Thermal Behavior and CO_2 Absorption of $Li_{2-x}Na_xZrO_3$ Solid Solutions

Heriberto Pfeiffer,*,† Carmen Vázquez,† Víctor H. Lara,‡ and Pedro Bosch†

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n, CU, Apdo. Postal 70-360, Coyoacán 04510, México DF, and Departamento de Química, Universidad Autónoma Metropolitana Iztapalapa, AV. Michoacán y la Purísima, Col. Vicentina, Del. Iztapalapa, México DF, Mexico

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Lithium−sodium metazirconate solid solutions, $Li_{2-x}Na_xZrO_3$, were tested as CO_2 captors. The thermal analyses of these materials showed that all the solid solutions present similar behaviors under air and N_2. The samples lost weight due to two different processes, desorption of physisorbed water (~100 °C) and a decarbonation process (400−700 °C). In fact, the quantities of water and CO_2 desorbed increased as a function of the sodium content. Thermal analyses into a CO_2 flux showed that $Li_{2-x}Na_xZr_2O_7$ solid solutions present a high CO_2 absorption. The solid solutions absorb CO_2 between 400 and 600 °C, but samples containing the sodium phase absorbed CO_2 in two distinct steps. First, at low temperatures, there is a CO_2 chemisorption, only at the surface of the particles, forming a carbonate shell. Later, when the temperature reaches 400 °C, or more, a second absorption process takes place. In this process lithium and/or sodium atoms diffuse from the core of the particles to the surface, through an external carbonate shell. The differences observed in the CO_2 sorption processes were explained with thermodynamic data.

Introduction

The main drawback to the use of fossil fuels is pollution. The flue gas from power plants contains high amounts of carbon dioxide (CO_2), which contributes to the greenhouse effect and the earth warming.[1−2] Thus, CO_2 has to be retained through either physical or chemical sorption, before it goes to the atmosphere.

In the past decade, several authors have reported the possible application of different ceramics as CO_2 absorbents, described as well as CO_2 captors.[2−8] These works have shown that lithium and sodium ceramics are able to retain CO_2. First, in 1998, Nakagawa and Ohashi reported the capture of CO_2 using Li_2ZrO_3 at high temperatures (400−600 °C).[9] Then, López-Ortiz and co-workers found that some sodium ceramics, Na_2ZrO_3 among them, absorb CO_2 in a similar interval of temperature.[10] Furthermore, Na_2ZrO_3 presents a better CO_2 sorption than Li_2ZrO_3.

The CO_2 chemisorption properties of Li_2ZrO_3 and Na_2ZrO_3 have been correlated to lithium or sodium mobility in the ceramics. Na_2ZrO_3 has a lamellar structure, where the sodium atoms are located among the ZrO_3^{2-} layers; sodium mobility is, then, favored. Instead, Li_2ZrO_3 has a much more packed structure, which limits lithium diffusion,[11,12] but the sodium size and weight are much higher than those of lithium.

However, a drawback that this kind of materials may present is correlated with its thermal stability. Studies have shown that lithium ceramics decompose at high temperatures, due to the lithium sublimation as lithium oxide.[5,13,14] Therefore, the use of these materials as CO_2 captors could be limited by their thermal stability.

Summarizing, $Li_{2-x}Na_xZrO_3$ solid solutions should present original behaviors as CO_2 absorbents, if both zirconates combine in a synergetic way. The synthesis and structure of these mixed oxides were already reported in a previous paper.[11] The aim of this work was to determine the thermal stability of $Li_{2-x}Na_xZrO_3$ solid solutions and to study their CO_2 absorption process.

Experimental Section

The synthesis of the materials was developed according to a previous paper.[11] $Li_{2-x}Na_xZrO_3$ samples were prepared by coprecipitation, where stoichiometric amounts of lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), and zirconium acetate ($Zr(OCH_3)_4$) were mixed and dissolved using different lithium:sodium molar ratios ($x = 0$, 0.2, 0.6, 1.0, 1.2, 1.4, and 2). Each solution

* To whom correspondence should be addressed. Phone: +52 (55) 5622 4627. Fax: +52 (55) 5616 1371. E-mail: pfeiffer@iim.unam.mx
† Universidad Nacional Autónoma de México.
‡ Universidad Autónoma Metropolitana Iztapalapa.

