

Chemical Sorption of Carbon Dioxide (CO₂) on Lithium Oxide (Li₂O)

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Received January 17, 2006. Revised Manuscript Received March 7, 2006

The behavior of lithium oxide (Li₂O) under an atmosphere of CO₂ was studied using thermogravimetric analysis, scanning electron microscopy, and X-ray diffraction techniques. Results show that Li₂O can be used for CO₂ retention. It is a better absorbent than other lithium ceramics. A chemisorption topochemical reaction is proposed to explain the sorption of CO₂. The kinetic parameters were obtained. First, the CO₂ sorption is controlled by a first-order reaction. Later, CO₂ sorption depends on the diffusion of lithium through the formed shell of Li₂CO₃, with an extraordinary increase of the diffusion at 600 °C, due to an unusual increase of lithium mobility.

Introduction

Many industries, such as power generation, produce carbon dioxide (CO₂) at high temperature. The CO₂ presence in the environment has increased the heat trapping capability of the atmosphere, that is, the greenhouse effect.^{1,2} Then, to have a cleaner environment, such emissions must be controlled.^{3,4}

Currently, different absorbents, such as polymer membranes, zeolites, some perovskite oxides, magnesia, or soda lime, are used to retain CO₂.^{5,6} Nevertheless, CO₂ sorption with these materials is a hard task in the industrial conditions due to high temperatures. Thus, new materials, with good cyclability, adequate absorption/desorption kinetics, and high selectivity and sorption capacity for CO₂ at high temperatures,^{3,7} have to be tailored. In this sense, some lithium ceramics (Li₂ZrO₃, Li₆Zr₂O₇, and Li₄SiO₄) seem to present adequate CO₂ sorption at high temperatures.^{3,4,6,8–13} These ceramics are recyclable, and they are selective at high temperature. In these ceramics, Li is the main component due to its ionic mobility and its affinity to CO₂.

However, other conditions may exist where the use of a CO₂ absorbent is required, for example, in spaceships or submarines for the CO₂ control produced by human activity. In these conditions the conventional absorbent is the LiOH·H₂O.¹⁴ Still, a hydroxide is hardly recyclable, and during storage it may decompose. In this case, Li₂O is an interesting alternative for this kind of applications.

Lithium oxide (Li₂O, lithia) is the most basic lithium ceramic, and it is used as a thermal stabilizer for glasses. An amount as low as 3% can reduce the melting temperature several grades and affect the melt surface tension. Furthermore, as Li₂O promotes devitrification in glass, it is employed during firing to soft the α–β quartz transition in the cooling cycle.¹⁵ In the nuclear industry, lithium oxide has been proposed as a breeder material for the new fusion reactor. Indeed, lithia has a low vapor pressure at high temperature, high tritium breeding capability, high thermal conductivity, low electrical conductivity, and low tritium solubility.¹⁶

As far as CO₂ retention is concerned, no reported studies were found. In this work, we evaluate the CO₂ sorption capacity of Li₂O as a function of temperature and time. A kinetic correlation is proposed between the CO₂ retained and the structural modifications of Li₂O particles. Last, results are compared to those reported in the references for other lithium ceramics.

Experimental Section

Commercial Li₂O (Aldrich) was used, and the purity of the CO₂ gas employed was 99 wt %. Thermal analyses were performed in TA Instruments equipment. First, for the thermogravimetric analysis (TGA), the sample was heat treated at a heating rate of 5 °C min⁻¹, under an atmosphere of CO₂. Then, isotherms were obtained at 200, 300, 500, and 600 °C, for 2 h. The powders obtained after the isothermal analyses were studied by X-ray diffraction (XRD), using

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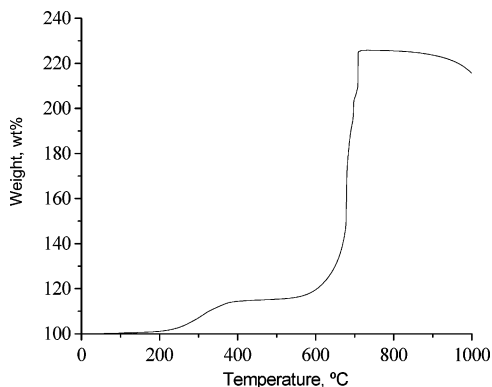


Figure 1. TGA curves of Li_2O in a CO_2 flux.

