

Thermochemical Capture of Carbon Dioxide on Lithium Aluminates (LiAlO₂ and Li₅AlO₄): A New Option for the CO₂ Absorption

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Received: March 19, 2009; Revised Manuscript Received: May 1, 2009

Lithium aluminates (LiAlO₂ and Li₅AlO₄) were synthesized, characterized, and tested as possible CO₂ captors. LiAlO₂ did not seem to have good qualities for the CO₂ absorption. On the contrary, Li₅AlO₄ showed excellent behavior as a possible CO₂ captor. Li₅AlO₄ was thermally analyzed under a CO₂ flux dynamically and isothermally at different temperatures. These results clearly showed that Li₅AlO₄ is able to absorb CO₂ in a wide temperature range (200–700 °C). Nevertheless, an important sintering effect was observed during the thermal treatment of the samples, which produced an atypical behavior during the CO₂ absorption at low temperatures. However, at high temperatures, once the lithium diffusion is activated, the sintering effect did not interfere with the CO₂ absorption. Eyring's model was used to determine the activation enthalpies of the CO₂ absorption (15.6 kJ/mol) and lithium diffusion (52.1 kJ/mol); the last one is the limiting process.

1. Introduction

In the last 10 years different lithium and sodium ceramics have been tested as possible carbon dioxide (CO₂) captors. These ceramics present a chemisorption reaction with CO₂, producing the respective alkaline carbonate and a residual metal oxide. For example, lithium metazirconate (Li₂ZrO₃) produces Li₂CO₃ and ZrO₂ because of the CO₂ absorption.^{1–3} Into this field, the lithium ceramics most studied until to now are: lithium zirconates (Li₂ZrO₃ and Li₆Zr₂O₇), lithium silicates (Li₄SiO₄ and Li₂SiO₃), and, more recently, lithium cuprate (Li₂CuO₂), lithium titanate (Li₄TiO₄), and lithium ferrite (LiFeO₂).^{1–13}

Among these materials, two of the most promising lithium ceramics are Li₄SiO₄ and Li₄TiO₄. These ceramics present good kinetic behaviors, and their theoretical CO₂ absorption capacities are the best, 0.73 (Li₄SiO₄) and 0.63 (Li₄TiO₄) g_{CO₂}/g_{ceram.}^{7,10} As can be deduced from previous data, CO₂ absorption capacity depends on the molecular weight of each ceramic. Consequently, the lighter the ceramic is, the higher the CO₂ absorption capacity would be. On the basis of this idea, lithium aluminates would present advantages over other lithium ceramics, even silicates, which were the lighter ceramics tested until now.

Lithium aluminates (LiAlO₂ and Li₅AlO₄) have been used for different applications. LiAlO₂ has been proposed as a breeder ceramic into the fusion reactors, a solid electrolyte for lithium batteries, and ceramic carrier material in the fabrication process of electrolyte tiles for molten carbonate fuel cells, among other applications.^{14–18} However, there is almost no information about Li₅AlO₄. There are only a few papers in which Li₅AlO₄ has been synthesized and tested for some electrical applications.^{19–21} Li₅AlO₄ ceramic presents two different crystal polymorphs α-Li₅AlO₄ and β-Li₅AlO₄, where both polymorphs have orthorhombic crystal structures.^{22,23}

If lithium aluminates were able to absorb CO₂, then following reactions may occur



The reactions proposed above are presented assuming that CO₂ is absorbed through the same mechanism observed for other lithium ceramics^{24–26} in which lithium aluminates react to produce lithium carbonate in addition to a residual oxide, Al₂O₃. The theoretical CO₂ absorption capacities for LiAlO₂ and Li₅AlO₄ are 0.33 and 0.87 g_{CO₂}/g_{ceramic}, respectively. Li₅AlO₄ has a very high theoretical CO₂ absorption capacity in comparison with that of the other lithium ceramics (Figure 1). In fact, only lithium oxide (Li₂O) possesses a higher theoretical capacity (1.46 g_{CO₂}/g_{Li₂O}) with the disadvantages of its high reactivity and corrosive characteristics.