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Table 1. Composition as Determined by X-ray Diffraction

nominal $Li_{2-x}Na_xZrO_3$	real composition[11]
Li_2ZrO_3	Li_2ZrO_3 (100%)
$Li_{1.8}Na_{0.2}ZrO_3$	Li_2ZrO_3 (100%)
$Li_{1.4}Na_{0.6}ZrO_3$	Li_2ZrO_3 (89%), Na_2ZrO_3 (11%)
$LiNaZrO_3$	Li_2ZrO_3 (46%), Na_2ZrO_3 (54%)
$Li_{0.8}Na_{1.2}ZrO_3$	Li_2ZrO_3 (28%), Na_2ZrO_3 (72%)
$Li_{0.6}Na_{1.4}ZrO_3$	Na_2ZrO_3 (100%)
Na_2ZrO_3	Na_2ZrO_3 (100%)

was heated at 70 °C until the precipitate dried. Finally, the powders were pulverized and heat treated at 900 °C for 4 h. The samples were labeled according to the x value on the general formula, for example, $Li_{1.8}Na_{0.2}ZrO_3$.

The composition of the samples was determined by X-ray diffraction (XRD), using Bruker AXS D8 Advance equipment, coupled to a copper anode X-ray tube. On the other hand, to obtain the radial distribution functions, an X-ray tube with a molybdenum wavelength was used to reach the required high values of the h parameter ($h = (4\pi \sin \theta)/\lambda$). This tube was coupled to a Siemens D-500 diffractometer. The Kα radiation was selected with a filter, and the data were measured by step scanning (1/8°) with a scintillation counter.

Thermogravimetric analyses (TGAs) were performed with TA Instruments equipment. The solid solutions were heat treated with a heating rate of 5 °C min^{-1} from room temperature to 1000 °C. These analyses were carried out under three different saturated atmospheres: air, N_2, and CO_2. Furthermore, another set of samples was analyzed isothermically at 400, 500, and 600 °C. All the isothermal analyses were performed under a saturated CO_2 atmosphere.

Results and Discussion

The characterization of the samples was presented in a previous paper.[11] The composition of the $Li_{2-x}Na_xZrO_3$ solid solutions is summarized in Table 1. Samples with a nominal composition of Li_2ZrO_3 and $Li_{1.8}Na_{0.2}ZrO_3$ presented only the X-ray diffraction peaks of Li_2ZrO_3, showing that 0.2 is the maximum solubility of sodium into the Li_2ZrO_3 structure. Samples with a nominal composition between $2 - x = 1.4$ and $2 - x = 0.8$ were a mixture of both zirconates, and finally, $Li_{0.6}Na_{1.4}ZrO_3$ had the same crystalline structure as Na_2ZrO_3. Hence, the solubility of lithium into the sodium phase is 0.6.

The experimental radial distribution functions of the reference samples, i.e., Li_2ZrO_3 and Na_2ZrO_3, are shown in Figure 1. As the structures were very different, the shapes of the curves and the peak positions differed. The Na_2ZrO_3 peaks fitted the theoretical peaks obtained for Zr−O. Only the peaks at 2.9 and 6.2 Å did not fit with the framework due to Zr and O atoms; these distances were found in the Zr−Zr and O−O radial functions. The contribution of Na−O distances to the experimental curve had to be found at $r =$ 2.3, 4.0, 5.1, and 7.0 Å. Unfortunately, these radii all overlap with the Zr−O distances.

The experimental radial distribution function of the lithium zirconate fitted well with the theoretical curve. All peaks were due to the Zr−O framework and may be attributed to Zr−O or O−O distances. No resolved peaks due to Li−O distances were observed. The radii corresponding to the Li−O neighbors were coincident with Zr−O or O−O distances. Lithium is a light element whose scattering power is small, and its contribution to the X-ray diffraction pattern and, thus, to the radial distribution is expected to be small.