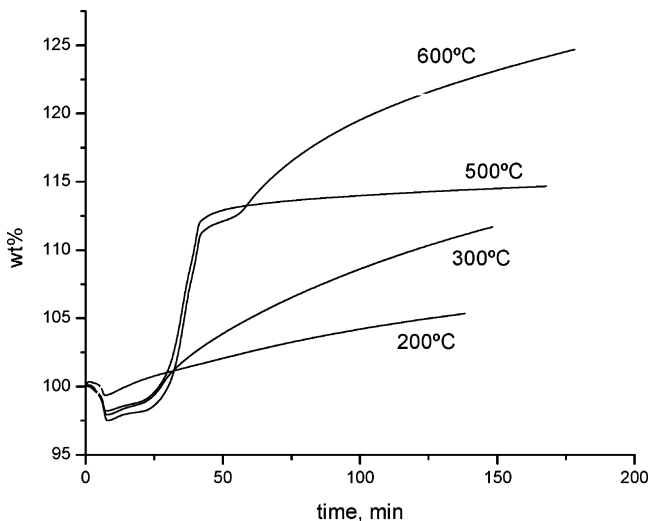


Figure 2. Isotherms of CO_2 sorption on Li_2O at several temperatures under a CO_2 atmosphere

a Bruker axis, D8 Advance diffractometer with a copper anode X-ray tube, where the $\text{Cu K}\alpha_1$ wavelength was selected with a monochromator. Compounds were identified using the JCPDS files. For comparison purposes, a Li_2O sample was exposed to air at room temperature for 22 days. A scanning electron microscope (SEM), Stereoscan 440, Cambridge, was used to determine the particle size and morphology of the materials before and after thermal treatments. The samples had to be recovered with gold to avoid the lack of conductivity.

Results

Figure 1 illustrates the thermogravimetric behavior of Li_2O under an atmosphere of CO_2 . The curve shows a first increase of weight (14.3 wt %) between 190 and 400 °C. At about 600 °C, weight increases dramatically up to 226 wt %. Although both weight differences have to be related to CO_2 incorporation, they are not continuous. Last, at temperatures higher than 800 °C, the sample presented a relatively low weight loss (10 wt %). From those curves, 200, 300, 500, and 600 °C temperatures were chosen to treat the samples and to follow the CO_2 sorption as a function of time, Figure 2. The CO_2 sorption kinetics increases as a function of temperature.

The weight loss at the beginning of the process is associated with water desorption. Then, the surface sorption takes place, slowly at 200 °C and 300 °C. On the other hand, at 500 °C and 600 °C the surface sorption is completed before

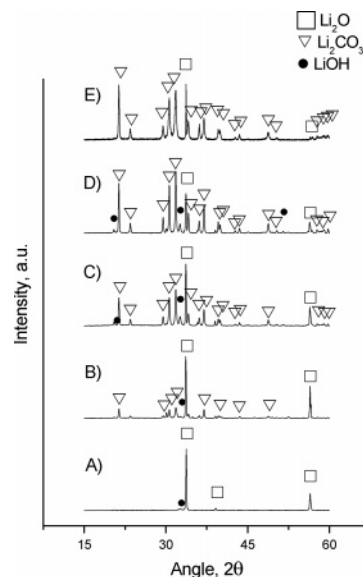


Figure 3. XRD patterns of Li_2O samples: (A) sample without CO_2 sorption, (B) heat treated at 300 °C for 2 h in a CO_2 flux, (C) heat treated at 500 °C for 2 h in a CO_2 flux, (D) heat treated at 600 °C for 2 h in a CO_2 flux, and (E) at room temperature in air for 22 days.

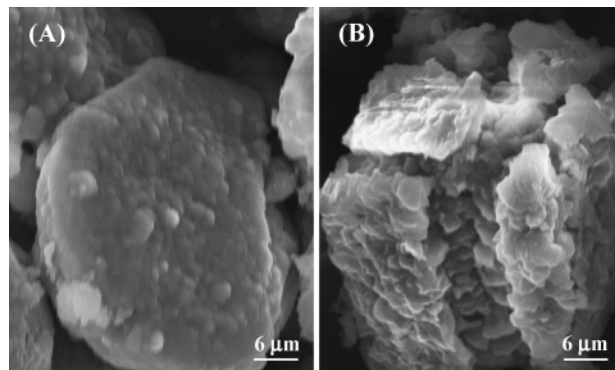


Figure 4. SEM analysis of Li_2O (A) before treatment and (B) heat treated at 600 °C for 2 h in a CO_2 flux.

