

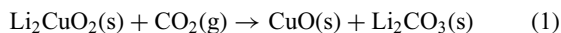
Synthesis and CO₂ Absorption Properties of Single-phase Li₂CuO₂ as a CO₂ Absorbent

Yusuke Matsukura, Takeshi Okumura, Ryota Kobayashi, and Katsuyoshi Oh-ishi*
Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University,
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551

(Received May 24, 2010; CL-100493; E-mail: oh-ishi@kc.chuo-u.ac.jp)

Synthesis and CO₂ absorption properties of single-phase Li₂CuO₂ oxide were studied by X-ray powder diffraction and thermogravimetry. Samples of Li₂CuO₂ were prepared in solid state using Li₂CO₃ and CuO as starting reagents. A mixture of Li₂CO₃ and CuO was heated at temperatures of 600–1000 °C and then quenched to room temperature. From XRD, it was found that single-phase Li₂CuO₂ can be obtained by heat treatment at 680–685 °C with the quenching operation. The single phase was never obtained without quenching; that is, quenching rate (°C s⁻¹) seems to be an important factor which determinates whether sample is obtained as a single phase or not. From thermogravimetry, it was found that Li₂CuO₂ begins to absorb CO₂ at around 230 °C, then drastically absorbs CO₂ at over 600 °C, reaching 40.2 mass % maximum CO₂ absorption, and finally emits CO₂ over 900 °C. The maximum CO₂ absorption (40.2 mass %) is larger than that (36.7 mass %) of Li₄SiO₄ CO₂ absorbent.

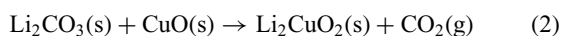
In 1998, Nakagawa and Ohashi reported that Li₂ZrO₂ can absorb CO₂ gas and suggested that the oxide could be a novel solid-ceramic CO₂ absorbent.¹ However, the CO₂ absorption rate is not impressive. Since their report, many studies have been reported on synthesis and CO₂ absorption properties for Li complex oxides including Li₂ZrO₃,^{2–15} As a result, Li₄SiO₄,^{11–13} LiFeO₂,¹⁴ and Li₄TiO₄¹⁵ were discovered and studied for their CO₂ absorption properties. According to previous reports,^{2–15} Li₄SiO₄ seems to be an excellent solid-ceramic CO₂ absorbent. However, recently, Palacios-Romero and Pfeiffer reported Li₂CuO₂ to be a new solid-ceramic CO₂ absorbent.¹⁶ If Li₂CuO₂ reacts with CO₂, the following reaction occurs.



According to this equation, the maximum CO₂ absorption is theoretically estimated as 40.2 mass % {molecular weight(CO₂)/molecular weight(Li₂CuO₂) = 0.402} when the reaction completes. However, it was reported that 40.2 mass % absorption was not confirmed because single-phase Li₂CuO₂ could not be obtained.¹⁶

In this letter, we report on the synthesis of perfect single-phase Li₂CuO₂ and the CO₂ absorption properties and compare this to those of the known solid-ceramic CO₂ absorbents like the Li₂ZrO₃, Li₄SiO₄, LiFeO₂, and Li₄TiO₄.

Samples of Li₂CuO₂ were prepared in solid state using Li₂CO₃ (99.999% purity, Rare Metallic Co., LTD) and CuO (99.99% purity, Rare Metallic Co., LTD) powder reagents and the following formation reaction.



Before these reagents were weighed for the synthesis, thermogravimetry was performed on these reagents in order to examine whether absorbed moisture was present. After thermogravimetry, these reagents were weighed in an appropriate molar ratio and mixed/ground in an agate mortar by hand for 1 h. Obtained

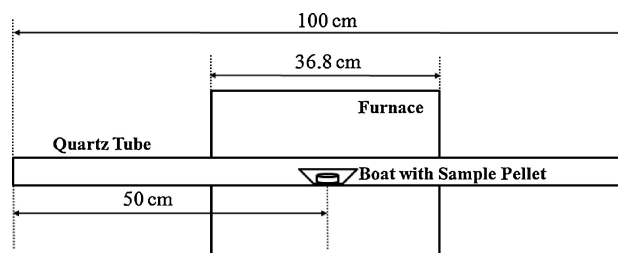


Figure 1. Schematic figure of the electric furnace used for sample synthesis for single-phase Li₂CuO₂.

