

Hydrothermal Stripping Synthesis of α -LiFeO₂ Nanoparticles from Qinghai Salt Lake Brine

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Abstract. A simple and green hydrothermal stripping synthesis route has been successfully developed for synthesis of α -LiFeO₂ nanoparticles from the organic phase containing Fe (III) and Li (I), which was prepared by mixing Qinghai salt lake brine, industrial FeCl₃·6H₂O and tributyl phosphate (TBP). The influence of synthesis conditions, such as Li/Fe molar ratio, time and temperature, on the samples was investigated, and spheroidal α -LiFeO₂ nanoparticles with diameter of about 150 nm have been synthesized at 210 °C with Li/Fe molar ratio of 30. Qinghai salt lake brine, as an important lithium resource, is supposed to be fully studied and utilized. Here, the application range of salt lake brine was expanded innovatively.

1. Introduction

With the fast development of the economies, increased demand for lithium raw materials is becoming common phenomena in many industries like battery, ceramics, glass, grease, metallurgy, etc. Therefore, as an important lithium resource in China, Qinghai salt lake brine (SLB), which has about 0.297 mol Li⁺ per litre, is advised to be fully studied and utilized. At present, one of mature methods to acquire Li element from Qinghai SLB is using organic solvent named tributyl phosphate (TBP) to extract Li⁺ after adding FeCl₃·6H₂O in the brine phase. Here, this extracting lithium method was innovatively combined with hydrothermal stripping technique to prepare α -LiFeO₂ material for the first time. The use of Qinghai SLB in the lithium ferrite preparation cut the costs considerably. Meanwhile, it provides us new ideas and perspectives on the exploitation and use of SLB.

α -LiFeO₂, as a member of lithium iron oxide compounds (Li_xFe_yO_z), deserves our attention and research since it is a versatile material and has shown great potential applications, including CO₂ absorbent material^[1], anode material^[2], cathode material^[3] of lithium ion battery and supercapacitor electrode^[4]. The synthesis of α -LiFeO₂ was explored extensively in the past 20 years. Now, α -LiFeO₂ can be synthesized with various methods, such as ionic exchange method^[5,6], molten salt method^[3,7-9], solid phase method^[10,11], hydrothermal method^[12,13], ethanol-thermal method^[14], etc. However, some of the synthesis

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methods need higher temperature, while some consume longer reaction times, or require the use of special materials, or demand strong oxidants, unavoidably have some defects. So it is well worth to develop other new methods to meet our needs in different situations.

In this method, Li(I) and Fe(III) which originally exit in water phase attached to organic phase in the extraction process firstly. Then these ions were stripped and precipitated in the form of LiFeO_2 with the assist of LiOH aqueous solution, called hydrothermal stripping. This novel synthesis has advantages of easy operation, fast preparation, economy of energy consumption, as well as environmental friendliness. Moreover, since the organic phase and the LiOH solution can be reused after the experiment, we are available to utilize the resources fully and reasonably.

2. Experimental

The nanosized $\alpha\text{-LiFeO}_2$ material was obtained as follows. A certain amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was first dissolved into the experimental Qinghai SLB, keeping the pH 1~2 to avoid the hydrolysis of Fe^{3+} . The tributyl phosphate (TBP) extracting agent was added into the brine and the mixture was stirred for 30min thereafter. The organic phase so obtained loading Fe(III) and Li(I) was mixed with freshly prepared LiOH aqueous solution and transferred into a stainless steel autoclave. Heat it for some time and cool down to ambient temperature naturally. The separation of particles and liquid phase were conducted by a fast centrifugation. After layering of the liquid phase, the aqueous and organic phases could be separated and were able to be reused in the next new stripping process. The precipitate obtained was washed with alcohol, dilute hydrochloric acid (pH = 3~4) and deionized water sequentially. The purpose of using muriate acid was mainly to remove the impurity of magnesium hydroxide that may contained in the sample, since tiny Mg^{2+} may move from the brine to organic phase in the extraction process. It has been proved that $\alpha\text{-LiFeO}_2$ didn't react with such dilute HCl solution. At last, the product was dried at 70°C for 12 h. The synthesis route was showed in Fig. 1.

