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Preparation of lithium zirconate nanopowder prepared by electrostatic spraying for CO_2 sorbent

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Electrostatic spray pyrolysis has been used to prepare Li_2ZrO_3 nanopowder for CO_2 sorbent. Final annealing was done at 900 °C for 30 min in air. The CO_2 sorption/desorption ability of the annealed powder has been investigated by thermogravimetric analysis and Fourier transform infrared spectroscopy. When Li_2ZrO_3 nanopowder was exposed to CO_2 environment at 500 °C, the theoretical absorption weight was gained within 250 min with high sorption rate. Absorbed CO_2 was mostly generated by heating at 800 °C.

Key words: *Li_2ZrO_3; nanopowder; CO_2; sorbent*

1. Introduction

Although coal is the most abundant fossil fuel in the world, the reduction of CO_2 emissions from coal-fired units is an imperative to mitigate global climate change, and consequently, to guarantee the sustainable key role of coal in the 21st century. Environmental concerns have stirred up much interest in CO_2 exhaust from energy power plants. The Kyoto protocol, adopted in 1997, requires a reduction in the release of CO_2. To achieve the goal, practical methods such as saving energy, improvement of conversion efficiency and development of alternative energy sources are required. Moreover, separation of CO_2 from the exhaust gas of power plants and factories and the absorption of CO_2 by forests and oceans are needed. Recently, importance of selecting high temperature CO_2 sorbent gained attention with respect to performing

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long-term multi-cycle. Currently, the most widely used high temperature CO_2 sorbent is dolomite, a natural mineral whose most attractive feature is low price. However, in order to use dolomite, energy intensive pre-treatment has to be performed prior to loading. In addition, it has tendency to significantly decrease its capacity through multi-cycle processing [1].

Therefore, a new generation of high temperature CO_2 sorbents such as Li_2ZrO_3, Li_4SiO_4, and Na_2ZrO_3 [2–6] have recently been developed. Among them, Li_2ZrO_3 has been investigated as a candidate of an additive material for molten carbonate fuel cell electrolyte plates. A durability test of this material revealed that Li_2ZrO_3 synthesized by heat-treatment of zirconia and lithium carbonate returned to the starting materials after 1000 h in the presence of CO_2 [7].

Kato el al. has developed a CO_2 separation technology based on a chemical reaction using Li_2ZrO_3 [8]. Since the method is effective in the temperature range from 450 to 700 °C, it has some advantages over the separation of CO_2 from power plants without lowering the temperature, and it can be used with catalysts for the CO shift reaction or methane reforming reaction. However, as far as we know, there is no information on the reaction of Li_2ZrO_3 nanopowder with CO_2, while several works corresponding to micron-sized powder or bulk were performed. Therefore, in this work, we tried to synthesize nanosized $LiZrO_3$ powder using electrostatic spray pyrolysis (ESP) and to evaluate its performance as CO_2 absorbent.

2. Experimental

Lithium nitrate ($LiNO_3$) and zirconyl nitrate (ZrN_2O_7) were used as reactants for synthesis of nanopowders. The sol was diluted with distilled water and methanol to adjust the concentration and viscosity for preparing nanopowders by ESP. Figure 1 shows the flow chart for the preparation of precursor sol and Li_2ZrO_3 nanopowder.

The electrostatic spray pyrolysis (ESP) method has been commonly used to synthesize nanosized particles of oxidic materials [7]. The working principles of the ESP method have been described elsewhere [7, 8]. A stainless steel needle (0.1 mm and 0.23 mm inner and outer diameters, respectively) was connected to a syringe pump (KD200, KD Scientific Inc., PA, U. S. A.) using a silicon rubber tube. The flow rate of the precursor solution was kept at 0.05 cm^3/60 min. In order to obtain a stable cone-jet mode of electrostatic atomization, high voltage, 10–30 kV, was applied between the needle tip and ground electrode by using DC power supply (SHV120-30K-RD, Convertech Co. Ltd., South Korea). A container was introduced on the ground electrode and was heated at 80–120 °C to vaporize organic compound in precursor solution during spraying. A precursor solution was pumped for 5 min through the nozzle placed 15 cm above the powder container. The sprayed powders were placed on the Si substrate and heated up to 900 °C for 30 min in a tube furnace in the presence of air (flow rate approximately 150–200 cm^3/min). The schematic of the set-up used in the study is shown in Fig. 2.