powder mixtures were pressed into a pellet. The pellet was put on a gold film on an alumina boat. The boat was put on an electric furnace. The furnace used for the synthesis is shown in Figure 1. After the sample pellet was heated for several hours, the boat with sample pellet was quickly moved from the center to outside of the quartz tube. In this way, the sample was quenched. Quenching rate was measured by monitoring temperature of the sample pellet with time. The temperature of the sample was monitored by an R-type thermocouple which was fixed to the alumina boat with sample pellet during the heat treatment. The quenching rate (°C s⁻¹) could be changed by changing the distance of the alumina boat from the center (synthesis temperature) to the end (room temperature) of the quartz tube. For example, a quenching rate of 3.7 °C s⁻¹ was measured when the distance from the center was 25 cm. In the same way, the quenching rate of 5.4 °C s⁻¹ was measured at 50 cm. The maximum quenching rate of 24.5 °C s⁻¹ in this study was achieved when the sample pellet on the gold film on a thin platinum boat was quickly moved from the center to the end of the quartz tube under an air stream of over 25 L min⁻¹. Inversely, the minimum quenching rate 0.1 °C s⁻¹ was measured when the boat with sample was furnace-cooled in air. After the synthesis with these quenching operations, obtained pellets were Li₂CuO₂ samples for X-ray powder diffraction (XRD) and thermogravimetry (TG-DTA) measurements.

XRD measurement to assess phase purity were carried out using a diffractometer (Rigaku Corp., Rint2100) with CuKα radiation. In order to examine CO₂ absorption of the samples, mass change and DTA signal of the samples were measured with a thermobalance (Ulvac-Riko, Inc., TGD9600) when the samples were heated in a 100 vol % CO₂ atmosphere from room temperature to 1000 °C with a heating rate of 5 °C min⁻¹.

For obtaining single-phase Li₂CuO₂, we tried to synthesize Li₂CuO₂ samples by changing synthesis temperatures and quenching rates. Single-phase Li₂CuO₂ could not be obtained at temperatures under 670 °C, and over 700 °C in air, despite the presence or absence of the quenching. Li₂CO₃ and CuO phases remained in the samples synthesized under the former con-

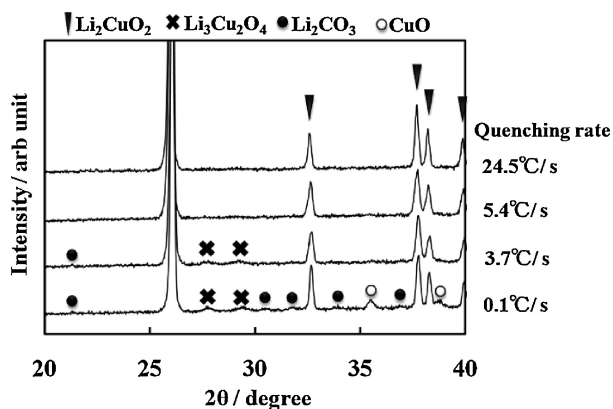


Figure 2. XRD profiles of synthesized Li_2CuO_2 with several quenching rates from 685 °C in air.

ditions, while samples under the latter conditions were found to be partially melted.

XRD profiles of the samples synthesized at 685 °C with several quenching rates are shown in Figure 2. From the figure, it is found that (i) the sample quenched at 5.4 °C s⁻¹ was single phase, (ii) CuO, Li₂CO₃, and Li₃Cu₂O₄¹⁷ of the extra phases were found in the samples quenched with the quenching rates of 3.7 and 1.0 °C s⁻¹, and (iii) intensity of these extra phases increased as the quenching rate decreased. Next, we tried to synthesize Li₂CuO₂ by changing synthetic temperatures at a constant quenching rate of 5.4 °C s⁻¹. From the results, it is found that single-phase Li₂CuO₂ could be obtained in the temperature region of 680 °C ≤ T ≤ 685 °C. In addition, the sample synthesized at 690 °C was found to be subtly melted, and very small diffraction peaks at 35.4 and 38.6° from CuO phase were detected. It is suggested that the melting seems to depend on the melting or instability of Li₂CO₃ phase around 700 °C. Moreover, powdery Li₂CuO₂ was instable against humidity because LiOH phase was detected in the powdery Li₂CuO₂ ground in a agate mortar for 15 min in the case that degree of humidity was over 50%. On the other hand, bulk (ceramic) Li₂CuO₂ was comparatively stable against humidity. Net volume of single-phase Li₂CuO₂ sample was almost 100% by XRD and thermogravimetry in the case that we ground the ceramic sample to powder fleetly or avoided high humidity day for the grinding.