Therefore, the aim of this work was to study and demonstrate whether LiAlO₂ and Li₅AlO₄ are able to capture CO₂ by a mechanism similar to that reported previously for other lithium ceramics. Special attention was given to Li₅AlO₄ because of its high theoretical CO₂ absorption capacity, which is mainly caused by its high Li/Al molar ratio equal to 5, and the fact that aluminum is a lighter atom than any other element tested, such as zirconium, copper, or even silicon.

2. Experimental Section

LiAlO₂ and Li₅AlO₄ were synthesized by solid state reaction using, in both cases, lithium oxide (Li₂O, Aldrich) and aluminum oxide (Al₂O₃, Aldrich). Initially, reagents were mixed mechanically and then heat-treated under different conditions. Whereas LiAlO₂ powders were thermally treated at 900 °C for 6 h, Li₅AlO₄ powders were heated at 900 °C for 24 h with two intermediate milling processes. To improve the synthesis of both lithium aluminates, 10 wt % of lithium excess was used because of the high tendency of lithium to sublime.²⁴

X-ray diffraction (XRD) patterns were obtained from a diffractometer (Bruker AXS, D8 Advance) coupled to a copper anode X-ray tube. Compounds were identified conventionally

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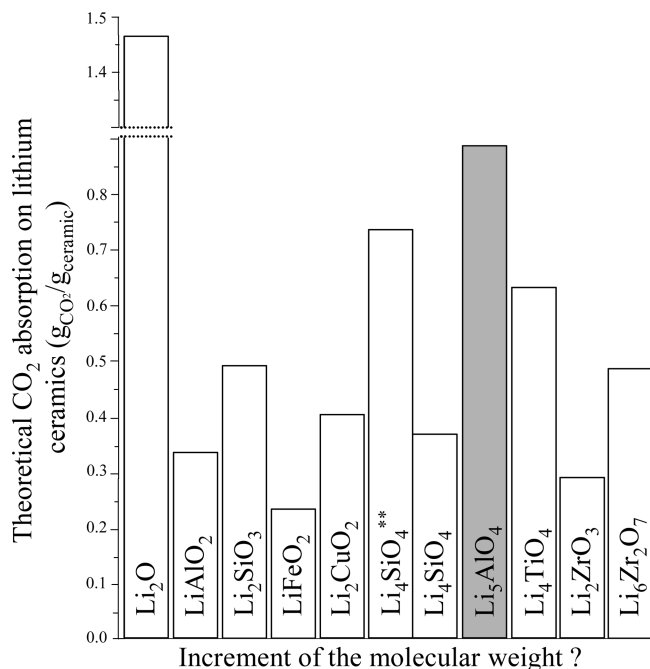


Figure 1. Comparison of the maximum theoretical CO₂ absorption capacities of different lithium ceramics. Li₄SiO₄** and Li₄SiO₄ represent the CO₂ absorption capacities, assuming a total and half lithium conversion to Li₂CO₃, respectively.

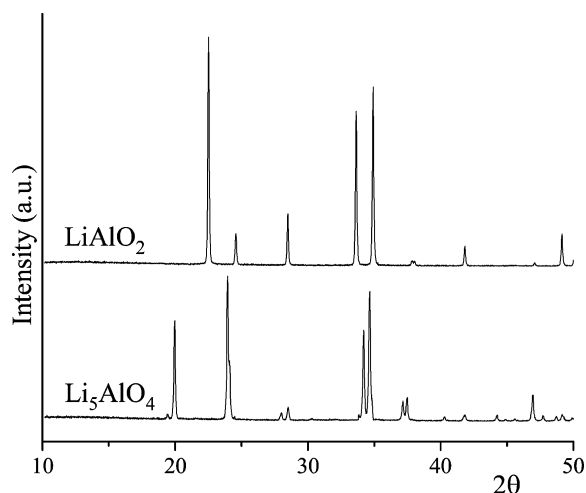


Figure 2. XRD patterns of the LiAlO₂ and Li₅AlO₄ powder samples.

by the corresponding Joint Committee Powder Diffraction Standards (JCPDS) files. We determined the particle size and morphology by scanning electron microscopy using a Stereoscan 440, Leica-Cambridge microscope. The samples were covered with gold to avoid the lack of electrical conductivity, and the particle size was determined using standard procedures. Finally, different thermal analyses were performed in a Q500HR equipment from TA Instruments. Initially, a set of samples was heat-dynamically treated with a heating rate of 5 °C/min from room temperature to 850 °C in a CO₂ flux (Praxair, grade 3.0). Then, Li₅AlO₄ sample was tested isothermally at different temperatures in the same CO₂ flux.

