

Short Communication

Synthesis and Characterization of Novel Cathode Material Li_5FeO_4 for Li-ion Batteries

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Antifluorite-type material Li_5FeO_4 was synthesized and characterized as novel cathode materials for using in a lithium secondary battery. It was prepared by high-temperature solid-state method, LiOH and Fe_2O_3 as raw materials. The obtained samples were featured by using TG/DTA, XRD, and its specific capacity and cycle property were also measured by LAND cell test system. The results showed that materials obtained by high-temperature solid-state method, that temperatures were 450°C for 10h, then 850°C for 20h and the mole ratios of Li to Fe is 6/1 exhibited single-phase and high capacity. Its first charge capacity and recharge capacity reaches 584.5 and 210.8 mAh/g respectively.

Keywords: lithium iron oxides; novel cathode materials; Li_5FeO_4 ; Li-ion battery; cobalt free.

1. INTRODUCTION

Owing to lithium iron oxides are always considered to have low cost and non-toxicity, they are paid more attention as a cathode of lithium secondary battery. LiFeO_2 [1,2,3] have been made great progress on its preparation, structure and modification due to extensive use of new preparation methods such as hydrothermal, low-temperature solid state reaction etc., and new analysis instruments such as Mössbauer spectra, HRTEM etc.. But the research work of Li_5FeO_4 [4,5,6] are very limited, there are only several papers report it, and the previous papers have strongly indicated that as potential

anode materials, Li_5FeO_4 can be applied in the lithium battery in the near future due to its low cost and its amity to environment.

Reported about Li_5FeO_4 was first seen in 1971, Demois-son and his colleagues[7] found new lithium iron oxides, high temperature and low temperature forms of Li_5FeO_4 in the system of Li_2O and Fe_2O_3 . Its crystalline structure belongs to the anti-fluorite type structure where three equivalent lithium vacancies ($\text{Li}_5\text{V}_2\text{FeO}_4$) are ordered among isolated FeO_4 tetrahedron. In 2010, Johnson[8] reported their researched works about Li_2O removal from Li_5FeO_4 , they think when Li_2O removed from Li_5FeO_4 , the material become a cathode precursor for lithium-ion batteries.

Although there are also some papers concerning Li_5FeO_4 [9], the properties of Li_5FeO_4 have been improved remarkably recently. However, there are many exact mechanisms we still don't know, need us to solve.

In this work, Li_5FeO_4 was prepared by high-temperature solid-state method, and the obtained samples were research deeply.

2. EXPERIMENTAL

2.1 Synthesis of Materials

The cathode material Li_5FeO_4 was synthesized by high-temperature solid-state method. The pink-colored samples was prepared by intimately mixing stoichiometric amounts of nanosized Fe_2O_3 with $\text{LiOH}\cdot\text{H}_2\text{O}$ and sintering the mixture under flowing nitrogen at 850°C for 20 h. Because Li_5FeO_4 has very high lithium content, it slowly decomposes in air, reacting with ambient moisture and CO_2 . Therefore we must avoid the samples contact with air in the series of operating process.

2.2 Characterization of the materials` structure and morphology

Netzsch sta 409 pc thermal analyzer was used for precursor from room temperature to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ in argon atmospheres. X-ray diffraction (XRD) analysis of the sample is carried out on a Bruker D8ADVANCE X-ray diffractometer equipped with a $\text{Cu-K}\alpha$ source ($\lambda = 0.154$ nm) at 40kV and 30mA. The 2θ angular region between 10° and 90° is recorded at a scan rate of $8^\circ/\text{step}$. X-ray Diffractometer was used to characterize the structure of Li_5FeO_4 powders.

2.3 Test of electrochemical performance

The electrochemical characterization was performed using CR2032 coin cells. The cell consisted of a cathode with the composition of 80wt% Li_5FeO_4 , 10wt% Super P carbon black, and 10wt% poly(vinylidene fluoride), and a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 mol/L $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{DMC}(1:1:1$ by volume). The cells were assembled in an MIKROUNA-Super-1220 glove box filled with pure argon. The charge-discharge tests were galvanostatically performed on LAND cell test system over 2.0~5.0V.

