A 3.9 V polyanion-type cathode material for Li-ion batteries

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Abstract: Monoclinic phase LiFeSO₄F was synthesized by a simple fast solid state reaction from the mixture of FeSO₄·7H₂O and LiF pulverized by high energy ball milling. m-LiFeSO₄F was confirmed by GITT measurement to be a 3.9 V polyanion-type cathode materials for Li-ion batteries. Its electrochemical activity can be enhanced by addition of carbon. A discharge capacity of 105 mA·h/g (70% of theoretical value) was achieved for a m-LiFeSO₄F/CNT composite. Phase separation behavior during lithium extraction and insertion was observed by ex-situ XRD test.

Key words: LiFeSO₄F; polyanion cathode; Li-ion battery

1 Introduction

Olivine LiFePO₄ [1] has been considered the most promising cathode candidate for the next generation large scale Li-ion batteries used for electrical vehicles and energy storage. Several other polyanion containing cathode materials, i.e. NASICON structure phosphates (LiₓM₂(PO₄)₃) [2], silicates (Li₂M(SO₄)₃) [3], borates (LiMBO₃) [4] and fluorophosphates (A₂FePO₄F) [5], have been also widely investigated. Their drawbacks of poor electronic and Li⁺ conducting properties can be overcome by carbon coating [6] and particle size reducing [7]. Recently, RECHAM et al [8] reported the reversible Li⁺ insertion/extraction in LiFeSO₄F with redox potential of 3.6 V and a much faster kinetics compared with LiFePO₄. A rather low migration energy for Li⁺ was predicted by a calculation due to its loose structure [9]. Though a raise of open-circuit voltage (OCV) by 0.8 V is observed when substituting PO₄³⁻ with SO₄²⁻ in the NASICON structure [10], LiFeSO₄F exhibits only a slightly higher OCV than that of LiFePO₄. Here we report a monoclinic phase LiFeSO₄F with OCV of 3.9 V (vs Li⁺/Li). This monoclinic phase was observed for LiMnSO₄F synthesized via an ionothermal method by BARPANDA et al [11], while LiMnO₄ (M=Fe, Co, Ni) as-obtained showed a triclinic phase. For convenience, we label the triclinic phase LiFeSO₄F as t-LiFeSO₄F and the monoclinic phase as m-phase.

2 Experimental

2.1 Synthesis

m-LiFeSO₄F was prepared by a solid-state reaction. All chemicals used were purchased without further purification. Stoichiometric amounts of FeSO₄·7H₂O (Alfa Aesar, 99%) and LiF (Sinopharm Chemical Reagent Co. Ltd, 99%) were mixed by using high energy ball milling with alcohol in a zirconia container for 5 h. TG-DSC-MS measurement was carried out on a TG-DSC-MS analyzer (Netzsch STA-449C) to optimize the synthesis temperature. The mixture was then sintered at 380 °C in a vacuum furnace under ambient pressure of about 33 Pa for 3 h. For comparison, a sample with the precursors mixed in an agate mortar was also prepared. m-LiFeSO₄F/acetylene black composite and m-LiFeSO₄F/CNT composite were prepared by adding 3% (mass fraction) acetylene black and 3% CNT respectively, into the container before milling. The resulted m-LiFeSO₄F, m-LiFeSO₄F/acetylene black composite and m-LiFeSO₄F/CNT composite were labeled as LFSF#1, LFSF#2 and LFSF#3, respectively.

2.2 Characterizations

The X-ray diffraction (XRD) patterns were recorded by an X-ray diffraction photometer (Rigaku Rint-2400) using Cu Kα radiation at a scan rate of 0.02 (°)/s. The morphology was observed by a field-emission gun
scanning electron microscope (Hitachi S-4700).

2.3 Electrochemical tests

The electrochemical performances of the \( m \)-LiFeSO\(_4\)F sample as cathode were evaluated using a Swagelok-type cell with a lithium metal counter electrode. The cathode was a mixture of \( m \)-LiFeSO\(_4\)F and acetylene black and polyvinylidene fluoride (PVDF) with a mass ratio of 80:10:10. The electrolyte was 1 mol/L LiPF\(_6\) dissolved in ethylene carbonate and dimethyl carbonate (EC/DMC 1:1 volume ratio) solution. The galvanostatic charge and discharge experiment was performed on a Land automatic batteries tester (KINQNUO Electrical Co. Ltd., China) at room temperature. Galvanostatic intermittent titration technique (GITT) test was performed by charging/discharging the cell for 30 min at a constant current density of 9 mA/g and by relaxing for 12 h.

3 Results and discussion

Considering that LiMSO\(_4\)F (M=Fe, Co, Ni) \([11]\) decomposes at elevated temperatures, mass spectra (MS) were recorded with the thermo-gravimetric analysis (TG) to detect the evolving gas. TG and MS curves of precursors mixed via high energy ball-milling (BM) and hand-milling (HM) are shown in Fig. 1. Most of the water of crystallization for the precursor made by HM was lost at around 100 °C, while this part of water for the BM sample was lost with alcohol during pre-drying and the last water of crystallization got lost at 280 °C. It can be seen that SO\(_2\) started to evolve at about 420 °C. The BM sample started to lose large amount of SO\(_2\) at obviously lower temperature, which may be attributed to the high reactive activity of the fine powders. Therefore, the synthesis temperature of LiFeSO\(_4\)F should be lower than 420 °C.

