2/\text{gm}$ and $0.0024\text{ m}^2/\text{gm}$ respectively. The surface area value of $8.36\text{ m}^2/\text{gm}$ point to an effective primary particle size of around 100nm and indicate the aggregated structure of the powder particles. The large differences in particle size and surface area values between the two samples evidence the enhanced particle growth on sintering at higher temperatures. This result was identical to the effect of heat-treatment on Li_2ZrO_3 powders. However, no change in crystalline structure was identified in the present case unlike Li_2ZrO_3 which has undergone phase transformation from tetragonal to monoclinic phase on heat-treating at temperatures higher than 900°C .

TG curves of the samples heat-treated at 700°C and 1000°C are shown in Figure 3. It is shown that Li_4SiO_4 sintered at 700°C absorbed CO_2 rapidly and the sample weight increased by 33 % within a duration of 1 – 2 minutes. The constant weight period in the data corresponding to this sample indicate that equilibrium was reached with a very short time. On the other hand, Li_4SiO_4 sintered at 1000°C showed slower take-up of CO_2 . This sample showed lower weight change than the 700°C -heat treated sample possibility because of under equilibrium. The results indicated that, CO_2 absorption rate of Li_4SiO_4 is affected by the particle size. The absorption and release rate of CO_2 by the sample made at 700°C is represented by TGA curve shown in Figure 4. The gas flow through the sample chamber was switched from CO_2 to Air to achieve the release of absorbed CO_2 at the temperature of absorption of 700°C . Free energy calculations have shown that at a CO_2 partial pressure of 0.0005 the reverse reaction would go ahead at a temperature of 436°C and at a CO_2 partial pressure of 0.1 the reaction would happen at a temperature of 622°C .

From figure 4 it is also clear that the rate of release of CO_2 , though lower than that of absorption, is very high. The difference between the rates of absorption and release of

CO₂ could be linked to the state of agglomeration of the particles. For well dispersed powders the absorption rate is generally found high during the first cycle of absorption but low for the first release cycle. Phase segregation of the carbonate phase produced by CO₂ absorption is easier in such well dispersed powders. Partial phase segregation could be the main reason for the incomplete and slow release of CO₂ during the first cycle of absorption and release in the present samples (Figure 4).

We have made membranes using the 700°C heat-treated lithium orthosilicate powder samples by dip coating. The membranes were sintered at 750°C after coating. Figures 5 (a) and (b) show the SEM micrographs of the surface of the substrate and the surface of the Li₄SiO₄ layer. The membranes as shown in Figure 5 (b) were not dense and therefore were coated with carbonate salt solution prior to gas permeance study (Figure 5 (c)). Previous studies with Li₂ZrO₃ materials have shown that the presence of some amount of excess carbonate salt introduced after crystallisation of the particles tend to accelerate the kinetics of CO₂ absorption [10] and also that the ratio Li₂CO₃/K₂CO₃ determines the rate of absorption. However in the case of Li₄SiO₄, K₂CO₃ had only a weaker influence in the absorption or release rates of CO₂ (*Weight change curves showing the influence of K₂CO₃ on CO₂ absorption and release rates of Li₄SiO₄ are included as supplementary information*). The influence of excess carbonate salt on the gas separation behaviour of this type of membrane system is difficult to establish clearly, though reduction in gas permeance occurs due to obvious changes in porosity. It should be noted that, independent measurements performed previously with carbonate salts supported on carbon layers did not show any selective CO₂ separation [11].

The results of gas permeance and separation studies performed with CO₂/N₂ mixtures are shown in Figure 6. Gas permeance value around 10⁻⁸ mol/m²sPa was measured in the temperature range 525-625°C. CO₂/N₂ separation factor values between 4 and 6 were obtained. The gas permeance through the membranes showed no significant dependence on the temperature of measurement. The separation performance of the membranes seems to be similar to that of Li₂ZrO₃ membranes reported in the previous paper [11]. As in the case of Li₂ZrO₃ membranes, we have failed to prepare a membrane with low amount of physical flux and therefore the measured separation factor was much lower than theoretically possible with the dual ion conducting

