Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting information

FeF_3@C nanotube arrays grown on the carbon fabric as free-standing cathode for lithium-ion batteries

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Experimental section

Synthesis of FeF_3@C nanotube arrays on CFC

Firstly, carbon fiber cloth (CFC) was ultrasonically cleaned in ethanol and ultrapure water for 15 min, separately. The Ni-Co basic carbonate ($(Co,Ni)(CO_3)_{0.5}OH$) nanowire arrays were synthesized by a typical hydrothermal deposition. Typically, 50 mmol urea, 10 mmol g $NiCl_2 \cdot 6H_2O$, and 20 mmol $CoCl_2 \cdot 6H_2O$ were dissolved in 160 mL deionized water with string to form a red-brown solution. After that, pre-treated CFC was vertically put into a 200 mL polytetrafluoroethylene-lined reactor and kept at 120 °C for 6 h in an oven. The attained Ni-Co basic carbonate precursor arrays were washed with ultrapure water and ethanol and dried at 80 °C for 10 h. To attain FeOOH-CFC, the dried precursor arrays were fully immersed in 300 mL 0.4 M $FeCl_3 \cdot 6H_2O$ aqueous solution and kept at 50 °C for 12 h. Finally, FeOOH-CFC film was immersed in 0.5 M glucose aqueous solution for 24 h and naturally dried. To obtain the FeF_3@C nanotube arrays, the modified FeOOH-CFC film was annealed at 500 °C for 3 h with 5 vol% H_2/Ar flowing, and then the temperature decreased to 300 °C converting the gas to 2 vol% NF_3/He and maintained at this temperature for 2h.

Materials characterization

X-ray diffraction (XRD) patterns of these films were collected by a PANalytical Empyrean XRD operating at 40 kV/45 mA equipped with a Cu Kα source. The morphology and microstructure information was revealed by scanning electron microscopy (SEM, Carl Zeiss Supra 40) with an operating voltage of 5 kV. Transmission electron microscopy (TEM) analyses were all conducted by a JEOL JEM-

2100F instrument. X-ray photoelectron spectroscopy (XPS) data was elucidated by an Axis Ultra DLD (Kratos Inc.) instrument using an Al Kα X-ray source. Raman spectrum was performed on a Thermo Fisher Micro DXR microscope motivated by He-Ne laser (532 nm) with a resolution of 2 cm^{-1}.

Electrochemical tests

Li^+ insertion/extraction properties of FeF_3@C-CFC cathode were measured by the assembled coin-cells (CR2025). FeF_3@C-CFC was cut into 8 mm circular disks as the cathode. The FeF_3@C mass loading of FeF_3@C-CFC was around 1.78 mg cm^{-2} and the CFC was about 11.53 mg cm^{-2}. Li//FeF_3@C-CFC cells were assembled in an Ar-filled glove box (both H_2O and O_2 below 0.1 ppm). 1 M $LiPF_6$ in a mixture of diethyl carbonate/ethylene carbonate (DEC/EC, 1: 2 by vol.) containing 10 wt% fluoroethylene carbonate (FEC) was applied as the electrolyte. Circular Li-foils and Celgard 2400 were used as counter electrodes and separators, respectively. A battery test system (Land 2001A) was taken to measure the cycling and rate performance of FeF_3@C-CFC in 1.0 V ~4.0 V or 2.0 V ~ 4.5 V, respectively. Cyclic voltammetry (CV) curves were conducted on an electrochemical workstation (Gamry Interface 1000). Electrochemical impedance spectroscopy (EIS) results were collected on the Gamry workstation in the frequency range of $0.01 \sim 1\times10^5$ Hz.