3. RESULTS AND DISCUSSION

In order to know about what was happened in the process of the sintering, thermo gravimetric (TG) and differential scanning calorimetry (DSC) analysis was carried out on Netzsch sta-409 pc. Fig.1 presents the TG-DSC curves of the samples which are respectively LiOH•H₂O and the mixture of LiOH•H₂O and Fe₂O₃ in argon atmospheres. The weight loss and weak endothermic peak in the range of 80~140°C are due to the removal of residual water molecules in the powder, and the weight loss is about 40% and 18% respectively. liquated and reacted with Fe₂O₃ at 420°C, and decomposed at 470°C. There is a small endothermic peak at 820°C, at which the reaction was happened between Li₂O and Fe₂O₃. Therefore, we can initially conclude that if we want to obtain the single phase samples, we need sinter the samples at higher temperature to 820°C.

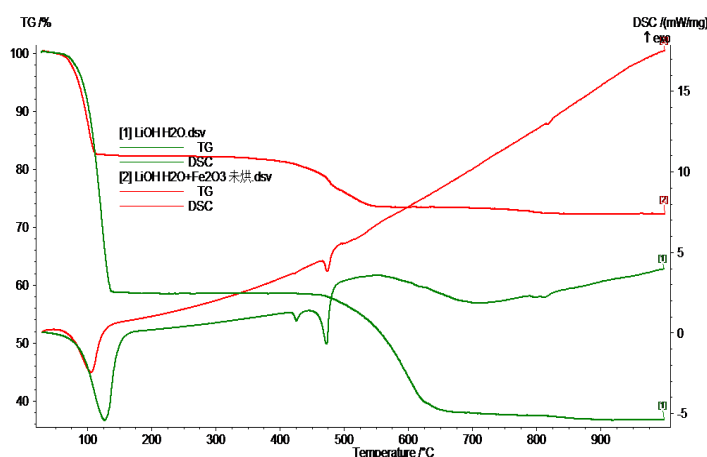


Figure 1. TG-DSC curves of the samples which are respectively LiOH•H₂O and the mixture of LiOH•H₂O and Fe₂O₃

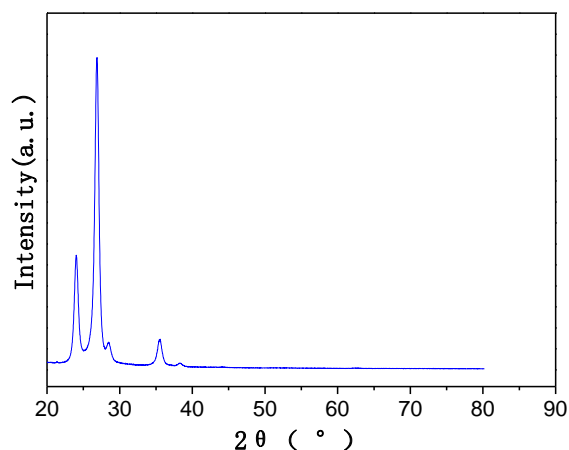


Figure 2. XRD pattern for the adhesive tape which covered samples

Antifluorite-type materials, Li_5FeO_4 has the very high lithium's content, it easily reacted with ambient moisture and CO_2 . For this reason, care will be taken to store and handle the Li_5FeO_4 samples in an inert atmosphere. Therefore, before testing XRD the powders were pressed into sample holder plates and covered by adhesive tape in the glove box. So the XRD pattern of adhesive tape is Fig.2. The XRD patterns of the samples Li_5FeO_4 synthesized by high-temperature solid-state method at 850°C for 20 h under flowing nitrogen are shown in Fig.3

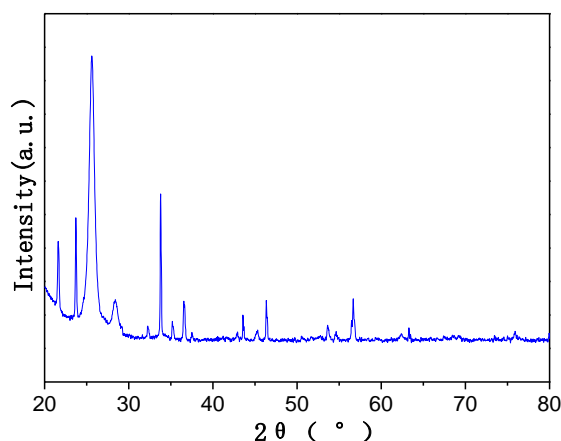


Figure 3. XRD pattern for the samples prepared from $\text{LiOH}\cdot\text{H}_2\text{O}$ and Fe_2O_3 . The molar ratio of Li and Fe is 6/1, the sintering temperature and time were 450°C for 10h and then 850°C for 20h.

