

Short communication

## Preparation of $\alpha$ -LiFeO<sub>2</sub>-based cathode materials by an ionic exchange method

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### Abstract

$\beta$ -FeOOH prepared with an enhanced hydrolysis method had been subjected to H<sup>+</sup>/Li<sup>+</sup> exchange with various lithium salts in ethanol for various duration. The effects of the kind of lithium salt used and the duration of ionic exchange on the composition, the crystalline structure, and the electrochemical properties of the prepared powders were investigated. It was found that  $\alpha$ -LiFeO<sub>2</sub> can be prepared from  $\beta$ -FeOOH by an ionic exchange reaction with LiOH in ethanol at 85 °C.  $\alpha$ -LiFeO<sub>2</sub> powders so prepared show electrochemical active properties with reversible capacity of 65–80 mAh g<sup>-1</sup>. The in situ XRD patterns of the cycled  $\alpha$ -LiFeO<sub>2</sub> cathode revealed that the crystalline structure remains unchanged while the lattice of cubic decreases and increases periodically upon charge/discharge cycling. The results of XANES suggest that the electrochemical reaction of the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple occurs as the prepared  $\alpha$ -LiFeO<sub>2</sub> electrode is charge/discharge cycled.

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**Keywords:** Lithium iron oxide; Cathode material; Ionic exchange reaction; Lithium-ion batteries

### 1. Introduction

Lithium iron oxides with formula of LiFeO<sub>2</sub> had got a lot of attention for their crystalline structure similar to LiCoO<sub>2</sub>, non-toxicity, and low cost. They are highly expected to be potential cathode materials for lithium-ion batteries [1–15]. Depending on the precursors and the synthetic methods used, LiFeO<sub>2</sub> can be prepared with various crystalline structures showing as  $\alpha$ -layered [1–3],  $\beta$ -layered [1],  $\gamma$ -layered [1], (structure similar to  $\alpha$ -NaFeO<sub>2</sub>) [4–6], corrugated layer (structure similar to  $\gamma$ -FeOOH) [6–11], goethite-type (structure similar to  $\alpha$ -FeOOH) [11], hollandite-type LiFeO<sub>2</sub> (structure similar to  $\beta$ -FeOOH) [12], and non-stoichiometric compounds with mixed structures [13–15]. Among the isomers, corrugated, goethite-type, and hollandite-type LiFeO<sub>2</sub> had been proved to be electrochemically active. Hollandite-type LiFeO<sub>2</sub> exhibits the highest reversible specific capacity of 170 mAh g<sup>-1</sup> within the cutoff voltages of 1.5 and 4.5 V among them. Solid-state reaction prepared  $\alpha$ -,  $\beta$ -, and  $\gamma$ -layered-type LiFeO<sub>2</sub> powders had been reported to be electrochemically inactive. However, Sakurai et al. showed that the low temperature prepared  $\alpha$ -LiFeO<sub>2</sub>, obtained from an ionic exchange reaction between  $\alpha$ -FeOOH

and LiOH in 2-phenoxyethanol, exhibits electrochemical activity in 1998 [2]. Recently, Wang et al. revealed that the  $\alpha$ -LiFeO<sub>2</sub> nanorods synthesized from  $\beta$ -FeOOH by a low-temperature molten salt method also manifest a reversible specific capacity of 60 mAh g<sup>-1</sup> [3]. In this study, nano-sized  $\alpha$ -LiFeO<sub>2</sub> powders were prepared from  $\beta$ -FeOOH by an ionic exchange method and their electrochemical properties were investigated.

### 2. Experimental

$\beta$ -FeOOH used for ionic exchange reaction was prepared by an enhanced hydrolysis of FeCl<sub>3</sub>·6H<sub>2</sub>O in aqueous solution by adding NaOH solution drop by drop to keep the pH of the solution between 1.5 and 2.0 at 80 °C [16,17].  $\beta$ -FeOOH so prepared and lithium salts, such as LiOH·H<sub>2</sub>O, Li<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COOLi, or LiNO<sub>3</sub>, were mixed with Li/Fe molar ratio of 2 and reacted in ethanol solution in closed vessels for various durations at 85 °C. The compositions, the crystalline structures, and the morphology of the prepared powders were studied with ICP-OES (Optima 2100, Perkin-Elmer), X-ray diffractometer (beam line 01C2, NSRRC, Taiwan), and SEM (JSM 6700, Hitachi). Thus, prepared powders were blended with acetylene black and polyvinylidene fluoride (PVDF) with weight ratio of 8:1:1 in adequate amount of *N*-methyl pyrrolidone (NMP) to become slurries. Then the slurries were coated on Al-foil substrate,

