Nanocrystalline Lithium Zirconate with Improved Kinetics for High-Temperature CO_2 Capture

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The removal of CO_2 from exhaust gases is becoming very significant in the field of energy production. It is generally accepted that the cost associated with the separation of CO_2 from flue gases introduces one of the largest penalties for power generation. CO_2 capture is always a point of discussion in processes such as natural gas treatment, purification of hydrocarbons, production of hydrogen, and aerospace. For example, pressure-swing adsorption is well-studied for the capture of CO_2 from any exhaust gas.[1] Capture of CO_2 at high temperature can, in principle, improve the energy efficiency by overcoming the need to cool the gas to ambient temperature prior to CO_2 removal. Another important application of high-temperature CO_2 acceptors is the sorption-enhanced steam methane reforming (SESMR) for hydrogen production.[2] For all these applications, there is a need for materials with a high CO_2 capture capacity at relevant working temperatures that are easy to regenerate and have a stable sorption capacity after many sorption/desorption cycles and have improved kinetic properties both for the sorption and desorption steps.

There has been extensive research on the equilibrium of CO_2 on adsorbents at ambient temperature and atmospheric pressure. However, there are few relevant investigations about the adsorption of CO_2 at high temperatures and pressures.[1] Recently, it has been reported that Li-containing materials (mainly Li_2ZrO_3 and Li_4SiO_4) are promising candidates with high CO_2 capture capacities and high stability levels.[3−10] Nakagawa et al. have reported that lithium zirconate can theoretically hold CO_2 in amounts up to 28 wt % acceptor weight at high temperatures according to the following reaction[3,4]

$$Li_2ZrO_3 + CO_2 \Leftrightarrow Li_2CO_3 + ZrO_2 \qquad (1)$$

The high capture capacity and stability at a temperature range of 723−873 K make it promising for application in SESMR. However, kinetic limitations are still the main obstacle.

The synthesis of lithium-containing ceramic powders has been extensively studied, especially lithium zirconate, because it is one of the candidates for tritium breeding for nuclear fusion reactors. Various solid-state processes have been employed for fabricating the lithium zirconate powders. Solid-state reactions between ZrO_2 and lithium peroxide (or carbonate) are the best-known processes.[3,4] In these processes, two types of powders are mechanically mixed and treated at high temperatures. Solid-state reactions normally require high temperatures and a long reaction time. In addition, the final particle size is normally large, partially due to sintering during the high-temperature treatment. There have been several efforts to reduce the starting powder size for solid-state processes. One example is the use of a sol−gel technique to prepare fine powders of ZrO_2.[5] However, this powder is subsequently reacted in the solid state with lithium carbonate at high temperatures with following sintering problems. A precipitation combustion process has also been reported to synthesize Li_2ZrO_3 powder as a breeding material for fusion reactors.[12] Li_2ZrO_3 can easily be obtained by this method by using a mixture of urea and citric acid in stoichiometric composition. The primary particle size of as-synthesized powders was smaller than 20 nm. However, the powder contains some impurities and requires high calcination temperatures.

Recently, Nair et al.[5] have done a systematic study on the properties of lithium zirconates with different crystal structures. They have compared the properties of powders prepared by the solid-state reaction of mixed powders, sol−gel prepared powders, and commercial grade powder. Their results indicated that small particle size and tetragonal phase are critical to enhancing the CO_2 capture. The reported materials do not meet the kinetic requirements for high-temperature CO_2 capture. The present work deals with the preparation of nanocrystalline lithium zirconate by a novel soft-chemistry route instead of the traditional solid-state reaction in order to improve the kinetic properties and stability of lithium zirconate. This preparation method works under milder conditions than those needed for a solid-state route, presenting an opportunity to minimize the particle size of the lithium zirconate.

Zirconyl nitrate ($ZrO(NO_3)_2 \cdot xH_2O$) and lithium acetate ($CH_3COOLi \cdot 2H_2O$) were used as precursors.[13] Appropriate amounts of each precursor were dissolved in deionized water.