XRD patterns of LiFeSO\(_4\)F synthesized are shown in Fig. 2. It has a similar crystallographic structure with LiMnSO\(_4\)F synthesized via an ionothermal method by BARPANDA et al \([11]\). In that literature, the LiMnSO\(_4\)F pattern was indexed to a monoclinic phase, different from the triclinic system for LiMSO\(_4\)F (M=Fe, Co, Ni). We named it as \( m \)-LiMSO\(_4\)F. The peaks marked with “■” cannot be indexed to any compound already reported and further work is required to eliminate this impurity. As for the HM sample, the product contains mainly FeSO\(_4\) and LiF. It means that high energy ball milling is necessary to guarantee the intimate contact of FeSO\(_4\) and LiF.

![Fig. 1 TG and MS curves of precursors mixed via high energy ball-milling (BM) and hand-milling (HM) (\( m/z = 18 \) curves corresponding to evolving of H\(_2\)O, while \( m/z = 64 \) curves corresponding to evolving of SO\(_2\))](image1)

![Fig. 2 XRD patterns of samples obtained with precursor mixed by ball-milling (BM) or hand-milling (HM)](image2)

In the solid state reaction process to synthesize \( t \)-LiFeSO\(_4\)F described by ATI et al \([12]\), the reaction kinetics can be enhanced by adopting larger values of \( r \) (molar ratio of LiF/FeSO\(_4\)·H\(_2\)O) at the price of introducing extra LiF. In our experiment, a similar phenomenon was observed. XRD patterns of the samples sintered with varied ratio of LiF/FeSO\(_4\)·H\(_2\)O are shown in Fig. 3. With increasing value of \( r \), several unidentified peaks become weaker while peaks indexed to LiF appear. The unidentified peaks marked with “■” in Fig. 3 can be eliminated by adding excess LiF into the precursor.

FESEM images of LFSF#1 and LFSF#3 (precursors and products) are shown in Fig. 4. LFSF#2 has similar morphology with LFSF#1. In both cases, the precursors were well pulverized (particle size less than 100 nm) and mixed. Notable particle growth happened in the sintering process. As for LFSF#3, it can be seen that CNT was well dispersed in the product.

GITT test was performed to study the Li\(^{+}\) extraction/insertion process in LFSF#1. As shown in Fig. 5, the open-circuit voltage curves exhibit clearly a 3.9 V plateau, indicating a two-phase reaction mechanism. The open-circuit voltage obtained from the GITT profile is
Assuming the voltage gap is only caused by the insufficient relaxation of GITT test, the electromotive force (emf) value could be 3.906 V, an ideal value that is comparable with widely used oxide cathode materials. The polarization is mainly contributed by ohmic polarization, which indicates that this material has a low electronic conductivity and a possible higher ionic conductivity.

The galvanostatic charge/discharge curves of $m$-LiFeSO$_4$F samples are shown in Fig. 6. The pristine $m$-LiFeSO$_4$F (LFSF#1) can only give an initial discharge capacity of 60 mA·h/g under 0.1 C rate (1 C denoting charge/discharge in 1 h), far below the theoretical value.
Fig. 6 Galvanostatic charge/discharge profiles of LFSF#1 (m-LiFeSO$_4$F), LFSF#2 (m-LiFeSO$_4$F/AB composite) and LFSF#3 (m-LiFeSO$_4$F/CNT composite) cycled from 2.2 V to 4.5 V at C/20.

Fig. 7 Cycling profiles of LFSF#1 ($\beta$-LiFeSO$_4$F), LFSF#2 ($\beta$-LiFeSO$_4$F/AB composite) and LFSF#3 ($\beta$-LiFeSO$_4$F/CNT composite) cycled from 2.2 V to 4.5 V at C/20.

(150 mA·h/g). Considering its low electronic conductivity indicated by GITT measurement, addition of carbon to form a composite was carried out to improve its electrochemical activity. A specific capacity of 82 mA·h/g was achieved for LFSF#2, the acetylene black/m-LiFeSO$_4$F composite. With CNT added as ideal path for electron transportation, LFSF#3 exhibited a discharge capacity of 105 mA·h/g, corresponding to 70% of the theoretical value.

To further confirm the structure change during Li$^+$ intercalation/deintercalation, ex-situ XRD patterns were recorded at different stages of the charge/discharge process. Patterns in the range of 2$\theta$ = 25°–35° were analyzed, as shown in Fig. 8. During the charging process, two peaks at 27.5° and 29.9° (marked with □) appeared and became stronger while two peaks at 27.8° and 31.6° (marked with △) became weaker and disappeared. The discharging process was in reverse. No peak shift was observed during the cycling. It indicates clearly a phase separation reaction mechanism.

Fig. 8 XRD patterns taken at different stages during charge/discharge process from 2 V and 4.5 V (Peaks appearing in charged state are marked with □ and discharged state with △).

4 Conclusions

In this work, we reported the synthesis of m-LiFeSO$_4$F with monoclinic crystal structure via a simple fast solid state reaction at low temperature. The 3.9 V discharge plateau of m-LiFeSO$_4$F is confirmed by GITT test, and the flat plateau indicates a two-phase reaction mechanism during charge/discharge process which is further confirmed by ex-situ XRD test. The electrochemical performance of m-LiFeSO$_4$F can be obviously enhanced by adding carbon to form a composite material. A discharge capacity of 105 mA·h/g (70% of the theoretical value) is achieved for a m-LiFeSO$_4$F/CNT composite, compared with 60 mA·h/g for m-LiFeSO$_4$F. It is a new 3.9 V polyanion-type cathode material for Li-ion batteries. This material has a high ionic conductivity and low electronic conductivity.

References