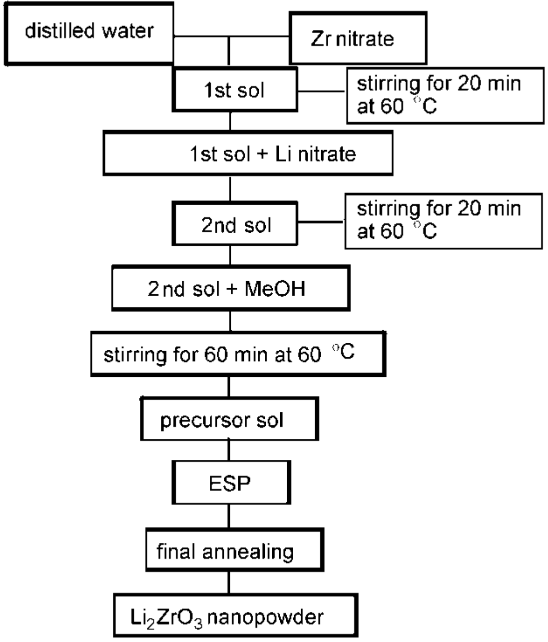

Fig. 1. The flow chart of the process

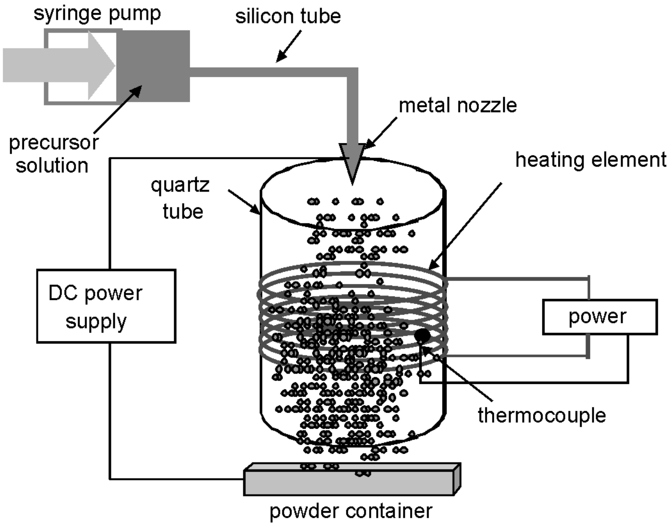

Fig. 2. The scheme of the set-up used in this study

The Fourier transform infrared (FTIR, FTS-60, BIO-RAD Digilab Co., U. S. A.) spectroscopy was performed to analyze chemical structure of the powders before and after CO_2 absorption. The morphology of the surface of the powders was evaluated by field emission – scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). CO_2 absorption properties were evaluated using a thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan). Samples were heated up to 500 °C in pure nitrogen and kept for 20 min. After that, the atmosphere was changed to CO_2 containing gases balanced by air, and kept for 275 min. After keeping at 500 °C for CO_2 absorption, the atmosphere was changed to N_2, heated up to 800 °C and kept for 30 min to release.

3. Results and discussion

FE-SEM images from the powders on Si substrate after annealing at 900 °C for 30 min in air were used to confirm the presence of Li_2ZrO_3 powders (Fig. 3). As can be seen, the average particle size decreases upon raising the heating temperature during spraying. Powders preheated at 120 °C during spraying are composed of nanosized particles, i.e., < 100 nm. A simple estimation of the average particle size gives 50–80 nm. From the FE-SEM results, the heating temperature during spraying was fixed at 120 °C.

