CO$_2$ absorption and structural phase transition of $\alpha$-LiFeO$_2$

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been synthesized using Fe$_2$O$_3$ and LiNO$_3$ under various conditions, and the relationship between the CO$_2$ absorption ability and structural phase transition of the synthesized $\alpha$-LiFeO$_2$ has been investigated by X-ray diffraction (XRD) analysis and thermogravimetry and differential thermal analysis (TG–DTA). Mixed powders of Fe$_2$O$_3$ and LiNO$_3$ were heated at 500°C for 5 h to synthesize $\alpha$-LiFeO$_2$. The CO$_2$ absorption reaction of the synthesized $\alpha$-LiFeO$_2$ was performed in the temperature range from 200 to 500°C for 2 h under CO$_2$ gas with a flow rate of 100 ml/min. It was found that the CO$_2$ absorption ratio of the synthesized $\alpha$-LiFeO$_2$ increased with increasing temperature up to 400°C but markedly decreased above 425°C. XRD analysis clarified that $\alpha$-LiFeO$_2$ underwent structural phase transition at 425°C, indicating that the structural phase transition suppressed the CO$_2$ absorption of $\alpha$-LiFeO$_2$. Results of the chemical composition analysis suggest that Li defects in LiFeO$_2$ promote structural phase transition.

Key-words: CO$_2$, LiFeO$_2$, Structural phase transition

1. Introduction

Various separation and collection methods for carbon dioxide (CO$_2$) from emission gases have been developed because of the increasing CO$_2$ concentration in the atmosphere, which is considered to be a factor contributing to global warming. From the viewpoint of the effective recovery of CO$_2$, collection at places with comparatively high CO$_2$ concentration is a valid method. Lithium ferrite (LiFeO$_2$) is suitable for the efficient separation of CO$_2$ from hot flue gases because it readily absorbs CO$_2$ at approximately 530°C to produce Li$_2$CO$_3$ and Fe$_2$O$_3$, and releases CO$_2$ at temperatures of approximately 530°C. Lithium ferrite has an advantage over other lithium salts such as Li$_2$ZrO$_3$, Li$_4$SiO$_4$, and Li$_4$TiO$_4$ because it absorbs CO$_2$ and releases CO$_2$ at lower temperatures than other compounds. However, the CO$_2$ absorption ratio of LiFeO$_2$ is low because the formation of Li$_2$CO$_3$ on the surface of LiFeO$_2$ prevents CO$_2$ molecules from diffusing inside the particles. In the above study, it was proposed that the mixing of K$_2$CO$_3$ and LiFeO$_2$ is effective for enhancing CO$_2$ diffusion in Li$_2$CO$_3$-coated LiFeO$_2$ particles because K$_2$CO$_3$ and Li$_2$CO$_3$ form a liquid phase on the surface of the particles.

$\alpha$-LiFeO$_2$ with a NaCl-type structure has been synthesized by various methods such as solid-state reaction, hydrothermal reaction and freeze-dry synthesis. However, a previous thermodynamic study has clarified that $\beta$-LiFeO$_2$ and $\gamma$-LiFeO$_2$ are more stable than $\alpha$-LiFeO$_2$ at low temperatures, suggesting that the $\alpha$-LiFeO$_2$ phase is a metastable phase at RT. In this study, LiFeO$_2$ powder has been synthesized using Fe$_2$O$_3$ and LiNO$_3$ under various conditions, and the relationship between the CO$_2$ absorption and structural phase transition of LiFeO$_2$ has been investigated by XRD analysis and TG–DTA.