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followed by heating at 80 °C for 24 h and punching into disk electrodes. After pressing and heating in vacuum oven at 80 °C for 8 h, the prepared electrodes were used as cathode or working electrode for assembling into coin-type cells, in situ cells, and three-electrode cells with lithium as anode, counter, and reference electrodes, Celgard 2400 as separator, and 1 M LiPF<sub>6</sub> in EC-DEC (1:1, v/v) as electrolyte.

Cyclic voltammetric study (CV) were carried out with the three-electrode cells on a potentiostat/galvanostat (Voltalab PGZ-402, Radiometer Analytical) by cycling the cells between potential limits of 1.3 and 4.7 V with scan rate of 1 mV s<sup>-1</sup>. The capacity retention study of the prepared powders was performed by cycling the coin-type cells with rate of 0.1 C between cutoff voltages of 1.5 and 4.5 V at 30 °C. The variation of the crystalline structure and the valence of iron in the  $\alpha$ -LiFeO<sub>2</sub> cathodes upon cycling were studied by in situ XRD and XANES with beam lines 01C2 and 17C of NSRRC in Taiwan, respectively.

### 3. Results and discussion

The XRD patterns of the  $\beta$ -FeOOH powders were prepared by various hydrolysis methods with FeCl<sub>3</sub>·6H<sub>2</sub>O as precursor are shown in Fig. 1. Though  $\beta$ -FeOOH can be obtained exclusively by these methods, enhanced hydrolysis was used to prepare  $\beta$ -FeOOH for further studies for larger quantity of  $\beta$ -FeOOH can be produced by this method than others. It may be caused by the removal of HCl that leads the equilibrium of hydrolysis reaction shifts to right according to the LeChatelier's principle.

Fig. 2 shows the XRD patterns of the powders prepared by ionic exchange reactions in ethanol at 85 °C for 24 h with  $\beta$ -FeOOH and various lithium salts as the starting materials. It is found that  $\alpha$ -LiFeO<sub>2</sub> formed in the sample prepared with LiOH/ $\beta$ -FeOOH molar ratio of 2, while the powders remained the characteristic pattern of  $\beta$ -FeOOH after been reacted with LiNO<sub>3</sub>, CH<sub>3</sub>COOLi, or Li<sub>2</sub>CO<sub>3</sub> in ethanol with the same Li/Fe molar ratio in the starting materials. For the samples prepared

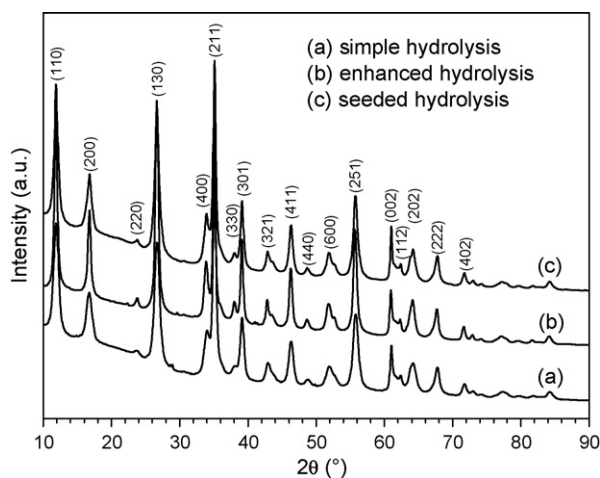


Fig. 1. XRD patterns of the  $\beta$ -FeOOH samples prepared by (a) simple hydrolysis, (b) enhanced hydrolysis by adding 1 M NaOH solution drop by drop, and (c) seeded hydrolysis by adding  $\beta$ -FeOOH at 80 °C.