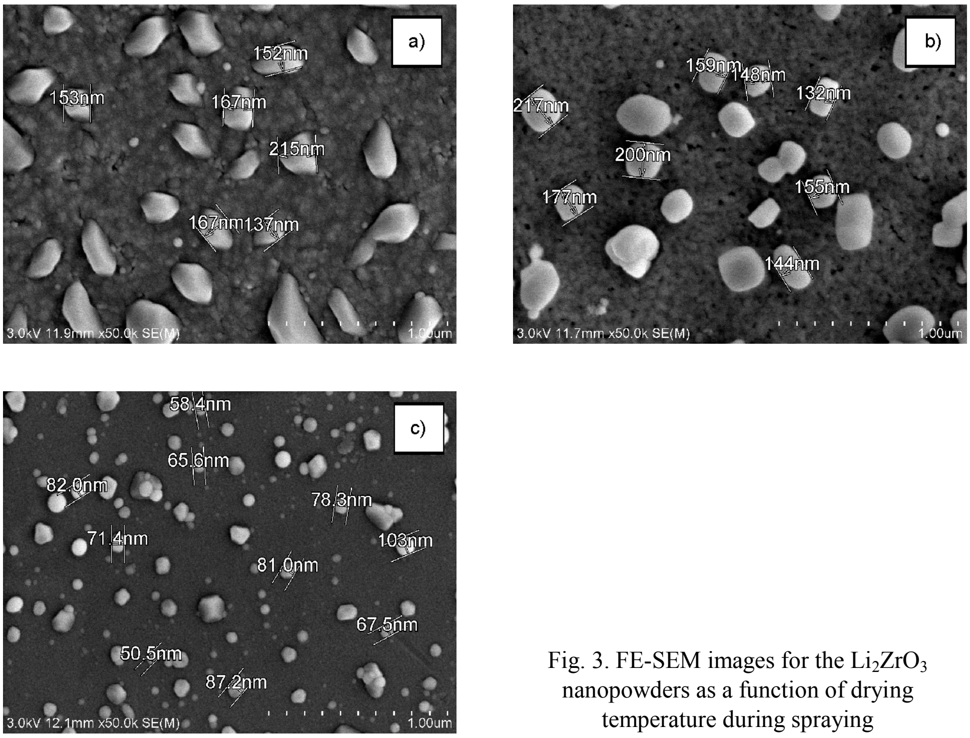

Fig. 3. FE-SEM images for the Li_2ZrO_3 nanopowders as a function of drying temperature during spraying

The following equation represents the reaction between lithium zirconate and CO_2:

$$Li_2ZrO_3 + CO_2 = Li_2CO_3 + ZrO_2 \quad (1)$$

The weight changes are indicators of the absorption and desorption of CO_2, respectively. Figure 4 shows the weight change of the powder during the temperature maintained at 500 °C and at 800 °C. Clear weight increase and decrease are observed during CO_2 sorption/desorption process at 500 °C/at 800 °C. The value of the weight increase was 27–30% at 500 °C in CO_2 after 250 min heating, which agrees with 29% expected of the theoretical maximum. The CO_2 capture rate was higher than for any other Li_2ZrO_3 reported. These values were very well comparable with previous results by Lin et al. [9]. While Li_2ZrO_3 prepared by the solid–solid reaction showed very slow kinetics [9], the nanosized powder prepared using liquid based method showed higher absorption rate probably due to larger surface area.

