

Low temperature synthesis and electrochemical characteristics of LiFeO₂ cathodes

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Abstract

Two rechargeable polymorphs of LiFeO₂ have been synthesized at low temperatures of less than 250 °C via a novel H⁺/Li⁺ ionic-exchange reaction in an alcoholic solution using stoichiometric amounts of lithium alkoxide and iron oxyhydroxide as the starting materials. The reaction, which proceeded in a topotactic manner, resulted in new polymorphs in the LiFeO₂ family with similar crystal structures to the parent materials. Two types of LiFeO₂, the corrugated layer and goethite type, were rechargeable in lithium cells with a cycling capacity of 0.2–0.4 Li/LiFeO₂ in the 1.5–4.5 V range, unlike the other six non-rechargeable polymorphs reported so far. A preliminary X-ray diffraction study on structural changes in the cathode during cycling showed a minimal lattice parameter change for corrugated layer LiFeO₂ and a noticeable *a*-lattice shrinkage/expansion of about 1% for goethite-type LiFeO₂. © 1997 Elsevier Science S.A.

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1. Introduction

A number of materials have been synthesized and evaluated for use as the cathode-active material in lithium secondary batteries and lithium-ion batteries at ambient temperature. Among them, a series of LiMO₂ (M = Co, Ni, Mn, Fe) cathodes have been extensively studied and LiCoO₂ is already employed in practical cells. Of the others, LiFeO₂ is a prospective candidate from the environmental friendliness and cost viewpoint. Although LiFeO₂ has several polymorphs such as α , β , β' , β'' , γ , layered (α -NaFeO₂ type) and corrugated layer (LiMnO₂ type) [1,2], only corrugated layer LiFeO₂ is reported to be electrochemically rechargeable in a lithium cell [3].

On the other hand, during the past decade, the concept of soft chemistry has attracted considerable attention as a new synthetic approach in the field of solid-state chemistry [4]. Soft chemical reactions involve a wide variety of low temperature processes, e.g. ionic exchange, redox, intercalation, de-intercalation and hydrolysis, and enable us to prepare novel materials, which are almost impossible to achieve by conventional routes through high temperature processes. We are investigating soft chemical synthesis routes based on cationic exchange in nonaqueous media with the aim of preparing novel lithium transition metal oxides as cathode-active

materials. Recently, we have developed a new low temperature synthesis method, which covers a reaction temperature range between room temperature and about 250 °C, by utilizing alcohol or an alcohol derivative (hereafter alcohol is used for simplicity) as a reaction medium [5].

In this paper, we report the synthesis methods and electrochemical cathode characteristics for both the corrugated layer LiFeO₂ and goethite-type LiFeO₂ (a new form of LiFeO₂).

2. Experimental

A lithium alkoxide solution was prepared by dissolving either lithium methoxide (LiOMe, Soekawa Chemicals), or lithium hydroxide (monohydrate) (LiOH·H₂O, Kanto Chemical) in an alcohol such as ethanol, 2-ethoxyethanol or 2-phenoxyethanol (Kanto Chemical). A stoichiometric amount of either α - or γ -type iron oxyhydroxide (α - or γ -FeOOH, Kanto Chemical and High Purity Chemicals, respectively), with Li/Fe = 1 in molar ratio, was then added to the solution to induce the following H⁺/Li⁺ ionic exchange reaction at a temperature below 250 °C [5]



where LiOR is lithium alkoxide and ROH is alcohol.

We used methanol or ethanol as a reaction medium for the reaction temperature range between room temperature and

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80 °C. 2-ethoxyethanol and 2-phenoxyethanol were used for reactions at 80–135 °C and 135–220 °C, respectively. The solution was magnetically stirred in a thermostatically controlled tetraethylene glycol bath. The resulting reaction product was filtered and washed with ethanol several times and then dried in vacuum at 90 °C.

The amounts of lithium and iron in the reaction products were analyzed by atomic absorption and inductively-coupled plasma atomic emission spectrometry. The crystal structure of the product was characterized by X-ray diffraction (XRD, Rigaku Rotaflex with Cu K α radiation). LiFeO₂ powder was mixed thoroughly with acetylene black and polytetrafluoroethylene powder in a weight ratio of 70:25:5, respectively, to form a cathode pellet (16 mm in diameter and about 0.5 mm thick). The electrochemical cathode characteristics were evaluated in coin-type lithium cells (23 mm in diameter and 2 mm thick) with an electrolyte consisting of 1 M LiPF₆ dissolved in a 50/50 vol.% mixture of ethylene carbonate and dimethyl carbonate. The separator we used was a Celgard 3501 microporous membrane. Cells were galvanostatically cycled between voltage limits of 1.5 and 4.5 V at a current density of 0.5 mA/cm² using a computer-controlled cycler system. Structural changes in the cathode during the charge/discharge cycle were evaluated by XRD measurement of the cycled cathode, which was first rinsed with dimethyl carbonate and dried in vacuum.