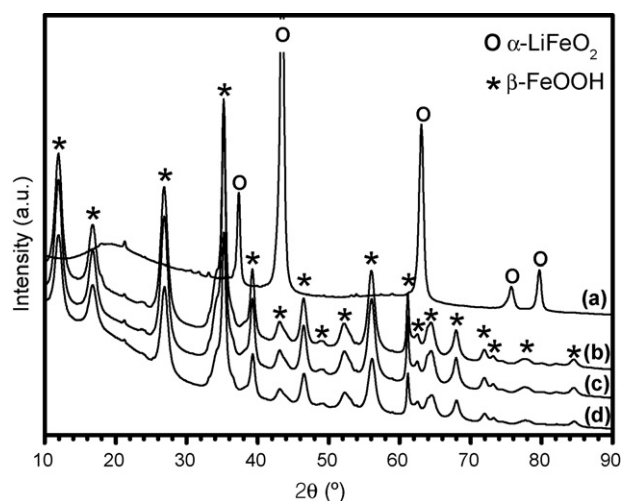


Fig. 2. XRD patterns of the powders prepared by having  $\beta$ -FeOOH reacted with (a) LiOH, (b) LiNO<sub>3</sub>, (c) LiCH<sub>3</sub>COO, and (d) Li<sub>2</sub>CO<sub>3</sub> with Li/Fe = 2 in ethanol at 85 °C for 24 h.

with LiOH/ $\beta$ -FeOOH = 2 in ethanol solution at 85 °C, the variation of the Li/Fe molar ratio in the prepared powders with the reaction duration is shown in Fig. 3. The Li/Fe molar ratio in the prepared powders rises steeply as the duration of ionic exchange reaction is shorter than 3 h. After that the ratio increases to 0.86 as the duration of reaction is extended to 12 h and increases gradually to a value of 0.91 in the 72 h reacted sample. The deviation from Li/Fe = 1/1 may be due to Li defects in the structure or insufficient time for ionic exchange reaction [12]. Though the samples obtained by the ionic exchange reaction might have the composition as Li<sub>1-x</sub>H<sub>x</sub>FeO<sub>2</sub> or Li<sub>1-x</sub>Fe<sub>1+x</sub>O<sub>2</sub>, the general composition, LiFeO<sub>2</sub>, instead of real composition is used thereafter.

From the XRD patterns (have not been shown in the manuscript) of the prepared powders, the diffraction peaks of cubic  $\alpha$ -LiFeO<sub>2</sub> were found in the samples prepared by the ionic exchange reaction for more than 3 h with LiOH/ $\beta$ -FeOOH = 2 in ethanol solution at 85 °C. The crystallinity of  $\alpha$ -LiFeO<sub>2</sub> phase

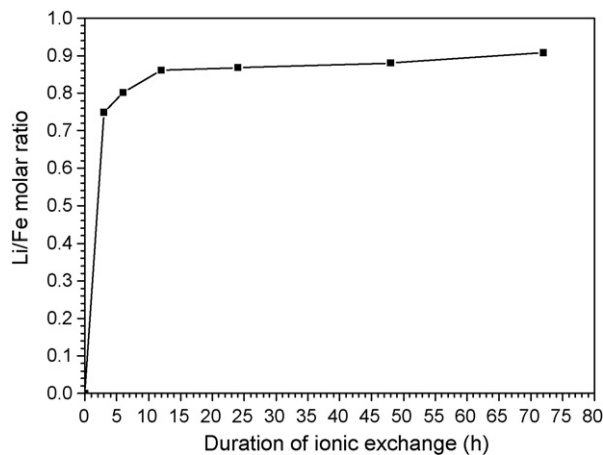


Fig. 3. Variation of Li/Fe molar ratio in the prepared powders with the duration of ionic exchange reaction in ethanol solution with LiOH/ $\beta$ -FeOOH = 2 at 85 °C in closed vessels.

increases while  $\beta$ -FeOOH phase diminishes with increasing duration of ionic exchange reaction. These results are different from the results reported by Matsumura et al. showed that the cubic  $\alpha$ -LiFeO<sub>2</sub> only formed at temperatures higher than 200 °C by the ionic exchange reaction with  $\beta$ -FeOOH/LiOH molar ratio of 5 in 2-phenoxyethanol [12]. A new form of LiFeO<sub>2</sub> that maintained the similar tetragonal structure as  $\beta$ -FeOOH formed after been reacted with LiOH for 12 h in ethanol solution at 80 °C with LiOH/ $\beta$ -FeOOH = 5. It may be attributed to the small particle size of the  $\beta$ -FeOOH used in this work that makes it easy to convert into  $\alpha$ -LiFeO<sub>2</sub>.