The specimen was identified by X-ray diffraction (XRD, D8-Focus) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the particles was characterized with scanning electron microscopy (SEM, Nanosem 430) and transmission electron microscope (TEM, Tecnai G2 F20).

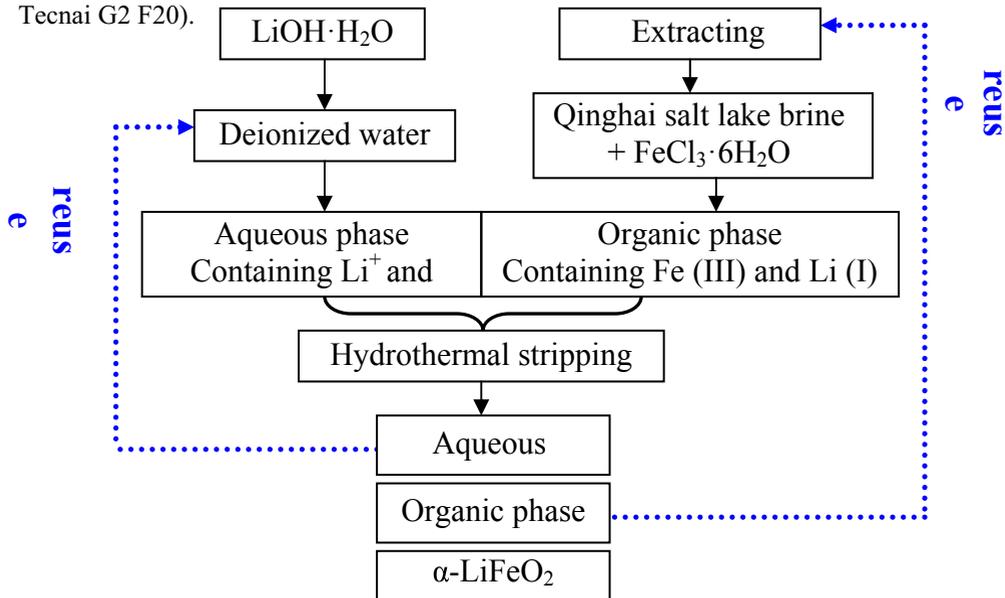
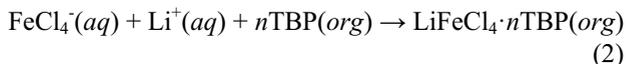


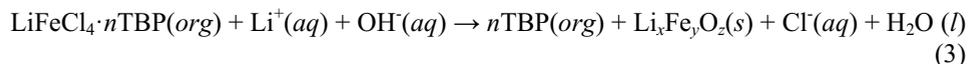
Fig. 1. Hydrothermal stripping synthesis route.

3. Results and Discussion

At room temperature, when TBP was added into Qinghai salt lake brine containing Li^+ naturally and Fe^{3+} artificially, extraction reaction happened soon. This mechanism was proved as follows:



And the hydrothermal stripping reaction may be written as:



Where the extractant of TBP was released and could be used again. $\text{Li}_x\text{Fe}_y\text{O}_z(\text{s})$ usually appeared in reaction (3) not otherwise than LiFe_5O_8 or LiFeO_2 ^[12], so we are supposed to prohibit the formation of LiFe_5O_8 to generate single $\alpha\text{-LiFeO}_2$ phase.