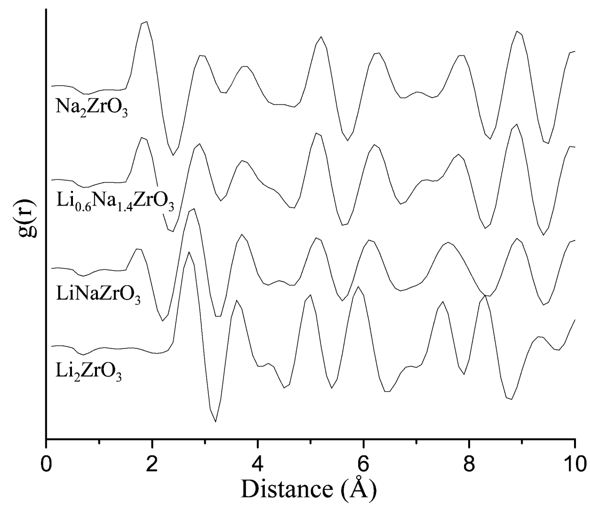

Figure 1. Radial distribution functions of $Li_{2-x}Na_xZrO_3$ solid solutions.

When sodium was incorporated into Li_2ZrO_3 to form $Li_{1.8}Na_{0.2}ZrO_3$, no effect was observed in the radial distribution function (data not shown). The structure remained the same, and hence, sodium only occupied the lithium positions. Instead, if lithium was incorporated into Na_2ZrO_3 to obtain $Li_{0.6}Na_{1.4}ZrO_3$, the corresponding radial distribution was shifted ca. 0.05 Å.

The $LiNaZrO_3$ sample, which was shown to be constituted by a mixture of lithium-enriched Na_2ZrO_3 (54%) and Li_2ZrO_3 (46%), confirms the results as the radial distribution, as expected, may be interpreted in terms of the previous curves. All the peaks present for Li_2ZrO_3 were found in the $LiNaZrO_3$ curve; they were slightly shifted toward larger values, ca. 0.2 Å. Also, the peaks present for $Li_{0.6}Na_{1.4}ZrO_3$ were found but shifted toward lower values, ca. 0.15 Å. Note that the peak at 1.8 Å can only be explained as due to $Li_{0.6}Na_{1.4}ZrO_3$. The peaks of $LiNaZrO_3$ were in an intermediate position between those of $Li_{0.6}Na_{1.4}ZrO_3$ and those of Li_2ZrO_3 as they were the convolution of the peaks of both materials.

Thermal Behavior. $Li_{2-x}Na_xZrO_3$ samples presented interesting thermal behaviors (Figure 2). The samples were analyzed as they were obtained from the synthesis process, without any further treatment. All the samples had a first weight loss between room temperature and 100 °C, which was attributed to physisorbed water over the zirconate particles. The amount of desorbed water increased with sodium content. While Li_2ZrO_3 practically did not lose weight, Na_2ZrO_3 lost up to 9 wt %.

After the dehydration process, Li_2ZrO_3 only lost 1 wt % in a large range of temperatures. This amount must be associated with the lithium sublimation present in all lithium ceramics treated at high temperatures.[5,13,14] $LiNaZrO_3$ lost 1.4 wt %, in a smaller interval of temperature (530−680 °C), compared to the $Li_{1.8}Na_{0.2}ZrO_3$ sample, which lost 3.5 wt % between 200 and 700 °C. Finally, $Li_{0.6}Na_{1.4}ZrO_3$ and Na_2ZrO_3 lost 3.6 and 5.7 wt % between 590 and 795 °C and between 585 and 825 °C, respectively. All these changes were attributed to decarbonation processes. Li_2ZrO_3 and Na_2-

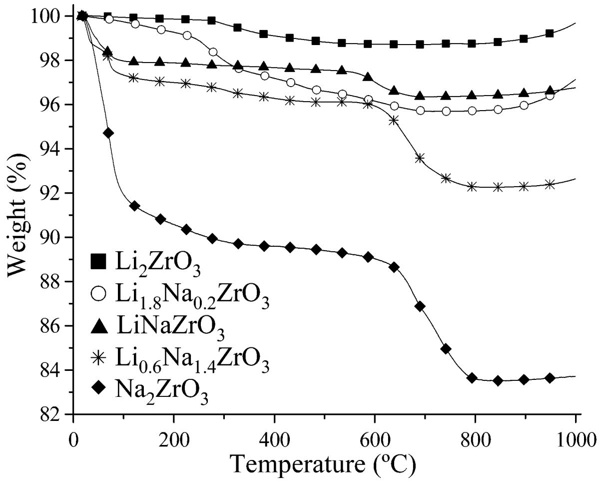

Figure 2. Thermogravimetric analyses of different $Li_{2-x}Na_xZrO_3$ solid solutions in a flux of air.