3. Results and Discussion

Figure 2 shows the XRD patterns of both lithium aluminates, Li₅AlO₄ and LiAlO₂. In both cases, the diffraction patterns fitted to their respective JCPDS files: 70-0432 for Li₅AlO₄ and 18-

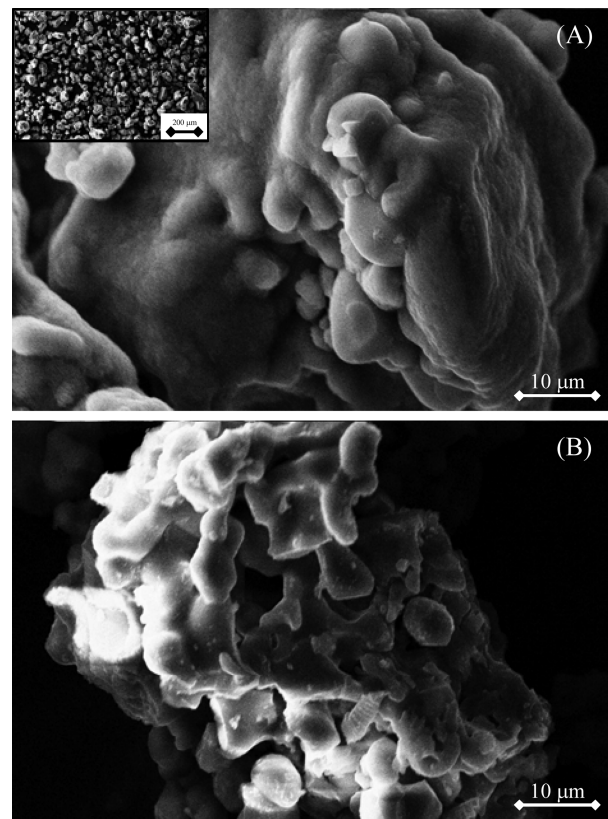


Figure 3. Scanning electron micrographs of the (A) Li₅AlO₄ and (B) LiAlO₂ samples. The rectangle inset shows a general view of the sample powders.

0714 for LiAlO₂. Therefore, both ceramics could be considered to be pure materials, at least at the XRD detection level. Then, particle size and morphology of the samples were obtained by SEM. Figure 3 shows the micrographs of Li₅AlO₄ and LiAlO₂. Li₅AlO₄ presented a particle size average of 60 μm, where the particle size was determined by standard procedures (inset of Figure 3A). These particles seemed to be highly sintered dense agglomerates, where their surface did not present any kind of texture (Figure 3A). This morphology can be merely explained by the high and long thermal treatment, in addition to the high lithium mobility, which tends to propitiate high sintering levels. A similar effect could be established for the LiAlO₂ sample in which the average particle size was equal to 50 μm. Perhaps the only difference observed on LiAlO₂ is that these particles seemed to be slightly less sintered (Figure 3B). Again, it can be explained by the shorter thermal-treatment time and lower lithium quantities present in the sample.

Once Li₅AlO₄ and LiAlO₂ were characterized, these materials were thermally treated under a CO₂ flux to analyze whether they were able to act as CO₂ captors. Figure 4 presents the dynamic thermograms of LiAlO₂ and Li₅AlO₄ into a CO₂ flux. It is more than evident that both ceramics presented very different behaviors. LiAlO₂ practically did not absorb CO₂. This ceramic was able to increase its weight percentage by only 0.13 wt % between 540 and 830 °C. This may be explained by its high thermal stability and its high dense structure.