Li/Fe molar ratio is a very important factor in the synthesis of $\alpha\text{-LiFeO}_2$, which has been confirmed by previous researchers. Fig. 2a represents the XRD patterns of the products prepared with different Li/Fe molar ratio and amplification of the XRD diagram with Li/Fe = 40 is shown in Fig. 2b. Each diffraction peak in Fig. 2b could be clearly ascribed to $\alpha\text{-LiFeO}_2$ (cubic rock salt structure, Space Group: $\text{Fm}\bar{3}\text{m}$, $a = 4.158 \text{ \AA}$)^[12], quite consistent with the JCPDS 17-0938 and the XRD spectrum of $\alpha\text{-LiFeO}_2$ prepared in other methods^[5-14]. The sharp and narrow peaks indicate good crystallinity of the sample. No impurities are observed, particularly $\beta\text{-LiFeO}_2$, which always accompany with $\alpha\text{-LiFeO}_2$ in the products synthesized by hydrothermal method. As can be seen from the Fig. 2a, pure $\alpha\text{-LiFeO}_2$ phase was obtained with the Li/Fe = 30 and 40, while spinel phase of $\beta\text{-LiFe}_5\text{O}_8$ (JCPDS 17-0114, disordered face centered cubic structure, Space Group: $\text{Fd}\bar{3}\text{m}$, $a = 8.333 \text{ \AA}$)^[15] was more likely to generate in the LiOH-poor region. Obviously, using such a high ratio of Li/Fe means that there are still a large number of Li^+ in the water phase after the preparation. However, it will not result in a waste since the aqueous solution can be recycled.

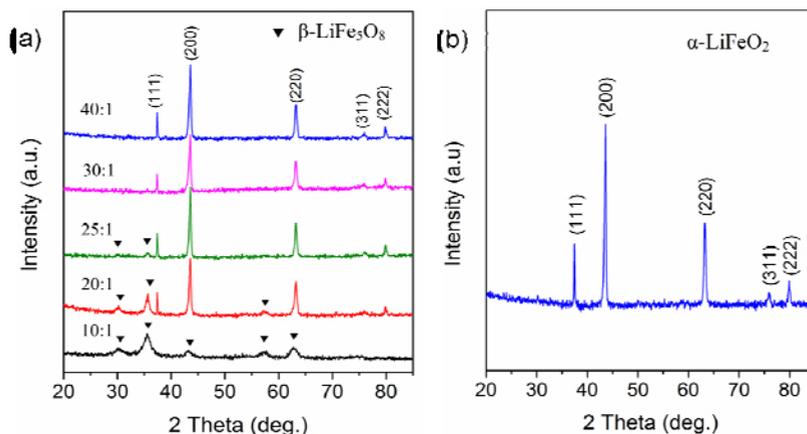


Fig. 2. XRD patterns of samples obtained at 210°C for 1h with Li/Fe molar ratio (a) differently, (b) 40:1.

Fig. 3 shows influence of reaction time on the product. The samples characterized in Fig. 3a still clearly showed weak diffraction peaks of β - LiFe_5O_8 when heating time lengthened to 2 or 3 hours. Pure phase failed to be obtained as expected by appropriately prolonging the reaction duration. It seems that there is no visible effect of heating time on phase composition. In the case in which Li/Fe molar ratio reached 30 (Fig. 3b), single α - LiFeO_2 phase was available after just half an hour, confirming the view once again. These phenomena also proved significance of Li/Fe molar ratio in the experiment.

The effect of temperature on the resulting product was also studied (Fig. 4). As we can see, pure α - LiFeO_2 was successfully generated at 200°C and 210°C, while β - LiFe_5O_8 became more obtainable at lower temperature. In other words, the main component of the obtained product experience a shift from α - LiFeO_2 to β - LiFe_5O_8 when reducing the temperature gradually. So temperature also plays a decisive role in the synthesis of α - LiFeO_2 .

The SEM and TEM experiments were conducted to observe the morphology and size of as-obtained α - LiFeO_2 particles. Fig. 5a and c show typical SEM images of a sample obtained at 200 and 210°C, respectively, which are quite consistent with their corresponding TEM pictures (Fig. 5b and d). Fig. 5a and b indicate that sample heated at 200°C has a cubes-like shape with average diameter of 200nm approximately. However, regular spheroidal particles, owning a smaller diameter (about 150nm), formed when the reaction temperature increased to 210°C. Therefore, morphology of the as-obtained α - LiFeO_2 particles can be interestingly altered by changing the reaction condition.

