Analysis and perspectives concerning CO_2 chemisorption on lithium ceramics using thermal analysis

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Abstract CO_2 removal from flue gas has been proposed as one of the most reliable solutions to mitigate global greenhouse emissions. Lithium ceramics are among several materials that have potential applications in CO_2 removal. Lithium ceramics are able to chemisorb CO_2 in a wide temperature range, presenting several interesting properties. All lithium ceramics present a similar CO_2 chemisorption reaction mechanism that has been described at the micrometric scale. However, there are several issues that have not been fully elucidated. The aim of this study is to re-analyze different experiments related to the CO_2 chemisorption on lithium ceramics and to propose how different factors control this process. This study focuses on diffusion controlled CO_2 chemisorption, which has been shown to be the limiting step of the CO_2 chemisorption process. Diffusion controlled CO_2 chemisorption appears to be mainly influenced by the chemical composition of a product's external shell.

Keywords CO_2 chemisorption · Greenhouse effect · Lithium ceramics · Thermal analyses

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Introduction

The combustion of various carbonaceous materials has increased the amount of carbon dioxide (CO_2) in the atmosphere, which has consequently produced the greenhouse effect [1–3]. In order to solve this threatening problem, several potential solutions have been proposed. One proposed solution to mitigate the greenhouse effect is to capture, separate, and concentrate CO_2 [2, 4, 5]. Different materials have been tested for utility in the CO_2 capture process [4, 6–15].

Lithium ceramics are a group of materials that can be potentially used in CO_2 capture [4, 13, 14, 16–52]. In 1998, Nakagawa and Ohashi [52] showed that lithium metazirconate (Li_2ZrO_3) could chemically trap CO_2 at relatively high temperatures (400–600 °C). Since then, several works have studied the CO_2 chemisorption of different lithium ceramics [16–62]. The ceramics that have been mainly studied are lithium zirconates (Li_2ZrO_3, $Li_6Zr_2O_7$, and Li_8ZrO_6), lithium silicates (Li_4SiO_4 and Li_2SiO_3), lithium aluminate (Li_5AlO_4), lithium cuprate (Li_2CuO_2), lithium ferrite ($LiFeO_2$), lithium titanate (Li_4TiO_4), and lithium gallate (Li_5GaO_4).

It is generally accepted that the CO_2 chemisorption on lithium ceramics is a two-step process. Initially, the lithium ceramic particles react with CO_2 at the particle surface. This superficial reaction involves the formation of an external shell composed of lithium carbonate. For a majority of these materials, a secondary lithium phase, which depends on the initial composition of the lithium ceramic, is also formed on the particle surface. Once the first stage is complete, bulk diffusion processes must be activated for the ceramic to continue CO_2 chemisorption. At this point, CO_2 chemisorption is controlled by diffusion processes [17, 21, 35, 52–54]. However, there is no agreement in the literature as to how the diffusion processes occur. While some papers suggest that

CO$_2$ bulk absorption is controlled by lithium diffusion [17, 35], other papers suggest that diffusion is CO$_2$ controlled [21, 54]. In the second case, it has been proposed that, once the external shell is produced, diffusion processes are controlled by the diffusion of CO$_2$ into the ceramic. Therefore, the movement of this molecule is the limiting step of the process. However, if this mechanism was occurring, the external shell of the particle would display some specific microstructural properties, which have not been reported. On the other hand, other groups [17, 35] have proposed that, once the external shell is produced, CO$_2$ chemisorption is controlled by lithium diffusion from the bulk particle to the surface. A few different mechanisms have been proposed for lithium diffusion through either a double layer composed of the products Li$_2$CO$_3$ and the corresponding metal oxide or a mixed external shell of these products [17, 35, 48]. These diffusion mechanisms have been supported by kinetic and lithium diffusion data [29, 41, 48, 50, 51, 55–60]. The CO$_2$ chemisorption process for bulk lithium ceramics is not completely understood. It is possible that the process does not depend on one factor but on a combination of several factors.

Different factors involved in the CO$_2$ chemisorption process are summarized below. It has been observed that the crystalline structure of a material modifies the CO$_2$ capture properties of that material. For example, the monoclinic and tetragonal Li$_2$ZrO$_3$ phases have different CO$_2$ chemisorption efficiencies [63–65]. Kinetic analysis of these phases showed that the rate of CO$_2$ absorption for the tetragonal phase is faster than for the monoclinic phase [24]. Apart from this example, it has not been possible to establish a correlation between CO$_2$ chemisorption and the crystalline structure of lithium ceramics. For example, monoclinic Li$_4$SiO$_4$ chemisorbs more CO$_2$ than the tetragonal Li$_2$ZrO$_3$ phase, which in turn chemisorbs more CO$_2$ than the monoclinic Li$_2$ZrO$_3$.

