Lithium Cuprate (Li_2CuO_2): A New Possible Ceramic Material for CO_2 Chemisorption

Luis M. Palacios-Romero and Heriberto Pfeiffer*
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Circuito Exterior s/n Cd. Universitaria, Del. Coyoacán, CP 04510, México DF, Mexico

(Received May 14, 2008; CL-080494; E-mail: pfeiffer@iim.unam.mx)

Li_2CuO_2 was used for the CO_2 chemisorption process. Li_2CuO_2 was thermally treated under a flux of CO_2, dynamically (from 25 to 1000 °C) and isothermically. The results clearly showed that Li_2CuO_2 is able to chemisorb CO_2 in a wider range of temperatures than those presented by other lithium ceramics. Therefore, this ceramic may become a new option as CO_2 captor.

In the last ten years, some lithium ceramics have been proposed as possible CO_2 captors because of the chemisorption process produced between CO_2 and lithium atoms present in the ceramic structure.[1–5] Some of the ceramics proposed up to now are; lithium oxide (Li_2O), lithium zirconates (Li_2ZrO_3 and $Li_6Zr_2O_6$), lithium orthosilicate (Li_4SiO_4), and lithium orthotitanate (Li_4TiO_4).[6–13] In general, all these materials show a similar chemisorption mechanism. First, CO_2 reacts over the ceramic particle surface, producing a lithium carbonate (Li_2CO_3) external shell and the corresponding residual oxide. Then, in order to continue the CO_2 chemisorption, lithium atoms have to diffuse from the core of the particles toward the surface to complete the reaction.[6] Additionally, it has been proposed that one of the most important steps, and perhaps the limiting one, of the whole process is the diffusion. On the other hand, lithium cuprate (Li_2CuO_2) has been used for different electrical applications such as cathodes for lithium batteries and as a superconductor material, owing to the excellent lithium diffusion.[14–19] The high lithium diffusion and structural characteristics have been reported for Li_2CuO_2; therefore, the aim of the work reported here was to study and demonstrate whether or not Li_2CuO_2 is able to capture CO_2, by a mechanism similar to that reported previously for other lithium ceramics.

Li_2CuO_2 sample was obtained by a coprecipitation method using 10 wt % excess of lithium, and its diffractogram is shown in Figure 1. Li_2CuO_2 was the main phase, and only small quantities of copper oxide (CuO) were detected. The presence of CuO indicates that excess lithium was not enough to complete the reaction. However, the volume fraction of this phase should not exceed 5% of the total system, and as CuO does not capture CO_2, it would not interfere with the CO_2 capture analysis. The same figure shows the morphology of the Li_2CuO_2 particles. As can be seen, the particles presented a dense polyhedral shape, with a particle size distribution of $11 \pm 2\,\mu m$. Additionally, the particles presented some kind of texture; the surface of the particles seems to be corrugated. This kind of morphology and particle size are similar to those obtained for other lithium ceramics that have been tested as CO_2 captors. It could be useful for comparison reasons.

Once Li_2CuO_2 was characterized, the material was thermally treated under a CO_2 stream to analyze whether or not this material is able to act as a CO_2 captor. If Li_2CuO_2 traps chemically CO_2, the following reaction may occur (reaction 1):

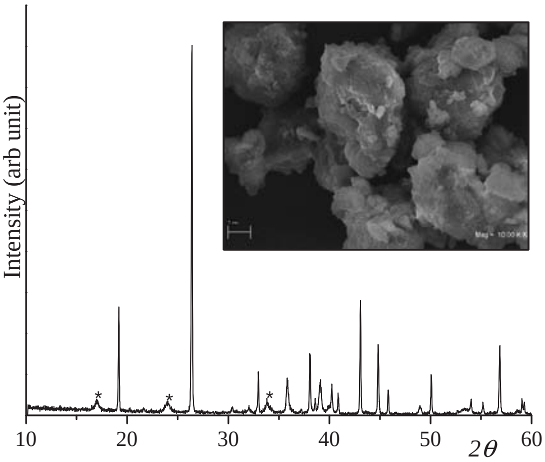

Figure 1. XRD pattern and SEM micrograph of the Li_2CuO_2 sample. Peaks labeled as (*) corresponds to the CuO phase.

$$Li_2CuO_2 + CO_2 \rightarrow Li_2CO_3 + CuO \qquad (1)$$

where the reaction is similar to those observed for other lithium ceramics,[1–6,8] in which lithium carbonate is produced in addition to a residual oxide, CuO in this case. For this reaction, the theoretical capacity is corresponds $0.412\ g_{CO_2}/g_{Li_2CuO_2}$.

Figure 2a presents the thermogram of Li_2CuO_2, and it is clear that different processes took place. First, at temperatures lower than 100 °C, a dehydration process was observed. It merely corresponds to the evaporation of some water molecules adsorbed over the surface of the ceramic. After that, two different increments of weight were produced between 120 and 400 °C, and 500 and 690 °C, respectively. Although this kind of thermal trend has not been observed for other lithium ceramics, it has been published that other alkali ceramics presents a similar behavior.[5,20] In those cases, the whole chemisorption process is divided in two steps: First, at low temperatures, a superficial reaction is produced. At this moment, an external alkali carbonate shell is formed over the surface of the ceramic particles. Then, when the temperature is increased sufficiently and the alkali metal diffusion is activated, the reaction continues through the bulk of the material, completing the CO_2 chemisorption. For Li_2CuO_2, a similar behavior can be described. The superficial reaction proceeds between 120 and 400 °C. Between 500 and 690 °C the lithium diffusion should be activated and the process is completed. In order to prove that Li_2CuO_2 is chemically trapping CO_2 in both ranges of temperature, two isothermal experiments were conducted at 350 and 650 °C (Figure 2b). These two temperatures were chosen, because they fit very well with the two processes identified as superficial and bulk chemisorption at the dynamic thermogram. As can be seen, the quantity of CO_2 trapped was dramatically increased as a function of the temperature. While Li_2CuO_2 only increased 4 wt % after 150 min at 350 °C, the total

