Enhancement of CO₂ Absorbance for Lithium Ferrite—Combinatorial Application of X-Ray Absorption Fine Structure Imaging

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Lithium ferrite powder was prepared at quite a low temperature by solid-state reaction, and its performance as a CO₂ absorbent was tested. In order to evaluate its performance efficiently, the idea of combinatorial-material development was introduced and combined with novel X-ray fluorescence (XRF) imaging analysis. The XRF of multiple samples on a combinatorial substrate were observed in parallel—and therefore in a short space of time—thus enabling the X-ray absorption fine structure (XAFS) of the samples to be compared with one another. Thermogravimetry (TG) was also used to estimate the absorption speed and absorbing mass of CO₂ quantitatively. The X-ray diffraction pattern showed that the obtained lithium ferrite was mainly α-LiFeO₂, and the broadening of the lines suggested a nano-crystalline product. LiFeO₂ reacted with CO₂ to form Li₂CO₃ and γ-Fe₂O₃. Changes in the XAFS spectra and the weight changes observed by TG with CO₂ exposure showed quick and voluminous absorbance by the low-temperature synthesized sample, and a higher performance was confirmed compared with samples prepared by the conventional ceramic method.

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1. Introduction

Global warming is one of the most serious issues to arise in recent years. The Kyoto protocol adopted at COP3 in 1997, which specifies a decrease in discharges of greenhouse gases such as carbon dioxide, CO₂, in 2008~2012, will be implemented in February 2005. In order to reduce CO₂, there are two main strategies; the development of alternative energy sources that do not generate any CO₂, and the effective collection and fixing of the gas before it is emitted into the environment. One procedure conforming to the latter method is absorption using chemical reactions. Recently, double oxides containing lithium have been proposed as an absorbent. They can react with CO₂ selectively. They are more stable than other known CO₂ absorbents at high temperature, and have a high absorbing capacity with low volumetric change.1) In this study, lithium ferrite was selected, because iron is cheap, common and nontoxic. Lithium ferrites can be observed in the Fe₂O₃–Li₂O pseudo-binary phase diagram, and LiFeO₂ has a composition of 1:1. It has already attracted attention as a cathode material for lithium-ion batteries.2–6) Several phases of various structures are known for LiFeO₂, but the α-type is the most stable phase and takes a rock-salt structure in which lithium and iron are disordered. In this research, LiFeO₂ was synthesized at low temperature to prepare micro particles that have large specific surfaces and this therefore gives them an advantage in reactions with gases that approach from the surface. Recently, combinatorial-material development based on parallel syntheses and characterization is being increasingly used to screen for excellent materials effectively. In this research, the concept of the combinatorial method was used to test the CO₂ absorption power. The X-ray fluorescence imaging technique was utilized for this purpose.

2. Experimental

Lithium ferrite was prepared by solid-state reaction at low temperature. An equimolar amount of catalyst-grade FeO(OH) (Sigma-Aldrich) and high-grade LiOH·H₂O (Wako Pure Chemical) were mixed in an agate mortar and precalcined at 100°C for 2 hours. The powder was ground again and pressed into a pellet, and was heated at various temperatures (100~400°C) for 10 hours under N₂ flow. LiFeO₂ was also prepared by the ordinary ceramic method, which heats the above mixture in an electric furnace at 800°C for 5 hours. All products were ground in an agate mortar into powder and used for the analysis. Powder X-ray diffraction (XRD) patterns of the obtained products were observed by a Rigaku RINT-2500 (12 kW) diffractometer using CuKα radiation. The change in the XRD pattern induced by CO₂ absorption was also observed. In order to evaluate the performance of the product as a CO₂ absorbent efficiently, the idea of combinatorial-material development was introduced. In this study, four samples obtained at different synthesis temperatures (100, 200, 300 and 400°C) were arranged on an 8 mm × 8 mm area of quartz-glass substrate. Four units of each sample were placed in individual columns (1st~4th for each), and were exposed to CO₂ under four different conditions. X-ray fluorescence (XRF) images were taken using a recently developed fast XRF camera.7,8) Highly brilliant synchrotron radiation Monochromatic X-rays from the multipole wiggler source at BL-16A1 of Photon Factory, KEK in Tsukuba were used for the XRF imaging. The beam taken from the flat Si(111) double-crystal monochromator was a wide homogeneous beam, and the width was restricted to 8 mm by slits and irradiated on the combinatorial substrate. A 2-D XRF image of the 8 mm × 8 mm (667 × 667 pixels) area was taken by a 3 s exposure of the CCD camera. We did not need any corrections on shading effects, because the uniformity was satisfactory. The X-ray absorption fine structure (XAFS) of each sample on the combinatorial substrate was observed in parallel from XRF images taken while scanning incident X-ray energies around the Fe–K edge. Thermogravimetry (TG) was also performed to measure the absorption speed and absorbing mass of CO₂.
quantitatively. The sample was put in a Pt cell, placed in thermal analysis equipment (Shimadzu DTG-60), and heated under CO$_2$ flow.

