

## Lithium Cuprate ( $\text{Li}_2\text{CuO}_2$ ): A New Possible Ceramic Material for $\text{CO}_2$ 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*

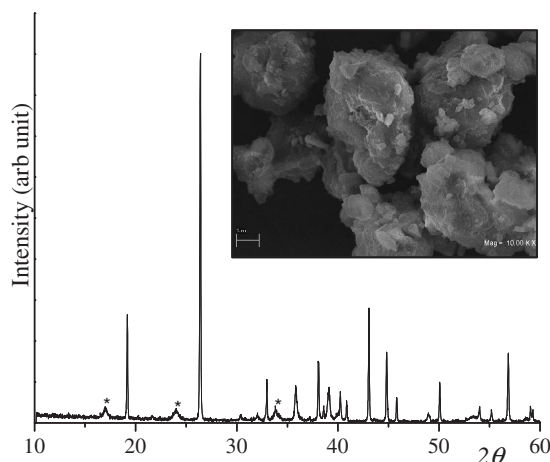
(Received May 14, 2008; CL-080494; E-mail: pfeiffer@iim.unam.mx)

$\text{Li}_2\text{CuO}_2$  was used for the  $\text{CO}_2$  chemisorption process.  $\text{Li}_2\text{CuO}_2$  was thermally treated under a flux of  $\text{CO}_2$ , dynamically (from 25 to 1000 °C) and isothermally. The results clearly showed that  $\text{Li}_2\text{CuO}_2$  is able to chemisorb  $\text{CO}_2$  in a wider range of temperatures than those presented by other lithium ceramics. Therefore, this ceramic may become a new option as  $\text{CO}_2$  captor.

In the last ten years, some lithium ceramics have been proposed as possible  $\text{CO}_2$  captors because of the chemisorption process produced between  $\text{CO}_2$  and lithium atoms present in the ceramic structure.<sup>1–5</sup> Some of the ceramics proposed up to now are; lithium oxide ( $\text{Li}_2\text{O}$ ), lithium zirconates ( $\text{Li}_2\text{ZrO}_3$  and  $\text{Li}_6\text{Zr}_2\text{O}_6$ ), lithium orthosilicate ( $\text{Li}_4\text{SiO}_4$ ), and lithium orthotitanate ( $\text{Li}_4\text{TiO}_4$ ).<sup>6–13</sup> In general, all these materials show a similar chemisorption mechanism. First,  $\text{CO}_2$  reacts over the ceramic particle surface, producing a lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) external shell and the corresponding residual oxide. Then, in order to continue the  $\text{CO}_2$  chemisorption, lithium atoms have to diffuse from the core of the particles toward the surface to complete the reaction.<sup>6</sup> 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 ( $\text{Li}_2\text{CuO}_2$ ) has been used for different electrical applications such as cathodes for lithium batteries and as a superconductor material, owing to the excellent lithium diffusion.<sup>14–19</sup> The high lithium diffusion and structural characteristics have been reported for  $\text{Li}_2\text{CuO}_2$ ; therefore, the aim of the work reported here was to study and demonstrate whether or not  $\text{Li}_2\text{CuO}_2$  is able to capture  $\text{CO}_2$ , by a mechanism similar to that reported previously for other lithium ceramics.

$\text{Li}_2\text{CuO}_2$  sample was obtained by a coprecipitation method using 10 wt % excess of lithium, and its diffractogram is shown in Figure 1.  $\text{Li}_2\text{CuO}_2$  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  $\text{CO}_2$ , it would not interfere with the  $\text{CO}_2$  capture analysis. The same figure shows the morphology of the  $\text{Li}_2\text{CuO}_2$  particles. As can be seen, the particles presented a dense polyhedral shape, with a particle size distribution of  $11 \pm 2 \mu\text{m}$ . 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  $\text{CO}_2$  captors. It could be useful for comparison reasons.

Once  $\text{Li}_2\text{CuO}_2$  was characterized, the material was thermally treated under a  $\text{CO}_2$  stream to analyze whether or not this material is able to act as a  $\text{CO}_2$  captor. If  $\text{Li}_2\text{CuO}_2$  traps chemically  $\text{CO}_2$ , the following reaction may occur (reaction 1):

