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Tavorite LiFeSO$_4$F cathode material is prepared by the solvothermal method. The thermal stability of delithiated Li$_x$FeSO$_4$F is characterized by X-ray diffraction, differential scanning calorimetry and thermogravimetric analysis. It shows that the side reactions between the cathode material and the electrolyte are moderate, which involves the decomposition of Li$_x$FeSO$_4$F forming Fe$_2$(SO$_4$)$_3$ and Li$_2$SO$_4$ phases and F$_2$ gas. The onset temperature of the exothermal process is 358 °C with a minimal heat release of 79.4 J g$^{-1}$. The material undergoes further decomposition above 500 °C, which forms Fe$_2$O$_3$, Fe$_2$O$_4$ and Li$_2$O, associated with the release of SO$_2$ gas.

1. Introduction

Li-ion batteries have attracted more and more attention with the developments of electric vehicles and energy storage for smart grid. In addition to the demands of large energy density, large power density and low price, high safety is extremely important for these new Li-ion battery techniques. Traditional layered cathode materials such as LiCoO$_2$, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ and the newly developed Li-excess layered cathode $x$Li$_2$MnO$_3$-(1-$x$)LiMO$_2$ (M = Ni, Co) are not suitable for high safe cathode materials due to the oxygen generation at overheated state.$^{[1-3]}$

Nowadays, the most safe cathode materials for Li-ion batteries are those built by polyanion frameworks such as LiFePO$_4$ $^{[4]}$, LiVPO$_4$F $^{[5]}$ and LiFeSiO$_4$ $^{[6]}$. The rigid polyanion frameworks can stabilize the crystal structure of the materials. In addition, it can limit the likelihood of oxygen generation, leading to good thermal stability. For example, the onset thermal release temperature of LiFePO$_4$ at the fully charged state is 250 °C, with a small thermal release of 147 J g$^{-1}$ $^{[4]}$. As a comparison, the corresponding data for LiCoO$_2$ is 176 °C and 2785 J g$^{-1}$, respectively. $^{[7]}

Recently, a new polyanion material, tavorite LiFeSO$_4$F, has been reported as a potential cathode material for Li-ion batteries $^{[8,9]}$. The material has a theoretical capacity of 151 mAh g$^{-1}$ and a working voltage of 3.6 V versus Li'/Li. It could be a strong contender to LiFePO$_4$ because of a greater cell voltage (150 mV), even though the theoretical energy density is 5% lower than that of LiFePO$_4$. This slight drawback can be counter balanced by the better ionic conductivity of LiFeSO$_4$F, which obviates the need for resorting to nanoparticles thus increases the material packing density $^{[8]}$. Given these advantages, it is important to characterize the thermal stability of the LiFeSO$_4$F cathode. In this communication, we report our new findings on the thermal stability of delithiated LiFeSO$_4$F cathode. The results show that the material has extremely high thermal stability which implies its potential uses in high safe lithium ion batteries.

2. Experimental

Our synthetic approach relied on the formation of FeSO$_4$·H$_2$O precursor by quick heating of FeSO$_4$·7H$_2$O at 100 °C for 3 h in Ar/H$_2$ atmosphere. The FeSO$_4$·H$_2$O precursor was mixed with LiF with a molar ratio of 1:1.1, and then ball-milled for 24 hours in acetone. Afterwards, the mixture was transferred into a 43 ml of Teflon-lined steel autoclave along with 30 ml of tetraethylene glycol (TEG) and kept at 260 °C for 60 h. The resulting white-gray powders were washed with acetone and then dried in vacuum-oven at 60 °C.

Electrochemical experiments were carried out using 2032-type coin cells. A metallic lithium foil served as the anode electrode. This journal is © The Royal Society of Chemistry [year]
The cathode electrode was composed of LiFeSO$_4$F active material (70 wt.%), carbon black conductive additive (20 wt.%), and poly (vinylidene fluoride) binder (PVDF, 10 wt.%). Each electrode was 8 × 8 mm$^2$ in size and contained about 2 mg of active material. The cathode and anode electrodes were separated by Celgard 2320 membrane. The electrolyte was a 1 mol·L$^{-1}$ LiPF$_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with EC: DMC: EMC = 1:1:8 by v/v ratio. Galvanostatic charge-discharge cycling was performed on a Land automatic battery tester at 25 °C and 60 °C, respectively.

After the first charge process completed, the battery cell was disassembled in glove box. The cathode composite was scrapped from the electrode and washed in DMC for several times. The delithiated Li$_{x}$FeSO$_4$F powders were then used for in-situ heat treatment X-ray diffraction (XRD) study on a Rigaku D/max-2550 diffractometer with Cu Kα radiation. The differential scanning calorimetry (DSC) of the material was studied on TA-Q2000 between room temperature and 450 °C with a heating rate of 10 °C min$^{-1}$. Thermogravimetric analysis (TGA) was performed on a SDTAR51E thermo analyzer between room temperature and 800 °C with a heating rate of 10 °C min$^{-1}$.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared material.

