Synthesis of $LiFePO_4$ by one-step annealing under the vacuum condition

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The mineral triphylite, having the formula $LiFePO_4$ and showing an ordered olivine structure is believed to be one of the most promising replacements of the cathode materials currently used, such as $LiCoO_2$, $Li_2Mn_2O_4$ and so on, due to the reasonable price of raw materials, the relative lack of toxicity, the operating voltage at 3.5 V versus Li/Li^+, cycling stability, and theoretical specific capacity as high as 170 mAh/g.

Since Padhi [1] and co-workers first synthesized $LiFePO_4$ by solid-state reaction in 1997, their synthesis route has been used extensively. This route is usually as follows: The raw materials are weighed in stoichiometric amounts and mixed homogenously. Then, the mixture is decomposed under a certain temperature. After the mixture is cooled, it is ground and transferred to the furnace and annealed at a high temperature for some time under the flow of inert gas (argon or nitrogen) in order to prevent oxidation. However, this process expends a lot of time, not to mention that it also consumes inert gas extensively. These two together occupy most of the cost of producing $LiFePO_4$.

It is universally known that two methods could be utilized to avoid oxidation: one is by the inert gas protection that is used by researchers in producing $LiFePO_4$, and the other by use of vacuum. This gave us the hint that $LiFePO_4$ might be synthesized under

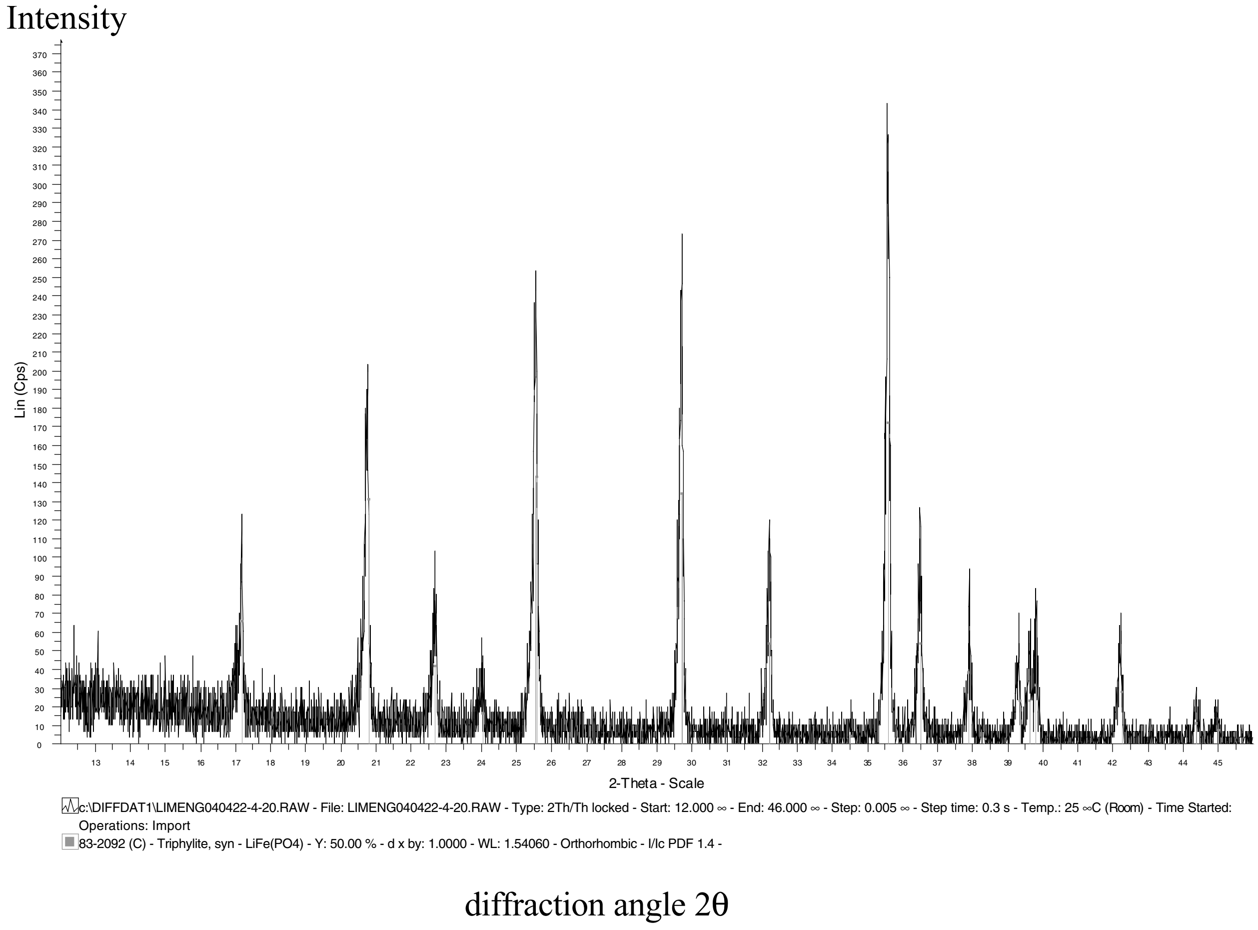

Figure 1 X-ray diffraction pattern of sample synthesized by one-step vacuum annealing.