mechanism illustrated in Figure 7. The pressure dependency of gas flux and permeance as shown in Figure 8 supports the illustrated mechanism of CO₂ gas transport. CO₂ flux through the membrane has two components; namely physical flux and reactive flux. Physical flux here, is the Fickian diffusive flux through the non-reactive portion of the membrane including defects without any reversible chemical reaction. The flux should be proportional to the driving force, which under the conditions employed is equivalent to, the partial pressure of CO₂. Therefore, we have evaluated the physical flux from CO₂ partial pressure; the dotted line in Figure 8 represents its value in the range of our measurement. Measured CO₂ flux is higher than this physical flux due to the facilitation effect [21-24].

As mentioned, Figure 8 indicates that the mechanism of gas separation is assisted by facilitated transport through the electrolytes [21]. In the feed side, the large partial pressure of CO₂ supports the formation of carbonate salt. CO₂ that dissolves in the material because of the feed side reaction diffuses (as CO₃²⁻) to the downstream side through the carbonate salt electrolyte by concentration gradient. Li₂CO₃ melt is a known conductor of CO₃²⁻ ions. In the downstream side the formation of gaseous CO₂ takes place because of the reverse reaction, which produces CO₂ and O²⁻ ions. These O²⁻ ions must diffuse towards the feed side to get the necessary charge balance. The skeleton material Li₂SiO₃, though not well known, is an oxygen ionic conductor. Based on molecular simulation it is reported in literature that the mobility of oxygen ions in Li₂SiO₃ is significantly high; with diffusivity values following the order $D_{Li} \gg D_O = D_{Si}$ [25, 26]. Hence, the skeleton of Li₂SiO₃ made by the reaction between CO₂ and the membrane matrix material of Li₄SiO₄ should be able to transfer O²⁻ ions across the membrane thickness. This result supports that selective CO₂ permeance through the membrane is assisted by carrier transport mechanism. In short, results show that carrier transport through mixed ion conducting electrolytes is a viable mechanism of gas separation. Figure 8 shows that the CO₂ permeance value measured with 10:90 (CO₂:N₂) mixture gas was almost double the value measured with equimolar mixture gas. This means that higher selectivity values against inert gas molecules could be attained in the low CO₂ partial pressure region. More studies, using membranes with lesser physical flux, however, is necessary for the complete confirmation of the mechanism we have proposed. Processing of membranes with much smaller and well dispersed particles should be the key points in this respect. The

use of smaller particles should help in the processing of membranes with lower defects and hence low amount of leakage flux. More importantly, the use of nanoparticles should allow the increase in interface area between the two electrolytes and hence a better local charge balance could be achieved. Carrier transport should enhance with the increase in interface area between the electrolytes and hence the effect of physical flux in the total gas permeance should become negligible. A more extensive study based on computer simulation of the structure of these CO₂ absorbing materials and the mechanism of gas absorption on them should give a better understanding of the phenomena.

Conclusions

In this study, we have studied the separation performance of a CO₂ absorbing materials based on lithium silicate. The high temperature CO₂ absorption rate of the material was found very fast; 33 wt.% of CO₂ could be absorbed in the material in less than 2 minutes. We have also prepared a membrane based on the material for the separation of CO₂. Using the membrane we have measured CO₂/N₂ selectivity between 4 and 6 in the temperature range of 525- 625°C. CO₂ transport mechanism through the membrane is possibly assisted by carrier transport of CO₃²⁻ and O²⁻ by the Li₂CO₃ and Li₂SiO₃ electrolytes.

Acknowledgements

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Figure 1: XRD peaks corresponding to lithium orthosilicate (Li_4SiO_4) samples are shown. Temperatures of heat-treatment of the samples in $^\circ\text{C}$ are shown inside the figure. Main peak data are as follows (JCPDS: 37-1472) [2 θ -22.61, d-3.93, hkl-011] [2 θ -28.23, d-3.16, hkl- -111] [2 θ -33.81, d-2.65, hkl-200], [2 θ -34.7, d-2.58, hkl-002].