3. Results and discussion

3.1. Synthesis of LiFeO₂

3.1.1. Corrugated layer LiFeO₂

Fig. 1 shows the powder XRD patterns of the reaction products synthesized at various temperatures for 4 h using stoichiometric amounts of LiOH·H₂O and γ -FeOOH as the starting materials. As seen in this figure, new reflections

appeared at the reaction temperature of 80 °C together with minor peaks of pristine γ -FeOOH. None of the peaks corresponding to γ -FeOOH was found for the reaction products synthesized at 115 °C and higher. The XRD pattern of the product obtained at 115 °C is very similar to that reported as corrugated layer LiFeO₂ (orthorhombic LiMnO₂-type) [3]. In Ref. [3], however, this phase was obtained with about 23% of α -LiFeO₂ as an impurity phase. By contrast, the XRD pattern of our product was indexed to an orthorhombic unit cell with space group *Pmnm*, without α -LiFeO₂ contamination (i.e. single phase corrugated layer LiFeO₂). The lattice parameters we thus obtained were $a = 4.041$ Å, $b = 2.965$ Å and $c = 6.068$ Å. Chemical analysis of the reaction product revealed that Li/Fe = 1, within the margins of experimental error, indicating a complete ionic exchange between H⁺ and Li⁺ during the reaction. The reaction was affected by temperature, reaction duration and lithium concentration. An almost single phase corrugated layer LiFeO₂ was also obtained in the LiOMe/ γ -FeOOH system even at room temperature, as shown in Fig. 2, although it took a week to complete the H⁺/Li⁺ ionic exchange reaction.

3.1.2. Goethite-type LiFeO₂

On the other hand, the ionic exchange reaction in the LiOH·H₂O/ α -FeOOH system required a higher reaction temperature than the corrugated layer LiFeO₂ synthesis mentioned above. New peaks started to appear when the reaction temperature reached 150 °C when the reaction duration was fixed at 4 h (Fig. 3). XRD analysis of the reaction product obtained after 4 h at 170 °C revealed that it is a new phase with the same symmetry as the parent α -FeOOH (goethite; orthorhombic, space group *Pnma*) and with lattice parameters $a = 9.677$ Å, $b = 2.934$ Å, $c = 5.005$ Å, with a trace of α -LiFeO₂. The complete ionic exchange was also confirmed by elemental analysis. Lithium ions in the structure are considered to reside in the (2 × 1) channels created by the corner-shared double FeO₆ octahedral chains as found in the

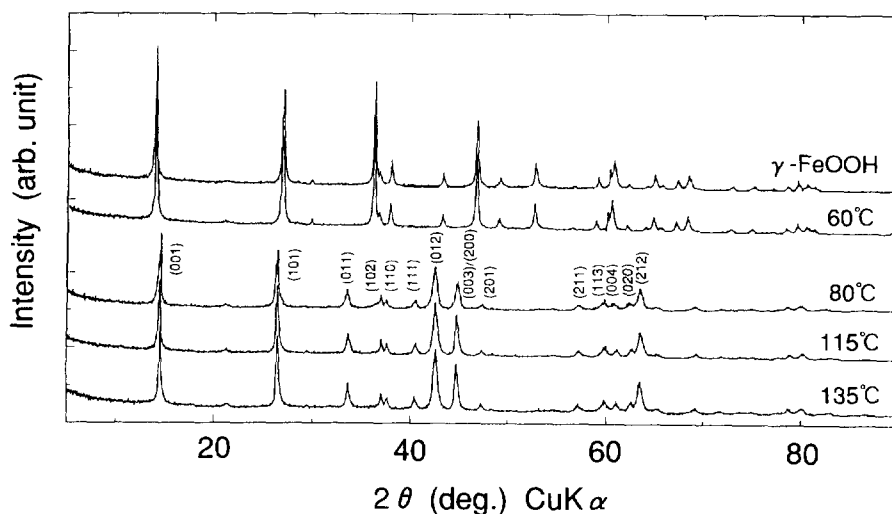


Fig. 1. Powder XRD patterns of reaction products in the LiOH/ γ -FeOOH system synthesized at various temperatures for 4 h. Miller indexes of the corrugated layer LiFeO₂ are indicated.