50 min, and finally at 600 °C the diffusion process begins immediately. The formation of lithium carbonate (Li_2CO_3) is shown by XRD after thermal treatments at 300, 500, and 600 °C for 2 h under a CO_2 atmosphere (Figure 3). In some samples, lithium hydroxides were also present as Li_2O may absorb H_2O . The XRD absorption coefficients (μ) of the phases did not allow evaluating straightforward from the diffractograms the amount of Li_2CO_3 ; the coefficients are 83.41 and 68.30 for Li_2CO_3 and for Li_2O , respectively. A Li_2O sample was exposed for 22 days to air at room temperature. The weight of the sample increased 90.9 wt %, it corresponds to 61.7 mol % of Li_2CO_3 .

The Li_2O particle morphology, before and after CO_2 sorption, was studied by the SEM (Figure 4). Most particles, before thermal treatment, are dense and with a relatively rough surface. Particles are agglomerates with sizes between 30 and 40 μm . After CO_2 sorption treatment, particles seem to explode, as shown by the surface fractures and cracks. The initial morphology of the Li_2O constituted by large grains with spherical surface features turns out to be, after reaction, fragmented showing lamellar entities. Note that the XRD patterns of the initial and final materials correspond to pure Li_2O and Li_2CO_3 with Li_2O .

Discussion

Our results show that lithia is highly reactive with CO₂ to form Li₂CO₃ even at room temperature in air in 22 days. This process is accelerated by temperature. From 190 to 400 °C the increase of weight is slow (14.3%), if compared to the increase of weight at temperatures higher than 600 °C. The XRD results show that such weight increase is due to the formation of new compounds (LiOH and Li₂CO₃), mainly, Li₂CO₃. LiOH is produced from the reaction with environmental water when the sample is put in contact with air. Carbon dioxide could be initially adsorbed, but it reacts with lithia to produce lithium carbonate.



This reaction is expected to be a surface reaction, and then a shell of Li₂CO₃ covers the lithia particles. The access of Li ions to CO₂ should be reduced; CO₂ cannot diffuse into the ceramic particle as it is too large. To react with CO₂, lithium, then, has to migrate and cross the Li₂CO₃ shell. Such diffusion is promoted by temperature, between 530 and 710 °C. Note that phase diagram¹⁷ guarantees that Li₂CO₃ is not liquid at temperatures lower than 705 °C. Furthermore, to avoid lithium sublimation the experiments were performed in a CO₂ atmosphere. Indeed, after Li₂CO₃ formation, the TGA curve shows a dramatic increase of weight between 530 and 710 °C. This amount is equal to 109.3 wt %. Lithium diffusion, in a Li₂O crystal, is known to increase considerably at temperatures higher than 600 °C.¹⁸

Last but not least, CO₂ desorption did not present an usual behavior, if compared with other lithium ceramics. Lithium ceramics can absorb CO₂ to produce Li₂CO₃ up to 700 °C, simply because the Li₂CO₃ melting point is 710 °C. In Li₂O treated at around 900 °C there was a weight loss of only 10%. Hence, under a CO₂ atmosphere in our conditions, almost as much Li₂CO₃ is dissociated as it is formed, and a metaequilibrium is reached.

Note that the morphology observed by the SEM, that is, cracks on the particle surface, agrees with the previous discussion. The diffusion of lithium atoms to reach CO₂ and the Li₂CO₃ formation are topochemical. Lithium carbonate acts as a wedge and increases the size of the lithia cracks. Indeed, a simple estimation shows that the volume occupied by 1 mol of Li₂O is 11.5 cm³/mol, while the volume of Li₂CO₃ is 28.46 cm³/mol; therefore, the volume increase is as high as 246.6%. The full process is schematized in Figure 5.

If $\ln [\text{Li}_2\text{O}]_{\text{surface}}$ is plotted as a function of time (t), a linear dependency is obtained for 200 and 300 °C, Figure 6. At 500 and 600 °C the data only adjust to the first part of the curve, before the Li₂CO₃ shell is completed. Therefore,

$$\ln [\text{Li}_2\text{O}]_{\text{surface}} = -kt \quad (2)$$

where k is the reaction rate constant, t is the time, and $[\text{Li}_2\text{O}]_{\text{surface}}$ is the molar concentration of lithia available in

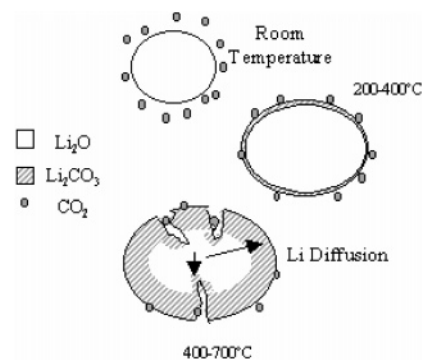


Figure 5. Scheme of the mechanism proposed for CO₂ absorption on Li₂O.