From the SEM photographs shown in Fig. 4, it is found that the needle-like  $\beta$ -FeOOH particles were pulverized into nano-sized particulate particles after they were reacted with LiOH for more than 3 h. There are no significant difference in morphology and average particle size among the samples prepared by the ionic exchange reaction with LiOH/ $\beta$ -FeOOH = 2 in ethanol for 3–72 h. However, it is clear that the morphology of the powders so prepared is different from the nanorod shape of the low-temperature molten salt synthesized powder reported previously [3].

The typical cyclic voltammogram of the prepared  $\alpha$ -LiFeO<sub>2</sub> powders is shown in Fig. 5. It was started with a reduction process from the OCV of a three-electrode cell with scan rate of 1 mV s<sup>-1</sup> and potentials between 1.3 and 4.7 V. During the initial cycle, the reduction peak at 1.8 V may be induced by the intercalation of Li<sup>+</sup> ions into  $\alpha$ -LiFeO<sub>2</sub> to form  $\alpha$ -Li<sub>1+x</sub>FeO<sub>2</sub> [7,10]. A broaden oxidation peak at 2.7 V may be attributed to the de-intercalation of Li<sup>+</sup> ions from Li<sub>1+x</sub>FeO<sub>2</sub> [7,10]. Whereas the steep increase in reduction current at potentials lower than 1.5 V that may be caused by the further reduction of Fe<sup>3+</sup> into Fe<sup>2+</sup>, the sharp rise in oxidation current at potentials higher than 4.0 V that may be caused by the oxidation of electrolyte or the oxidation of LiFeO<sub>2</sub> into Li<sub>1-x</sub>FeO<sub>2</sub> are also observed [7,12]. In addition to the peaks and current rises shown in the initial cycle, a small reduction peak at 2.8 V is found in the second cycle that may be ascribed to the intercalation of Li<sup>+</sup> into Li<sub>1-x</sub>FeO<sub>2</sub>.

For comparisons, the cells for capacity retention and in situ XRD studies were cycled by charging the cells before discharging as previous reports [2,3,8–12,15]. The results of capacity retention study of the prepared  $\alpha$ -LiFeO<sub>2</sub> powders are plotted in Fig. 6. It is found that the discharge capacity decreases with increasing duration of the ionic exchange reaction, though Li/Fe molar ratio in the prepared powders were increased by extending the duration of reaction. This might be due to the powder prepared with shorter reaction duration has higher concentration of  $\beta$ -FeOOH than those prepared with longer ionic exchange time, since it had been reported by Funabiki et al. that the  $\beta$ -FeOOH exhibits high reversible specific capacity of 230 mAh g<sup>-1</sup> [17]. The 72 h reacted sample with Li/Fe molar ratio of 0.91 shows a reversible specific capacity of about 70 mAh g<sup>-1</sup>. It is consistent with the result reported by Sakurai et al. that low-temperature prepared disordered rock-salt  $\alpha$ -LiFeO<sub>2</sub> is rechargeable in a lithium cell with a cycling capacity of ca. 0.2 Li/LiFeO<sub>2</sub> [2].

The typical charge/discharge curves of the  $\alpha$ -LiFeO<sub>2</sub>/Li cells are shown in Fig. 7. The cell voltage increases rapidly from 2.3 to 3.0 V followed by a steep increase to 4.0 V and then a