Mass change and DTA signal of the single-phase Li₂CuO₂ were measured under 100 vol % CO₂ atmosphere from room temperature to 1000 °C at 5 °C min⁻¹ of the heating rate by a thermobalance procedure described in the experimental section. The TG data are shown in Figure 3. From the figure, it is found that the mass of the sample weakly increases around 230 °C, then drastically increases at over 600 °C, reaching the maximum at about 875 °C, and finally decreases over 875 °C. The maximum mass increase was measured to be 40.2%. Exothermic DTA signals were detected corresponding to the mass increases, respectively. XRD measurement was performed on a sample heated until 875 °C under 100 vol % CO₂. The measurement showed that only Li₂CO₃ and CuO phases existed, while Li₂CuO₂ phase was not detected in the sample. From the results of the TG and XRD measurements, the reaction between Li₂CuO₂ and CO₂ could be described by eq 1. According to reaction (1), the calculated maximum mass increase is 40.2%

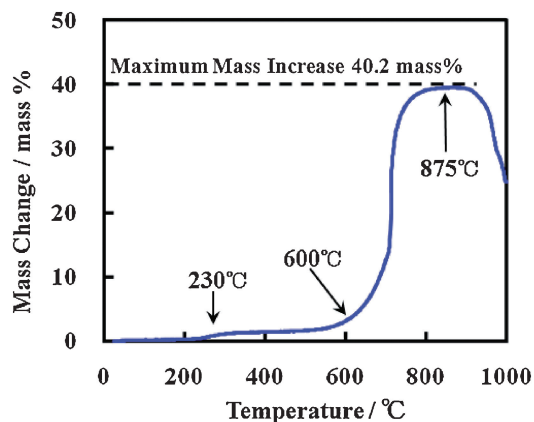


Figure 3. Temperature dependence of mass increase of single-phase Li₂CuO₂.

when the reaction completes. It is found that the measured maximum mass increase was consistent with the calculated value. This has not been shown in previous reports.¹⁶ From these experimental results one may surmise that the quenching is necessary. The reason seems to be as follows. According to the formation reaction (2) of Li₂CuO₂, CO₂ emission is necessary in order to complete the reaction. On the other hand, CO₂ absorption reaction of Li₂CuO₂ is shown as reaction (1). The reactions (1) and (2) are opposite, each other. Therefore, there is a possibility that formed Li₂CuO₂ returns to Li₂CO₃ and CuO in the suitable temperature region (680–685 °C) if CO₂ remains in the furnace, and the formed Li₂CO₃ and CuO react each other and form Li₃Cu₂O₄ phase around 300 °C.

The single-phase Li₂CuO₂ can be obtained in the solid state at 680–685 °C in air with quenching rates over 5.4 °C s⁻¹. The single-phase Li₂CuO₂ can absorb 40.2 mass % of CO₂. The value of 40.2 mass % is consistent with the maximum CO₂ absorption value estimated from the reaction between Li₂CuO₂ and CO₂.

The authors thank Mr. N. Togashi and Ms. K. Gotou for useful discussion.

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. Vázquez, 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 K. Essaki, K. Nakagawa, M. Kato, *J. Ceram. Soc. Jpn.* **2001**, *109*, 829.
- 12 M. Kato, K. Nakagawa, *J. Ceram. Soc. Jpn.* **2001**, *109*, 911.
- 13 M. E. Bretado, V. G. Velderrain, D. L. Gutiérrez, V. Collins-Martínez, A. L. Ortiz, *Catal. Today* **2005**, *107–108*, 863.
- 14 M. Kato, K. Essaki, K. Nakagawa, Y. Suyama, K. Terasaka, *J. Ceram. Soc. Jpn.* **2005**, *113*, 684.
- 15 N. Togashi, T. Okumura, K. Oh-ishi, *J. Ceram. Soc. Jpn.* **2007**, *115*, 324.
- 16 L. M. Palacios-Romero, H. Pfeiffer, *Chem. Lett.* **2008**, *37*, 862.
- 17 M. T. Weller, D. R. Lines, D. B. Currie, *J. Chem. Soc., Dalton Trans.* **1991**, 3137.