When lithium ceramics are doped with K or Na, the CO$_2$ chemisorption process is significantly improved [21, 22, 41, 54, 66, 67]. This has been explained as the result of CO$_2$ diffusion through molten lithium–potassium or lithium–sodium carbonate because these materials produce a eutectic phase that is a liquid at lower temperatures than the undoped material. As this eutectic phase is liquid at temperatures where CO$_2$ chemisorption occurs, diffusion processes become more efficient. Results show that the external shell produced on the surface of lithium ceramic particles plays an important role in the CO$_2$ chemisorption process. However, if lithium carbonate alone controls the second part of the CO$_2$ chemisorption process, all the ceramics should behave identically once the external carbonate shell is produced. This similarity in chemisorption is not observed.

Different papers in the literature have presented kinetic analyses showing that diffusion controlled CO$_2$ chemisorption is the limiting step of the reaction process [29, 41, 48, 50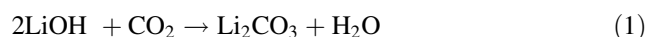, 51, 55–60]. Additionally, these reports show that the constants of both direct CO$_2$ chemisorption (k_1) and diffusion controlled CO$_2$ chemisorption (k_2) depend on temperature, and that these kinetic constants vary among lithium ceramics.

Importance of the lithium external shell

The results described above confirm that the lithium ceramic is important for the CO$_2$ chemisorption process. CO$_2$ is initially chemisorbed on the lithium ceramic and the identity of the initial lithium ceramic determines the external shell composition. The composition of the external shell plays a significant role in the CO$_2$ chemisorption process of the bulk lithium ceramic. The external shells should be examined in further detail due to the significance of this area. For this analysis, lithium ceramics are divided as a function of the external shell composition. There are three possible compositions: (1) pure Li$_2$CO$_3$, (2) Li$_2$CO$_3$ mixed with a metal oxide such as ZrO$_2$; and (3) Li$_2$CO$_3$ mixed with a secondary lithium phase such as Li$_2$SiO$_3$. It is also possible that more than one secondary lithium phases can be formed. An example of this is seen in the synthesis of the solid solution Li$_{4+x}$Si$_{1-x}$Al$_x$O$_4$, where Li$_2$SiO$_3$ and LiAlO$_2$ are produced on the external shell.

External shells composed of Li$_2$CO$_3$

The formation of a pure Li$_2$CO$_3$ external shell is only possible on lithium hydroxide (LiOH) and lithium oxide (Li$_2$O) (reactions 1 and 2) [55, 68]. Figure 1 shows the CO$_2$ capture process for Li$_2$O [55]. Initially, CO$_2$ is only captured at the Li$_2$O particle surface, which absorbs up to 15% of the mass at approximately 250 °C. At high temperature (600 °C), the CO$_2$ bulk chemisorption is induced once the diffusion processes have been activated. This activation increases the final absorption to 226%. In this case, the diffusion process only depends on the Li$_2$CO$_3$ produced over the surface of the Li$_2$O particles.

$$2\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O} \qquad (1)$$

$$\text{Li}_2\text{O} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 \qquad (2)$$

External shells composed of Li$_2$CO$_3$ and metal oxides

CO$_2$ chemisorption on Li$_2$CuO$_2$ produces Li$_2$CO$_3$ and CuO (reaction 3) [43, 44, 69]. The presence of CuO might not interfere with the diffusion process. In contrast, Li$_2$ZrO$_3$ produces a Li$_2$CO$_3$–metal oxide external shell as seen for lithium cuprate (reaction 4) through different CO$_2$ chemisorption behaviors (Fig. 1). Initially, these differences can be explained in terms of lithium reactivity. While the superficial reaction of CO$_2$ on Li$_2$CuO$_2$ occurs at
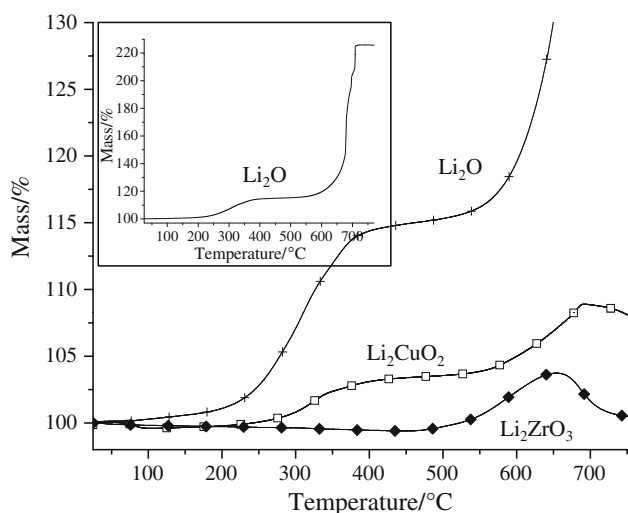
Fig. 1 Comparative dynamic TG analyses of Li_2O, Li_2CuO_2, and Li_2ZrO_3 into a CO_2 flux. The *square inset* shows the complete thermogram of the Li_2O sample

