**Supporting Information**

**Iron Fluoride/Multiwalled Carbon Nanotubes Cathode for High Performance Aluminum-ion Batteries**

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**Experimental Section**

**Material synthesis**

0.5 g of multi-walled carbon nanotubes (MWCNTs) was added to 200 ml of HF solution (48-51%), and then sonicated for 2 hours to obtain solution A. 3 mg CTAB was added to 50 ml $FeCl_3$ solution (5M) and stirred for 30 min to obtain solution B. Solution B was added dropwise to solution A, and stirred at room temperature for 24 hours. After the reaction, the mixed solution was centrifuged and washed with deionized water several times, and the precipitate was freeze-dried to obtain the product $FeF_3 \bullet 3H_2O$/MWCNTs. The product was heated to 220 °C under an inert atmosphere for annealing and kept for 4h to obtain the final product $FeF_3$/MWCNTs.

**Electrochemical measurements**

Anhydrous aluminum chloride ($AlCl_3$) and vacuum-dried 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) were mixed in an argon-filled glove box ($O_2$, $H_2O$<0.1ppm) at a molar ratio of 1.3:1 to prepare an ionic liquid electrolyte. The

prepared FeF₃/MWCNTs, acetylene black, and PVDF were mixed in a mass ratio of 6:3:1, NMP was used as a solvent, and the slurry was coated on a molybdenum foil (Mo) current collector, and vacuum dried at 70°C for 12 hours. The battery is assembled into a Swagelok battery, using high-purity aluminum foil as the anode and Whatman (GF/D) glass fiber filter paper as the separator. The cyclic voltammetry curve was tested using an electrochemical workstation (CHI660e, Shanghai Chenhua, China). The galvanostatic charge/discharge measurements uses Wuhan LANHE test system.

**Materials Characterization**

The crystal structures of the samples were analyzed by powder X-ray diffraction (XRD, X' Pert Pro MPD, PANalytical, Netherlands) with CuKα radiation at 40 kV and 40 mA. The microscopic morphology and microstructure of the samples were observed by field-emission scanning electron microscopy (SEM, JSM-7900F，JEOL) and Field emission scanning transmission electron microscopy (FE-STEM, Thermo Scientific Talos F200X). X-ray photo- electron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, ULVAC-PHI, USA) with an Al Kα X-ray source (1486.6 eV) was used to study the surface chemical composition and valent state of the elements of the samples. Raman spectroscopy (HORIBA HR Evolution with excitation at 532 nm) are used to characterize the structural changes of materials. The thermogravimetric analyzer (TG, METTLER TOLEDO) was used to determine the component content of the sample. Nitrogen adsorption and desorption (BET, ASAP2020 HD88) was used to characterize the specific surface area and pore size distribution of the material.
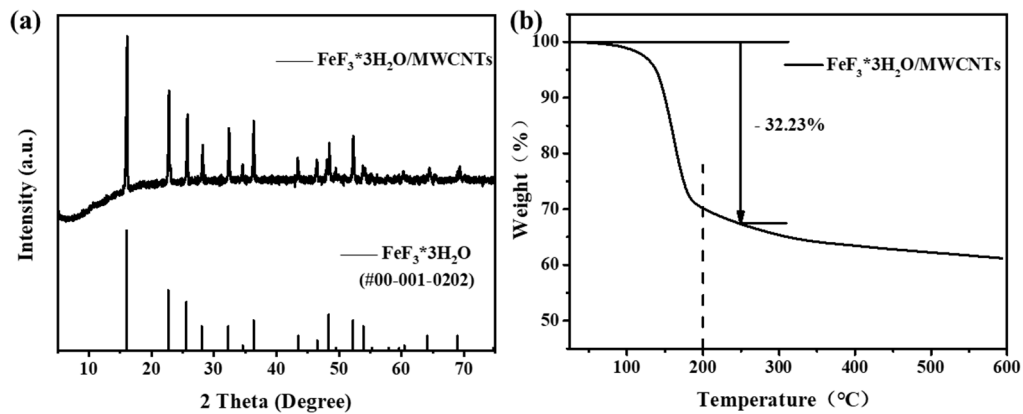
Figure S1 (a) XRD curves of FeF₃·3H₂O/MWCNTs; (b) Thermogravimetric curve of FeF₃·3H₂O/MWCNTs under nitrogen atmosphere.
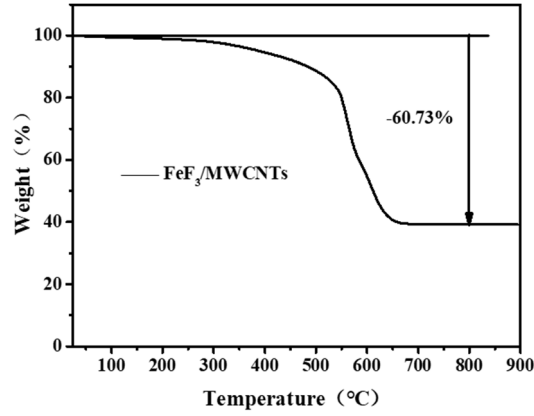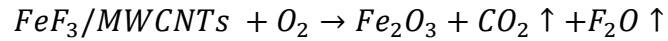


