Antifluorite-type material Li$_5$FeO$_4$ 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$_2$O$_3$ 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$_5$FeO$_4$; 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$_5$FeO$_4$[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$_5$FeO$_4$ can be applied in the lithium battery in the near future due to its low cost and its amity to environment.

Reported about Li$_5$FeO$_4$ was first seen in 1971, Demois-son and his colleagues[7] found new lithium iron oxides, high temperature and low temperature forms of Li$_5$FeO$_4$ in the system of Li$_2$O and Fe$_2$O$_3$. Its crystalline structure belongs to the anti-fluorite type structure where three equivalent lithium vacancies (Li$_5$V$_2$FeO$_4$) are ordered among isolated FeO$_4$ tetrahedron. In 2010, Johnson[8] reported their researched works about Li$_2$O removal from Li$_5$FeO$_4$, they think when Li$_2$O removed from Li$_5$FeO$_4$, the material become a cathode precursor for lithium-ion batteries.

Although there are also some papers concerning Li$_5$FeO$_4$[9], the properties of Li$_5$FeO$_4$ have been improved remarkably recently. However, there are many exact mechanisms we still don't know, need us to solve.

In this work, Li$_5$FeO$_4$ 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$_5$FeO$_4$ was synthesized by high-temperature solid-state method. The pink-colored samples was prepared by intimately mixing stoichiometric amounts of nanosized Fe$_2$O$_3$ with LiOH·H$_2$O and sintering the mixture under flowing nitrogen at 850°C for 20 h. Because Li$_5$FeO$_4$ 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°C /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 Cu-Kα source (λ =0.154 nm) at 40kV and 30mA. The 20 angular region between 10° and 90° is recorded at a scan rate of 8°/step. X-ray Diffractometer was used to characterize the structure of Li$_5$FeO$_4$ 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% Li5FeO4, 10wt% Super P carbon black, and 10wt% poly(vinylidenefluoride), and a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 mol/L LiPF$_6$ /EC+DEC+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 decompounded 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](image1)

![Figure 2. XRD pattern for the adhesive tape which covered samples](image2)
Antifluorite-type materials, Li$_3$FeO$_4$ 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$_3$FeO$_4$ 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$_3$FeO$_4$ synthesized by high-temperature solid-state method at 850°C for 20 h under flowing nitrogen are shown in Fig.3.

![Figure 3](image1.png)

**Figure 3.** XRD pattern for the samples prepared from LiOH·H$_2$O and Fe$_2$O$_3$. 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 antifluorite 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](image2.png)

**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$_2$CO$_3$ appeared in the spectrum.

The first charge-discharge curves of the Li$_5$FeO$_4$ 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$_5$FeO$_4$ 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$_2$O per Li$_5$FeO$_4$ formula unit. For the discharge curves, no plateau is observed due to the irreversible reaction of Li$_2$O extraction from Li$_5$FeO$_4$ component, which causes large irreversible capacity loss, and about 60% capacity loss is observed at the first discharge.

![Figure 5](image)

**Figure 5.** First charge-discharge curves of Li$_5$FeO$_4$ synthesized at 800°C

### 4. CONCLUSION

Pure phase uniform Li$_5$FeO$_4$ 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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