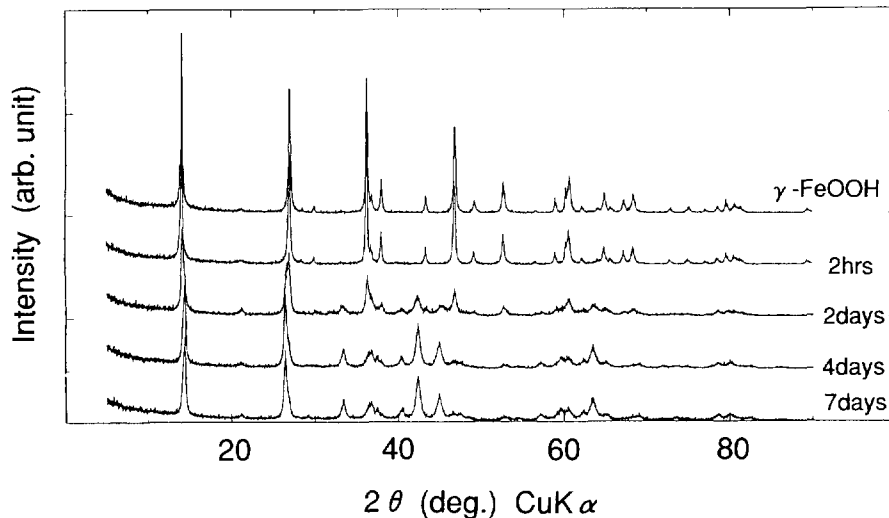


Fig. 2. Dependence of the powder XRD patterns of reaction products in the LiOMe/ γ -FeOOH system on reaction duration at room temperature

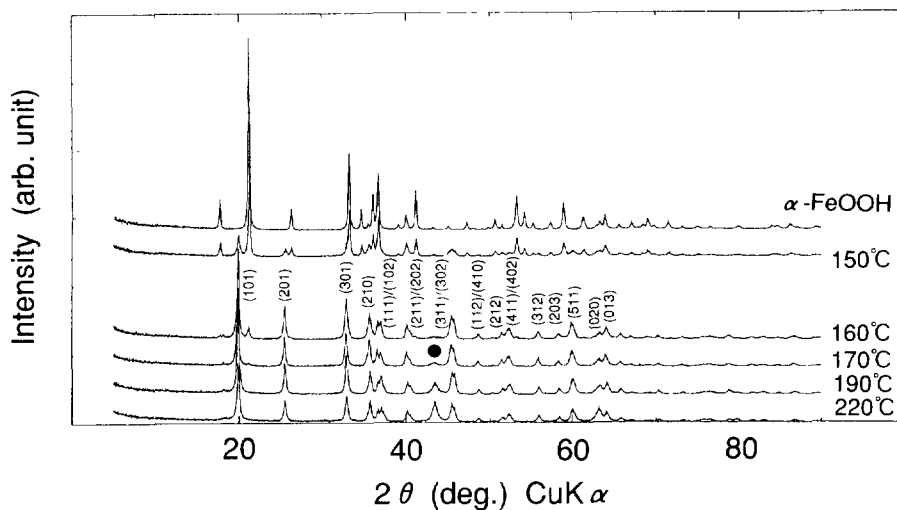


Fig. 3. Powder XRD patterns of reaction products in the LiOH/ α -FeOOH system synthesized at various temperatures for 4 h. Miller indexes of the goethite-type LiFeO₂ are indicated and an α -LiFeO₂ peak is marked with a filled circle.

framework of ramsdellite-MnO₂. We found that the amount of α -LiFeO₂ phase tends to increase with reaction temperature.