Figure S2 Thermogravimetric curve of FeF₃/MWCNTs under air atmosphere.

Calculation results of component content:

$$FeF_3/MWCNTs + O_2 \rightarrow Fe_2O_3 + CO_2 \uparrow + F_2O \uparrow$$

$$100\% \qquad\qquad 39.27\%$$

If $\qquad\qquad$ 100 g $\qquad\qquad$ 39.27 g

As known $\quad$ M(Fe₂O₃) = 159.7 g/mol $\qquad$ M(FeF₃) = 112.85 g/mol

$\qquad\qquad$ m(FeF₃) = 39.27 ÷ 159.7 × 2 × 112.85=55.50 g

$\qquad\qquad$ FeF₃% = 55.50 g ÷ 100 g × 100% = 55.5%

$\qquad\qquad$ MWCNTs% = 100% - 55.5% = 44.5%



| Element | Wt% |
|---------|------|
| C | 46.97 |
| O | 5.40 |
| Fe | 27.94 |
| F | 19.68 |
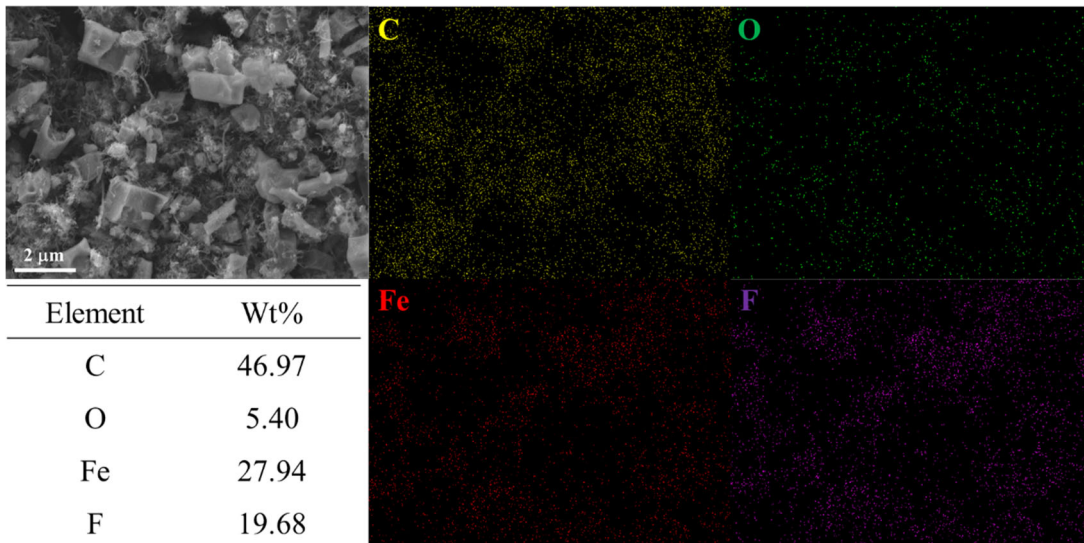
Figure S3 Content of the elements in FeF$_3$/MWCNTs composites determined by EDS mapping.