Figure 2: SEM photographs of Li_4SiO_4 samples made (a) 700 $^\circ\text{C}$ (b) 1000 $^\circ\text{C}$.

Figure 3: TGA curves representing the CO_2 absorption of Li_4SiO_4 particles made at 700 $^\circ\text{C}$ and 1000 $^\circ\text{C}$

Figure 4: TGA curves representing the CO_2 absorption and release of Li_4SiO_4 particles made at 700 $^\circ\text{C}$. CO_2 absorption was carried out by flowing CO_2 through the TGA sample chamber. Release of absorbed CO_2 was made by changing the gas flow to air at isothermal condition

Figure 5: SEM photographs of (a) alumina support (b) Li_4SiO_4 layer surface (c)Final membrane surface

Figure 6: CO_2/N_2 mixed gas permeance and separation results of Li_4SiO_4 membrane system.

Figure 7: Proposed mechanism of the selective component of CO_2 gas permeance.

Figure 8: Pressure dependency of CO_2 flux through Li_4SiO_4 membrane measured using CO_2/N_2 mixture feed gas of varying compositions.

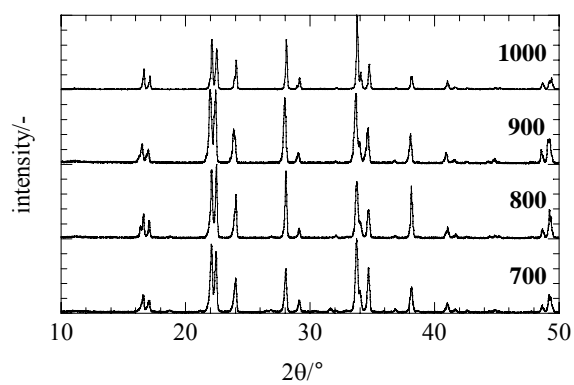


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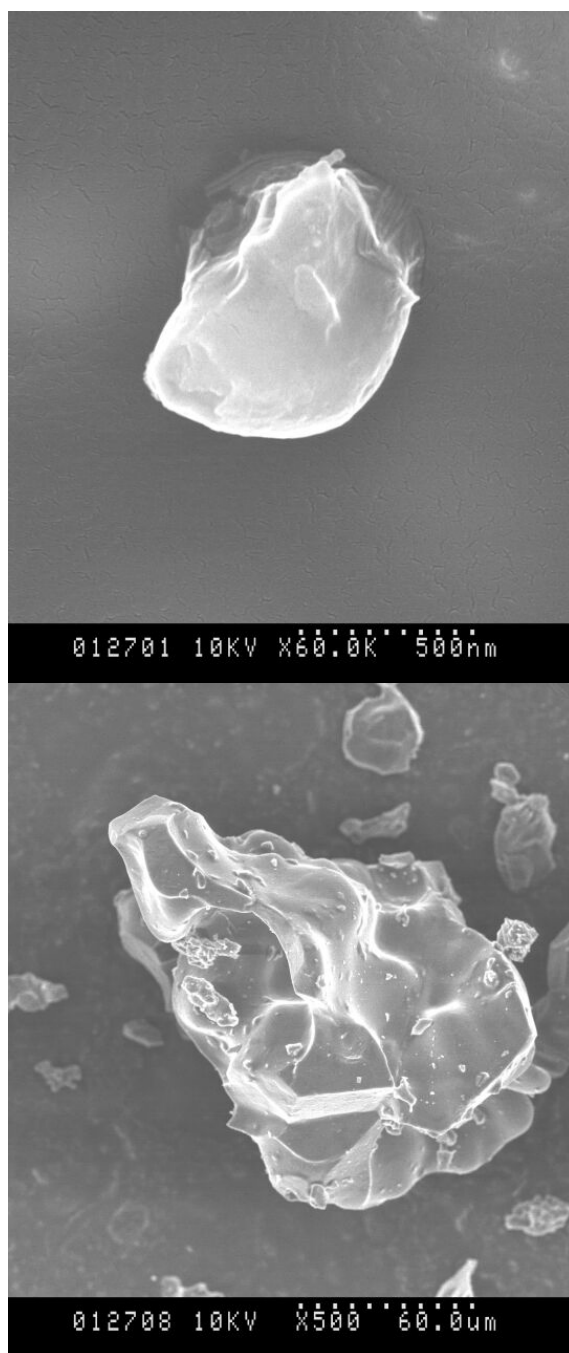