2. Experimental

Commercially available $\gamma$-Fe$_2$O$_3$ powder (99% purity, Wako Pure Chemical Industries, Ltd.), $\alpha$-Fe$_2$O$_3$ powder synthesized from $\alpha$-FeOOH prepared using FeCl$_3$ and NaOH aqueous solutions, and LiNO$_3$ powder (> 99.9% purity, Wako Pure Chemical Industries, Ltd.) were used as starting raw materials. LiNO$_3$ and $\gamma$-Fe$_2$O$_3$ or $\alpha$-Fe$_2$O$_3$ powders were mixed at a molar ratio of LiNO$_3$/Fe$_2$O$_3 = 2.00$ to 2.40. The mixing procedure was performed in ethanol for 24 h by ball milling using Al$_2$O$_3$ balls. After removing ethanol by evaporation, the mixed powder was dried and then heated at 500°C for 5 h to synthesize $\alpha$-LiFeO$_2$ with cubic symmetry. The crystalline phases of the synthesized LiFeO$_2$ powder were investigated using an X-ray diffraction (XRD) apparatus (Rad-C, Cu K$_\alpha$, 40 kV, 30 mA, Rigaku Co.) equipped with a graphite monochromator. The structural phase transition ratio of the synthesized $\alpha$-LiFeO$_2$ powder was calculated from the ratio of the main peak of the transitioned phase to that of $\alpha$-LiFeO$_2$. The lattice constants of the synthesized $\alpha$-LiFeO$_2$ were refined by the least-squares method, using the diffraction peaks of the (111), (200), and (220) planes of the synthesized $\alpha$-LiFeO$_2$. Here, silicon powder was used as the external standard. The morphologies of the $\alpha$-LiFeO$_2$ powder synthesized under various conditions and Fe$_2$O$_3$ powders were observed by field-emission scanning electron microscopy (FE-SEM; S4100, Hitachi, Ltd.). The specific surface areas of the LiFeO$_2$ and Fe$_2$O$_3$ powders were measured from the adsorption isotherm of nitrogen at –196°C by the Brunauer–Emmett–Teller method (BET; Sorptomatic 1990, CE Instruments). The molar ratio of Li to Fe of the synthesized $\alpha$-LiFeO$_2$ was examined by inductively coupled plasma spectrometry (ICP; ICP–S8100, Shimadzu Co.).

CO$_2$ absorption of the synthesized LiFeO$_2$ was performed in a mullite tube in the temperature range from 200 to 500°C for 2 h under CO$_2$ gas with a flow rate of 100 ml/min. The CO$_2$ absorption ratio of the synthesized LiFeO$_2$ was investigated from the mass decreasing ratio of the CO$_2$-absorbed LiFeO$_2$ in the temperature range from 200 to 500°C for 2 h under CO$_2$ gas with a flow rate of 100 ml/min. The CO$_2$ absorption ratio of the synthesized LiFeO$_2$ was investigated using an X-ray diffraction (XRD) apparatus (Rad-C, Cu K$_\alpha$, 40 kV, 30 mA, Rigaku Co.) equipped with a graphite monochromator.
Hence, the CO$_2$ absorption ratio of the synthesized LiFeO$_2$ was calculated for the theoretical absorption ratio of 23.2%. The CO$_2$ absorption-desorption properties of the synthesized LiFeO$_2$ powder were investigated in the temperature range from 25 to 600°C under CO$_2$ gas with a flow rate of 100 ml/min by TG–DTA.

3. Results and discussion

Similarly to those in previous studies, cubic LiFeO$_2$ hereafter α-LiFeO$_2$ (M), was synthesized by solid-state reaction using γ-Fe$_2$O$_3$ (magnemite) although the α-LiFeO$_2$ phase is thermodynamically metastable at RT. Figures 1(a), (b), (c) and (d) show the XRD patterns of α-LiFeO$_2$(M) heated at temperatures from 200 to 425°C for 2 h under CO$_2$ flow. The peak intensity of the γ-Fe$_2$O$_3$ phase increased with increasing temperature, indicating that LiFeO$_2$ absorbed CO$_2$, while the peak of the β-LiFeO$_2$ phase appeared at 400°C and markedly increased at 425°C. No γ-LiFeO$_2$ phase with a main peak at approximately 2θ = 24° was observed. The above XRD behavior shows that α-LiFeO$_2$(M) underwent structural phase transition due to CO$_2$ absorption, which resulted in the production of the four phases of α-LiFeO$_2$, β-LiFeO$_2$, γ-Fe$_2$O$_3$ and Li$_2$CO$_3$ at 400 and 425°C. Figure 2 shows the relationship between the CO$_2$ absorption ratio of α-LiFeO$_2$(M) and the heating temperature under CO$_2$ flow. The CO$_2$ absorption ratio increased with increasing heating temperature up to 400°C but markedly decreased above 425°C. Considering that α-LiFeO$_2$(M) underwent structural phase transition at 425°C, it is clear that the CO$_2$ absorption of α-LiFeO$_2$(M) was suppressed by structural phase transition.