Table S1 Content of Fe element in FeF$_3$/MWCNTs measured by ICP-AES.

| Sample | Sampling quality/g | Solution volume/ml | Dilution coefficient | Measured element | Instrument reading | Unit | Conversion content | Unit | Percentage |
|---|---|---|---|---|---|---|---|---|---|
| Pure FeF$_3$ | 0.0223 | 50 | 100 | Fe | 2.207 | mg/L | 494856 | mg/kg | 49.4856 |
| FeF$_3$/MWCNTs | 0.0219 | 50 | 100 | Fe | 2.461 | mg/L | 561979 | mg/kg | 27.8126 |

Notes: Conversion Content=Intrument reading*Soultion volume*Dilution coefficient/Sampling quality.
10000 mg/kg=1.0 %

Content of FeF$_3$: M(Fe) = 55.85 g/mol, M(FeF$_3$) = 112.85 g/mol

m(FeF$_3$) %=m(Fe)%/M(Fe)*M(FeF$_3$) = 27.8126/55.85*112.85 = 56.1979%

m(MWCNTs) %=100%- m(FeF$_3$) %=43.8021%
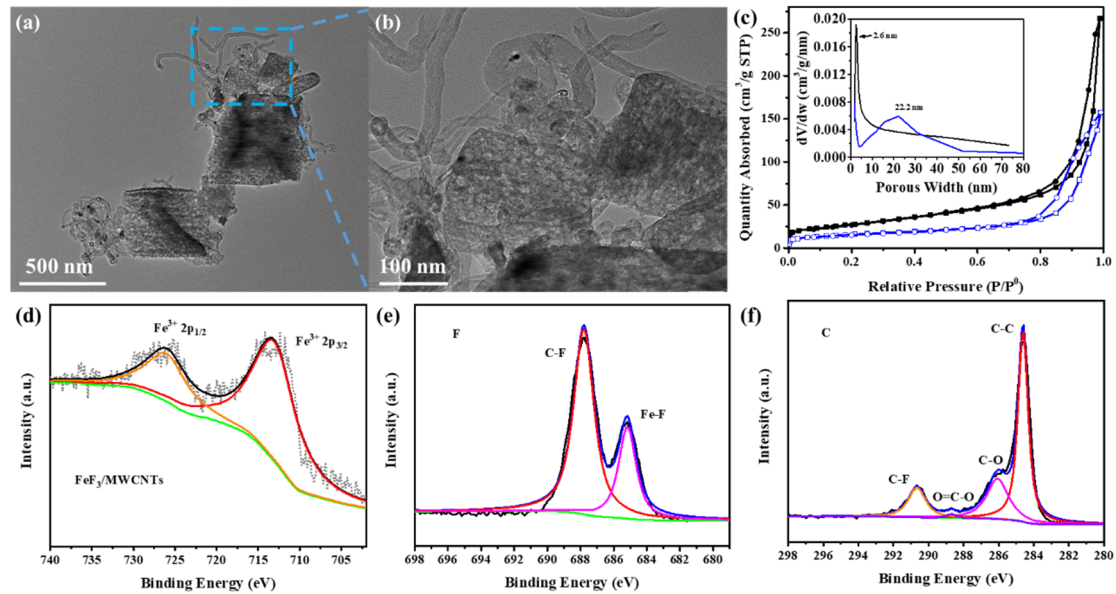


Figure S4 (a, b) TEM images of FeF$_3$/MWCNTs; (c) Nitrogen adsorption and desorption curves of MWCNTs (Black) and FeF$_3$/MWCNTs (Blue) and corresponding pore size distribution diagrams; (d, e, f) XPS spectrum of Fe 2p, F 1s and C 1s for FeF$_3$/MWCNTs.
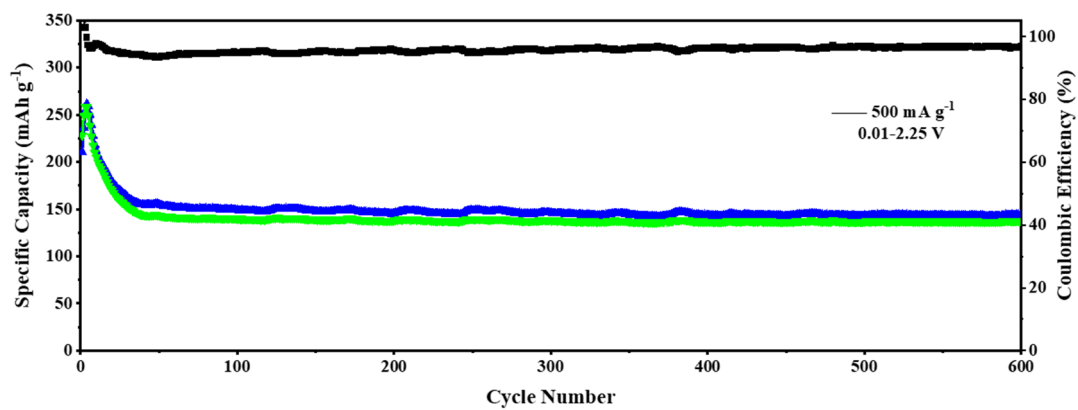
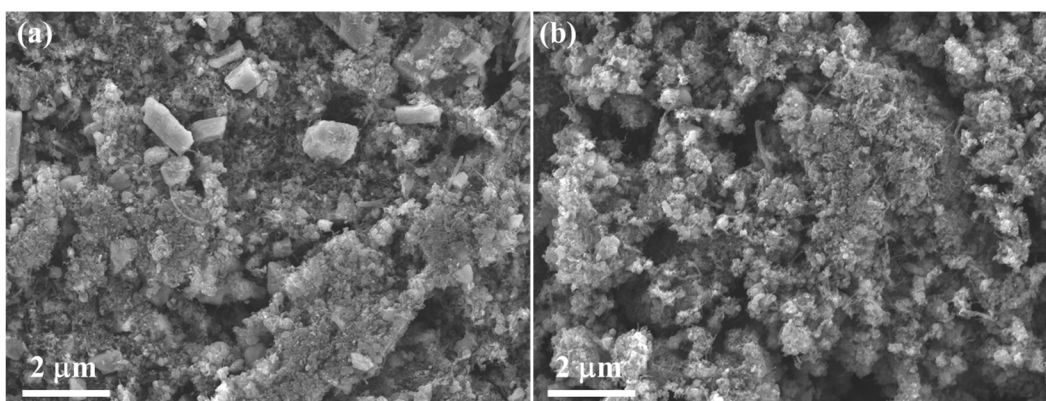Figure S5 Long cycle curves of FeF$_3$/MWCNTs in the voltage range of 0.01-2.25 V at 500 mA g$^{-1}$.



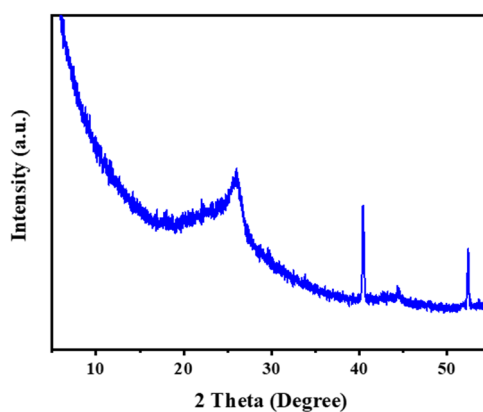Figure S6 SEM images of FeF$_3$/MWCNTs cathodes (a) before and (b) after cycling.