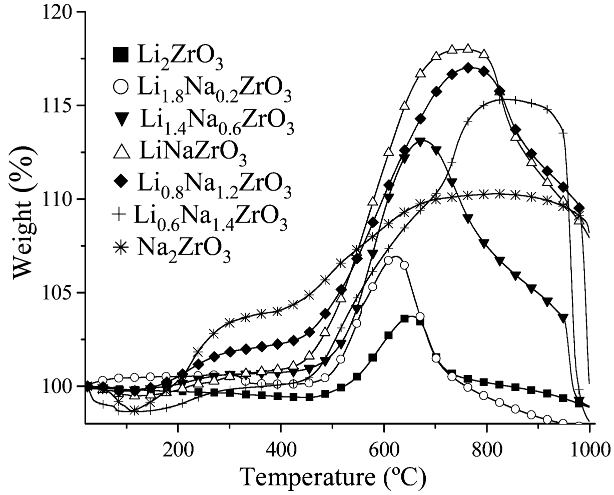

Figure 3. Thermogravimetric analyses of different $Li_{2-x}Na_xZrO_3$ solid solutions in a flux of CO_2.

ZrO_3 absorb CO_2, and their desorption processes occur at 720 and 800 °C, respectively.[9,10] Additionally, CO_2 sorption of Na_2ZrO_3 is higher than that of Li_2ZrO_3. This explains why the temperatures and weight loss increased as a function of the nominal x in $Li_{2-x}Na_xZrO_3$. Moreover, the carbonation process of the samples must occur during cooling and storage of the samples.

Samples analyzed under a N_2 flux presented exactly the same behavior. Hence, none of these processes (dehydration, decarboxylation, or decomposition) depend on the environmental gas. In other words, oxygen, present in air, does not accelerate any of these processes, as could be expected. For example, it has been shown that, in other lithium ceramics, such as $Li_6Zr_2O_7$, air modifies the thermal stability.[5]

CO_2 Absorption. Both zirconates Li_2ZrO_3 and Na_2ZrO_3 are good CO_2-absorbent materials. Then if $Li_{2-x}Na_xZrO_3$ solid solutions present a synergetic effect, they should capture more CO_2 than the amount predicted by a linear relationship, through the following reaction:

$$Li_{2-x}Na_xZrO_3 + CO_2 \rightarrow (Li_{2-x}Na_x)CO_3 + ZrO_2 \quad (1)$$

where $(Li_{2-x}Na_x)CO_3$ represents merely a mixture of both carbonates Li_2CO_3 and Na_2CO_3.

All samples analyzed by TGA presented some CO_2 absorption (Figure 3). First, Li_2ZrO_3 presented a standard CO_2 absorption. Li_2ZrO_3 increased its weight by about 4 wt %, which is in good agreement with previous reports,[5,15] and the maximum absorption was obtained at 656 °C.

Then the $Li_{1.8}Na_{0.2}ZrO_3$ sample showed a significant improvement in the CO_2 absorption. It increased to 6.9 wt %, and the maximum absorption temperature was shifted toward lower temperatures, 626 °C. Besides, the absorption peak became broader than the Li_2ZrO_3 peak.

In the third sample, $Li_{1.4}Na_{0.6}ZrO_3$, the CO_2 absorption was almost duplicated (13.1 wt %). Furthermore, the curve revealed two different sorption processes. First, a sorption was shown by a small peak, between 200 and 350 °C (1 wt %). Later, at higher temperatures (between 500 and 650 °C), the absorption increased to 12.1 wt %. This CO_2 sorption mechanism was more evident as the sodium content increased. Perhaps the absorption observed at low temperatures is due to a chemical sorption only at the surface of the particles, as reported for other ceramics.[8] However, lithium phases did not seem to produce this surface reaction, which was observed only on the sodium-containing particles.