3.2. Electrochemical characteristics of LiFeO₂ cathodes

We evaluated the electrochemical cathode characteristics of both the corrugated layer LiFeO₂ and goethite-type LiFeO₂ in lithium cells in the 1.5–4.5 V range at 0.5 mA/cm². There were rest periods between charge and discharge. Fig. 4 shows typical charge/discharge curves of the above two types of LiFeO₂. It was possible to remove lithium ions from the host structures of both types of LiFeO₂ by initial charging, resulting in a voltage plateau somewhere around 4.2 V. The possibility of electrolyte oxidation or anion doping into carbon being causes for this voltage plateau were denied by the fact that the initial charging of an Li/ α -LiFeO₂ cell delivered negligible capacity under the charge conditions described

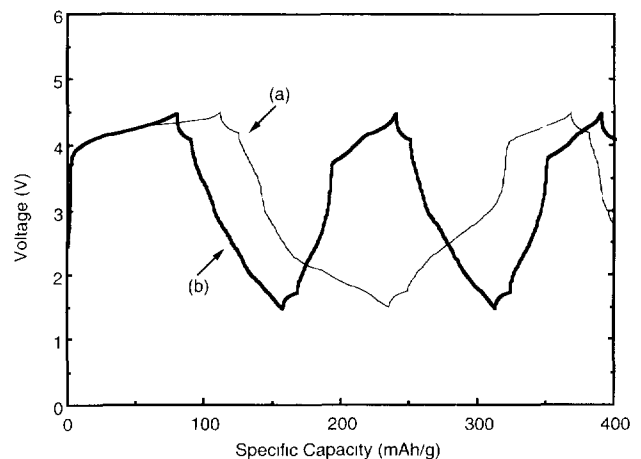


Fig. 4. Charge/discharge curves of (a) corrugated layer LiFeO₂ synthesized at 135 °C for 4 h, and (b) goethite-type LiFeO₂ synthesized at 190 °C for 1 h

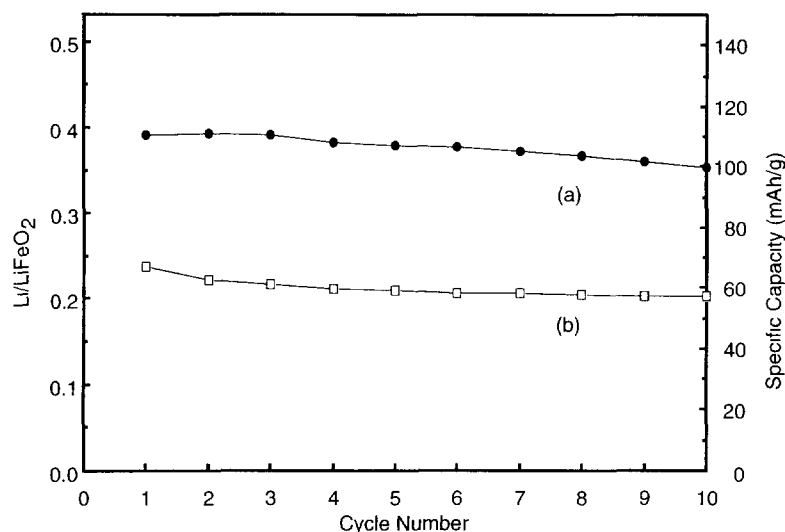


Fig. 5. Relation between cycling capacity and cycle number of: (a) corrugated layer LiFeO_2 , and (b) goethite-type LiFeO_2 .

above. In addition, an unequivocal deposition of metallic lithium was observed on the anode upon initial charging. The chemical compositions of these cathodes at the end of initial charging can be expressed as $\text{Li}_{0.6}\text{FeO}_2$ and $\text{Li}_{0.7}\text{FeO}_2$ for corrugated layer LiFeO_2 and goethite-type LiFeO_2 , respectively. Slanted discharge voltage profiles were observed for the subsequent discharge as is the case for corrugated layer LiFeO_2 synthesized by a different method, i.e. heating pressed admixtures of $\text{LiOH} \cdot \text{H}_2\text{O}$ and $\gamma\text{-FeOOH}$ in a silver tube at $150\text{--}250^\circ\text{C}$ [3]. The distinct difference between our corrugated layer LiFeO_2 and that in Ref. [3] is the slight but clear appearance of a high discharge voltage region above 3 V. This may be due to the difference in charge cutoff voltage (4.5 versus 4.3 V). The relationships between the cycling capacity of the two types of LiFeO_2 and cycle number are shown in Fig. 5. We found that corrugated layer LiFeO_2 and goethite-type LiFeO_2 are both rechargeable with cycling capacities of about 0.4 Li and 0.2 Li/ LiFeO_2 , respectively. The cycling capacity of the latter may be gained by making this a single phase material.

