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Communication

Excellent thermal stability of tavorite Li$_x$FeSO$_4$F used as a cathode material for lithium ion batteries

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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 ₁₀ 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 ₁₅ process is 358 ^{o}C with a minimal heat release of 79.4 J g^{-1}. The material undergoes further decomposition above 500 ^{o}C, which forms Fe$_2$O$_3$, Fe$_3$O$_4$ and Li$_2$O, associated with the release of SO$_2$ gas.

1. Introduction

₂₀ 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 ₂₅ 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 xLi$_2$MnO$_3$.(1-x)LiMO$_2$ (M = Ni, Co) are not suitable for high safe cathode materials due to the oxygen generation at overcharged state [1-3]. Nowadays, the most safe cathode materials for Li-ion batteries ₃₀ are those built by polyanion frameworks such as LiFePO$_4$ [4], LiVPO$_4$F [5] and Li$_2$FeSiO$_4$ [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 ₃₅ temperature of LiFePO$_4$ at the fully charged state is 250 ^{o}C, with a small thermal release of 147 J g^{-1} [4]. As a comparison, the corresponding data for LiCoO$_2$ is 176 ^{o}C and 2785 J g^{-1}, respectively [7].

Recently, a new polyanion material, tavorite LiFeSO$_4$F, has been ₄₀ 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 ₄₅ 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 ₅₀ communication, we report our new findings on the thermal stability of delithiated Li$_x$FeSO$_4$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

₅₅ 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 ₆₀ 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.

₆₅ Electrochemical experiments were carried out using 2032-type coin cells. A metallic lithium foil served as the anode electrode.

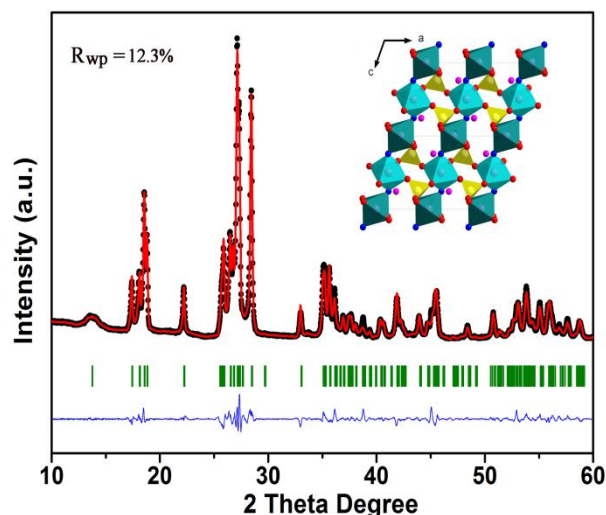Fig. 1 Rietveld refinement of the material based on LiFeSO$_4$F/LiF two phases.
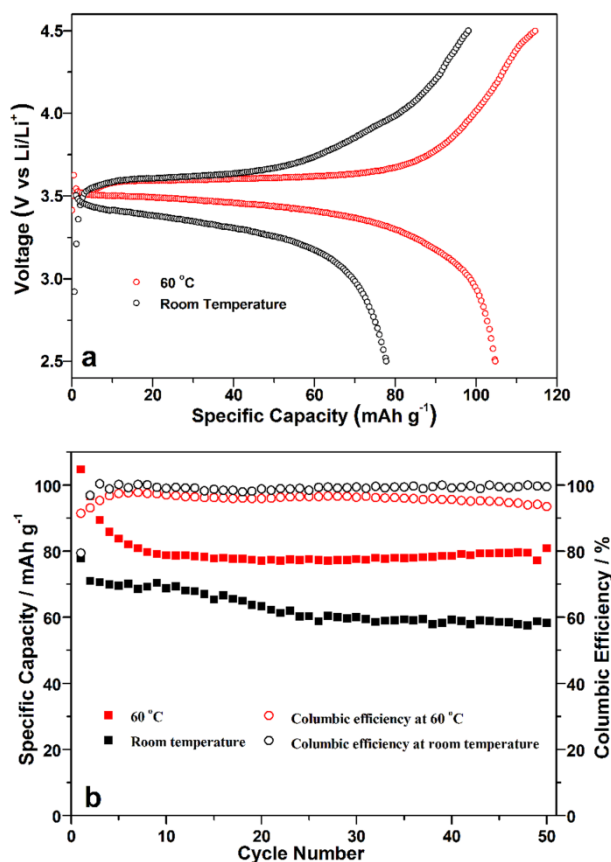
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Fig. 2 (a) Charge-discharge curves and (b) cycling performance of LiFeSO$_4$F at room temperature and 60 ^{o}C.