However, Li₅AlO₄ presented a very high CO₂ absorption. It is clear that two different sorption processes took place; the first one between 200 and 380 °C and a second one between 590 and 750 °C. Although this kind of thermal trend has already been observed for other lithium ceramic, for example Li₂CuO₂,^{9,27} it is not the most common behavior among the lithium ceramics,

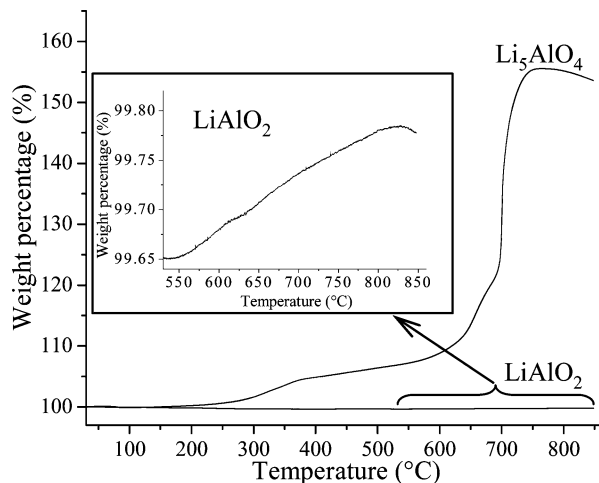


Figure 4. Dynamic thermogravimetric curves of Li₅AlO₄ and LiAlO₂ in a CO₂ flux. The rectangular inset shows an enlargement of the LiAlO₂ thermogram, 530–880 °C.

where the absorption is produced in just one step.^{4,11} In other words, the superficial and bulk absorption processes are not distinguishable on lithium ceramics. Nevertheless, in the Li₂CuO₂ case, the whole absorption process was divided into two thermal steps: Initially, at low temperatures, a superficial reaction is produced. At this moment, an external lithium carbonate and residual oxide shell are formed over the surface of the ceramic particles, inhibiting the CO₂ absorption process. Then, when the temperature is increased and the lithium diffusion is activated, the reaction continues through the bulk of the ceramic, completing the CO₂ chemisorption.^{9,27} For Li₅AlO₄, a similar behavior could be described. The superficial reaction takes place between 200 and 380 °C, where the sample increased its weight by 4.5 wt %. Then, an increment of weight, equal to 3.8 wt % (8.3 wt % in total), was observed between 380 and 590 °C. In this temperature range, CO₂ absorption is highly controlled by the diffusion process, considering that the Li₂CO₃ external shell has already been formed during the first process. Finally, between 580 and 750 °C, the lithium diffusion is activated, and the process is completed through the bulk of the particles. In this case, the weight increased by 47.2 wt % (55.5 wt % in total). In addition, it can be observed in Figure 4 that at temperatures higher than 780 °C, the CO₂ desorption process began.

To analyze the CO₂ absorption process on Li₅AlO₄ further, different isothermal experiments were performed (Figure 5). At the lowest temperature (250 °C), the isothermal showed an exponential behavior, which had not reached the plateau after 4 h, and it absorbed 3.35 wt %. Then, samples treated at 300 and 350 °C presented the same exponential behavior, increasing their weights by 3.7 and 4.22 wt %. Then, the sample treated at 400 °C presented an atypical behavior. Although this sample showed a fast CO₂ absorption at short times (in comparison with the previous isotherms), the final absorption was smaller than that observed for the samples heat treated at 300 and 350 °C. The same effect, but more dramatically, was observed for the sample heat treated at 450 °C, where the sample increased its weight by only 0.65 wt %. This atypical behavior has been reported for the CO₂ absorption on other alkaline ceramics such as Na₂ZrO₃ and Li₂CuO₂.^{27,28} This behavior has been associated with a sintering process produced during the heating of the samples, which produces an important decrement of the surface area. This phenomenon is usually observed at low temperatures because once the diffusion process is activated, sintering and