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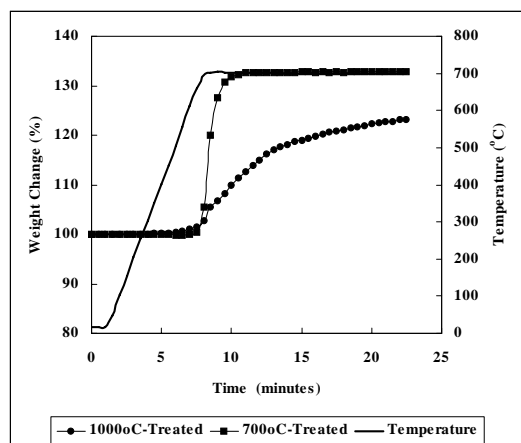


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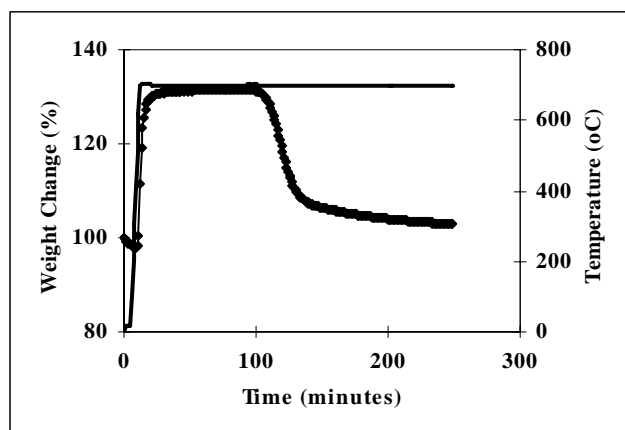


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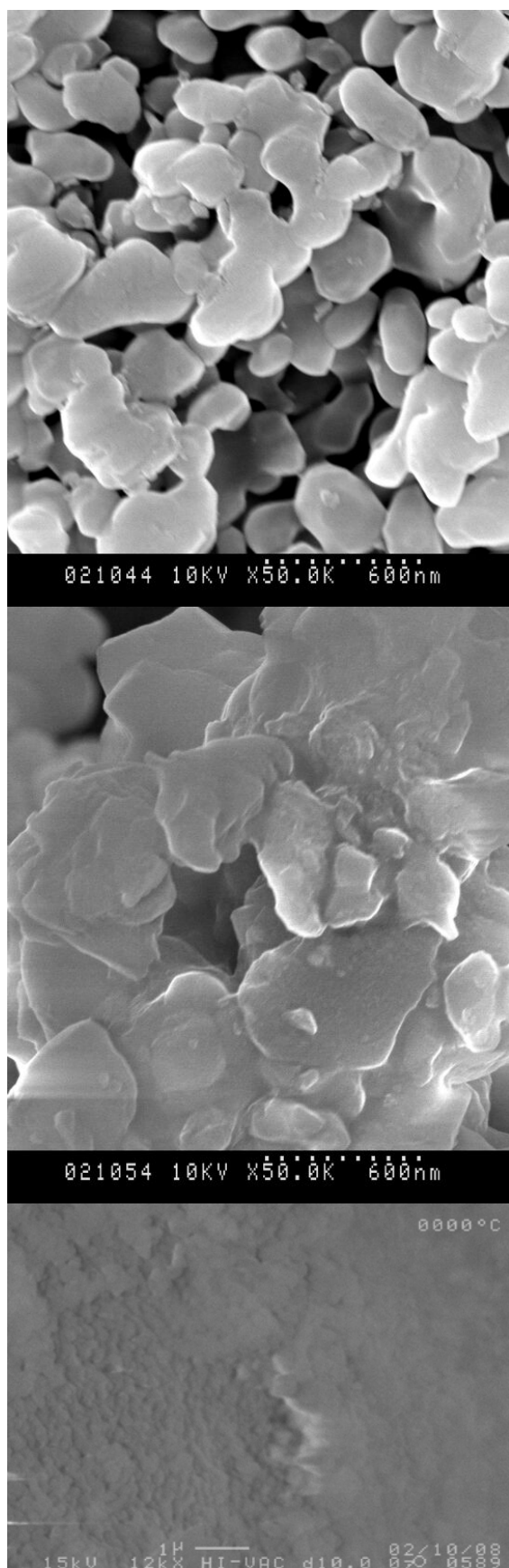