Fig. 2 Comparative dynamic TG analyses of Li_4SiO_4 and Li_5AlO_4 into a CO_2 flux. The *square inset* amplifies the CO_2 superficial chemisorption produced on the Li_4SiO_4 sample

approximately 200–250 °C, the same reaction on Li_2ZrO_3 only commences at 450–500 °C [17, 20, 70]. For Li_2ZrO_3, it is not possible to differentiate the superficial and the bulk CO_2 chemisorption processes. These results strongly suggest that CO_2 chemisorption is more limited for Li_2ZrO_3 than for Li_2CuO_2. In fact, the final CO_2 mass absorption obtained for these ceramics was 8.7% for Li_2CuO_2 and 3.8% for Li_2ZrO_3.

$$Li_2CuO_2 + CO_2 \rightarrow Li_2CO_3 + CuO \qquad (3)$$

$$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2 \qquad (4)$$
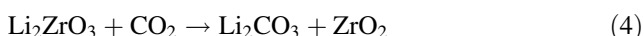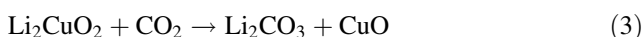
How does one explain the CO_2 chemisorption differences observed between Li_2CuO_2, Li_2ZrO_3, and Li_2O after the production of the external shell? The three ceramics have the same lithium phase (Li_2CO_3) in the external shell and different metal oxide phases (CuO and ZrO_2) as secondary phases. Lithium does not diffuse in these metal oxide phases. However, the efficiency of CO_2 chemisorption was found to vary significantly: Li_2O (85.8%) > Li_2CuO_2 (21.9%) > Li_2ZrO_3 (12.5%). If the CO_2 chemisorption behavior of Li_2CuO_2 and Li_2O are compared (Fig. 1), it can be seen that both superficial and bulk CO_2 chemisorption processes occur in similar temperature ranges. However, the mass gained is much more significant in Li_2O. As the chemisorption processes occurred in the same temperature range, qualitatively, both ceramics have a similar CO_2 reactivity. The only difference is the production of CuO in the Li_2CuO_2 case. CuO cannot improve lithium diffusion, but it may interfere with the process because the volume percentage occupied by CuO in the external shell is approximately 26. Therefore, the presence of CuO produces a barrier through which lithium is not able to diffuse. Additionally, if present on the particle surface, CuO will
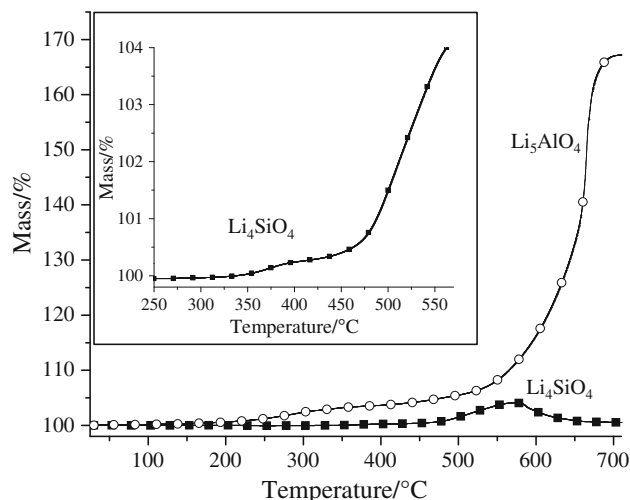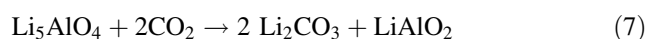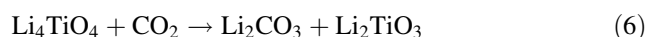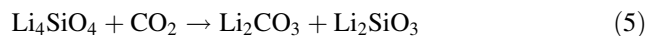
reduce the quantity of active sites where the CO_2 reaction can occur. A similar effect will be observed for Li_2ZrO_3, where the ZrO_2 volume percentage in the external shell is approximately 38.2. Li_2CO_3 does not undergo any type of phase transformation in the temperature range of interest that could activate or limit the diffusion of lithium [71, 72].