Fig. 2 (a) Charge-discharge curves and (b) cycling performance of LiFeSO$_4$F at room temperature and 60 °C.

The irreversible capacity is immediately minimized after the first cycle, resulting in a stable columbic efficiency of 80 %. The irreversible capacity could be due to the difficulty in insertion more Li ions into the crystal structure. Also, a part of the irreversible capacity could be caused by the formation of solid electrolyte interface (SEI) film which has been reported by J. M. Tarascon et al. [11]. The irreversible capacity is immediately minimized after the first cycle, resulting in a stable columbic efficiency of 96 %. The material is also charge-discharged at 60 °C as shown in Fig. 2. At this elevated temperature, the initial charge and discharge capacities are increased to 120 mAh g$^{-1}$ and 110 mAh g$^{-1}$, respectively. A discharge capacity of 80 mAh g$^{-1}$ is obtained after 50 cycles, which is much larger than the 60 mAh g$^{-1}$ that measured at room temperature. Here it should be noted that the electrochemical performance of the as-prepared LiFeSO$_4$F is

Fig. 3 DSC curves of the chemically and electrochemically delithiated Li$_{0.35}$FeSO$_4$F, together with that of the LiPF$_6$/EC+DMC+EMC electrolyte.

Rietveld refinement shows that the material is composed of triclinic LiFeSO$_4$F with a little amount of LiF impurity. The percent of LiF impurity in the material is calculated to be 4.3 wt.%. The as-prepared LiFeSO$_4$F material has a triclinic structure with space group of P-1. Its lattice parameters are refined to be $a = 5.1841(4)$ Å, $b = 5.5058(1)$ Å, $c = 7.2286(7)$ Å, $\alpha = 106.535(1)^\circ$, $\beta = 107.201(7)^\circ$, $\gamma = 97.775(3)^\circ$, which fit well with those reported in the literature [8]. The framework of triclinic LiFe$_2$O$_4$F is built of two independent FeO$_6$ octahedra linked by fluorine vertices in the trans position forming chains along the c axis. The chains are bridged by isolated SO$_4$ tetrahedra, creating a three-dimensional (3D) framework and delimiting three tunnels along the [100], [010] and [101] directions where the Li$^{+}$ ions reside. This unique structure is more favor for Li$^{+}$ ion transport comparing with the 1D Li$^{+}$ diffusion pathway in LiFePO$_4$. As has been reported, the ionic conductivity of LiFeSO$_4$F is about three orders of magnitude higher than that of LiFePO$_4$ (i.e. $4 \times 10^{-6}$ S cm$^{-1}$ vs. $2 \times 10^{-9}$ S cm$^{-1}$) [8,10].

Galvanostatic charge-discharge cycling is performed at room temperature in the voltage window of 2.5 - 4.5 V at the C/10 rate (I = 15.1 mA g$^{-1}$). As shown in Fig. 2, the first charge profile of the material shows a voltage plateau at around 3.6 V. About 0.65 mol of Li ions are removed from the material, associated with an initial charge capacity of 98 mAh g$^{-1}$. However, only 0.52 mol of Li ions can be inserted in the subsequent discharge, corresponding to a small columbic efficiency of 80 %. The irreversible capacity could be due to the difficulty in insertion more Li ions into the crystal structure. Also, a part of the irreversible capacity is caused by the formation of solid electrolyte interface (SEI) film which has been reported by J. M. Tarascon et al. [11]. The irreversible capacity is immediately minimized after the first cycle, resulting in a stable columbic efficiency of 96 %. The material is also charge-discharged at 60 °C as shown in Fig. 2. At this elevated temperature, the initial charge and discharge capacities are increased to 120 mAh g$^{-1}$ and 110 mAh g$^{-1}$, respectively. A discharge capacity of 80 mAh g$^{-1}$ is obtained after 50 cycles, which is much larger than the 60 mAh g$^{-1}$ that measured at room temperature. Here it should be noted that the electrochemical performance of the as-prepared LiFeSO$_4$F is...
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Conclusions

In summary, majorite LiFeSO_4F cathode has been prepared by the solvothermal method. The side reactions between the delithiated LiF_eSO_4F and the electrolyte are moderate. The onset temperature of thermal release, 358 °C, is much higher than that of LiFePO_4 which is between 240 °C and 300 °C according to different literatures [3, 12, 13]. The associated minimal heat release is due to the decomposition of LiFeSO_4F accompanied with the

Fig. 4 (a) Temperature dependent XRD patterns and (b) TG curve of the electrochemically delithiated Li_{0.35}FeSO_4F.
release of F₂ gas. The superior thermal stability of delithiated LiFeSO₄F indicates that LiFeSO₄F can be used as a potential high safe cathode material for lithium ion batteries.

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Notes and references