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Supporting Information

Synthesis and Electrochemical Evolution of Mesoporous LiFeSO₄ $F_{0.56}$ (OH)_{0.44} with High Power and Long Cyclability

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Experimental Section

Synthesis. -- The mixture of FeSO₄·7H₂O and LiF (Guoyao Chemistry Co., Ltd, >99.9 %) at the same mole were ground before some PEG-400 (Shanghai Lingfeng Chemistry Co., Ltd, 99%) was added into the mixture, followed by continuously grinding until a homogeneous and yellow paste (sample A) was obtained. The paste was placed in an incubator at 45 °C for 60 hours followed by rinsing with anhydrous alcohol and dichloromethane, filtration and vacuum drying. The resulting precursor powders (sample B) were calcined at 120 °C for 10 hours under Argon to form LiFeSO₄F_y(OH)_{1-y} (sample C). The determination of y value via the chemical titration method was followed the Ref. [s1].

Physical properties. -- The thermal behavior of the obtained precursor powders was analyzed with thermogravimetric-differential scanning calorimetry (TG-DSC, STA-449C, Netzsch, Germany) under Nitrogen in the temperature range from 50 to 900 °C at a heating rate of 10 °C ·min⁻¹. The crystal structure of the precursor and the resulting LiFeSO₄F_y(OH)_{1-y} was examined by X-ray powder diffraction (Model X'TRA, Thermo Electron, USA). The morphology was characterized using field emission scanning electron micro-scope (JSM-6700F, JEOL, Japan) and transmission electron microscope (JEM-1010, JEOL, Japan). Infrared spectroscopy (IR) spectra were collected using a TENSOR 27 Fourier transform spectrometer over the range of 4000–400 cm⁻¹ at 25 °C (NEXUS870, NICOLET, USA). X-ray photoelectron spectroscopy (XPS) was carried out on a PHI5000 Versa Prboc model X-ray photoelectron spectrometer (Ulvac-Phi Inc., Japan) using *Mg Ka* radiation (1253.6 eV) exciting source.

Electrochemical Properties. -- The obtained $LiFeSO_4F_y(OH)_{1-y}$ was mixed with carbon black and polyvinylidene fluoride (PVDF) (70 wt%:20 wt%:10 wt%) in N-methylpyrrolidinon (NMP) to

form a slurry, which was then cast on an aluminum foil and vacuum dried at 120 °C for 12 hours. The dried foil with an active material loading of ~ 5 mg.cm⁻² was punched to disk electrodes with the diameter of 13 mm. Electrochemical properties of the cathode material were investigated by fabricating 2032 coin cells using lithium foil as negative electrode. The electrolyte employed was 1 mol·L⁻¹ LiPF₆ in ethylene carbonate and diethyl carbonate (50 vol%:50 vol%). The galvanostatic charge/discharge was studied at room temperature in the voltage range of 2.5–4.2 V by a BTS-3000 battery testing system (NEWARE, China). The cyclic voltagramma (CV) scan was started from the open-circuit potential (OCP), going in the anodic direction with the potential range between 2.5 V and 4.2 V. CV was carried out by a CHI660B electrochemical testing system (Chenhua, China).





The XRD pattern of the top one shows that the slurry sample A contains FeSO₄·7H₂O and LiF. The XRD pattern of the middle one is the PDF card of FeSO₄·7H₂O (PDF Number: 22-0633) and of the bottom one is the PDF card of LiF (PDF Number: 45-1460).





XRD pattern of the top one shows that the sample D (prepared by maintaining the mixture of $FeSO_4.7H_2O$ and PEG400 at 45 °C for 60 hours) is composed of $FeSO_4.4H_2O$, while sample B is composed of an amorphous phase with LiF. The composition of this amorphous phase is under investigation. The XRD pattern of the middle one is the PDF card of $FeSO_4.4H_2O$ (PDF Number: 16-0699) and of the bottom one is the PDF card of LiF (PDF Number: 45-1460).