$LiNaZrO_3$ was the sample presenting the best CO_2 retention. It absorbed 19 wt %, and the maximum absorption was obtained at 749 °C. This temperature is 93 °C higher than that for Li_2ZrO_3. The $Li_{0.8}Na_{1.2}ZrO_3$ sample had a behavior similar to that of the $LiNaZrO_3$ sample, although reaching a weight increased by 2 wt % less (17 wt %).

Last, in $Li_{0.6}Na_{1.4}ZrO_3$ and Na_2ZrO_3 (samples where Na_2ZrO_3 was the only crystalline phase detected), the absorption decreased to 15.3 and 10.3 wt %, respectively. These samples presented the same trends, the peaks being broader and the maximum temperature shifted to higher temperatures.

In a previous paper,[11] a structural model for $Li_{2-x}Na_xZrO_3$ solid solutions was proposed, where the sodium phase is trapped in the lithium phase. This proposition is in good agreement with the thermal and CO_2 sorption results. As Li_2ZrO_3 was found to be the external phase, the surface CO_2 sorption on Na_2ZrO_3 increases when this phase is more exposed. Furthermore, as the sodium content increased, two processes were modified: (1) The maximum absorption temperature moved toward higher temperatures, and (2) the CO_2 absorption process began at lower temperatures, producing broader peaks. These two effects can be explained by the differences in the formation enthalpies (ΔH_f) and the melting points of Li_2CO_3 and Na_2CO_3. ΔH_f values of lithium and sodium carbonates are −1215.4 and −1130.8 kJ/mol, respectively.[16] As the ΔH_f of Na_2ZrO_3 is 84.6 kJ mol^{-1} lower than that of Li_2ZrO_3, Na_2ZrO_3 needs less energy to be produced. In other words, Na_2ZrO_3 can be produced at lower temperatures than Li_2ZrO_3. This can explain the CO_2 sorption at low temperatures when sodium is added to the solid solution. On the contrary, the melting point of Na_2ZrO_3 (851 °C) is 131 °C higher than that of Li_2ZrO_3 (720 °C).[16] Then,

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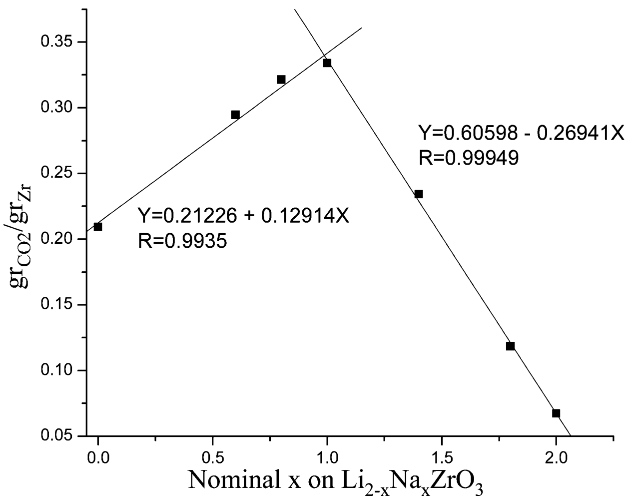

Figure 4. Number of grams of CO_2 captured per gram of zirconium as a function of x on $Li_{2-x}Na_xZrO_3$.

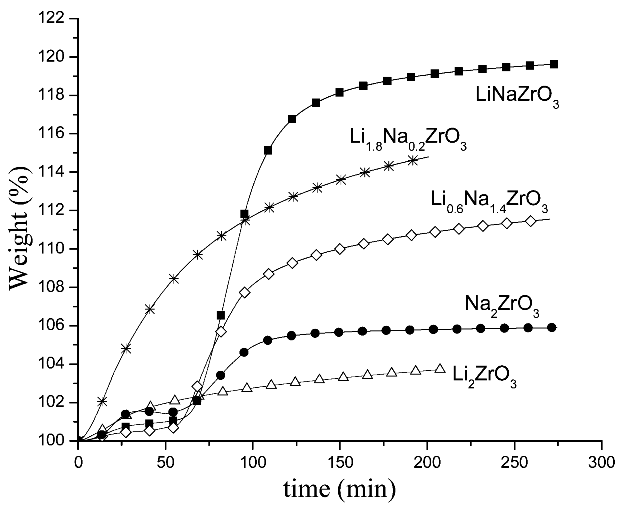

Figure 5. Isothermal analyses of $Li_{2-x}Na_xZrO_3$ solid solutions heat treated at 600 °C in a flux of CO_2.