Figure 3(a) shows the XRD pattern of as-synthesized α-LiFeO$_2$(M). Figures. 3(b) and (c) show the XRD patterns of the α-LiFeO$_2$(M) powders annealed at 480°C for 25 and 100 h in air, respectively. The annealing treatment enhanced the structural phase transition of the LiFeO$_2$, and the LiFeO$_2$ powders annealed for 25 and 100 h had structural phase transition ratios of 23 and 92%, respectively. The γ-LiFeO$_2$ phase was also recognized in the XRD pattern of the sample annealed at 480°C for 100 h, in addition to the β-LiFeO$_2$ phase. The γ-LiFeO$_2$ phase was considered to produce owing to the long annealing treatment, similar to those in other studies. The CO$_2$ absorption properties of the prepared α-LiFeO$_2$(M) powders with phase transition ratios of 0, 23, and 92% were investigated by TG–DTA in the temperature range from 25 to 600°C under CO$_2$ flow. The results are shown in Fig. 4. The maximum CO$_2$ absorption ratios of the prepared LiFeO$_2$ powders at approximately 500°C differed from each other. α-LiFeO$_2$(M) with the phase transition ratio of 0% had the highest CO$_2$ absorption ratio, and α-LiFeO$_2$(M) with the phase transition ratio of 23% had a higher ratio than that with the phase transition ratio of 92%. The CO$_2$ absorption ratio of each sample rapidly decreased above 500°C owing to the decomposition of Li$_2$CO$_3$. The specific surface areas of α-LiFeO$_2$(M) phase transition of the LiFeO$_2$, and the LiFeO$_2$ powders annealed for 25 and 100 h had structural phase transition ratios of 23 and 92%, respectively. The γ-LiFeO$_2$ phase was also recognized in the XRD pattern of the sample annealed at 480°C for 100 h, in addition to the β-LiFeO$_2$ phase. The γ-LiFeO$_2$ phase was considered to produce owing to the long annealing treatment, similar to those in other studies. The CO$_2$ absorption properties of the prepared α-LiFeO$_2$(M) powders with phase transition ratios of 0, 23, and 92% were investigated by TG–DTA in the temperature range from 25 to 600°C under CO$_2$ flow. The results are shown in Fig. 4. The maximum CO$_2$ absorption ratios of the prepared LiFeO$_2$ powders at approximately 500°C differed from each other. α-LiFeO$_2$(M) with the phase transition ratio of 0% had the highest CO$_2$ absorption ratio, and α-LiFeO$_2$(M) with the phase transition ratio of 23% had a higher ratio than that with the phase transition ratio of 92%. The CO$_2$ absorption ratio of each sample rapidly decreased above 500°C owing to the decomposition of Li$_2$CO$_3$. The specific surface areas of α-LiFeO$_2$(M)

\[
2\text{LiFeO}_2 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Fe}_2\text{O}_3
\] (1)

Hence, CO$_2$ absorption ratio was calculated for the theoretical CO$_2$ absorption ratio of LiFeO$_2$ using Eq.(1).

![Fig. 1. XRD patterns of α-LiFeO$_2$(M) after CO$_2$ absorption at 200°C (a), 300°C (b), 400°C (c), and 425°C (d) for 2 h under CO$_2$ gas with a flow rate of 100 ml/min. α-LiFeO$_2$ (●), β-LiFeO$_2$ (○), γ-Fe$_2$O$_3$ (□), and Li$_2$CO$_3$ (▲)].

![Fig. 2. CO$_2$ absorption ratio of α-LiFeO$_2$(M) in the temperature range from 200 to 500°C for 2 h under CO$_2$ gas with a flow rate of 100 ml/min. Here, CO$_2$ absorption ratio was calculated for the theoretical CO$_2$ absorption ratio of LiFeO$_2$ using Eq.(1).]

![Fig. 3. XRD patterns of (a) α-LiFeO$_2$, (b) α-LiFeO$_2$ with β-phase ratio of 23%, and (c) α-LiFeO$_2$(M) with β-phase ratio of 92%. α-LiFeO$_2$ (●), β-LiFeO$_2$ (○), γ-LiFeO$_2$ (□), γ-Fe$_2$O$_3$ (▲), and Li$_2$CO$_3$ (▲).]
Fig. 4. CO2 absorption and desorption behaviors of α-LiFeO2(M) with β'-phase ratio of (a) 0%, (b) 23%, and (c) 92% in the temperature range of 25 to 600°C. CO2 absorption ratio was calculated for the theoretical CO2 absorption ratio of LiFeO2 using Eq.(1).

Fig. 5. SEM photographs of (a) γ-Fe2O3, (b) α-LiFeO2(M), (c) α-Fe2O3, and (d) α-LiFeO2(H) powders.

with the phase transition ratios of 0, 23, and 92% were 25, 13, and 5 m²/g, respectively. It was therefore considered that structural phase transition reduced the specific surface area of the LiFeO2 powder, which resulted in a decrease in the CO2 absorption ratio of the LiFeO2 powder.