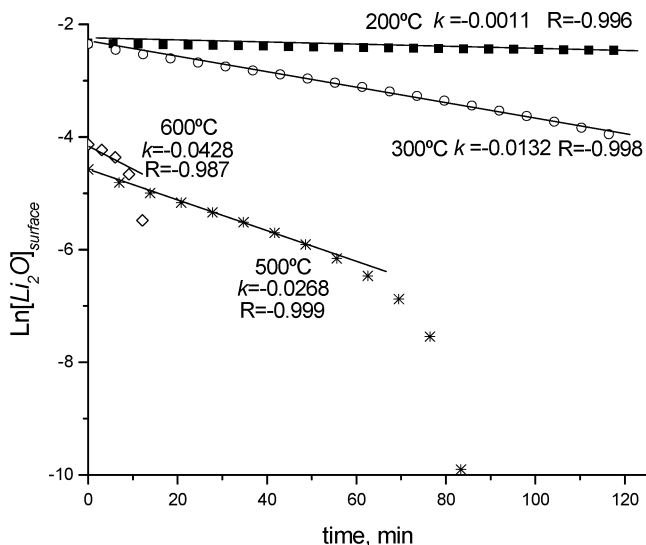


Figure 6. Plot of $\ln [\text{Li}_2\text{O}]_{\text{surface}}$ vs time. The data at 200 and 300 °C present a linear behavior. Data at 500 and 600 °C follow a straight line only for short times.

the surface, which corresponds to 9% of the lithia total concentration. Hence, deriving eq 2 as follows:

$$\frac{1}{[\text{Li}_2\text{O}]_{\text{surface}}} d[\text{Li}_2\text{O}]_{\text{surface}} = -k dt \quad (3)$$

$$d[\text{Li}_2\text{O}]_{\text{surface}}/dt = -k[\text{Li}_2\text{O}]_{\text{surface}} \quad (4)$$

which corresponds to a first-order reaction with respect to Li₂O.

The reaction rate constants follow an Arrhenius type behavior:

$$k = k_0 \exp^{-E_a/RT} \quad (5)$$

where E_a is the activation energy of reaction (eq 1), R is the gas constant, T is absolute temperature, k is the reaction rate constant, and k_0 is the global reaction rate constant. From the k constants obtained from Figure 6 a plot of $\ln |k|$ versus $1/T$ is a straight line, Figure 7. The obtained value of $E_a = -3554$ J/mol is very small.

Samples treated at 500 and 600 °C follow a linear behavior only at the beginning of the process, Figure 6, as the limiting step in those samples is a diffusional process. Sharp and co-workers have developed several diffusional models.¹⁹ If the

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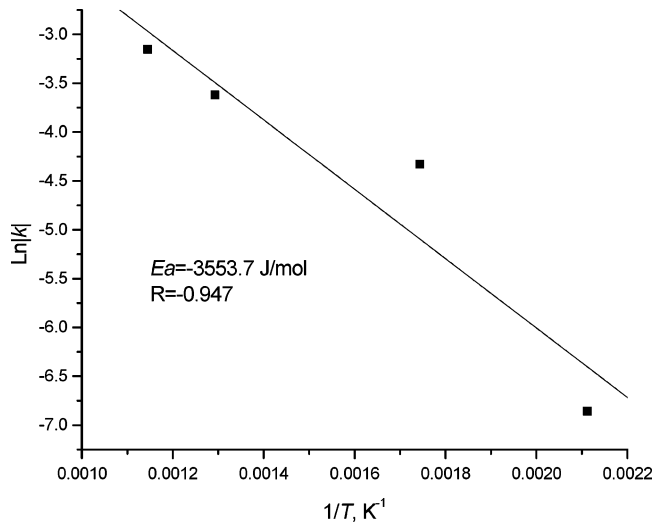


Figure 7. Arrhenius type plot of $\ln |k|$ vs $1/T$.