External shells composed of Li_2CO_3 and a lithium secondary phase

For the analysis of external shells consisting of Li_2CO_3 and a secondary lithium phase, Li_4SiO_4 and Li_5AlO_4 ceramics will be considered because these ceramics are two of the most promising lithium ceramics for CO_2 capture [16, 32, 35, 40, 41, 45, 47, 50]. Figure 2 compares the dynamic CO_2 chemisorption of these ceramics. Again, two different behaviors are observed. Both the ceramics behave similar to Li_2O. However, Li_5AlO_4 begins the superficial CO_2 chemisorption at approximately 200–250 °C (3%), while Li_4SiO_4 only begins the superficial CO_2 chemisorption at approximately 360 °C (0.4%). These results suggest that Li_5AlO_4 has a higher reactivity than Li_4SiO_4. As shown in the literature, Li_4TiO_4 behaves in a similar manner [16, 41, 46]. These ceramics produce external shells composed of Li_2CO_3 and the corresponding lithium secondary phase (reactions 5, 6, and 7).

$$Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3 \qquad (5)$$

$$Li_4TiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2TiO_3 \qquad (6)$$

$$Li_5AlO_4 + 2CO_2 \rightarrow 2\,Li_2CO_3 + LiAlO_2 \qquad (7)$$

The volume percentages occupied by Li_2SiO_3, $LiAlO_2$, and Li_2TiO_3 in the external shell are 50.4, 26.6 and 47.7,

respectively. Additionally, the reaction of CO_2 with any of these lithium secondary phases is not favored due to thermodynamic factors in the temperature range of interest [73, 74].

If the diffusion process only depends on the lithium carbonate, the CO_2 chemisorption behavior would be almost identical for all samples. However, this is not observed. For example, Li_4SiO_4 and Li_5AlO_4 behave very differently. While Li_4SiO_4 chemisorbs CO_2 between 350 and 570 °C (4.5%), the CO_2 chemisorption of Li_5AlO_4 occurs over a much wider temperature range (220–700 °C), absorbing up to 166.8%. The bulk diffusion controlled CO_2 chemisorption process was activated at different temperatures: 500–570 °C for Li_4SiO_4 and 580–700 °C for Li_5AlO_4. In fact, the CO_2 chemisorption varied both as a function of the lithium ceramic, with Li_5AlO_4 showing more reactivity than Li_4SiO_4, and as a function of the external shell produced. Therefore, the secondary phases of lithium must be involved in the diffusion processes.

The secondary lithium phases, such as Li_2CO_3, may promote lithium diffusion in Li_4SiO_4 and Li_5AlO_4, consequently enhancing CO_2 chemisorption. Based on this hypothesis, and by analyzing the lithium diffusion coefficients of these ceramics, several different relationships can be established. Table 1 shows the lithium diffusion coefficients of several lithium ceramics. The lithium diffusion coefficient of Li_2SiO_3 shows a one order of magnitude increase between 500 and 600 °C, which correlates with the temperature range where the CO_2 bulk chemisorption is activated on Li_4SiO_4. Similar to lithium carbonate, Li_2SiO_3 does not have a phase transformation in the temperature range of interest that could activate lithium diffusion [77].

A similar behavior can be observed for CO_2 bulk chemisorption in Li_5AlO_4. In this case, $LiAlO_2$ has a one order of magnitude lithium diffusion increment between 600 and 700 °C. This is the same temperature range where CO_2 chemisorption is significantly activated for Li_5AlO_4. Once lithium diffusion is thermally activated in each secondary phase, lithium diffusion is enhanced on Li_2CO_3–Li_2SiO_3 or Li_2CO_3–$LiAlO_2$ external shells when compared to pure Li_2CO_3 or Li_2CO_3–metal oxide external shells.