The cathode electrode was composed of LiFeSO$_4$F active
5 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}
10 lithium hexafluonophosphate (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. Galvonostatic charge-discharge cycling was performed on a Land automatic battery tester at 25 °C and 60 °C, respectively.
15 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-
20 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 SDTA851E thermo analyzer between room
25 temperature and 800 ^{o}C with a heating rate of 10 °C min^{-1}.

3. Results and discussion
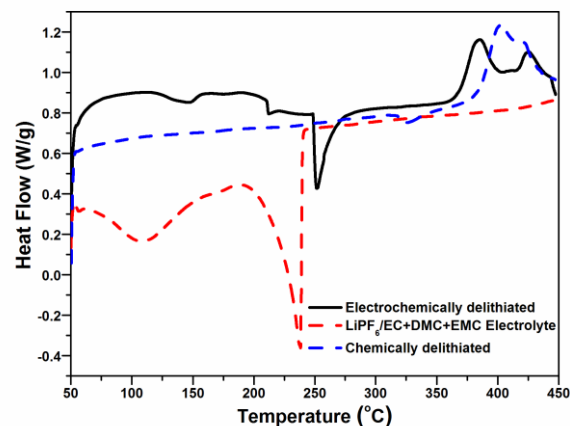
Fig. 1 shows the XRD pattern of the as-prepared material.

Fig. 3 DSC curves of the chemically and electrochemically delithiated
30 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 tavorite 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
35 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, *α* = 106.535(1)°, *β* = 107.201(7)°, *γ* = 97.775(3)°, which fit well with those reported in the literature [8]. The framework of tavorite LiFeSO$_4$F is built of two independent FeO$_4$F$_2$ octahedra linked by
40 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
45 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 × 10^{-6} S cm^{-1} vs. 2 × 10^{-9} S cm^{-1}) [8,10].

Galvanostatic charge-discharge cycling is performed at room
50 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
55 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
60 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 ^{o}C as shown in Fig. 2. At this elevated temperature, the initial
65 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
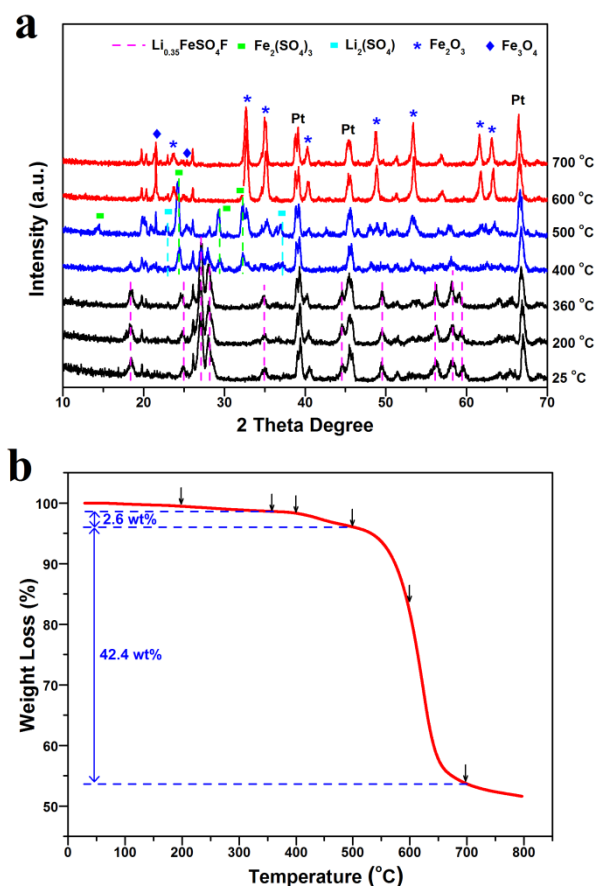
Fig. 4 (a) Temperature dependent XRD patterns and (b) TG curve of the electrochemically delithiated $Li_{0.35}FeSO_4F$.

not as good as expected which could be due to several reasons such as (1) The electronic conductivity of the material is low because it is not carbon coated; (2) The particle size of the material is too large for a polyanion cathode material (Supporting Information Fig. S1); (3) The upper cutoff voltage is high enough to cause electrolyte decomposition. (4) The SEI film formed during the initial charge-discharge cycle (Fig. S2). (5) The LiF impurity is not only electrochemical inactive but also electronic insulative. Future work should be done to resolve the above problems for preparing high performance $LiFeSO_4F$ cathode.