3. Results and Discussion

3.1 XRD analysis

The product obtained at 800°C was $\alpha$-LiFe$_2$O$_3$ according to the XRD pattern shown in Fig. 1(a). $\alpha$-LiFe$_2$O$_3$ was also the main phase of the 400°C product (Fig. 1(b)), although lines attributed to spinel-type iron oxide were also observed. While the 800°C product showed an ideal XRD pattern of sharp lines, the 400°C product had broad lines, suggesting a nanocrystalline product. The spinel phase is LiFe$_2$O$_4$. As FeO(OH) is dehydrated and becomes Fe$_2$O$_3$, the phase must be $\gamma$-Fe$_2$O$_3$, or FeO(OH). As the diffraction patterns overlap one another, it is difficult to distinguish them especially when the lines broaden. As FeO(OH) is dehydrated and becomes Fe$_2$O$_3$ at 400°C, the phase must be $\gamma$-Fe$_2$O$_3$, or LiFeO$_2$. Weak but sharp lines of Li$_2$CO$_3$ produced in the course of synthesis by the undesirable absorption of CO$_2$ were also observed.

Figure 1(f) is the XRD pattern of the 400°C product heated at the rate of 10°C/min up to 500°C with a CO$_2$ flow of 200 ml/min. In tandem with CO$_2$ absorption, the diffraction lines from the spinel phase ($\gamma$-Fe$_2$O$_3$, LiFe$_2$O$_3$, or a mixture of the two) became intense. Therefore, the reaction process of LiFe$_2$O$_3$ and CO$_2$ is expressed by equation (i), or equation (ii) followed by (iii):

$$2\text{LiFe}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \gamma\text{-Fe}_2\text{O}_3 \quad (i)$$
$$5\text{LiFe}_2\text{O}_3 + 2\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{LiFe}_2\text{O}_3 \quad (ii)$$
$$2\text{LiFe}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + 5\gamma\text{-Fe}_2\text{O}_3 \quad (iii)$$

If LiFe$_2$O$_3$ reacts completely with CO$_2$ to become Fe$_2$O$_3$, the equivalent amount of CO$_2$ absorbable by 1 g LiFe$_2$O$_3$ is 120 cm$^3$ in volume.

In the case of the products obtained at lower temperatures (Fig. 1(c) 300°C and (d) 200°C), the spinel lines were intense and had relatively smaller portions of $\alpha$-LiFe$_2$O$_3$. Also, the lines of Li$_2$CO$_3$ could be observed clearly even though we were unwilling to perform exposure to CO$_2$ before the XRD experiment. This may demonstrate the excellent performance of the lower-temperature synthesized product as a CO$_2$ absorbent, because the formation of Li$_2$CO$_3$ appears to be rapid. On the other hand, it was also inferred that the synthesis was imperfect, that is a mixture of lithium-poor spinel ($\gamma$-Fe$_2$O$_3$ and LiFe$_2$O$_3$) and the lithium ingredient were produced, because of low reactivity at low temperatures. In this case, the lithium ingredient failed to combine with iron but reacted with CO$_2$ directly. In the case of the 100°C product, XRD showed a very broad spinel pattern that was almost identical to that of the FeO(OH) reagent used for the synthesis. The pattern of unreacted LiOH, produced by dehydration of LiOH·H$_2$O, could be detected also, and therefore the reaction seemed to be incomplete, because the temperature is too low.