External shells composed of Li_2CO_3 and two or more lithium secondary phases

In order to further explore the previous statements, Li_4SiO_4 and Li_5AlO_4 were doped with different elements to produce mixtures of different lithium secondary phases on the external shell. The solid solutions produced were $Li_{4.2}(Si_{0.8}Al_{0.2})O_4$, $Li_{3.8}(Si_{0.8}V_{0.2})O_4$, $Li_5(Al_{0.8}Ga_{0.2})O_4$, and $Li_5(Ga_{0.8}Al_{0.2})O_4$. These solid solutions were characterized by X-ray diffraction (data not shown), and no phases other than Li_4SiO_4 or Li_5AlO_4 were detected because Li_5GaO_4 is isostructural to Li_5AlO_4. These results confirmed the incorporation of Si, V, Ga, and Al into their respective phases. Figures 3 and 4 show the CO_2 chemisorption dynamic thermograms of all the solid solutions. In the Li_4SiO_4 solid solutions, it is evident that Al or V addition significantly modified the CO_2 capture process (Fig. 3). For the $Li_{3.8}(Si_{0.8}V_{0.2})O_4$ sample, initial CO_2 chemisorption appears to be slightly favored in comparison to the Li_4SiO_4 sample ($T \leq 300$ °C). V addition may modify the superficial reactivity of the lithium orthosilicate. However, at high temperatures where the CO_2 chemisorption is controlled by diffusion processes, the CO_2 chemisorption significantly decreased for the sample containing vanadium. In fact, the CO_2 capture slopes of Li_4SiO_4 and $Li_{3.8}(Si_{0.8}V_{0.2})O_4$ between 450 and 560 °C decreased approximately five times from 0.0351 to 0.0074. Additionally, although it is a qualitative analysis, the mass gained in these samples varied from 4.3% for Li_4SiO_4 to 0.7% for $Li_{3.8}(Si_{0.8}V_{0.2})O_4$. The external shell of $Li_{3.8}(Si_{0.8}V_{0.2})O_4$ is composed of Li_2CO_3, Li_2SiO_3, and Li_3VO_4 (reaction 8). From the data presented in Table 1, it is evident that Li_3VO_4 has a lithium diffusion coefficient

Table 1 Lithium diffusion coefficient (D) on different lithium ceramics [16, 75, 76]

Temp./°C	D/cm^2 s^{-1}			
	Li_2CO_3	Li_2SiO_3	Li_3VO_4	$LiAlO_2$
500	1.3×10^{-38}	2.9×10^{-37}	6.4×10^{-41}	1.1×10^{-37}
600	1.8×10^{-37}	1.5×10^{-36}	9.8×10^{-40}	2.8×10^{-37}
700	–	4.5×10^{-36}	4.9×10^{-38}	1.9×10^{-36}

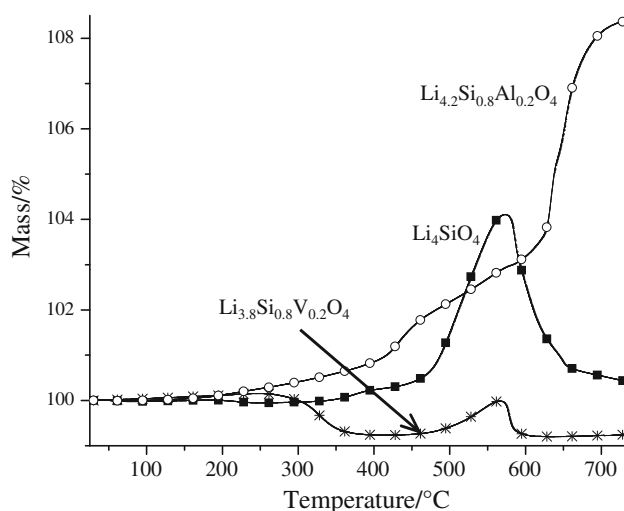D values calculated from; $D = \sigma \left[(nz^2e^2)/(kT) \right]$

Fig. 3 Comparative dynamic TG analyses of Li_4SiO_4 and two different solid solutions of it; $Li_{4.2}Si_{0.8}Al_{0.2}O_4$ and $Li_{3.8}Si_{0.8}V_{0.2}O_4$. All these thermograms were performed into a CO_2 flux

that is three orders of magnitude slower than the diffusion coefficient of Li$_2$CO$_3$ and Li$_2$SiO$_3$. Therefore, the presence of Li$_3$VO$_4$ on the external shell of the material must reduce the CO$_2$ chemisorption by decreasing the rate of lithium diffusion compared to the pure Li$_4$SiO$_4$ sample.