Na_2CO_3 decomposes and consequently desorbs the CO_2 at higher temperature than Li_2ZrO_3. This can explain why the maximum absorption temperature moved to higher temperatures and why the peaks became broader as a function of the sodium content.

Figure 4 shows the amount of captured CO_2 per gram of zirconium by the various $Li_{2-x}Na_xZrO_3$ samples. This graph showed two different linear trends. This behavior suggests a synergetic effect between lithium and sodium zirconates. Furthermore, the incorporation of lithium into the sodium zirconate seems to favor CO_2 sorption, 2 times more than the incorporation of sodium into the lithium structure, as may be concluded from the two different slopes (0.27 and 0.13).

Figure 5 shows the isothermal graphs at 600 °C. When the Li_2ZrO_3 curve was compared to the $Li_{1.8}Na_{0.2}ZrO_3$ curve, it was found that Li_2ZrO_3 only absorbed 3.7 wt %, after 200 min, whereas $Li_{1.8}Na_{0.2}ZrO_3$ solid solution absorbed 4 times that amount (14.7 wt %) in the same period of time. The CO_2 sorption in Li_2ZrO_3 was much lower than in $Li_{1.8}Na_{0.2}ZrO_3$, at any time. This was obvious at short times (between 0 and 40 min), as shown by the slopes of the curves, 0.16 and 0.04 wt % min^{-1} for $Li_{1.8}Na_{0.2}ZrO_3$ and Li_2ZrO_3, respectively. These differences were associated with the sodium presence in the Li_2ZrO_3 structure. Sodium atoms must locally modify locally the structure of Li_2ZrO_3. As sodium atoms are larger than lithium atoms, the Li_2ZrO_3 structure was probably expanded, favoring an easier diffusion of the lithium atoms to reach the CO_2 molecules. It has to be pointed out that only one sorption process can be seen in both samples.

Table 2. Number of Grams of CO_2 Absorbed per Gram of Sample in the Isothermal Processes after 275 min

solid solution	$g_{CO_2}/g_{ceramic}$ 400 °C	500 °C	600 °C
Li_2ZrO_3	0.004	0.026	0.037
$Li_{1.8}Na_{0.2}ZrO_3$	0.018	0.104	0.147
$LiNaZrO_3$	0.040	0.135	0.196
$Li_{0.6}Na_{1.4}ZrO_3$	0.034	0.073	0.115
Na_2ZrO_3	0.026	0.029	0.060

All the other samples contained Na_2ZrO_3 (Table 1), and all of them presented a double-step sorption process, during the isothermal analyses. First, there was a small sorption of about 2 wt %, in the first hour, which corresponded to a CO_2 sorption over the surface of the particles. At higher temperatures, once lithium and sodium atoms had the energy necessary to diffuse from the core to the surface of the particles, the second and more important absorption process took place. These experimental data were in total agreement with those from previous papers that report a similar CO_2 sorption mechanism for this kind of ceramics.[8]

The sample $LiNaZrO_3$ was the ceramic that presented the best absorption properties. $LiNaZrO_3$ absorbed almost 20 wt % after 270 min. As in the TGA analysis, CO_2 absorption by $LiNaZrO_3$ was 4 times higher than the absorption by the pure zirconates Li_2ZrO_3 and Na_2ZrO_3. Additionally, once the second absorption process started, CO_2 sorption in $LiNaZrO_3$ was faster than in $Li_{1.8}Na_{0.2}ZrO_3$ and Li_2ZrO_3. In this case, the slope of the curve, at short times, was 0.76 wt % min^{-1}, which is 5 times more rapid. Last, CO_2 absorption decreased in the $Li_{0.6}Na_{1.4}ZrO_3$ and Na_2ZrO_3 samples. These solid solutions only absorbed 11.5 and 6.0 wt %.