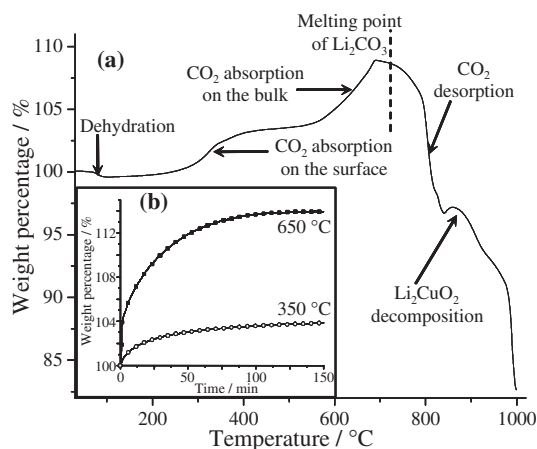


**Figure 1.** XRD pattern and SEM micrograph of the  $\text{Li}_2\text{CuO}_2$  sample. Peaks labeled as (\*) corresponds to the CuO phase.



where the reaction is similar to those observed for other lithium ceramics,<sup>1–6,8</sup> in which lithium carbonate is produced in addition to a residual oxide, CuO in this case. For this reaction, the theoretical capacity is corresponds  $0.412 \text{ gCO}_2/\text{gLi}_2\text{CuO}_2$ .

Figure 2a presents the thermogram of  $\text{Li}_2\text{CuO}_2$ , 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.<sup>5,20</sup> 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  $\text{CO}_2$  chemisorption. For  $\text{Li}_2\text{CuO}_2$ , 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  $\text{Li}_2\text{CuO}_2$  is chemically trapping  $\text{CO}_2$  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  $\text{CO}_2$  trapped was dramatically increased as a function of the temperature. While  $\text{Li}_2\text{CuO}_2$  only increased 4 wt % after 150 min at 350 °C, the total



**Figure 2.** Thermogravimetric, dynamic and isothermic, analyses of the  $\text{Li}_2\text{CuO}_2$  into a flux of  $\text{CO}_2$ .

weight increment observed at  $650^\circ\text{C}$  was 13.6 wt % in the same period of time. It means that at  $650^\circ\text{C}$   $\text{Li}_2\text{CuO}_2$  is able to trap more than three times as much  $\text{CO}_2$  than at  $350^\circ\text{C}$ , 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  $650^\circ\text{C}$ , 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  $\text{CO}_2$  is being trapped chemically, the residual powders obtained after the two isothermal reactions were analyzed by XRD. In both cases, a mixture of  $\text{Li}_2\text{CuO}_2$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{CuO}$  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  $\text{Li}_2\text{CuO}_2$  decomposed at high temperatures. Between 700 and  $840^\circ\text{C}$ ,  $\text{Li}_2\text{CuO}_2$  undergoes a  $\text{CO}_2$  desorption, which is in agreement with the  $\text{Li}_2\text{CO}_3$  melting point. This fact may be used to regenerate the ceramic, which is one of the basic conditions for using these ceramics as  $\text{CO}_2$  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  $840^\circ\text{C}$ , the sample showed a small weight increase. This behavior has been associated with a second trapping of  $\text{CO}_2$  produced during lithium sublimation as  $\text{Li}_2\text{O}$ .<sup>10</sup> It seems that  $\text{Li}_2\text{O}$  reacts with  $\text{CO}_2$  producing  $\text{Li}_2\text{CO}_3$  that disappears later by thermal decomposition. This data, as well as the fact that the sample lost more than 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  $\text{Li}_2\text{O}$ . Therefore, at temperatures higher than  $840^\circ\text{C}$ , the following thermal decomposition reaction is taking place (reaction 2):



Summarizing,  $\text{Li}_2\text{CuO}_2$  was synthesized by the coprecipitation method, and it presented a dense polyhedral morphology with some corrugated texture and particle size of about 11  $\mu\text{m}$ . The thermal analysis performed in a  $\text{CO}_2$  stream, clearly showed that  $\text{Li}_2\text{CuO}_2$  would be a new alternative for the  $\text{CO}_2$  chemisorp-

tion among the lithium ceramics.  $\text{Li}_2\text{CuO}_2$  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  $\text{CO}_2$  chemisorption goes on through the bulk material. Finally, the  $\text{CO}_2$  desorption occurs between 700 and  $840^\circ\text{C}$ , and  $\text{Li}_2\text{CuO}_2$  decomposes through the lithium sublimation at temperatures higher than  $840^\circ\text{C}$ .