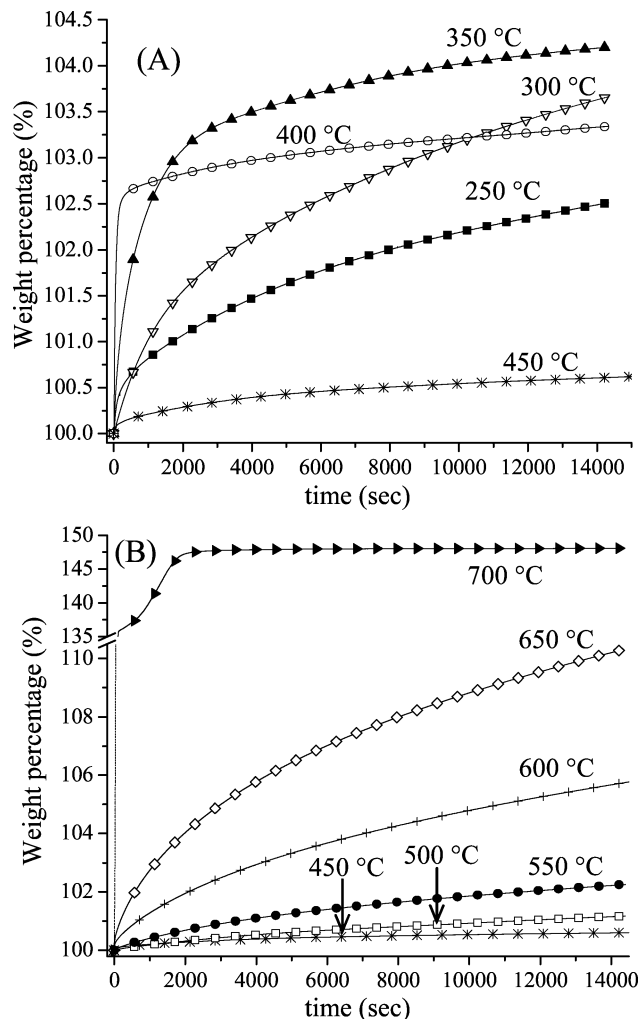


Figure 5. Isotherms of CO₂ absorption on Li₅AlO₄ at different temperatures into a flux of CO₂. (A) Isotherms obtained between 250 and 450 °C. (B) Isotherms obtained between 450 and 700 °C.

surface area are not preponderant factors on the CO₂ absorption. Therefore, in the isothermal analyses at 500, 550, 600, and 650 °C, the weight gained increased again, absorbing more CO₂ as a function of the temperature (Figure 5B). This means that although the sintering effect must be produced in those samples, the lithium diffusion was activated. Finally, the behavior presented at 700 °C should be pointed out, where the quantity and rate of the CO₂ absorption were very high and fast, presenting a totally different isothermal shape. In the first 3 min, the sample absorbed 35.7 wt %. Then, the absorption rate, between 3 and 30 min, decreased, getting a CO₂ maximum total absorption of 47.8 wt %. After that time, the isotherm reached the plateau. This means that in the first few minutes, the CO₂ absorption efficiency reached 53.7%, and after 30 min, the maximum efficiency under these thermal conditions, 68.5%, was obtained.

These results clearly show that the sintering process affects CO₂ absorption on Li₅AlO₄. Therefore, to corroborate and eliminate the presence of this effect, a second set of isotherms was performed. In this case, all of the Li₅AlO₄ samples were initially heated to 675 °C at 100 °C/min with a subsequent isothermal treatment of 60 min. Then, each sample was cooled to its respective isothermal temperature for the CO₂ absorption. All of these procedures were carried out under an inert atmosphere (N₂). Once the sample reached the corresponding temperature, the flux gas was switched from N₂ to CO₂ and the

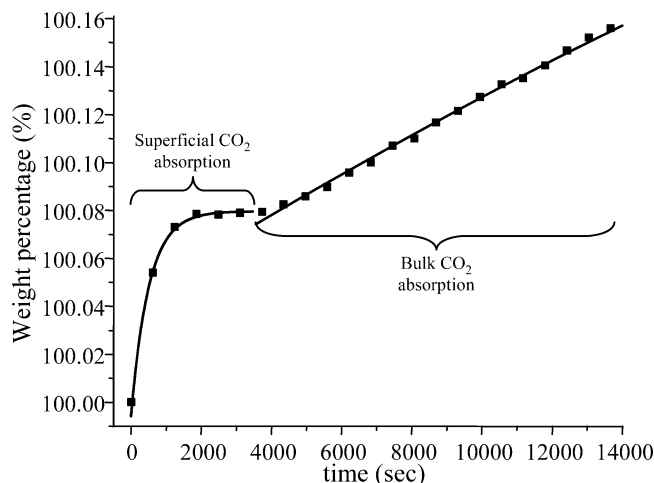


Figure 6. CO₂ absorption isotherm of Li₅AlO₄ at 350 °C after a sintering process at 675 °C.

isothermal experiments were performed. As could be expected, all of the isothermals followed the typical behavior. In other words, the CO₂ absorption on Li₅AlO₄ increased as a function of the temperature.