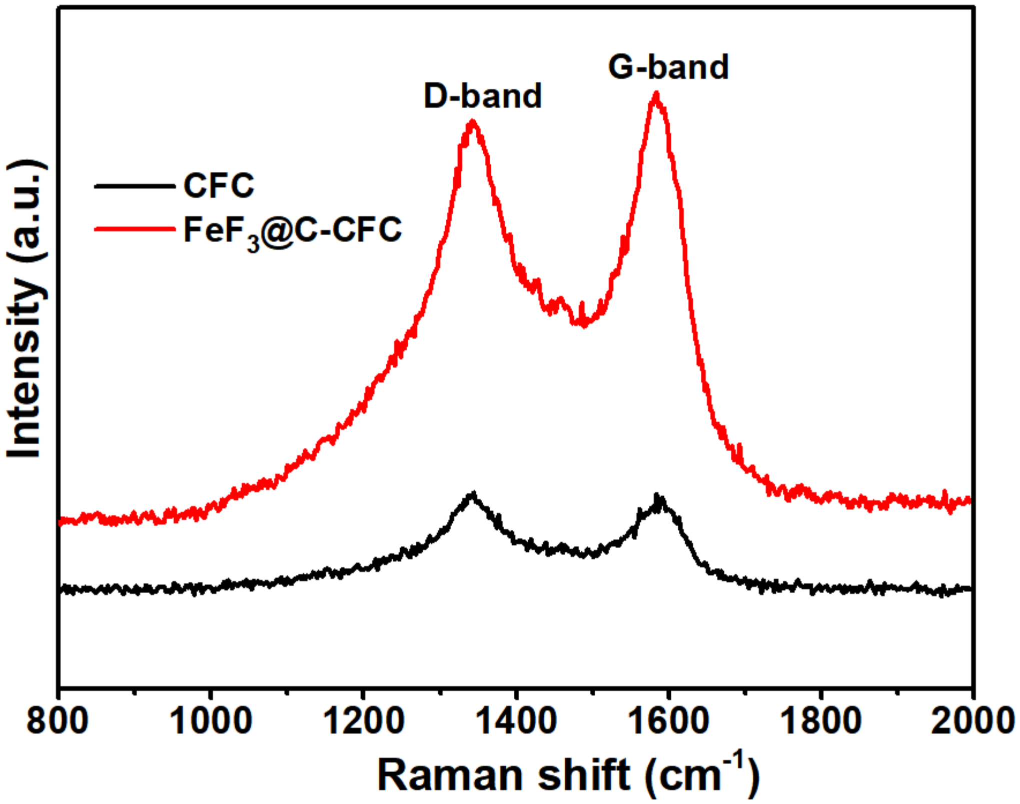

Figure S1 Raman spectra of CFC and FeF_3@C-CFC.

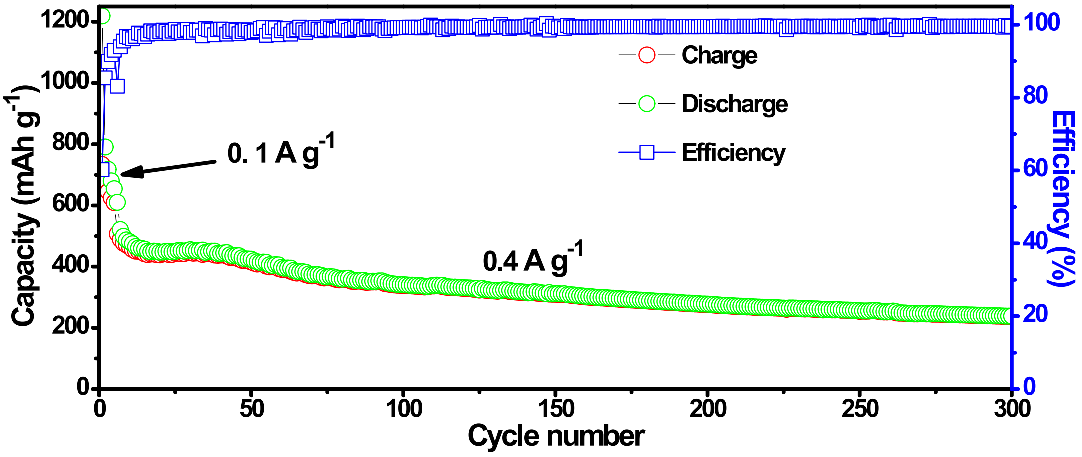

Figure S2 Cycling performance of FeF_3@C nanoarray at 0.4 A g^{-1}.