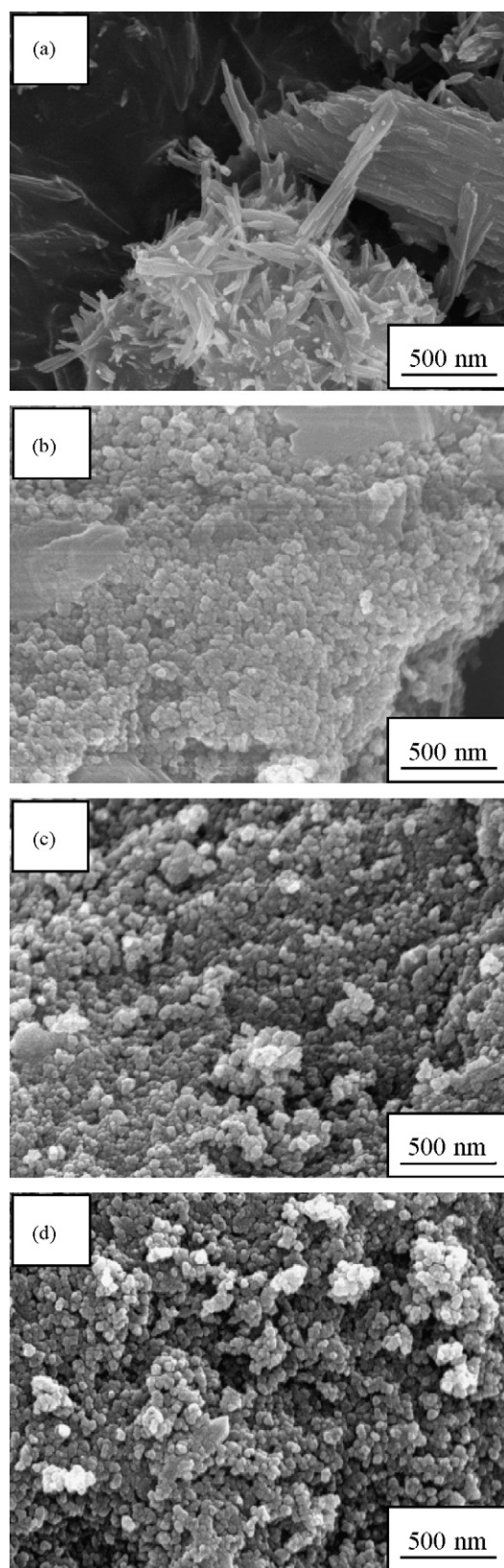


Fig. 4. SEM photographs of (a)  $\beta$ -FeOOH and the powders prepared by ionic exchange reaction with LiOH/ $\beta$ -FeOOH = 2 for (b) 3 h, (c) 24 h, and (d) 72 h in 85 °C ethanol solution.

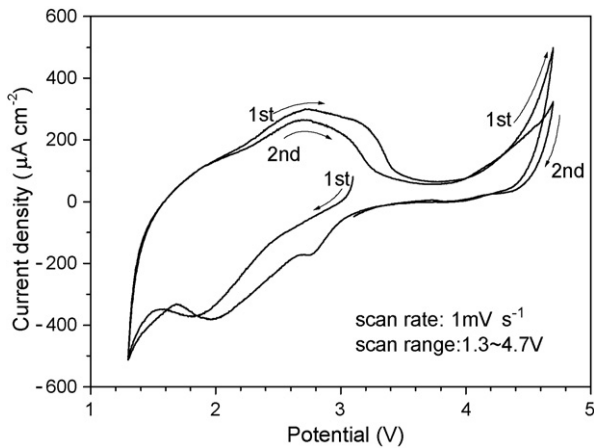


Fig. 5. Cyclic voltammogram of the powder prepared by ionic exchange reaction with  $\text{LiOH}/\beta\text{-FeOOH} = 2$  in  $85^\circ\text{C}$  ethanol solution for 72 h in a closed vessel.

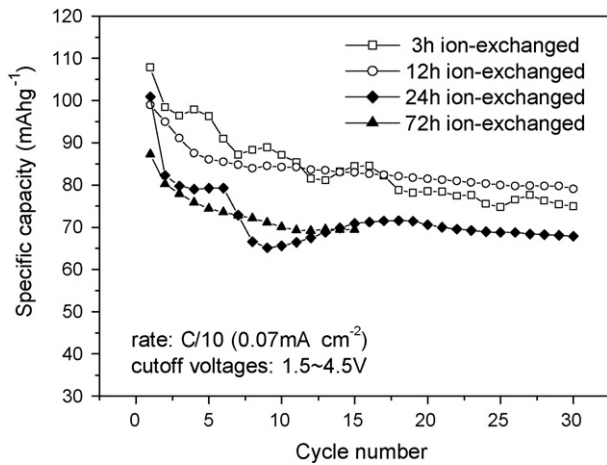


Fig. 6. Results of capacity retention study of the coin-type cells comprised with powders prepared with  $\text{LiOH}/\beta\text{-FeOOH} = 2$  in  $85^\circ\text{C}$  ethanol solution in closed vessels for various durations.