$$Li_{3.8}(Si_{0.8}V_{0.2})O_4 + 0.8CO_2 \rightarrow 0.8Li_2CO_3 + 0.8Li_2SiO_3 + 0.2Li_3VO_4 \quad (8)$$
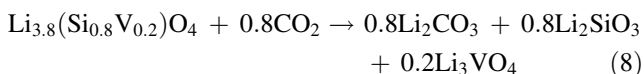
Conversely, Al addition enhanced the CO$_2$ chemisorption of Li$_4$SiO$_4$ (Fig. 3). At low temperatures, the Li$_{4.2}$(Si$_{0.8}$Al$_{0.2}$)O$_4$ thermogram shows a considerable CO$_2$ chemisorption improvement (0.9%) beginning at around 200 °C. This is in comparison to the Li$_4$SiO$_4$ sample (0. 4%), which presented this initial process between 360 and 450 °C. This observation can potentially be explained by the combination of two factors: a higher CO$_2$ superficial reaction rate produced by the Al addition and the presence of extra lithium atoms that compensate the electro-neutrality of the system. However, the most interesting part of the CO$_2$ chemisorption process was observed at high temperatures, where the external shell limits the process. In this case, the diffusion controlled CO$_2$ chemisorption processes on Li$_{4.2}$(Si$_{0.8}$Al$_{0.2}$)O$_4$ can be divided into two different processes that occur between 415 and 570 °C and between 600 and 720 °C where the mass percentage increments were equal to 3.1 and 8.2, respectively. Therefore, the maximum CO$_2$ chemisorption increased from 4.3% for Li$_4$SiO$_4$ to 8.2% for Li$_{4.2}$(Si$_{0.8}$Al$_{0.2}$)O$_4$. Qualitatively, the addition of Al increased the CO$_2$ chemisorption by a factor of 2. In this case, the lithium external shell is composed of Li$_2$CO$_3$, Li$_2$SiO$_3$, and LiAlO$_2$ (reaction 9). Therefore, the diffusion controlled CO$_2$ chemisorption of Li$_{4.2}$(Si$_{0.8}$Al$_{0.2}$)O$_4$ is potentially determined by different lithium secondary phases as a function of varying temperatures. Between 415 and 570 °C, Li$_2$CO$_3$ and Li$_2$SiO$_3$ must control the lithium diffusion as seen for Li$_4$SiO$_4$. At temperatures higher than 600 °C, a second diffusion process must be activated due to the presence of LiAlO$_2$, which increases the final amount of CO$_2$ chemisorbed. In fact, this CO$_2$ chemisorption temperature range is very similar to that observed for the Li$_5$AlO$_4$ sample (see Fig. 2). From these results, it can be concluded that Al addition enhances the superficial CO$_2$ reaction and significantly modifies the diffusion processes at the lithium external shell particularly at high temperatures where Li diffusion is activated for LiAlO$_2$ (600–700 °C).

$$Li_{4.2}(Si_{0.8}Al_{0.2})O_4 + 1.2CO_2 \rightarrow 1.2Li_2CO_3 + 0.8Li_2SiO_3 + 0.2LiAlO_2 \quad (9)$$
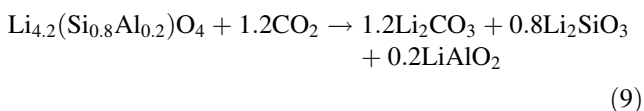
As a second example of the proposed mechanism, Fig. 4 shows the CO$_2$ dynamic thermograms of the following samples: Li$_5$AlO$_4$, Li$_5$(Al$_{0.8}$Ga$_{0.2}$)O$_4$, Li$_5$(Ga$_{0.8}$Al$_{0.2}$)O$_4$, and Li$_5$GaO$_4$. There is no lithium diffusion data for any lithium
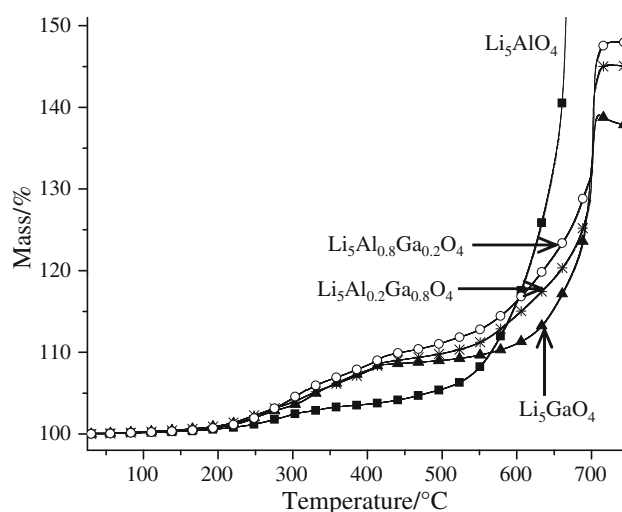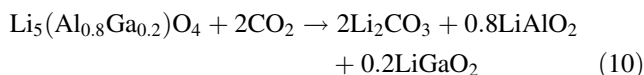