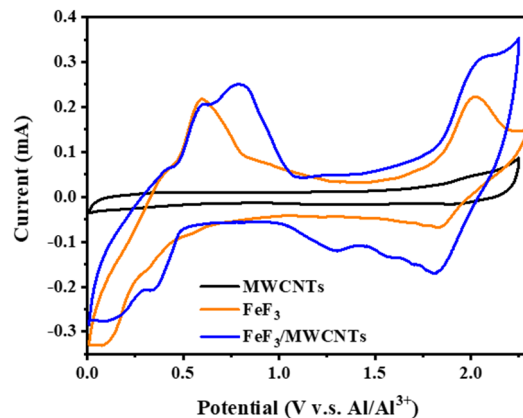Figure S7 XRD pattern of FeF$_3$/MWCNTS electrode after 100 cycles at 100 mA g$^{-1}$.

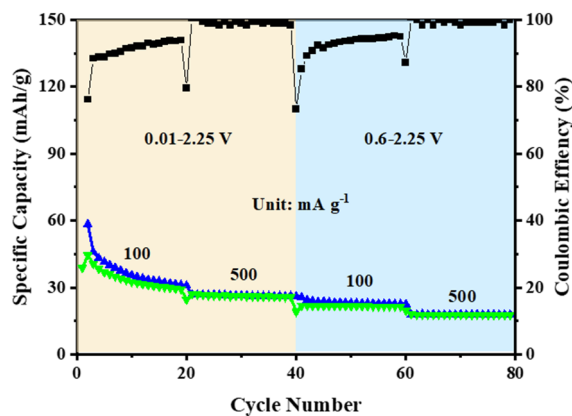Figure S8 Comparison of CV curves of FeF$_3$, MWCNTs and FeF$_3$/MWCNTs at 1.0 mV s$^{-1}$.



Figure S9 Discharge capacity of MWCNTS in different voltage range and different current density.
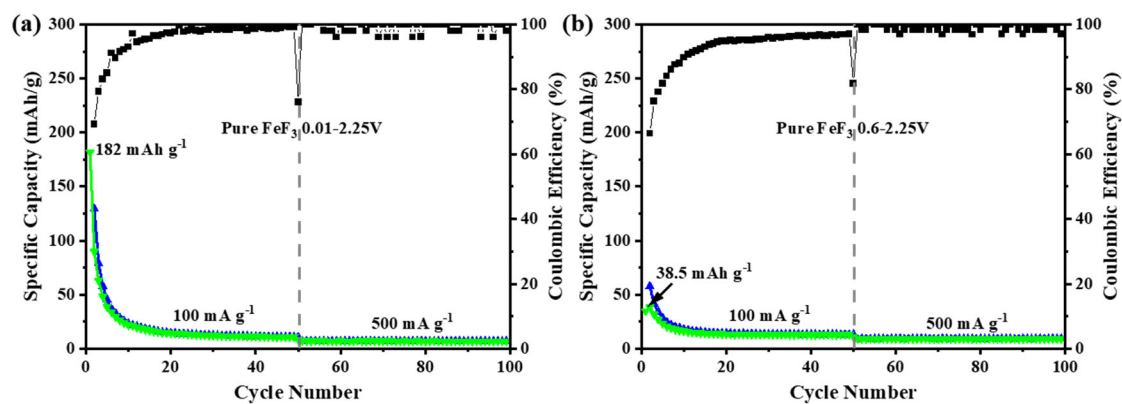