After comparing them we can see the peaks between 22° and 30° are considered to be attributed to the adhesive tape, and all the other diffraction peaks can be indexed based on the anti-fluorite type structure. The single phase was obtained at the starting composition of around 6:1 (Li/Fe) ratio. The actual composition of Li/Fe ratio of the sample was confirmed to be 5:1 by the XRD patterns. The evaporation of some amount of Li occurred during heating at high temperature.

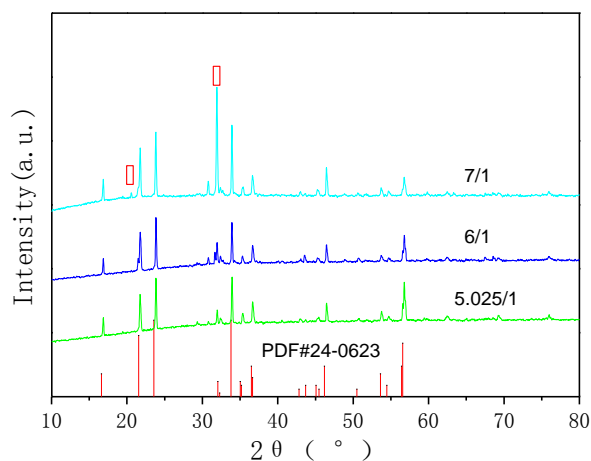


Figure 4. XRD pattern of the samples

According to the original work we chose 5.025/1, 6/1 and 7/1 as the mole ratios of Li to Fe, The Fig.4 are the XRD pattern of the samples we obtained in the characterizing work. As we can see in the pattern, when the mole ratios of Li to Fe is 6/1 the material was sintered at 850°C has a nearly perfect crystal structure and without impurity, but when the mole ratio is increasing, Characteristic peaks of Li_2CO_3 appeared in the spectrum.

The first charge-discharge curves of the Li_5FeO_4 synthesized by high-temperature solid-state method at 850°C for 20h are shown in Fig.4. For the charge curves, we can see when we Charging our Li/ Li_5FeO_4 cells to 4.55V, the voltage suddenly fell down to about 4.3V, then the voltage grow up slowly. At the same time the structure undergoes a phase change as the removal of lithium progresses. Corresponding to the charge curves that lithium removal takes place in two steps. The first between ~3.0 and 4.5 V and the second on a voltage plateau at about 4.7V, each step corresponding to the removal of one Li_2O per Li_5FeO_4 formula unit. For the discharge curves, no plateau is observed due to the irreversible reaction of Li_2O extraction from Li_5FeO_4 component, which causes large irreversible capacity loss, and about 60% capacity loss is observed at the first discharge.

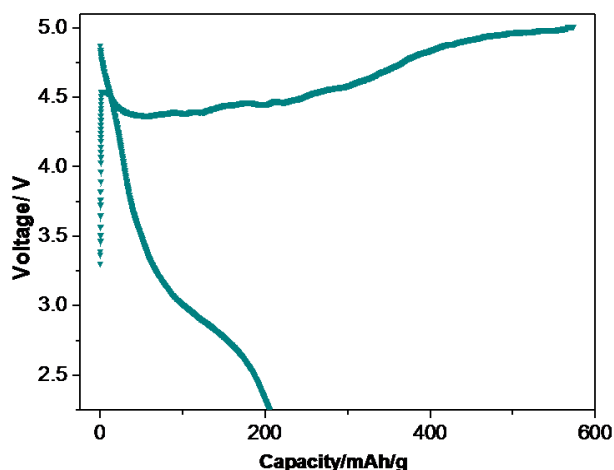


Figure 5. First charge-discharge curves of Li_5FeO_4 synthesized at 800°C

4. CONCLUSION

Pure phase uniform Li_5FeO_4 powder can be successfully prepared by high-temperature solid-state method and temperatures were 450°C for 10h and then 850°C for 20h. The samples sintered at optimized the mole ratios of Li to Fe is 6/1 shows uniform fine well-crystallized particles and high capacity. Its first charge capacity and recharge capacity reaches 584.5 and 210.8mAh/g respectively.

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