The isotherms performed at the lowest temperatures (300, 350, and 400 °C) clearly showed the presence of two different processes (Figure 6). Initially, during the first 3000 s, CO₂ is absorbed only over the surface. Then, at larger times, the absorption occurred on the bulk, although the total quantity of CO₂ absorbed over time is very poor. In fact, the only difference among these three samples is that the total CO₂ absorbed slightly increased progressively as a function of the temperature (0.15, 0.16, and 0.57 wt % for 300, 350, and 400 °C, respectively). The behavior and the quantity of CO₂ absorbed are very different than those observed when the samples were not previously sintered. In these cases, as Li₅AlO₄ powders were sintered, their surface area must have dramatically decreased, reducing the possibility of CO₂ reacting with the surface, and because the lithium diffusion is very slow at those temperatures, the final CO₂ absorbed decreased.

However, all other isotherms performed at higher temperatures (450, 500, 550, 600, 650, and 675 °C) presented an exponential typical behavior. In these cases, samples increased their weights from 0.88 (450 °C) to 34.2 wt % (675 °C) after 4 h. These results are presented in Figure 7. Additionally, it is clearly evident that CO₂ absorption at short times was dramatically increased as a function of the temperature. However, the isothermal slopes became almost the same in long time periods. It can be explained as follows: in short time periods, the increase in weight depends on the CO₂ absorption reaction, whereas in long time periods, it depends on the lithium diffusion.

To prove these qualitative observations, we fitted all isotherms to simple (300–400 °C) or double (450–675 °C) exponential models because there are two different processes taking place: the CO₂ absorption and the lithium diffusion. In the first three samples, the isotherms were divided and adjusted to a simple exponential model, whereas in the other cases, a double exponential model was used because the reaction and diffusion processes were undistinguished. From these results, it was possible to obtain two different constant values, k_1 and k_2 , which represent the kinetic constant values of the CO₂ absorption and lithium diffusion, respectively. Table 1 shows the different parameters obtained from the isotherms. From these data, it can be seen that CO₂ absorption constants (k_1) are at least one order of magnitude higher than lithium diffusion constants (k_2). In

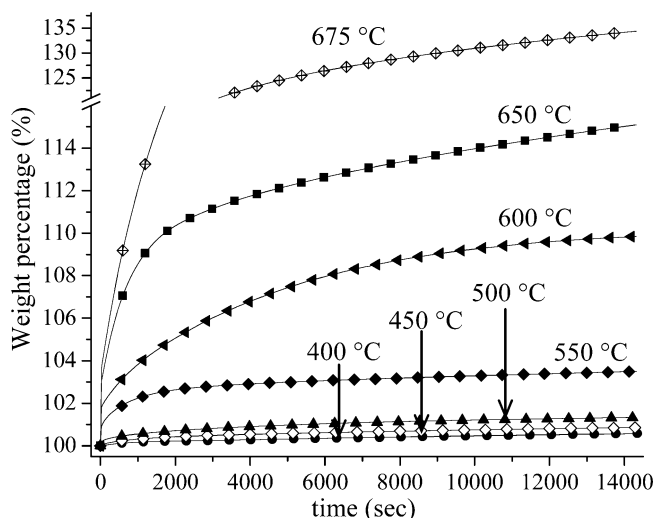


Figure 7. Isotherms of CO₂ absorption on Li₅AlO₄ at different temperatures (400 to 675 °C) in a flux of CO₂ after a sintering process at 675 °C.

TABLE 1: Kinetic Parameters Obtained from Li₅AlO₄ Isotherms Fitted to Exponential Models

temp (°C)	k_1 (1/s)	k_2 (1/s)
300 ^a	0.00073	6.7802×10^{-6}
350 ^a	0.00097	5.2696×10^{-6}
400 ^a	0.00092	1×10^{-5}
450	0.00116	2×10^{-5}
500	0.00175	3×10^{-5}
550	0.00153	8×10^{-5}
600	0.00276	2.7×10^{-4}
650	0.00257	2.7×10^{-4}
675	0.00736	6.8×10^{-4}

^a Isotherms fragmented and fitted to a simple exponential model. All other isotherms were fitted to a double exponential model.

other words, the limiting step of the total process is the lithium diffusion. Additionally, CO₂ absorption and diffusion constant values were enhanced as a function of the temperature, as was already qualitatively described in Figures 6 and 7. In both cases, the processes were improved by one (k_1) or two (k_2) orders of magnitude, increasing the temperature from 300 to 675 °C.