3.3. Structural change in LiFeO_2 cathodes during cycling

We used XRD measurements to obtain preliminary results on the structural changes which occur in cathodes during the charge/discharge process. Figs. 6 and 7 show the XRD patterns of corrugated layer LiFeO_2 and goethite-type LiFeO_2 cathodes, respectively, obtained at several charge/discharge states, i.e. uncycled ('uncycled' in the figures), after initial charging to 4.5 V ('init. C'), after a subsequent discharge to 1.5 V ('1st D') and then charging again to 4.5 V ('1st C'). It can be seen by comparing Figs. 1 and 3 with Figs. 6 and 7, respectively, that the relative XRD peak intensities of cathode pellets are different from those of cathode powder itself. This implies that there might be preferred orientations in the two types of LiFeO_2 and that some reflections are intensified by the physical stress caused by pressing and/or rolling during

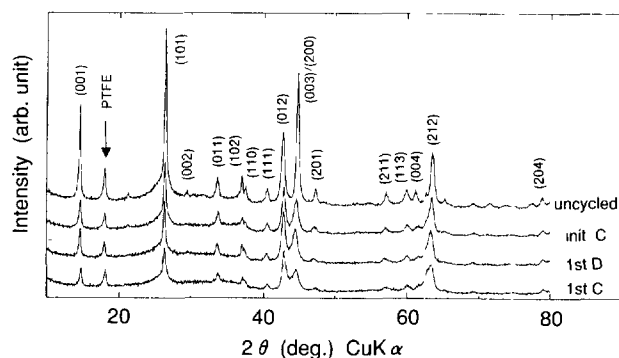


Fig. 6. XRD patterns of corrugated layer LiFeO_2 cathode obtained at various charge/discharge states.

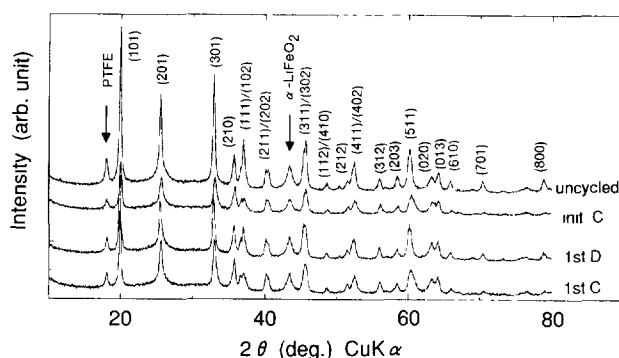


Fig. 7. XRD patterns of goethite-type LiFeO_2 cathode obtained at various charge/discharge states.

the cathode fabrication process. With corrugated layer LiFeO_2 , the lattice parameters were almost unchanged during cycling, while the peak intensities weakened. By contrast, the goethite-type LiFeO_2 cathode exhibited noticeable peak shifts which accounted for a shrinkage/expansion of about 1% in the a -lattice parameter, after charge/discharge, respectively. However, these results cannot explain why the two types of LiFeO_2 exhibit asymmetric voltage profiles during cycling from the viewpoint of crystal structure, since we

found that their crystal structures are basically maintained during cycling. Similar voltage asymmetry has been reported for orthorhombic LiMnO_2 [6–8]. In this case, however, a clear phase transition, from corrugated layer to spinel structure, was observed which well explained the voltage hysteresis during cycling.

It is of interest to note that the voltage profiles of corrugated layer LiFeO_2 and goethite-type LiFeO_2 are similar, despite their different crystal structures. Considering the similar large voltage hysteresis found in the extraction/insertion process of NaFeO_2 [9] and Li_5FeO_4 [10], unusual Fe^{4+} ions generated during charging may play an important role in the occurrence of voltage hysteresis. Further work is needed to clarify the reason for the large voltage hysteresis found in Li/LiFeO_2 cells.

4. Conclusions

Corrugated layer LiFeO_2 and goethite-type LiFeO_2 (a new polymorph in the LiFeO_2 family) were synthesized at low temperature via the H^+/Li^+ ionic exchange reaction between lithium alkoxide and iron oxyhydroxide. Corrugated layer LiFeO_2 was obtained even at room temperature. These two types of LiFeO_2 were rechargeable in lithium cells with a cycling capacity of 0.2–0.4 Li/LiFeO_2 . These are the only two rechargeable polymorphs yet found in the LiFeO_2 family.

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