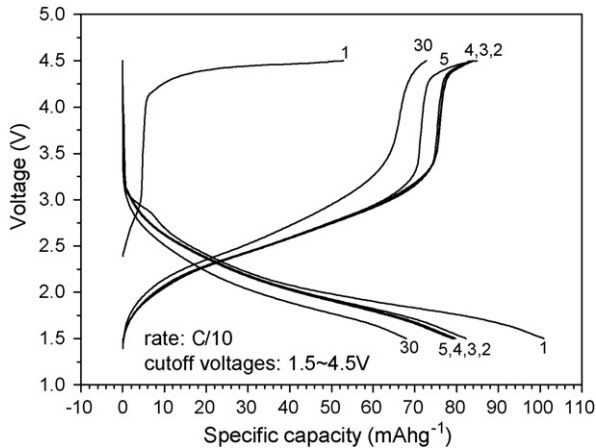


Fig. 7. Typical charge/discharge curves of a coin-type cell comprised with  $\alpha\text{-LiFeO}_2$  powder prepared with  $\text{LiOH}/\beta\text{-FeOOH} = 2$  in  $85^\circ\text{C}$  ethanol solution in a closed vessel for 24 h.

gradual increase to 4.5 V as a plateau is observed in the initial charge curve. The plateau voltage is slightly higher than the value reported by Sakurai et al. [2]. For the initial discharge, cell voltage decreases rapidly to 3.1 V and then decreases slowly to the cutoff voltage of 1.5 V. A small plateau at 2.9 V that corresponds to the reduction peak at 2.8 V on the cyclic voltammogram is also observed. In the following cycles, the cell voltage increases rapidly to 1.7 V, then increases steadily to 3.2 V followed by a abrupt increase to 4.5 V plateau in the charging curves, while a quick drop to 3.0 V and a slanted decrease in voltage to 1.5 V is observed in the discharge curves. The charge/discharge curves are quite similar to those of previous reports [2,3], though the discharge plateau at 4.2 V reported by Sakurai et al. is not found. Moreover, they are also similar to the charge/discharge curves of other electrochemical active  $\text{LiFeO}_2$  isomers [6–12,15].

Fig. 8(A) reveals the in situ XRD patterns of the  $\alpha\text{-LiFeO}_2$  cathodes in the  $\alpha\text{-LiFeO}_2/\text{Li}$  in situ cells quasi-equilibrated at various states upon cycling. It can be found that the cathodes remain cubic rock-salt structure when the cells were charged to

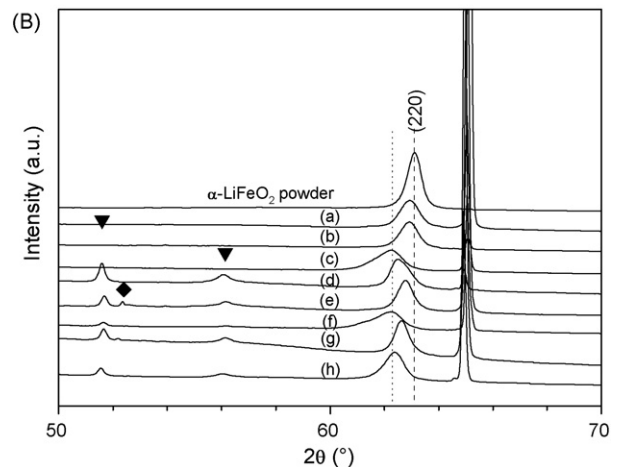
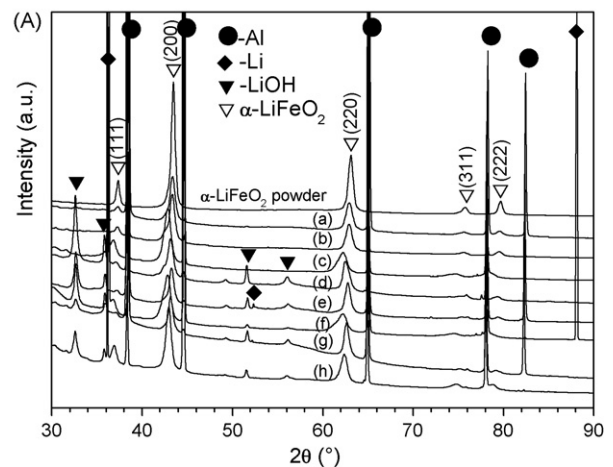


Fig. 8. (A) In situ XRD patterns of 24 h exchanged  $\alpha\text{-LiFeO}_2$  cathodes quasi-equilibrated at (a) 4.5 V of 1st charged cycle, (b) 3.0 V of 1st discharged cycle, (c) 1.5 V of 1st discharged cycle, (d) 3.0 V of 2nd charged cycle, (e) 4.5 V of 2nd charged cycle, (f) 1.5 V of 2nd discharged cycle, (g) 3.0 V of 3rd charged cycle, and (h) 1.5 V of 3rd discharged cycle. (B) The detailed view of (A) with  $2\theta$  between  $50$  and  $70^\circ$ .