Figures 5(a), (b), (c) and (d) show SEM photographs of the powders of γ-Fe2O3, α-LiFeO2(M), α-Fe2O3, and α-LiFeO2(H) synthesized using α-Fe2O3, respectively. The morphology of α-LiFeO2(H) did not reflect that of α-Fe2O3 particles, whereas the morphology of α-LiFeO2(M) reflected that of γ-Fe2O3 particles. The γ-Fe2O3 and α-Fe2O3 powders had specific surface areas of 30 and 87 m²/g, and the synthesized α-LiFeO2(M) and α-LiFeO2(H) had specific surface areas of 25 and 32 m²/g, respectively. The difference between the specific surface areas of Fe2O3 and LiFeO2 indicates that the prepared α-Fe2O3 had very fine pillar particles, making it difficult for α-Fe2O3 to maintain its morphology. Figures 6(a) and (b) show the XRD patterns of the as-synthesized α-LiFeO2(H) and the α-LiFeO2(M) heated at 425°C for 2 h under CO2 flow, respectively. α-LiFeO2(M) deposed to γ-Fe2O3 and Li2CO3 without the β'-LiFeO2 phase, which was different from α-LiFeO2(M). The lattice constants and chemical compositions of the synthesized α-LiFeO2(M) and α-LiFeO2(H) are shown in Table 1. The lattice constants differed from each other and distinct Li defects were recognized in α-LiFeO2(M). Such differences between α-LiFeO2(M) and α-LiFeO2(H) suggest that the chemical reactivity between LiNO3 and Fe2O3 is of importance for the synthesis of the α-LiFeO2 single phase with few Li defects because the α-Fe2O3 used for α-LiFeO2 synthesis had a larger specific surface area than γ-Fe2O3. α-LiFeO2 has disordering sites of Li+ and Fe3+ ions in its crystal structure, while β'-LiFeO2 has ordering sites of Li+ and Fe3+ ions.10,17) Li defects in α-LiFeO2 were considered to enhance the rearrangement for the ordering of Li+ and Fe3+ ions resulting in the production of the β'-LiFeO2 phase. This is because the vacancy sites derived from the Li defects were useful for the migration of the ions, which led to the enhancement of the structural phase transition of α-LiFeO2 to β'-LiFeO2 accompanied by CO2 absorption.

Figures 7 shows the relationship between the mixing ratio of LiNO3 to γ-Fe2O3 and the lattice constant of the synthesized α-LiFeO2. The increase in the lattice constant with increasing mixing ratio means that the increase in the mixing ratio of LiNO3 is effective for preventing the production of Li defects in α-LiFeO2. This is because the decrease in the lattice constant of α-LiFeO2 corresponded to the increase in the number of Li defects in α-LiFeO2, as shown in Table 1. Figure 8 shows the relationship between the lattice constant of the synthesized α-LiFeO2 and the phase transition ratio of α-LiFeO2 to β'-LiFeO2 induced by CO2 absorption at 425°C for 2 h. Here, α-LiFeO2 was synthesized under various LiNO3 mixing conditions ranging from 0 to 20 mol% excess for the stoichiometric composition of LiFeO2.

Table 1. Lattice Constant and Chemical Composition of α-LiFeO2

<table>
<thead>
<tr>
<th>Lattice constant /Å</th>
<th>Chemical composition /molar ratio</th>
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</thead>
<tbody>
<tr>
<td>α-LiFeO2(M)</td>
<td>Λ : Fe = 0.71 : 1.0</td>
</tr>
<tr>
<td>α-LiFeO2(H)</td>
<td>Λ : Fe = 0.93 : 1.0</td>
</tr>
</tbody>
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card to prevent the production of Li defects in α-LiFeO2 because the vacancy sites derived from the Li defects were useful for the migration of the ions, which led to the enhancement of the structural phase transition of α-LiFeO2 to β'-LiFeO2, accompanied by CO2 absorption.

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From the relationship shown in Fig. 8, it was found that the phase transition ratio decreased with increasing lattice constant, indicating that increasing the mixing ratio of LiNO₃ leads to the suppression of the structural phase transition of $\alpha$-LiFeO₂.

4. Conclusions

$\alpha$-LiFeO₂ was synthesized by heating a mixture of LiNO₃ and Fe₂O₃ powders at 500°C for 5 h. The CO₂ absorption ratio of the synthesized $\alpha$-LiFeO₂ increased with increasing heating temperature from 200 to 400°C but decreased above 425°C. It was considered that the CO₂ absorption of $\alpha$-LiFeO₂ was suppressed by the structural phase transition as determined from the XRD result showing that $\beta$-LiFeO₂ emerged clearly when heating temperature increased up to 425°C. Results of the chemical composition analysis of the synthesized $\alpha$-LiFeO₂ suggest that Li defects in $\alpha$-LiFeO₂ affect structural phase transition.

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References