3.2 Performance evaluation using XRF imaging

While quick and efficient characterization of combinatorial samples has been a significant issue, the fast XRF imaging technique developed by the authors proved to be useful in this study. Figure 2 is an XRF image of a LiFe$_2$O$_3$ combinatorial sample taken in just 3 s by 7130 eV monochromatic X-ray irradiation. The Fe-K XRF from each sample unit can be observed as a bright square. The XRF intensity of each unit was calculated by integrating the pixel data constituting each square. From the XRF images collected around the Fe-K absorption edge, the fluorescence-XAFS spectrum of each sample unit was obtained by plotting the intensity values against the incident X-ray energy. One of the advantages of observing Fe-XAFS is the ability to focus on only iron and its compounds. By this, we mean that when it comes to performance evaluation, even if unreacted lithium that also absorbs CO$_2$ coexists in the product, only the contribution of lithium ferrite can be observed. Figure 3(a) shows the XAFS of the material in the bottom column of Fig. 2 (synthesis temperature is 400°C). As observed by the above XRD experiment, $\gamma$-Fe$_2$O$_3$ is finally produced by CO$_2$ absorption. In our previous
measurements of XAFS, it was observed that the absorption edges of $\gamma$-Fe$_2$O$_3$ have a higher energy compared with those of LiFeO$_2$. Figure 3(a) shows that the absorption edge shifts to the high-energy side by CO$_2$ exposure. Furthermore, the higher the exposure temperature, the faster the reaction rate—the shift is large at 350 °C exposure. Even at 200 °C, the shift can be observed clearly by an exposure of only 30 min. Therefore, excellent reactivity is confirmed. In Fig. 3(b), the XAFS of the 200 °C product (2nd column from the top) is shown. The absorption edge shift by CO$_2$ exposure can also be observed. Even though the $\alpha$-LiFeO$_2$ portion was lower in this sample as the XRD result showed, the shift even at low-temperature exposure (100 °C or 200 °C) seemed to be larger than that for the 400 °C product in just a short period of time (30 min). Generally speaking, the lower the temperature at which a material is produced, then the smaller the crystallite size, and the higher the reactivity. As the result, in spite of impurities, the product exhibits a decent capability overall. Accordingly, a future issue is how to prepare pure $\alpha$-LiFeO$_2$ at lower temperatures. On the other hand, the spinel-type phase contained in the product may show substantial potential. The phase was also obtained by Kim and Manthiram and Lee et al. in the course of cathode material development, and the phase presented a high discharge capacity, while $\alpha$-LiFeO$_2$ was electrochemically inactive because of the structural difficulty of inserting/extracting lithium. In the case of the CO$_2$ absorption reaction, the ease of migration of lithium probably promotes the reactivity of lithium and CO$_2$ to result in Li$_2$CO$_3$. As the lithium fraction is smaller in the spinel-type phase LiFe$_2$O$_3$ compared with LiFeO$_2$, the total capacity of CO$_2$ absorption is smaller in LiFe$_2$O$_3$. However, apart from capacity, it may show high reactivity and quick absorption in a short space of time. Therefore, the formation of spinel phase in the lower-temperature synthesized sample might not be inconvenient, although further experiments are necessary for understanding the details. In the case of the 100 °C product, the chemical shift by CO$_2$ exposure was not so large compared with that of the 200 °C product, and we concluded the reason must be the incompleteness of the synthesis reaction.

The result of combinatorial XAFS imaging proved that the 400 °C product has excellent CO$_2$ absorbing power. The product synthesized at lower temperature (the 200 °C product) showed quicker absorption and therefore superior power by low-temperature exposure of CO$_2$. However, obviously, too low a temperature for the synthesis around 100 °C resulted in unsuccessful production.

### 3.3 Quantitative analysis using TG

TG curves were observed for both products obtained by low-temperature synthesis at 400 °C and by the ceramic method at 800 °C. CO$_2$ was flowed at the rate of 200 ml/min and the samples were heated from room temperature at the rate of 10 °C/min. An increase in weight accompanying CO$_2$ absorption started to be observed at below 100 °C for the 400 °C product. The weight showed the maximum value at around 500 °C and was followed by a steep decrease at around 550 °C upon CO$_2$ release. A similar weight change was observed for the 800 °C product, although both the initial rise and the maximum value were far lower. CO$_2$ absorption behavior was also measured using TG in the following program. The samples were kept at 400 °C and CO$_2$ was flowed at a rate of 200 ml/min. Weight changes against duration time, expressed by percentage as the increment from the initial value of the samples, are shown in Fig. 4. A rapid increase in weight in the initial stage can be observed for the 400 °C product. The total increase in weight reached more than 16% 150 min. later, and was still increasing. In contrast, the 800 °C product showed a slower absorption speed, and the absorption mass was only 2% at a time of 150 min. Theoretically, LiFeO$_2$ can absorb CO$_2$ corresponding to a 23.2% increase in weight according to the equation (i). Therefore, 16% absorption is inadequate and unsatisfactory. However, the low-temperature synthesis sample is far superior to the ceramic-method sample in terms of CO$_2$ absorbing power. The best temperature for low-temperature synthesis has not been examined by TG analysis, but a temperature of 400 °C or lower must be better in consideration of XAFS imaging results.
4. Conclusions

A new CO$_2$ absorbent, LiFeO$_2$, was successfully synthesized by a low-temperature process. Using the XAFS imaging technique, absorption edge shifts accompanied by CO$_2$ absorption were observed for multiple samples at the same time. The technique can be used for extremely quick surveying of the optimum conditions for the synthesis. The performance of the low-temperature synthesized product is excellent mainly because of the increase of the active area effectively corresponding to the reduction of the particle size, and so the speed and total amount of CO$_2$ absorption were significant.

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