4.5 V or discharged to 1.5 V as reported previously [2]. In addition to the diffraction peaks of rock-salt structure, new peaks are found in the cathodes after the cells had been charged/discharged for more than one cycle. While the peaks at around  $32^\circ$ ,  $36^\circ$ ,  $52^\circ$  and  $56^\circ$  manifest the existence of LiOH, the peaks at around  $36^\circ$  and  $53^\circ$  reveal the appearance of Li. It is different from the results reported previously [2,18]. Though, Sakurai et al. found the cathode remains rock-salt without the formation of any other new phase upon cycling within the same voltage window as this study [2].  $\text{Li}_2\text{O}$  and Fe were observed during the first discharge by Obrovac et al. when the solid-state reaction method prepared  $\alpha\text{-LiFeO}_2$  cathode was cycled with C/60 rate within voltage window between 0 and 2.5 V [18]. This may be attributed to the patterns of Sakurai et al. were performed with ex situ method with samples first rinsed by dimethylcarbonate before XRD study and different cycling voltage window was used by Obrovac et al. The discrepancy between the results reported by Obrovac et al. and this work may also be caused by the residual H atoms in the powders prepared in this study. However, the mechanisms of the formation of Li and LiOH are unclear.

From Fig. 8(B), a partial enlargement of Fig. 8(A), it is found that the diffraction peaks of rock-salt structure shift to left slightly as the cell was charged from OCV (about 3.0 V) to quasi-equilibrate at 4.5 V and then discharged to quasi-equilibrate at 3.0 V of initial cycle. This may be caused by the different sample holders were used for powder sample and in situ cell, though they had been designed and manufactured carefully. The positions of the characteristic diffraction peaks of rock-salt shift to left as the cell was quasi-equilibrated at 1.5 V and shift to right as the cell was quasi-equilibrated at 3.0 and 4.5 V in the further cycles. This indicates that the lattice parameter decreases and increases periodically between values around 4.17 and 4.22 Å upon charge/discharge cycling. It is different from the results obtained by Sakurai et al. that the lattice parameter is almost unchanged during cycling [2]. By comparing the peak positions of (2 2 0) as the cathodes were quasi-equilibrated at 4.5 V during initial and second cycles, shown in patterns (a and e) in Fig. 8(B), it is found that the peak position shifts slightly to lower angle as the cell was further cycled. It manifests the lattice parameter of rock-salt structure in the cathode at its charged state is increased slightly by further cycling. This may be ascribed to the remaining  $\text{Li}^+$  ions in the tetrahedral sites intercalated during the previous cycles which had not been de-intercalated upon charging.

Since it had been suggested by Koyama et al. that the energy required to remove  $\text{Li}^+$  ion from  $\text{LiFeO}_2$  is so high that the  $\text{Fe}^{4+}/\text{Fe}^{3+}$  couple tends to be lie far from  $\text{Li}/\text{Li}^+$  and the OCV versus  $\text{Li}/\text{Li}^+$  of  $\text{Fe}^{4+}/\text{Fe}^{3+}$  should be higher than 4 V [19]. The charge/discharge curves of the samples prepared in this study show charge/discharge plateaus at around 2.6 and 2.1 V after initial cycle. It suggests that the prepared nano-sized  $\alpha\text{-LiFeO}_2$  samples are electrochemical active due to the reactions of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple and the intercalation of  $\text{Li}^+$  ions into the tetrahedral sites of the random, so the rock-salt structure occurs as the cell is discharged. Though it is very difficult to explain the reason why the intercalation can proceed in such a structure from