Fig. 4 Comparative dynamic TG analyses of Li$_5$AlO$_4$, two different solid solutions with gallium (Li$_5$Al$_{0.8}$Ga$_{0.2}$O$_4$ and Li$_5$Ga$_{0.8}$Al$_{0.2}$O$_4$) and Li$_5$GaO$_4$. All these thermograms were performed into a CO$_2$ flux

gallate in the temperature range of interest. However, in a previous work [78], it was observed that Li^{1+} diffusion in a Li$_4$SiO$_4$ ceramic was increased when the ceramic was doped with either Al or Ga. Additionally, the Al-doped Li$_4$SiO$_4$ sample had a higher lithium diffusion rate than that observed for the Ga-doped sample. Therefore, in the present case it would be expected that Ga addition would modify the CO$_2$ chemisorption not only during the initial reaction on the surface but also during the diffusion controlled chemisorption. The reaction of CO$_2$ with these materials produces different lithium external shells as shown by reactions 7 and 10–12.

$$Li_5(Al_{0.8}Ga_{0.2})O_4 + 2CO_2 \rightarrow 2Li_2CO_3 + 0.8LiAlO_2 + 0.2LiGaO_2 \quad (10)$$

$$Li_5(Ga_{0.8}Al_{0.2})O_4 + 2CO_2 \rightarrow 2Li_2CO_3 + 0.2LiAlO_2 + 0.8LiGaO_2 \quad (11)$$

$$Li_5GaO_4 + 2CO_2 \rightarrow 2Li_2CO_3 + LiGaO_2 \quad (12)$$
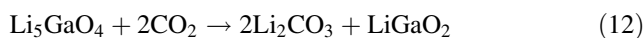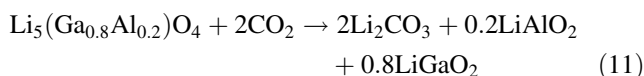
Initially, Li$_5$AlO$_4$ chemisorbs the amount of CO$_2$ at the surface between 200 and 430 °C. Gallium addition enhances superficial CO$_2$ chemisorption. However, a completely different behavior is observed at high temperatures ($T > 500$ °C) during the diffusion controlled CO$_2$ chemisorption. The CO$_2$ chemisorption process of Li$_5$AlO$_4$ occurs at the lowest temperature (535 °C) and occurs at a faster rate than observed for the other samples. For the other samples, the diffusion controlled CO$_2$ chemisorption was consecutively hindered as a function of Ga addition as follows: Li$_5$(Al$_{0.8}$Ga$_{0.2}$)O$_4$, Li$_5$(Ga$_{0.8}$Al$_{0.2}$)O$_4$, and Li$_5$GaO$_4$. The observed reduction of CO$_2$ chemisorption can be correlated to the amount of LiGaO$_2$ produced in each compound. These

results show that diffusion controlled CO_2 chemisorption is highly dependent on the secondary lithium phases produced on the external shell, as in the previous case described above.

Based on all these results and previous reaction models, [17, 21, 35, 52–54] there are potentially several factors that may enhance or limit the CO_2 chemisorption of lithium ceramics. Although there are some papers proposing that the CO_2 chemisorption process depends on CO_2 diffusion [21, 54], the results and interpretation presented here support the idea that lithium diffusion is the key component of the reaction mechanism. The initial lithium phase controls the initial reaction between CO_2 and the lithium ceramic. However, once the external lithium shell is produced, the external shell controls the CO_2 chemisorption process.

The external shell of the lithium ceramic always contains Li_2CO_3. However, in most cases, Li_2CO_3 is mixed with other secondary phases that may or may not contain lithium. A general scheme for the different possible external lithium shells is presented in Fig. 5. This scheme only applies for cases where Li_2CO_3 is a solid. If the external shell is composed of Li_2CO_3 and a metal oxide (for example, ZrO_2 in the Li_2ZrO_3 case, Fig. 5B), the presence of the metal oxide may reduce the CO_2 chemisorption process in two different ways. CO_2 chemisorption may be inhibited if the metal oxide occupies superficial sites where CO_2 molecules could potentially be initially captured. Alternatively, the metal oxide may produce a

barrier for lithium diffusion into the lithium external shell. This type of secondary phase will reduce lithium diffusion both physically and indirectly.

If the lithium external shell is composed of Li_2CO_3 and other lithium-containing phases, the following two scenarios may occur (Fig. 5C, D). The secondary lithium phase or phases may enhance or reduce the lithium diffusion depending on the lithium diffusion capacity of the phase. If the secondary lithium phase has similar or better lithium diffusion properties than Li_2CO_3, the lithium diffusion process will be improved because the lithium atoms present in the original lithium phase would have more than one material to be transported through. However, if the secondary lithium phase does not possess good lithium diffusion properties, lithium diffusion will not be improved. Even if lithium diffusion is considerably low, this secondary lithium phase may present a similar effect to that observed for the metal oxide case where the lithium diffusion is also hindered.