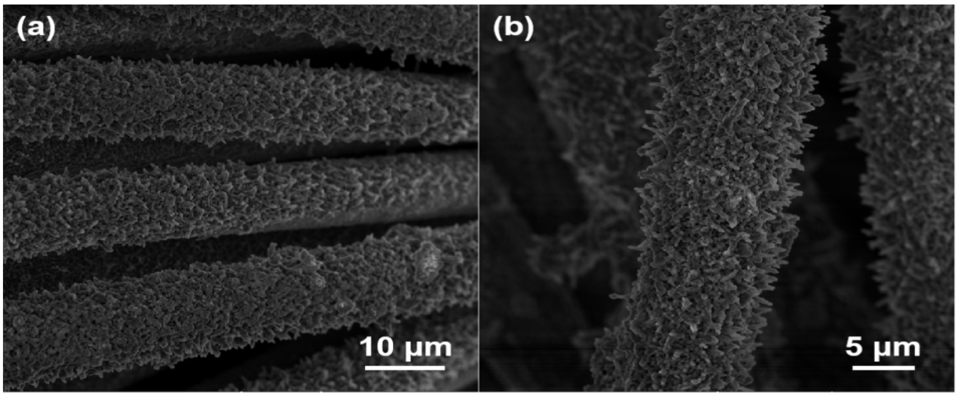

Figure S3 SEM images of FeF_3@C nanoarray after 50 cycles at 1.0 A g^{-1}.

Detailed calculation processes of Li^+ transfer coefficient

The Li^+ diffusion is measured based on the analysis of impedance and according to Equations (1) and (2):

$$D_{K^+} = R^2T^2 / 2n^4F^4\sigma_w{}^2A^2C^2 \qquad (1)$$

$$Z^{'} = R + \sigma_w w^{-1/2} \qquad (2)$$

EIS was employed to calculate the Li^+ diffusion coefficient to study the effect of crystallinity on potassium storage performance. In Equations (1) and (2), R, T, n, F, A, C, and σ_w are the gas constant (8.314 J mol^{-1} K^{-1}), the absolute temperature (303.15 K), the number of electrons per molecule during oxidation (2), the Faraday's constant (96485 C mol^{-1}), the surface area of the electrode (1.13 cm^2), the Li^+ concentration in the electrode material (1.0 mol L^{-1}), and the Warburg coefficient, respectively.

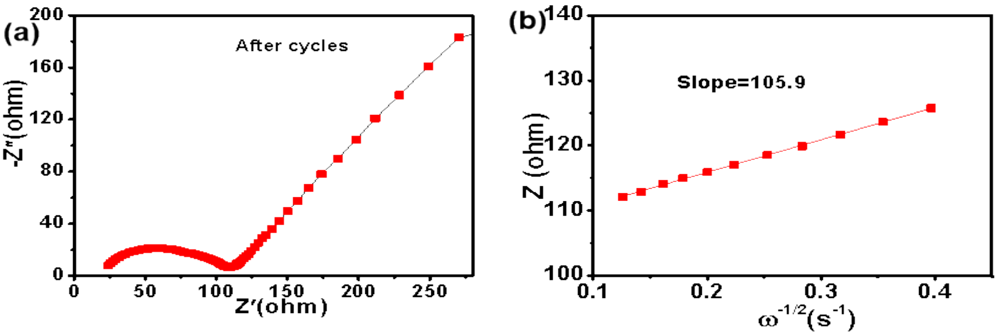

Figure S4 (a) EIS of FeF_3@C nanoarrays after cycles. (b) The plot of Zre with $w^{-1/2}$ within the low-frequency range of FeF_3@C nanotube arrays.

Table S1. A comparison of cycling performance between the current FeF_3@C nanotube arrays with recently reported fluoride cathode materials for LIBs.

Anode	**Current density ($mA\ g^{-1}$)**	**Discharge capacity ($mAh\ g^{-1}$)**	**Cycle number (cycles)**	**Voltage region (V)**	**Reference**
$FeF_3 \cdot 0.33\ H_2O$	237	95	45	1.7-4.5	Ref. S1
FeF_3-CNT	23.7	140	50	1.3-4.5	Ref. S2
Yolk-like FeF_3	712	125	40	1.5-4.2	Ref. S3
FeF_3/C/RGO	100	220	200	**1.0-4.0**	Ref. S4
O-$FeF_3 \cdot 0.33H_2O$	474	90	1000	1.5-4.5	Ref. S5
$FeF_3 \cdot 0.33H_2O$ nanosheets array	400	96	1000	1.7-4.5	Ref. S6
FeF_3/rGO	356	378-8	100	1.5-4.5	Ref. S7
FeF_3-C -NF	100	500	400	**1.0-4.0**	Ref. S8
FeF_3@C nanotube arrays	**100**	**300**	**700**	**1.0-4.0**	**This work**
	400	**235**	**300**		

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