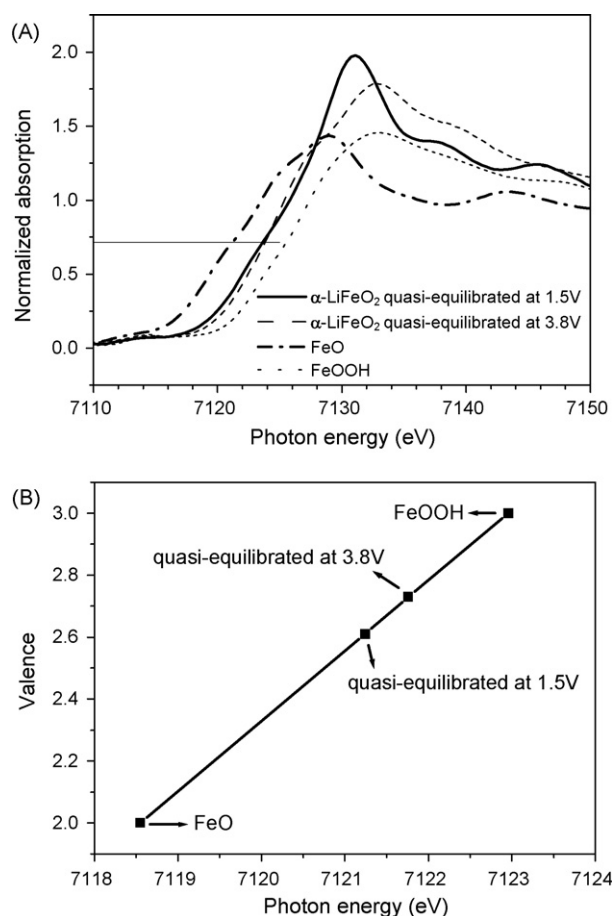


Fig. 9. (A) In situ XANES of the  $\alpha\text{-LiFeO}_2$  cathodes quasi-equilibrated at 3.8 V charged and 1.5 V discharged states in company with those of FeO and FeOOH for comparison. (B) Estimated valence of iron in  $\alpha\text{-LiFeO}_2$  cathode quasi-equilibrated at charged and discharged states.

the crystallographic point of view. It may be attributed to the size effect of the prepared powders.

The in situ XANES of the nano-sized  $\alpha\text{-LiFeO}_2$  cathodes of the  $\alpha\text{-LiFeO}_2/\text{Li}$  cells quasi-equilibrated at 3.8 and 1.5 V states of initial cycle are shown in Fig. 9 (A). The Fe adsorption edges of FeO and FeOOH are also shown for comparison. The Fe adsorption edge of the cathode moves to lower photon energy as the cell was discharged to quasi-equilibrate at 1.5 V while the absorption edge move to higher photon energy as the cell was charged to 3.8 V. The valences of iron in the cathode at its charged and discharged states were estimated from the energies of centre of the jump with FeO and FeOOH as references. As shown in Fig. 9 (B), the estimated valences of iron in the  $\alpha\text{-LiFeO}_2$  cathode are 2.61 as the cell was discharged and 2.73 as the cell were charged. Though the specific capacity estimated from the change of valence of iron in the cathode upon cycling is smaller than those obtained from capacity retention studies. The results of in situ XANES also suggest that the redox couple and the reversible electrochemical reaction occurs in the  $\alpha\text{-LiFeO}_2$  cathode upon charge/discharge cycling are  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Li}_{1+x}\text{FeO}_2 \rightarrow \text{LiFeO}_2 + x\text{Li}^+ + xe^-$ , as those proposed by Kanno et al. and Lee et al. for other  $\text{LiFeO}_2$  isomers [7,10]. Only limited amount of  $\text{Li}^+$  ions can be intercalated into the

tetrahedral sites without destroying the integrality of rock-salt structure. However, the amount of lithium can be intercalated into  $\alpha$ -LiFeO<sub>2</sub> powders that may depend on its preparing method and the size of the prepared powders.

#### 4. Conclusions

Nano-sized  $\alpha$ -LiFeO<sub>2</sub> particulate powders can be prepared from needle-like  $\beta$ -FeOOH nanoparticles by an ionic exchange reaction with LiOH in ethanol solution at 85 °C. The extent of ionic exchange not only depends on the duration of reaction, but also on the lithium salt used. The  $\alpha$ -LiFeO<sub>2</sub> powders prepared in this study shows electrochemical activity with reversible capacity of 65–80 mAh g<sup>-1</sup> by cycling between 1.5 and 4.5 V versus Li<sup>+</sup>/Li. From the results of in situ XRD and XANES studies, it is proposed that the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox couple occurs during the charge/discharge cycling within the voltage range.

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