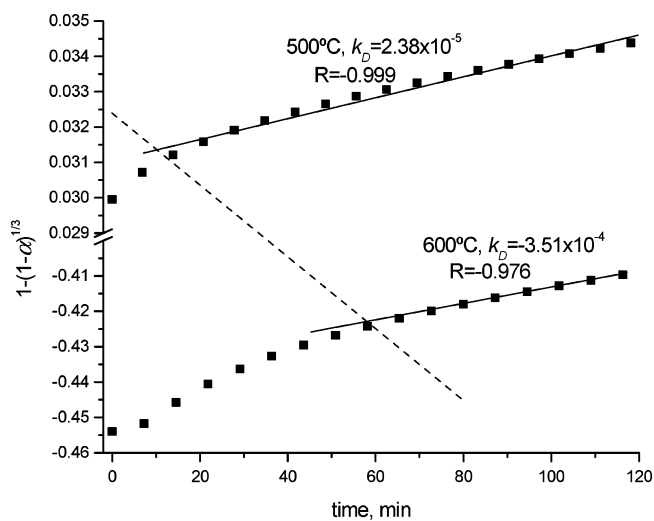


Figure 8. Plot of $1 - (1 - \alpha)^{1/3}$ vs time for the samples heat treated at 500 and 600 °C. The dashed line indicates the beginning of the diffusional behavior of these samples.

reaction is controlled by the interface movement from the surface inward it can be described by the following equation:

$$k_D t = 1 - (1 - \alpha)^{1/3} \quad (6)$$

where α is the molar fraction of Li_2CO_3 produced, t is time, and k_D is a constant which depends on the diffusion coefficient, particle size, and temperature.

A plot of $1 - (1 - \alpha)^{1/3}$ versus t is a straight line, Figure 8. The experimental results, then, agree with the predicted curve, and therefore the diffusion is controlled by the interface movement from the surface inward. It has to be emphasized, however, that the two constants, $k_D^{500^\circ\text{C}} = 2.38$

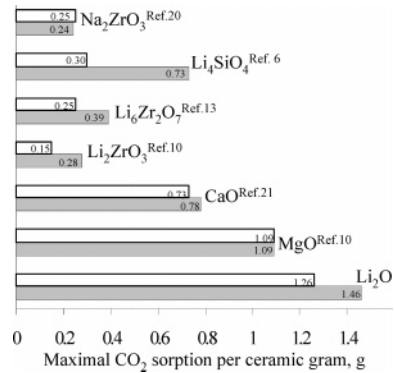


Figure 9. Comparison of the theoretical (gray) and experimental (white) CO_2 sorption capacities of Li_2O with others ceramics.^{6,10,13,20,21}

$\times 10^{-5}$ and $k_D^{600^\circ\text{C}} = 3.5 \times 10^{-4}$, differ in 1 order of magnitude. Thus, the diffusion process at 600 °C is 10 times faster than at 500 °C. Again, lithium mobility is clearly determined by temperature; such a conclusion agrees with a previous work.¹⁸

Quantitatively, the final weight fraction of CO_2 absorbed (126 wt %) at 600 °C corresponds to 86 mol % conversion from Li_2O to Li_2CO_3 , which turns out to be a fairly good efficiency. Moreover, it means that 1.26 g of CO_2 react per gram of Li_2O . It is more than twice the theoretical amount retained by other lithium ceramics, whose performance is between 0.2 and 0.73 g of CO_2 per gram of ceramic.^{1,8,13} Other oxides such as MgO and CaO are only able to absorb up to 1.09 and 0.78 g of CO_2 per gram of material, Figure 9.

Conclusions

Li_2O can be used as a material for CO_2 retention. The CO_2 is absorbed through two different mechanisms. First, at low temperatures, the retention is due to a surface reaction with the formation of Li_2CO_3 controlled by the diffusion of lithium atoms through a shell of Li_2CO_3 . This reaction temperature is in good agreement with previous reports that mention that lithium mobility increases at 600 °C. Hence, this mobility favors the diffusion through the Li_2CO_3 shell present on the surface of the Li_2O particles. The isothermal curves respond to two competitive models: A first-order surface reaction and a diffusional mechanism controlled by the movement of an interface moving from the surface inward. At a temperature close to 600 °C or more the second mechanism is the determining step. Finally, the CO_2 desorption process was not observed in a CO_2 atmosphere, as it occurs on other lithium ceramics.

Acknowledgment. This work has been performed in the frame of the Project of Nanotechnology IMPULSA, UNAM. H.A.M. thanks the National Council of Science and Technology Mexico (CONACYT), for financial support.

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