Finally, it must be emphasized that CO_2 chemisorption of lithium ceramics depends not only on the intrinsic factors analyzed here but also on external factors such as the flow gas where the solid–gas interface may present different regimes [50], the gas composition, variations in CO_2 concentrations [16, 58, 62], and competition from other gases for the lithium ceramic's active sites [48, 49]. One specific topic to be further analyzed is oxygen diffusion because a complete analysis has not been performed on this topic.

Fig. 5 Scheme of the lithium diffusion processes controlled by different possible external shell compositions. (A) Lithium diffusion controlled exclusively by Li_2CO_3 in solid state; (B) lithium diffusion controlled by Li_2CO_3, but limited by the metal oxide presence; (C) lithium diffusion controlled by Li_2CO_3, which is reduce by the presence of other lithium secondary phase with a smaller lithium diffusion capacity; (D) lithium diffusion controlled by Li_2CO_3, which is enhanced, at a determined temperature, by the presence of the other lithium secondary phase with a larger lithium diffusion capacity
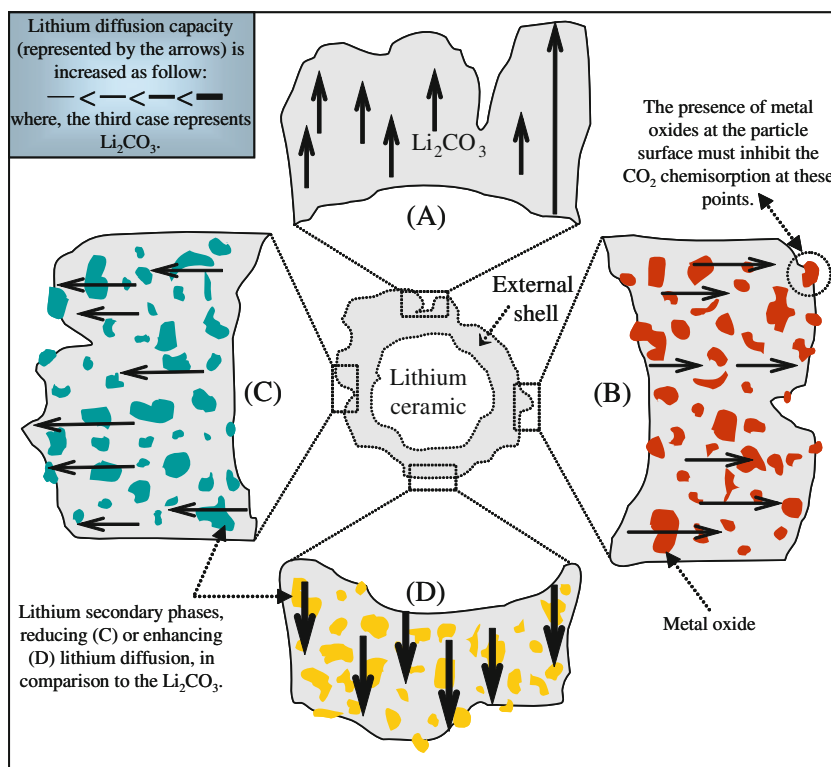
Conclusions

Different lithium ceramics were dynamically tested by TG analysis using a CO_2 flux. All obtained results clearly show that CO_2 chemisorption of lithium ceramics is controlled by various different factors. Initially, CO_2 chemisorption is controlled by the reactivity of the lithium ceramic. However, once the external lithium shell is produced at the surface of the lithium ceramic particles, this external shell controls the CO_2 chemisorption process. The portion of the CO_2 chemisorption controlled by the external shell is usually the larger of the two processes.

Li_2CO_3 is always present in the external shell but in most cases a mixture of different phases is present. The external phases may or may not contain lithium. When the external shell is composed of Li_2CO_3 and metal oxides, the presence of metal oxides reduces CO_2 chemisorption. If the external lithium shell is composed of Li_2CO_3 and another lithium phase, the CO_2 chemisorption process can be enhanced or decreased depending on the lithium diffusion coefficients of the secondary lithium phases. To elucidate this hypothesis, different solid solutions were prepared and tested. Results showed that the CO_2 chemisorption process is significantly enhanced at temperatures where the lithium secondary phase or phases increased lithium diffusion coefficients when the lithium diffusion coefficients were higher than that of Li_2CO_3.

Therefore, although there are several factors that determine the CO_2 chemisorption process, the external shell plays a significant role in the process. Consequently, when selecting a lithium ceramic for CO_2 chemisorption, the secondary lithium phase produced should be considered, in addition to the reactivity of CO_2 with the ceramic, because the external shell dictates a significant portion of the CO_2 chemisorption process.

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