Fig. 3 shows the DSC curve of the electrochemically delithiated Li_xFeSO_4F (x = 0.35) cathode, together with those of the $LiPF_6/EC+DMC+EMC$ electrolyte and the chemically delithiated Li_xFeSO_4F powders (x = 0.35, which was prepared by soaking the $LiFeSO_4F$ powders in a NO_2BF_4 and acetonitrile oxidation agent). The DSC curve of the electrochemically delithiated Li_xFeSO_4F shows an endothermic process in the temperature range of 248-280 °C and an exothermic process in the temperature range of 358-443 °C. The corresponding heat evolved in the above processes are -25.4 J g^{-1} and 79.4 J g^{-1}, respectively. Combining with the DSC curves of the electrolyte and chemically delithiated Li_xFeSO_4F, the endothermic process is attributed to the decomposition of remaining electrolyte whose existence can be observed by fourier transform infrared spectroscopy (Fig. S3), and the exothermic process is due to the Li_xFeSO_4F phase. Additional experiments show that the fully

chemically de-lithiated $FeSO_4F$ also have similar TG and DSC curves as those of $Li_{0.35}FeSO_4F$ (Fig. S4 and Fig. S5). This indicates that $LiFeSO_4F$ has excellent thermal stability not only in partially de-lithiated state but also in fully de-lithiated state. In addition, Fig. 3 shows that the electrochemically and chemically delithiated $Li_{0.35}FeSO_4F$ have similar exothermic temperatures and thermal release. This indicates that the side reactions between the Li_xFeSO_4F cathode and the electrolyte are moderate, which do not lower the exothermic temperature or bring additional thermal release in the battery system. In comparison, our recent study on another fluorine-based polyanion cathode material, $LiVPO_4F$, exhibits more violent side reactions with the electrolyte. The exothermal peak of Li_xVPO_4F itself is as high as 342 °C, but it decreases to 235 °C when coupled with a $LiPF_6/EC+EMC$ electrolyte [5]. Additional DSC experiments show that Li_xFeSO_4F have similar thermal behavior in different $LiPF_6$ based electrolytes (Fig. 6S). This demonstrates the good thermal stability of Li_xFeSO_4F in conventional electrolyte mixtures.

Temperature dependent XRD are performed to study the phase transformations of $Li_{0.35}FeSO_4F$ during heat treatment. A Pt holder is used as an internal standard for calibration of the XRD peaks. Both the chemically and electrochemically delithiated samples show similar XRD patterns (Fig. 7S) indicating that the phase transformation is only correlated with the structure properties of $Li_{0.35}FeSO_4F$ itself. It is seen from Fig. 4a that the structure of $Li_{0.35}FeSO_4F$ is well reserved before 360 °C. Thereafter, the $Li_{0.35}FeSO_4F$ phase continuously decomposes between 360 °C and 500 °C, accompanied with the formation of $Fe_2(SO_4)_3$ and Li_2SO_4 phases. Meanwhile, the TG curve of $Li_{0.35}FeSO_4F$ (Fig. 4b) shows a weight loss about 2.6 wt.% in the same temperature range. This suggests that the exothermic process is associated with the decomposition of $Li_{0.35}FeSO_4F$ which forms $Fe_2(SO_4)_3$ and Li_2SO_4 phases and F_2 gas. With the heat temperature increasing to 700 °C, the XRD pattern mainly shows the co-existence of Fe_2O_3 and Fe_3O_4. In addition, the TG curve shows an abrupt weight loss about 42.4 wt.% between 500 °C and 700 °C. Therefore, it is reasonable to say that the material undergoes further decomposition at high temperature, which forms metal oxides including Fe_2O_3, Fe_3O_4 and Li_2O accompanied with the release of SO_2 gas. Note that Li_2O is not observed in the XRD patterns due to its small amount or amorphous state. According to the above phase transformations, the calculated weight losses for the F_2 and SO_2 evolutions are 7.3 wt.% and 36.9 wt.% respectively. The differences between the calculation and experimental values may be due to the thermal hysteresis effects of the TG experiment. In spite of this, the total experimental weight loss (45.0 wt.%) is consistent well with that of the calculation result (44.2 wt.%).

Conclusions

In summary, tavorite $LiFeSO_4F$ cathode has been prepared by the solvothermal method. The side reactions between the delithiated Li_xFeSO_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 [4, 12, 13]. The associated minimal heat release is due to the decomposition of Li_xFeSO_4F accompanied with the

release of F_2 gas. The superior thermal stability of delithiated Li_xFeSO_4F indicates that $LiFeSO_4F$ can be used as a potential high safe cathode material for lithium ion batteries.

Acknowledgements

10 Notes and references

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