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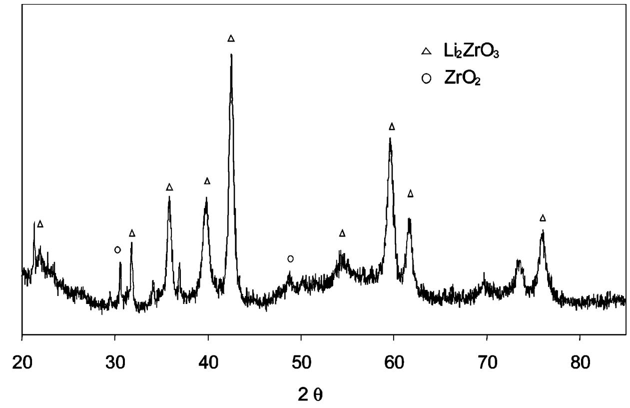

Figure 1. XRD pattern of Li_2ZrO_3 calcined at 873 K.

After standardizing the solutions by thermogravimetric analysis, we mixed the precursors for several hours in appropriate amounts to form a complex solution. The solution was spray-dried (Büchi, Mini Spray-Drier B-191) with an input temperature of 423 K and a pump rate of 2 mL/min. The resulting solid products were further decomposed/oxidized in a certain temperature range, forming powders with a homogeneous atomic mixture of Li and Zr. The powders were calcined at three different temperatures: 673, 873, and 1073 K in air, which led to ignition of the organic compounds. The crystal structures of the prepared powders were characterized by X-ray diffraction (XRD) analysis using Cu Kα radiation (Siemens D5005). As shown in Figure 1, this method yields pure nanocrystals of Li_2ZrO_3 with pure tetragonal phase when the calcination temperature was 873 K. Calcination at 673 K did not yield pure lithium zirconate, whereas calcination at 1073 K yielded formation of the undesired monoclinic lithium zirconate and crystal growth. Consequently, calcination of powders at 873 K is selected in the present work. The crystallite size of the sample calcined at 873 K was calculated using the Scherrer equation and was 13 nm. The morphology of the Li_2ZrO_3 powders was examined in a Hitachi S-4300se field-emission scanning electron microscope (SEM). Examples of SEM images are presented in Figure 2. The results indicate that the individual lithium zirconate crystallites stick together to form large porous particles with a relatively uniform size between 1 and 2 μm. All particles display a characteristic geometry; large spheres with holes resembling a doughnutlike shape were found. This might be a result of the calcination process. As presented above, when the dried powders are heated to a certain temperature, the oxidation of the organic compounds leads to a smouldering process involving gas evolution. This significant gas evolution results in loosely agglomerated particles with mesopores and maropores.

CO_2-capture properties were evaluated using a tapered-element oscillating microbalance (TEOM). The measurement of the mass change in the fixed bed is on the basis of changes in the natural frequency of an oscillating quartz element containing the sample. High mass resolution and a short response time make the TEOM particularly suitable for performing the uptake measurements.[14] The tapered element was loaded with 20 mg of Li_2ZrO_3 together with quartz particles. The samples were heated to 848 K with a heating rate of 10 K/min in pure argon gas and kept there for 60 min. The CO_2 capture was initiated by switching from Ar to 100% CO_2 at the same temperature. The flow rates of Ar and CO_2 were kept constant at 100 mL/min. The partial pressures of Ar and CO_2 were both fixed at 1 atm. After saturation of the acceptor, we increased the temperature at 10 K/min to 923 K, and changed the flow gas from CO_2 to Ar to release the CO_2.