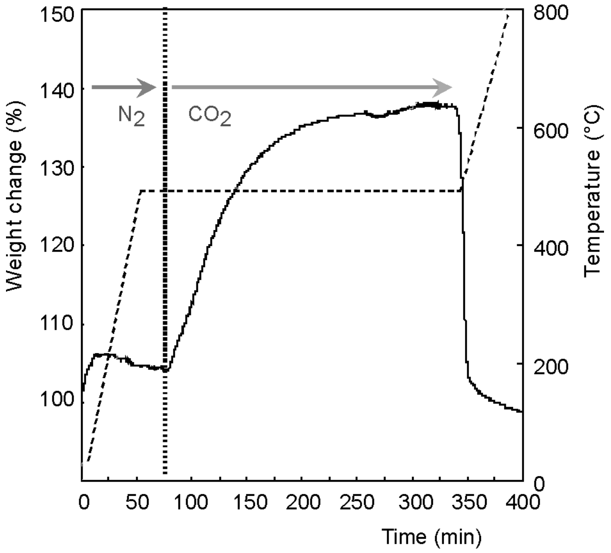

Fig. 4. Weight change of the powder between 500 °C and 800 °C

When Li_2ZrO_3 is exposed to CO_2 at 500 °C, CO_2 molecules move to the surface of Li_2ZrO_3 and react with Li_2ZrO_3 to form ZrO_2 and Li_2CO_3 nuclei (Eq. (1)). As reaction proceeds, ZrO_2 and Li_2CO_3 nuclei touch each other and form a dense Li_2CO_3 shell on the outer surface and a dense ZrO_2 shell in the middle covering the unreacted Li_2ZrO_3 core. Both Li_2CO_3 and ZrO_2 shells are in solid state because their melting points are higher than the operating temperature. After the formation of double shells, CO_2 can diffuse through the solid Li_2CO_3 shell and react with Li^+ and O^{2-} on the outer surface of the ZrO_2 shell [10]. At the same time, another reaction occurs on the surface of unreacted Li_2ZrO_3 to generate Li^+ and O^{2-}. Because ZrO_2 contains a large number of oxygen vacancies in its crystal [11], O^{2-} can diffuse through the ZrO_2 shell. Similarly Li^+ can also diffuse interstitially through the ZrO_2 shell.

In order to analyze chemical structural changes of Li_2ZrO_3 nanopowder during the CO_2 sorption/desorption process, Li_2ZrO_3 samples were rapidly quenched at the room temperature after CO_2 sorption at 500 °C and after CO_2 desorption at 800 °C, respectively. Then, the quenched samples were analyzed by FTIR. To compare, the spectrum of pure Li_2ZrO_3 annealed at 900 °C was determined (curve a in Fig. 5). Results of the FTIR analysis of the obtained samples are shown in Fig. 5.

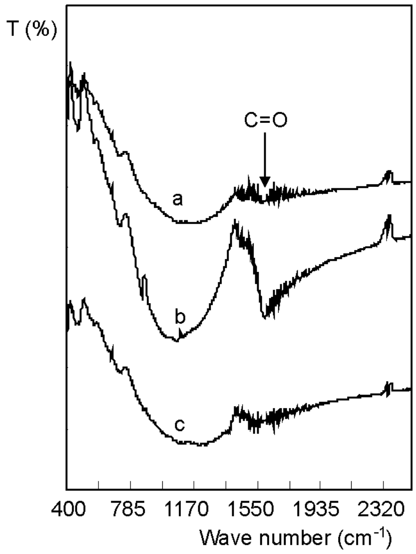

Fig. 5. FTIR patterns of Li_2ZrO_3 nanopowders: a) after annealing at 900 °C, b) after CO_2 absorption at 500 °C, c) after desorption of CO_2 at 800 °C

The FTIR pattern in Li_2ZrO_3 nanopowder after CO_2 sorption clearly includes a peak at 1550–1650cm^{-1} corresponding to C=O bond, as shown in Fig. 5, curve b. This result indicates that after CO_2 sorption, Li_2ZrO_3 reacted with CO_2 to form Li_2CO_3 and ZrO_2. Comparing to curve b in Fig. 5, the FTIR pattern in Fig. 5, curve c after CO_2 desorption shows that the peak corresponds to C=O bond completely disappeared. This means that after CO_2 desorption at 800 °C, Li_2CO_3 and ZrO_2 react to Li_2ZrO_3 again. These results clearly indicate that the reaction represented by Eq. (1) is reversible with reaction rates enabling its use in practice, and is applicable to the CO_2 capture from high-temperature gases.

4. Conclusions

Li_2ZrO_3 nanopowder for CO_2 sorbent was fabricated by the ESP process. Powders preheated at 120 °C during spraying are composed of nanosized particles, 50–80 nm. From the TGA result, clear weight changes are observed during CO_2 sorption/desorption process at 500 °C/at 800 °C. Nanosized powder prepared using liquid based method showed higher absorption rate probably due to larger surface area. FTIR results clearly indicate that the CO_2 reaction is reversible with practical reaction rates and is applicable to the CO_2 capture from high-temperature gases.

Acknowledgements

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