If both processes, CO₂ absorption (k_1) and lithium diffusion (k_2), follow a linear trend as a function of temperature, then the gradients of these best fit lines should fit the Eyring's model. These results are illustrated in Figure 8. It is clear that plots of $\ln(k/T)$ versus $1/T$ describe linear trends, fitting Eyring's model. Therefore, the activation enthalpies (ΔH) of the two different processes could be determined. The ΔH values obtained were 15.6 kJ/mol for CO₂ absorption and 52.1 kJ/mol for lithium diffusion. Therefore, this result clearly shows that lithium diffusion on Li₅AlO₄ is more dependent on temperature in comparison to the CO₂ absorption. It is very clear that lithium diffusion is the limiting step in the whole temperature range, although it is highly activated as a function of the temperature in comparison with the CO₂ absorption process.

4. Conclusions

Lithium aluminates (LiAlO₂ and Li₅AlO₄) were synthesized by solid state reaction and then characterized by XRD and SEM. In both cases, pure materials were obtained, and they presented a considerably large particle size. Then, during the dynamic thermal analyses, both ceramics presented very different behaviors for the CO₂ absorption. Whereas LiAlO₂ practically did

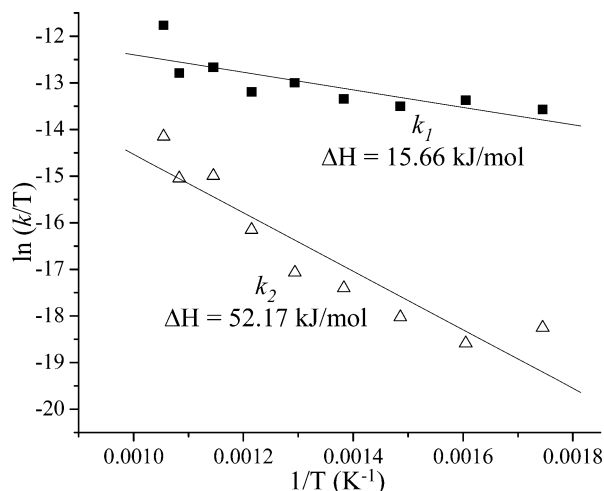


Figure 8. Eyring's plots for the rate constants of CO₂ absorption (k_1) and lithium diffusion (k_2).

not absorb CO₂ at all, Li₅AlO₄ presented a high CO₂ absorption. Li₅AlO₄ absorbed CO₂ in a wide temperature range from 200 to 700 °C, but it sintered as a function of temperature. At low temperatures, the CO₂ absorption decreased because of the sintering effect, which implies a reduction of the surface area. However at high temperatures, this phenomenon was not observed because lithium diffusion was activated.

To avoid the sintering effect and to perform a kinetic analysis, a different set of samples was homogeneously sintered before the isothermal experiments were carried out. All of these isotherms were fitted to exponential models, which described two different processes: the CO₂ absorption reaction and the lithium diffusion from the core of the particles to the surface. It could be determined that the diffusion process is the limiting step of the whole process. Additionally, the ΔH values obtained for the CO₂ absorption and lithium diffusion processes were 15.6 and 52.1 kJ/mol, respectively. This means that lithium diffusion is more dependent on the temperature.

Last but not least, it has to be mentioned that aluminum is a lighter element in comparison with the other elements used as structural ceramics for this application, for example silicates (Li₄SiO₄ and Li₂SiO₃), cuprates (Li₂CuO₂), zirconates (Li₂ZrO₃ and Li₆Zr₂O₇), or titanates (Li₄TiO₄). Therefore, because Li₅AlO₄ has the best theoretical CO₂ chemisorption capacity per gram of ceramic among the lithium ceramics and because of the results obtained, Li₅AlO₄ may become an important case of study as a CO₂ captor.

Acknowledgment. This work has been performed into the PUNTA IMPULSA-UNAM framework, and it was financially

supported by the projects 23418-CONACYT-SEMARNAT, 99102-CONACYT, and IN100609-PAPIIT-UNAM. We thank L. Baños and E. Fregoso for technical help.