Although the general mechanism for  $\text{CO}_2$  capture by  $\text{Li}_2\text{CuO}_2$  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)  $\text{Li}_2\text{CuO}_2$  begins to react with  $\text{CO}_2$  at lower temperatures ( $120^\circ\text{C}$ ) than any other lithium ceramic reported up to now, which usually begin to react with  $\text{CO}_2$  at around  $400\text{--}450^\circ\text{C}$ . 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  $\text{Li}_2\text{CuO}_2$  possesses one of the best theoretical  $\text{CO}_2$  chemisorption capacities per gram of ceramic,  $0.401 \text{ gCO}_2/\text{gceramic}$ . For example, alkali zirconates,  $\text{Li}_2\text{ZrO}_3$ , and  $\text{Na}_2\text{ZrO}_3$ , only can absorb  $0.287 \text{ gCO}_2/\text{gceramic}$  and  $0.237 \text{ gCO}_2/\text{gceramic}$ , respectively.<sup>4,5,20</sup> Finally,  $\text{Li}_4\text{SiO}_4$  is able to absorb theoretically up to  $0.733 \text{ gCO}_2/\text{gceramic}$ , assuming that the whole lithium participate in the reaction. But most of the papers published have shown that  $\text{Li}_4\text{SiO}_4$  only reacts partially with  $\text{CO}_2$ , producing  $\text{Li}_2\text{CO}_3$  and  $\text{Li}_2\text{SiO}_3$ .<sup>3,7,11</sup> Therefore, the real  $\text{CO}_2$  absorption capacity is  $0.366 \text{ gCO}_2/\text{gceramic}$ . It means a capacity lower than that of  $\text{Li}_2\text{CuO}_2$ . Although this work is not enough to consider  $\text{Li}_2\text{CuO}_2$  as a good option for  $\text{CO}_2$  capture, it presents encouraging results to continue studying this ceramic into this research field.

This work was supported by the projects 46522-Q CONACYT and 23418-CONACYT-SEMARNAT, IMPULSA-UNAM and IN103506-PAPIIT.

#### References

- 1 K. Nakagawa, T. Ohashi, *J. Electrochem. Soc.* **1998**, *145*, 1344.
- 2 K.-H. Choi, Y. Korai, I. Mochida, *Chem. Lett.* **2003**, *32*, 924.
- 3 R. Xiong, J. Ida, Y. S. Lin, *Chem. Eng. Sci.* **2003**, *58*, 4377.
- 4 M. Y. Veliz-Enriquez, G. Gonzalez, H. Pfeiffer, *J. Solid State Chem.* **2007**, *180*, 2485.
- 5 H. Pfeiffer, C. Vazquez, V. H. Lara, P. Bosch, *Chem. Mater.* **2007**, *19*, 922.
- 6 H. Mosqueda, C. Vazquez, P. Bosch, H. Pfeiffer, *Chem. Mater.* **2006**, *18*, 2307.
- 7 J. Ida, R. Xiong, Y. S. Lin, *Sep. Purif. Technol.* **2004**, *36*, 41.
- 8 E. Ochoa-Fernández, M. Rønning, T. Grande, D. Chen, *Chem. Mater.* **2006**, *18*, 1383.
- 9 E. Ochoa-Fernández, M. Rønning, T. Grande, D. Chen, *Chem. Mater.* **2006**, *18*, 6037.
- 10 H. Pfeiffer, P. Bosch, *Chem. Mater.* **2005**, *17*, 1704.
- 11 M. E. Bretado, V. G. Velderrain, D. L. Gutiérrez, V. Collins-Martínez, A. L. Ortiz, *Catal. Today* **2005**, *107–108*, 863.
- 12 C. Gauer, W. Heschel, *J. Mater. Sci.* **2006**, *41*, 2405.
- 13 K. B. Yi, D. Ø. Eriksen, *Sep. Sci. Technol.* **2006**, *41*, 283.
- 14 E. M. L. Chung, G. J. McIntyre, D. M. Paul, G. Balakrishnan, M. R. Lees, *Phys. Rev. B* **2003**, *68*, 144410.
- 15 A. S. Prakash, D. Larcher, M. Morcrette, M. S. Hegde, J.-B. Leriche, C. Masquelier, *Chem. Mater.* **2005**, *17*, 4406.
- 16 G. Vitins, E. A. Raekelboom, M. T. Weller, J. R. Owen, *J. Power Sources* **2003**, *119–121*, 938.
- 17 K. Nakamura, K. Kawai, K. Yamada, Y. Michihiro, T. Moriga, I. Nakabayashi, T. Kanashiro, *Solid State Ionics* **2006**, *177*, 2775.
- 18 S. Giri, H. Chudo, H. Nakamura, M. Shiga, *J. Alloys Compd.* **2001**, *326*, 61.
- 19 H. Arai, S. Okada, Y. Sakurai, J. Yamaki, *Solid State Ionics* **1998**, *106*, 45.
- 20 I. Alcerreca-Corte, E. Fregoso-Israel, H. Pfeiffer, *J. Phys. Chem. C* **2008**, *112*, 6520.