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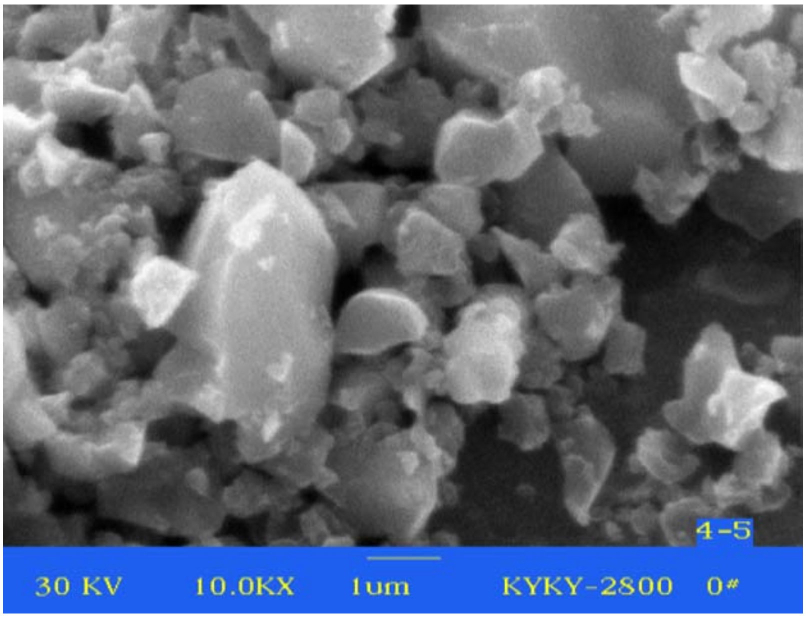

Figure 2 SEM image of Lithium iron phosphate synthesized by one-step annealing under the vacuum condition.

vacuum conditions and the decomposing step might also be removed.

In this paper, we used one-step annealing under vacuum conditions as our route (in which the traditional decomposing step is removed and the inert gas protection is cancelled simultaneously). We also investigated the physical and electrical properties of our product to test our route.

We choose the stoichiometric mixture of Li_2CO_3 (Analysis Pure), $(NH_4)H_2PO_4$ (Analysis Pure) and $FeC_2O_4{\cdot}2H_2O$ (Industrial) as the starting materials. The mixture was then homogenized and wet ball milled for 1 hr, and transferred to vacuum furnace for final annealing. The final annealing was at 700 °C under the vacuum condition(−0.099 MPa) for 10 hr. When the mixture was cooled to room temperature under the vacuum condition, the black powder $LiFePO_4$ was achieved.

X-ray diffraction (XRD) experiments were performed with a BRUKER AXS D8 advance diffractometer using Cu K_α radiation. The morphology of the powders was observed by scanning electron microscopy (SEM) by means of KYKY2800.

Electrochemical performance was carried out in a coin-type cell (Type 2320) with a lithium metal anode and 1 M LiPF6 in EC and DMC (1:1) electrolyte was employed to evaluate the charge-discharge properties of our product. We used the celgard 3501 microporous membrane as the separator. The positive electrode was made in the following way: the $LiFePO_4$ powder was mixed with acetylene black and polytetrafluoroethylene (PTFE) according to the weight ratio of 82:10:8. Then we applied the mixture to aluminum foil. The cell was finally assembled in a glove box filled with argon gas. Charge/discharge property was evaluated at constant current density between 2.75 and 4.2 V at $C/8$ and 15 °C.

Fig. 1 shows the X-ray diffraction pattern of a typical sample, synthesized by the one-step annealing process. All diffraction lines could be attributed to the orthorhombic olivine type phase $LiFePO_4$ and to minor impurity phase. Further more, the profiles of the reflection peaks are quite narrow and symmetric. Therefore, this indicates that this process can produce nearly phase pure homogeneous and well-crystallized $LiFePO_4$ powder.

Fig. 2 shows the SEM image of a one-step annealing product under the vacuum condition. The picture shows there are well-dispersed particles, except a few aggregations. The average particle size is about 1 μm which is smaller than 20 μm the average size of $LiFePO_4$ reported by Yamada *et al.* [2].

Fig. 3 depicts the specific charge and discharge capacities of a $LiFePO_4$ sample under cycling test. The weight of the active material is 7.8 mg. By calculation, the discharge capacity of our product is about 112 mAh/g (theoretical value: 170 mAh/g) at the first four

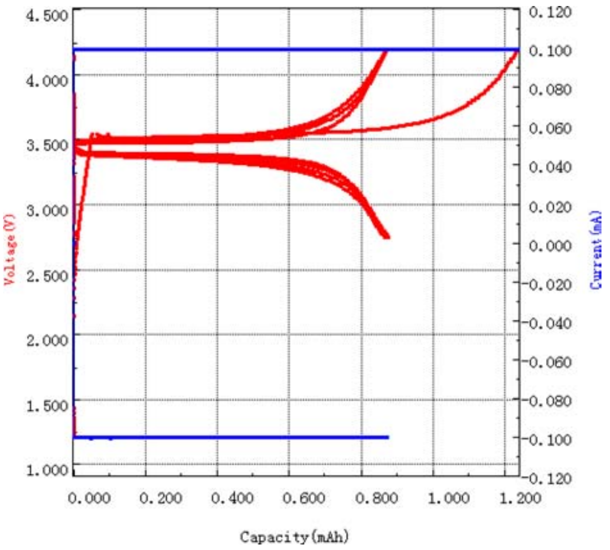

Figure 3 Electrochemical performance of $LiFePO_4$ sample.

cycles, together with a high reversibility and a good cycling stability. And the charge and discharge capacity of the first cycle are 159 and 111 mAh/g respectively. The corresponding potential capacity diagram for the first four cycles shows the typical flat potential plateau at 3.5 V versus Li/Li^+, resulting from the phase transition of triphylite $LiFePO_4$ to heterosite $FePO_4$ [1].

To conclude, nearly pure phase and well-crystallized lithium iron phosphate $LiFePO_4$ can be synthesized by one-step annealing under vacuum conditions. The average particle size is small (1 μm). Excellent electrochemical properties in concerns of capacity, reversibility and cycling stability are achieved.

References

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