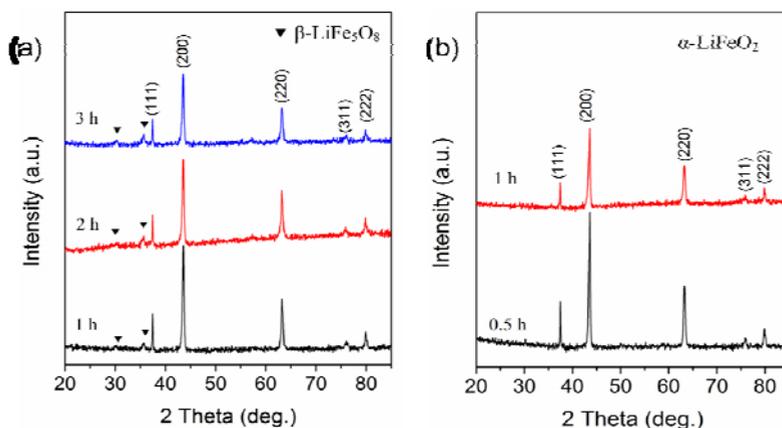


Fig. 3. XRD patterns of samples obtained at 210°C for different time with Li/Fe molar ratio (a) 25 and (b) 30.

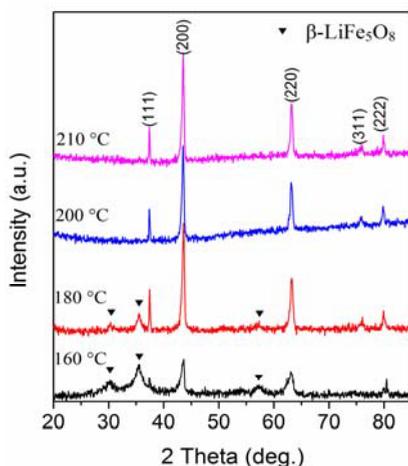


Fig. 4. XRD patterns of samples obtained at different temperature for 1h with Li/Fe molar ratio 30.

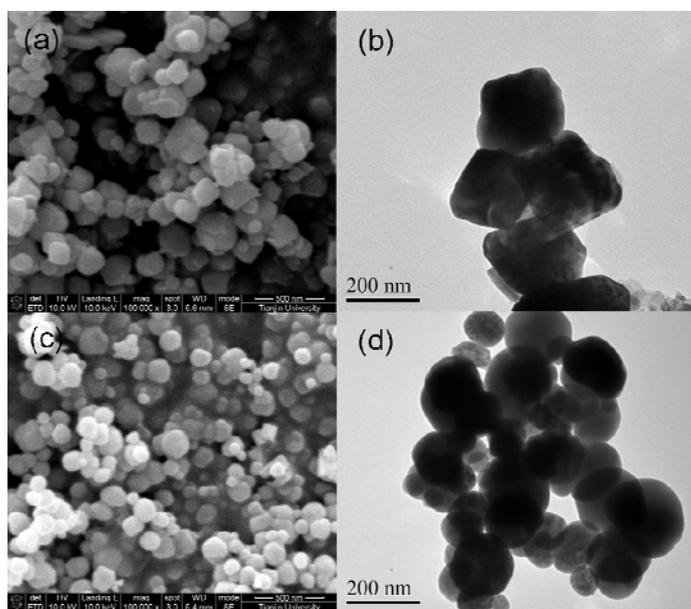


Fig. 5. Typical SEM (a and c) and TEM (b and d) images of as-obtained α -LiFeO₂ powders under different conditions ((a) and (b): 200 °C 1h with Li/Fe = 30; (c) and (d): 210 °C 1h with Li/Fe = 30).

4. Summary

Using Qinghai salt lake brine, industrial FeCl₃·6H₂O, tributyl phosphate (TBP) and LiOH·H₂O, the spheroidal α -LiFeO₂ nanoparticles with diameter of about 150 nm were successfully synthesized by hydrothermal stripping at 210 °C with Li/Fe molar ratio of 30. The structure, composition and particle size of LiFeO₂ can be controlled by changing the Li/Fe molar ratio, heating duration and temperature. The hydrothermal stripping route exhibits fast, simple, low-cost and environmentally friendly merits.

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