References and Notes

- (1) Ochoa-Fernández, E.; Rønning, M.; Yu, X.; Grande, T.; Chen, D. *Ind. Eng. Chem. Res.* **2008**, *47*, 434–442.
- (2) Hwang, K. S.; Lee, Y. H.; Hwangbo, S. *Mater. Sci. Poland* **2007**, *25*, 969–975.
- (3) Yi, K. B.; Eriksen, D. Ø. *Sep. Sci. Technol.* **2006**, *41*, 283–296.
- (4) Nakagawa, K.; Ohashi, T. *J. Electrochem. Soc.* **1998**, *145*, 1344–1346.
- (5) Rodríguez, M. T.; Pfeiffer, H. *Thermochim. Acta* **2008**, *473*, 92–97.
- (6) Pfeiffer, H.; Bosch, P. *Chem. Mater.* **2005**, *17*, 1704–1710.
- (7) Togashi, N.; Okumura, T.; Oh-ishi, K. *J. Ceram. Soc. Jpn.* **2007**, *115*, 324–328.
- (8) Kato, M.; Essaki, K.; Nakagawa, K.; Suyama, Y.; Terasaka, K. *J. Ceram. Soc. Jpn.* **2005**, *113*, 684–686.
- (9) Palacios-Romero, L. M.; Pfeiffer, H. *Chem. Lett.* **2008**, *37*, 862–863.
- (10) Escobedo-Bretado, M.; Guzmán-Velderrain, V.; Lardizabal-Gutiérrez, D.; Collins-Martínez, V.; López-Ortiz, A. *Catal. Today* **2005**, *107–108*, 863–867.
- (11) Essaki, K.; Kato, M.; Uemoto, H. *J. Mater. Sci.* **2005**, *18*, 5017–5019.
- (12) Kalinkin, A. M.; Kalinkina, E. V.; Zalkind, O. A.; Makarova, T. I. *Colloid J.* **2008**, *70*, 33–41.
- (13) Yamaguchi, T.; Niitsuma, T.; Nair, B. N.; Nakagawa, K. *J. Membr. Sci.* **2007**, *294*, 16–21.
- (14) Johnson, C. E.; Hollenberg, G. W. *J. Nucl. Mater.* **1981**, *103*, 547–556.
- (15) Oda, T.; Oya, Y.; Tanaka, S.; Weber, W. J. *J. Nucl. Mater.* **2007**, *367*, 263–268.
- (16) Sundaram, N. T. K.; Subramania, A. *Electrochim. Acta* **2007**, *52*, 4987–4993.
- (17) Li, T. K.; Ng, D. H. L. *Mater. Sci. Eng., A* **2007**, *445–446*, 652–656.
- (18) Ribeiro, R. A.; Silva, G. G.; Mohallem, N. D. S. *J. Phys. Chem. Solids* **2001**, *62*, 857–864.
- (19) Andreev, O. L.; Zelyutin, G. V.; Martemyanova, Z. S.; Batalov, N. N. *Inorg. Mater.* **2001**, *37*, 177–179.
- (20) Follstaedt, D. M.; Biefeld, R. M. *Phys. Rev. B* **1978**, *18*, 5928–5937.
- (21) La-Ginestra, A.; Lo-Jacono, M.; Porta, P. *J. Therm. Anal.* **1972**, *4*, 5–17.
- (22) Stewner, F.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1971**, *380*, 241–243.
- (23) Hoppe, R.; König, H. *Z. Anorg. Allg. Chem.* **1977**, *430*, 211–217.
- (24) Pfeiffer, H.; Knowles, K. M. *J. Eur. Ceram. Soc.* **2004**, *24*, 2433–2443.
- (25) Mosqueda, H. A.; Vazquez, C.; Bosch, P.; Pfeiffer, H. *Chem. Mater.* **2006**, *18*, 2307–2310.
- (26) Xiong, R.; Ida, J.; Lin, Y. S. *Chem. Eng. Sci.* **2003**, *58*, 4377–4385.
- (27) Palacios-Romero, L. M.; Lima, E.; Pfeiffer, H. *J. Phys. Chem. A* **2009**, *113*, 193–198.
- (28) Alcérreca-Corte, I.; Fregoso-Israel, E.; Pfeiffer, H. *J. Phys. Chem. C* **2008**, *112*, 6520–6525.

JP902501V