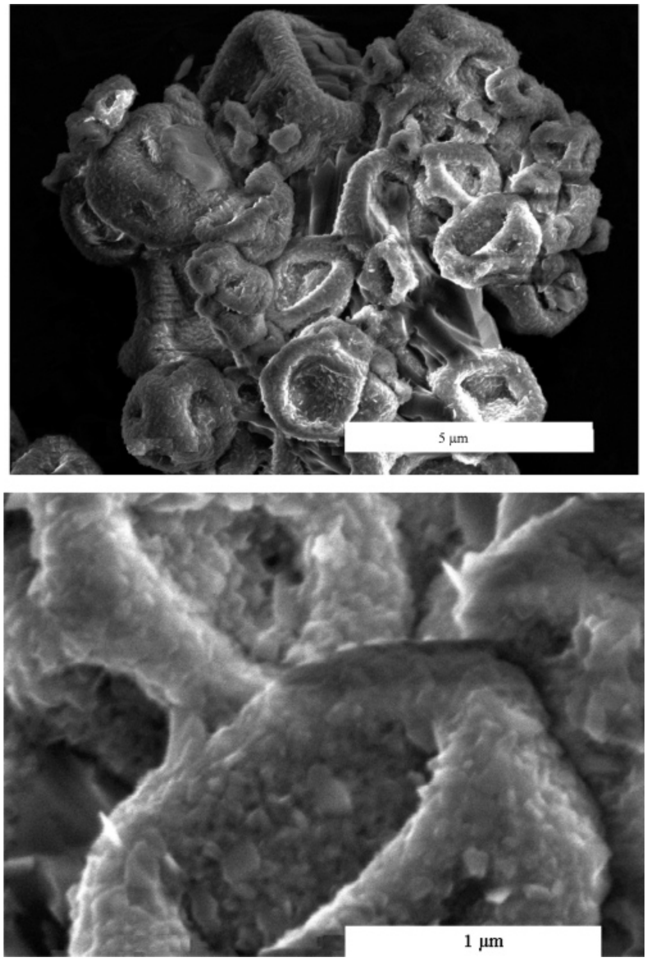

Figure 2. SEM images of Li_2ZrO_3 calcined at 873 K.

Figure 3 shows the CO_2 capture at 848 K and the temperature-programmed regeneration curve of the Li_2ZrO_3 up to 923 K. As shown, lithium zirconate prepared by the soft-chemistry method can hold CO_2 in amounts equivalent to 27 wt % sample weight, and saturation is reached in less than 5 min. XRD patterns of the saturated acceptor were also recorded and indicated the formation of lithium carbonate and zirconium oxide, according to reaction 1. Small traces of unreacted lithium zirconate were also found.

These results represent important improvements in the carbon dioxide capture rate reported so far. Ida et al.[7] carried out a detailed study about the capture properties of pure and modified lithium zirconate prepared by solid-state reactions. According to their investigation, pure lithium zirconate

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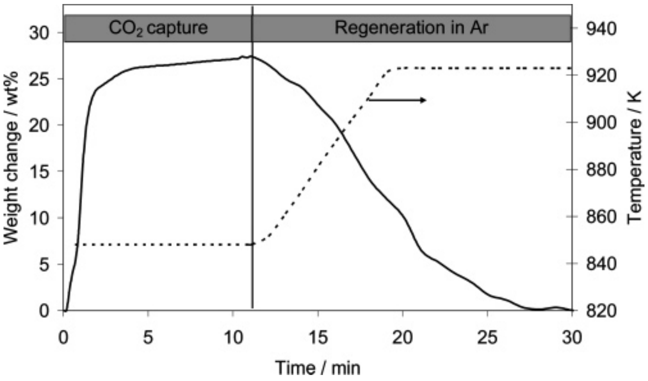

Figure 3. CO_2 capture at a CO_2 pressure of 1 atm and 848 K on Li_2ZrO_3 and temperature-programmed regeneration in Ar.