The isothermal sorption trends at 400 and 500 °C were similar to those at 600 °C. Table 2 compares the maximum CO_2 absorbed for each material at those temperatures. As expected, the CO_2 absorbed changed as a function of temperature. For instance, in $LiNaZrO_3$, when CO_2 absorption was performed at 400 °C, only 0.04 $g_{CO_2}/g_{LiNaZrO_3}$ was retained after 180 min. However, when the absorption processes were performed at 500 and 600 °C, the amounts of CO_2 absorbed were 0.135 and 0.19 $g_{CO_2}/g_{LiNaZrO_3}$, in the same time period. Similar behaviors were observed for the other solid solutions.

Figure 6 displays the efficiency of the solid solutions at the different temperatures. In this case, the efficiency should be defined as

$$E\ (\%) = \frac{\text{experimental } CO_2 \text{ absorbed (wt \%)}}{\text{theoretical maximum } CO_2 \text{ absorbed (wt \%)}} \times 100 \quad (2)$$

where the theoretical maximum CO_2 absorbed was calculated for each nominal composition. For example, $LiNaZrO_3$ was

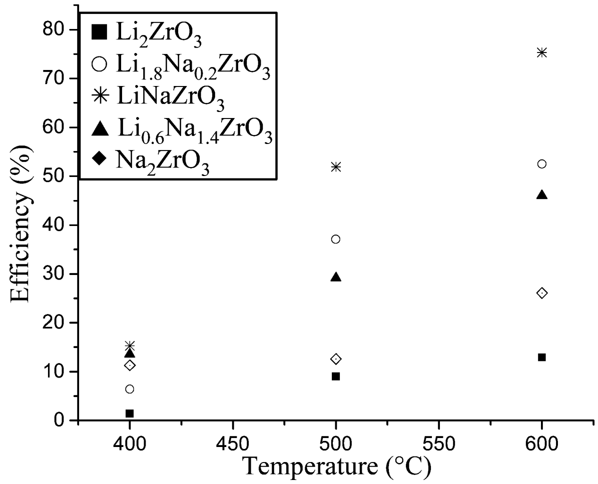

Figure 6. Efficiency of $Li_{2-x}Na_xZrO_3$ solid solutions for CO_2 absorption at different temperatures.

the nominal composition that presented the best efficiency. This sample absorbed up to 75.3% of the total CO_2 that could be absorbed according to reaction 3.

$$LiNaZrO_3 + CO_2 \rightarrow {}^1/_2Li_2CO_3 + {}^1/_2Na_2CO_3 + ZrO_2 \qquad (3)$$

It seems that sodium located at the surface of the particles is very reactive, while bulk lithium and sodium atoms require higher temperatures to diffuse through the carbonate phase and react with CO_2.

Conclusions

Thermal analyses showed that all the solid solutions presented similar behaviors under air and N_2. The first weight loss occurred between room temperature and 100 °C, and it was attributed to physisorbed water over the zirconate particles. The water desorbed increases with sodium content due to a higher hydration of the sodium phase. All samples present a second weight loss due to a decarbonation process.

$Li_{2-x}Na_xZr_2O_7$ solid solutions presented a high CO_2 absorption, compared to pure alkaline zirconates Li_2ZrO_3 and Na_2ZrO_3. All compounds absorbed CO_2 between 400 and 600 °C, but ceramics containing the sodium phase absorbed CO_2 in two distinct steps. At low temperatures (200−300 °C), there was a surface CO_2 absorption. Later, the CO_2 absorption process continued when the temperature reached 400 °C or more. In this case, lithium and sodium atoms diffused from the core of the particles to the surface through the carbonate external shell. The sample presenting the best conditions for CO_2 chemical sorption was $LiNaZrO_3$ at 600 °C, where the CO_2 absorbed was 0.196 $g_{CO_2}/g_{LiNaZrO_3}$, which means an efficiency of 75.3%. Furthermore, $LiNaZrO_3$ absorbed CO_2 faster than any of the other ceramics at short times.

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