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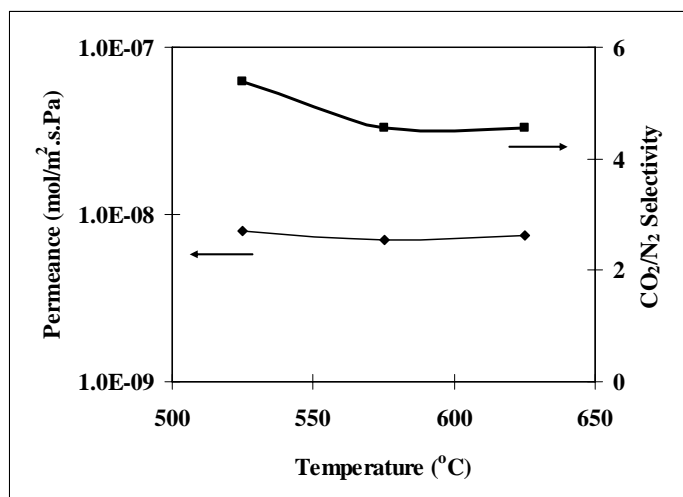


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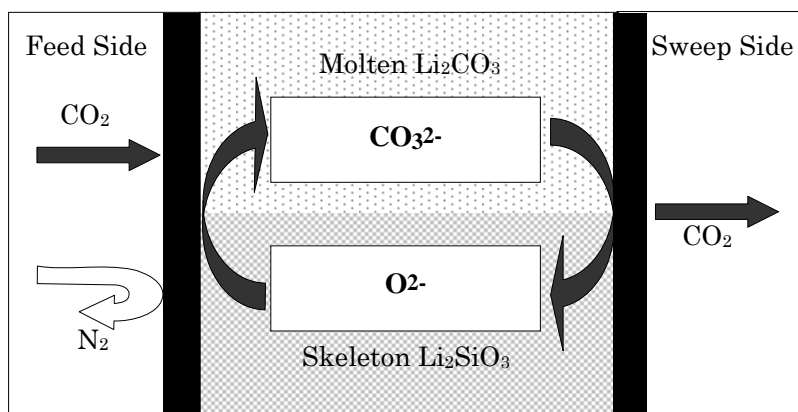


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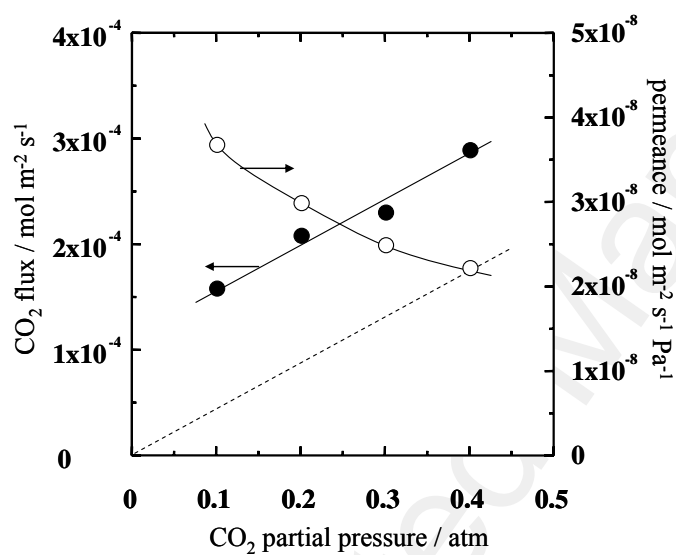


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