needed more than 24 h to reach 18 wt % capacity at 878 K.[7] Doping of Li/K carbonate on lithium zirconate improved the CO_2 capture rate considerably; modified Li_2ZrO_3 could contain 18 wt % sample weight within 40 min at 923 K in this case. Nakagawa et al. have reported similar results.[3] Ida and Lin[8] have studied the effect of a Li_2CO_3/K_2CO_3 dopant on the CO_2 capture rate. Doping Li_2CO_3/K_2CO_3 into Li_2ZrO_3 increases the rate because of the formation of a eutectic molten carbonate at high temperatures. This molten carbonate can significantly reduce CO_2 diffusion resistance relative to that of the solid shell in the pure Li_2ZrO_3 case. Nevertheless, the capture rate of the pure lithium zirconate prepared in the present work is more than three times faster than the capture rate of the reported Li/K-modified Li_2ZrO_3.[8]

As shown in Figure 3, the regeneration temperature used in this investigation was 923 K. This temperature is considerably lower than the desorption temperature reported for lithium zirconate prepared by solid-state reactions (973−1053 K). The narrow temperature gap between capture and regeneration make the acceptor better suited for heat management in industrial applications such as SESMR.

In addition, the pure lithium zirconate shows a high level of stability. After a number of capture cycles, the acceptor displayed the same capacity and capture/regeneration kinetics. One example is shown in Figure 4. The sample was kept in an inert atmosphere for 7 days at 848 K, and the capture capacity was found unchanged. Figure 5 shows a SEM image of the acceptor after being exposed to 15 cycles, indicating a high stability of the prepared lithium zirconate.

Hence, this preparation method represents several advantages relative to present technologies. First, it is simple and allows for the preparation of pure powder in a single step. Second, the method yields pure nanocrystals of Li_2ZrO_3 with pure tetragonal phase while using a relatively low calcination temperature. As a result, properties of the powders, such as the capture rate of CO_2 and the regeneration temperature, have been significantly improved. The improved properties of the material make the preparation process much simpler and reduce the need for doping with K for certain applications. As a result, the new preparation method is expected to open new applications of Li_2ZrO_3 in high-temperature CO_2 capture, for example, in post- and precombustion processes in power generation with CO_2 management.

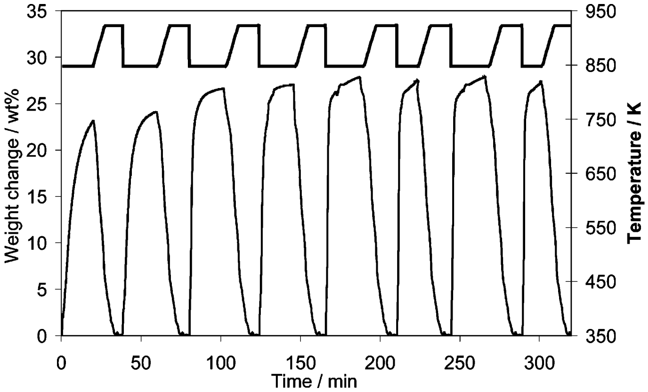

Figure 4. Stability of lithium zirconate during capture/regeneration cycles. The sequence of capture and regeneration is the same as that stated in Figure 3.

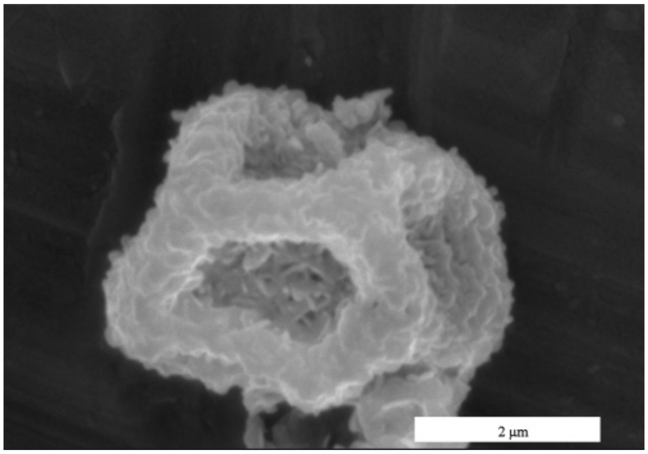

Figure 5. SEM image of lithium zirconate after 15 capture/regeneration cycles.

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