TG-DSC curves for the sample B obtained from room temperature to 900 °C with a heating rate of 10 °C ·min⁻¹ under N₂. There are three distinct mass loss stages. 1) 17 wt% mass loss from 50 °C to 120 °C with an endothermic peak centered at 120 °C. This stage is attributed to the formation of LiFeSO₄F_y(OH)_{1-y} according to Eq. [3] in the manuscript. 2) 8 wt% mass loss between 250 °C and 300 °C with another endothermic peak detected at 280 °C in the DTA curve. This stage is claimed to the formation of FeSO₄F_y(OH)_{1-y} which also exhibits a reversible electrochemical performance and will be presented in the next paper. 3) 15 wt% mass loss in the third stage between 400 °C and 800 °C can be claimed to the decomposition of FeSO₄F_y(OH)_{1-y} to form several phases, including Li₂SO₄, Fe₂O₃, FeS₂ and Fe₂(SO₄)₃ ^[s2]. It is reported that LiFeSO₄F and LiFeSO₄OH are stable up to 300 °C ^[s1], therefore LiFeSO₄F_y(OH)_{1-y} is less stable since it decomposes at ~250 °C. However, regarding the thermal stability, LiFeSO₄F_y(OH)_{1-y} is superior to most of the commercialized layer cathodes, such as LiCoO₂, LiNi_{0.8}Co_{0.2}O₂ and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, which are reported to decompose at 150-230 °C in the delithiated state.^[83-65]



CV scans at 0.1 mV \cdot s⁻¹ of the LiFeSO₄F_{0.56}(OH)_{0.44} sample.



The LiFeSO₄ $F_{0.56}$ (OH)_{0.44} cathode reaches its maximum discharge capacity 98.4 mAh g⁻¹ after 120 charge/discharge cycles at 0.1 C (15 mA g⁻¹).



Rate capability test of the $LiFeSO_4F_{0.56}(OH)_{0.44}$ sample.



SI-Figure S7

The bottom line (original sample) is the XRD pattern of the fresh LiFeSO₄F_{0.56}(OH)_{0.44} sample; The top line (aged sample) is the XRD pattern of the LiFeSO₄F_{0.56}(OH)_{0.44} electrode reaching the maximum capacity after ~ 470 cycles at 1C (the peaks under the * are the characteristic peaks of Al foil).

It can be seen clearly that the aged sample still possesses the same crystal structure (the triclinic P-1 tavorite structure) as the original sample, suggesting that there is no obvious phase change occurred during the electrochemical activation process.

LiFeSO ₄ F _{0.56} (OH) _{0.44}					
	Х	у	Z	frac	U _{iso}
S	0.329271	0.571733	0.213436	0.9840	0.16179
Fe(1)	0.000000	0.000000	0.500000	0.9830	0.28929
Fe(2)	0.000000	0.000000	0.000000	1.0000	0.80000
F	0.141062	0.868765	0.739577	0.5557	0.18597
O(1)	0.552433	0.799044	0.345573	1.0986	0.20336
O(2)	0.073392	0.562234	0.359039	1.2258	0.80000
O(3)	0.299367	0.352657	0.147840	0.9734	0.13879
O(4)	0.297510	0.745169	0.094513	0.9224	0.34704
Li	0.152553	0.557058	0.799691	0.5197	0.80000
ОН	0.141062	0.868765	0.739577	0.4443	0.39281

SI-Table 1

Atomic parameters of LiFeSO₄F_{0.56}OH_{0.44} refined from powder X-ray diffraction data. LiFeSO₄F_{0.56}(OH)_{0.44} was tested from 15° to 70 ° and data points were collected every 0.002° 20 and scan speed of 0.5°/s. The tavorite LiFeSO₄F_{0.56}(OH)_{0.44} phase is fitted with the P-1 space group as previously reported, possessing lattice parameters of a = 5.3158(8) (Å), b = 5.4248(8) (Å), c = 7.2010(1) (Å), $\alpha = 106.834(1)$ °; $\beta = 106.472(1)$ °; $\gamma = 99.199$ (1)° and V = 183.864 (5) (Å³). Agreement factors: $R_p = 9.23$ %, $R_{wp} = 11.56$ %. References:

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