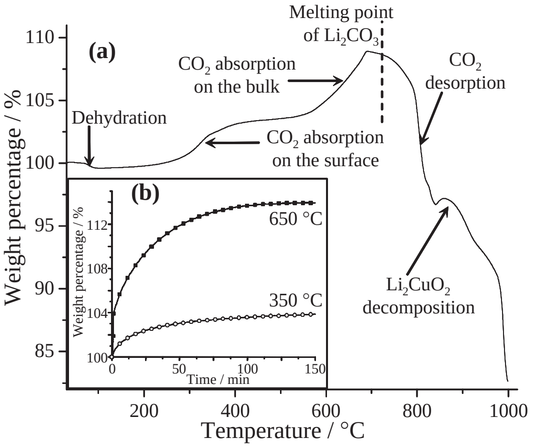

Figure 2. Thermogravimetric, dynamic and isothermic, analyses of the Li_2CuO_2 into a flux of CO_2.

weight increment observed at 650 °C was 13.6 wt % in the same period of time. It means that at 650 °C Li_2CuO_2 is able to trap more than three times as much CO_2 than at 350 °C, but its efficiency is only equal to 33.8%. Additionally, at the beginning of the absorption process, the reaction rate seems to be much faster. In fact, the differences observed on the slopes of the isotherms were 12.4 and 30.1 wt %/min at 350 and 650 °C, respectively. Later, both slopes became close to zero. It means that in both cases, the reaction almost has reached equilibrium. Hence, the difference observed in the total weight gained can be associated to the lithium diffusion process which must be activated at high temperatures but not at low temperatures. Finally, in order to confirm that CO_2 is being trapped chemically, the residual powders obtained after the two isothermal reactions were analyzed by XRD. In both cases, a mixture of Li_2CuO_2, Li_2CO_3, and CuO were detected (data not shown). Therefore, reaction 1 does occur, and it can be established that the trapping mechanism is a chemisorption process. Coming back to the dynamic thermogram, it seems that Li_2CuO_2 decomposed at high temperatures. Between 700 and 840 °C, Li_2CuO_2 undergoes a CO_2 desorption, which is in agreement with the Li_2CO_3 melting point. This fact may be used to regenerate the ceramic, which is one of the basic conditions for using these ceramics as CO_2 captor, in other words cyclability. Nevertheless, more and different studies must be done to really elucidate the cyclability of this ceramic. Finally, in the dynamic thermogram at around 840 °C, the sample showed a small weight increase. This behavior has been associated with a second trapping of CO_2 produced during lithium sublimation as Li_2O.[10] It seems that Li_2O reacts with CO_2 producing Li_2CO_3 that disappears later by thermal decomposition. This data, as well as the fact that the sample lost more that 15 wt % of its original weight, confirms the lithium sublimation. In total 55 wt % of the total lithium present in the sample is lost as Li_2O. Therefore, at temperatures higher than 840 °C, the following thermal decomposition reaction is taking place (reaction 2):

$$Li_2CuO_2 \rightarrow Li_2O + CuO \qquad (2)$$

Summarizing, Li_2CuO_2 was synthesized by the coprecipitation method, and it presented a dense polyhedral morphology with some corrugated texture and particle size of about 11 μm. The thermal analysis performed in a CO_2 stream, clearly showed that Li_2CuO_2 would be a new alternative for the CO_2 chemisorption among the lithium ceramics. Li_2CuO_2 presented the following mechanism: A superficial reaction proceeds at low temperatures, forming an external shell of lithium carbonate and copper oxide. At higher temperatures, lithium diffusion is activated and the CO_2 chemisorption goes on through the bulk material. Finally, the CO_2 desorption occurs between 700 and 840 °C, and Li_2CuO_2 decomposes through the lithium sublimation at temperatures higher than 840 °C.

Although the general mechanism for CO_2 capture by Li_2CuO_2 is similar to those of other lithium ceramics, this material seems to have some advantages over those ceramics. Specially, two different aspects have to be pointed out: 1) Li_2CuO_2 begins to react with CO_2 at lower temperatures (120 °C) than any other lithium ceramic reported up to now, which usually begin to react with CO_2 at around 400–450 °C. Hence, this material may be used on different applications or under different thermal conditions. 2) Last but not least, copper is 31 wt % lighter than zirconium, and of course, copper is cheaper. Therefore, it may have several implications thinking about the design of a prototype for industrial applications. Actually, it should be mentioned that Li_2CuO_2 posses one of the best theoretical CO_2 chemisorption capacities per gram of ceramic, 0.401 $g_{CO_2}/g_{ceramic}$. For example, alkali zirconates, Li_2ZrO_3, and Na_2ZrO_3, only can absorb 0.287 $g_{CO_2}/g_{ceramic}$ and 0.237 $g_{CO_2}/g_{ceramic}$, respectively.[4,5,20] Finally, Li_4SiO_4 is able to absorb theoretically up to 0.733 $g_{CO_2}/g_{ceramic}$, assuming that the whole lithium participate in the reaction. But most of the papers published have shown that Li_4SiO_4 only reacts partially with CO_2, producing Li_2CO_3 and Li_2SiO_3.[3,7,11] Therefore, the real CO_2 absorption capacity is 0.366 $g_{CO_2}/g_{ceramic}$. It means a capacity lower than that of Li_2CuO_2. Although this work is not enough to consider Li_2CuO_2 as a good option for CO_2 capture, it presents encouraging results to continue studying this ceramic into this research field.

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