Figure S10 Discharge capacity of pure FeF$_3$ in different voltage range (a: 0.01-2.25 V, b: 0.6-2.25 V) and different current density.
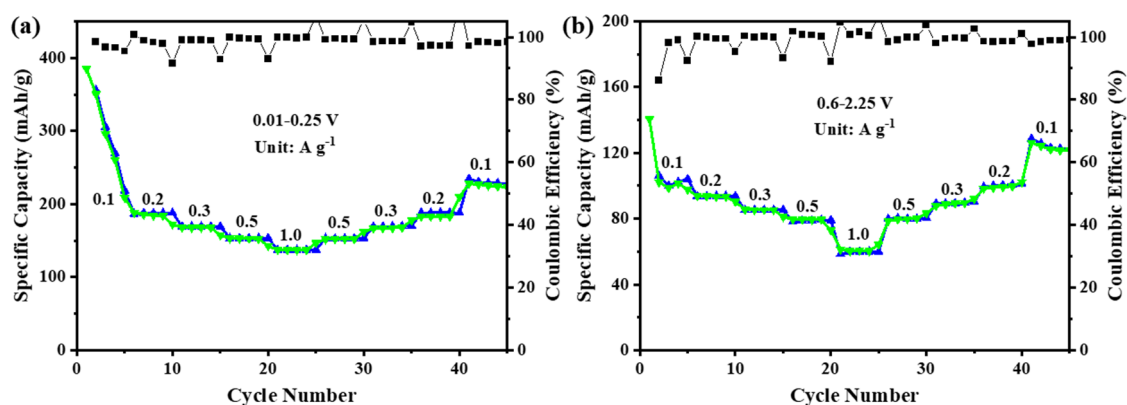
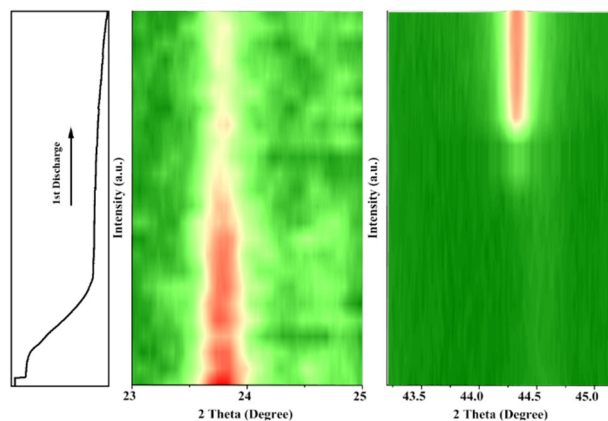Figure S11 Rate performance of FeF$_3$/MWCNTs cathode in different voltage range (a: 0.01-2.25 V, b: 0.6-2.25 V).



Figure S12 In-situ XRD patterns of FeF$_3$/MWCNTS cathode during the first discharge at 100 mA g$^{-1}$.
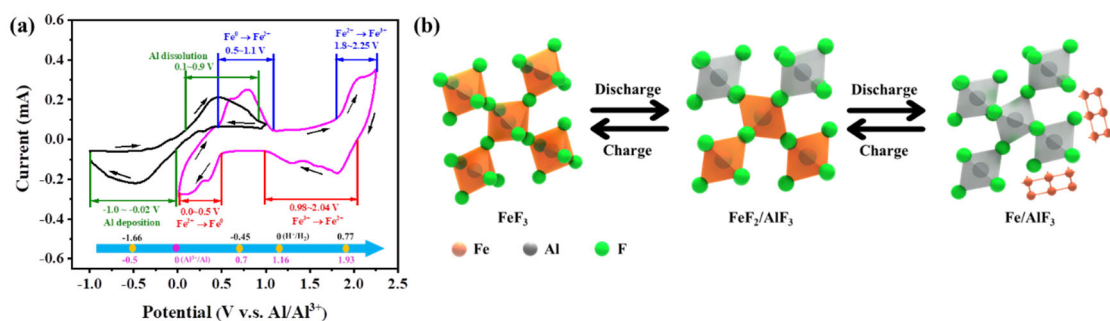


Figure S13 (a) CV curves of Al foil and FeF$_3$/MWCNTs at 1.0 mV s$^{-1}$ against an Al reference electrode; (b) Schematic diagram of the energy storage mechanism of FeF$_3$ cathode in aluminum ion battery.