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**Electronic Supplementary Information (ESI)**

# iron oxyfluorides as lithium-free cathode materials for solid-state Li metal batteries

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# Experimental

## Materials synthesis

$Fe(NO_3)_3 \cdot 9H_2O$ (99%), hydrofluoric acid (HF, 48 w.t.%), absolute ethanol and acetonitrile (99%) were purchased from Sinopharm chemical reagent, Beijing, China. 1-proponal (99%), 3,4-ethylenedioxythiophene (EDOT, 98%) were purchased from Sigma Aldrich. $FeCl_3$ (98%) was purchased from Alfa Aesar. All chemicals were analytical grade without further purification before use.

## $FeF_2 \cdot 4H_2O$ NWs Growth

0.4 g $Fe(NO_3)_3 \cdot 9H_2O$ was added into 10 mL absolute ethanol and stirred for 15 minutes until dissolved as solution A. 40 mL absolute ethanol and 10 mL HF were added into a 100 mL plastic centrifuge tube (with lid) and stirred carefully to mix as solution B. Then, inject solution A into solution B, close the lid and keep them at 60 ˚C for 10 h in oven. The resulting nanowires were centrifuged and washed with ethanol for three times. Finally, the white cloudy production was dried in vacuum oven under 80 ˚C overnight.

## Conversion of $FeF_2 \cdot 4H_2O$ NWs to FeOF nano-rods

150 mg $FeF_2 \cdot 4H_2O$ NWs was firstly grinded in a mortar and then dispersed in 45 mL 1-proponal. After stirring for two hours, the suspension was transferred into a Teflon-lined stainless-steel autoclave and kept in 210 ˚C for ten hours. The resulting production with light brown color was centrifuged and washed with ethanol and dried in vacuum oven overnight under 80 ˚C.

## Preparation of the PEDOT coated FeOF nano-rods

70 mg of the as-prepared FeOF was dispersed in 20 mL deionized water by ultrasonic dispersion for one hour. After that, 46 mg $FeCl_3$ dissolved in 5 mL deionized water was added in the suspension and stirred for another one hour. 10 uL EDOT was dissolved in a mixed solution of 7 mL deionized water and 3 mL acetonitrile, and then added this solution into the suspension dropwise. The mixed solution was kept stirring for 24 h at room temperature to complete the polymerization process. Finally, the dark brown

precipitate was collected, centrifuged, washed with ethanol and kept in vacuum oven under 80 ˚C overnight.

## Polymer Electrolyte Synthesis

Ethoxylated trimethylolpropane triacrylate (Mw = 428), 2-hydroxy-2-methyl-1phenyl-1-propanon, polyethylene oxide (Mw = $10^6$) and dimethyl sulphoxide (DMSO, 99%) were all purchased from Aldrich. 1 M $LiPF_6$ in 1:1:1 (by volume) ethylene carbonate/dimethyl carbonate/diethyl carbonate containing 2 vol% vinylene carbonate as electrolyte.

The PEA polymer electrolyte was obtained by UV curing the precursor as described previously.[1] Firstly, mixing ethoxylated trimethylolpropane triacrylate (monomer), liquid electrolyte and PEO (2.5 wt%, in anhydrous DMSO) in the volume ratio of 1:4:1.5 to form the precursor. The UV lasted for about 5 minutes, wherein 2-hydroxy-2-methyl-1phenyl-1-propanon (photoinitiator) was fixed at 1.0 wt% of monomer.

After that, the mixed solution was dropped onto the surface of Li foil and exposed to UV irradiation for few minutes.

## Materials characterizations

The morphology and particle size of the obtained samples were examined by scanning electron microscopy (SEM, JEOL 6701F) operated at 10 kV and transmission electron microscopy (TEM, JEM 2100F) with energy dispersive spectroscopy (EDS) operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 diffractometer with filtered Cu Kα radiation ($\lambda = 1.5405$ Å). Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific) with a laser wavelength of 532 nm.

## Electrochemical measurements

The 2032 coin type battery was assembled using the coated FeOF as cathode and pure Li foil as anode in an argon-filled glove box ($H_2O$, $O_2 < 0.1$ ppm) to evaluate the electrochemical property of the as-prepared electrodes. The working electrode was prepared by casting 70 wt % active materials, 20 wt % super P and 10 wt % poly(vinyl difluoride) (PVDF) onto the Al foil. The solid electrolyte was a kind of PEA electrolyte membrane.[1] 1 M $LiPF_6$ in 1:1:1 (by volume) ethylene carbonate/dimethyl carbonate/diethyl carbonate containing 2 vol% vinylene carbonate was used as liquid electrolyte for comparison. The cells were assembled with a polypropylene microporous film as the separator when using liquid electrolyte and the loading mass of the active materials for the electrode is around 1.5 mg cm$^{-2}$. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a ParSTAT MC electrochemical work station (Princeton). Galvanostatic tests were carried out in the voltage range of 2–3.8 V vs Li$^+$/Li using LAND cycler (Wuhan Kingnuo Electronic Co., China) at 25 ˚C.

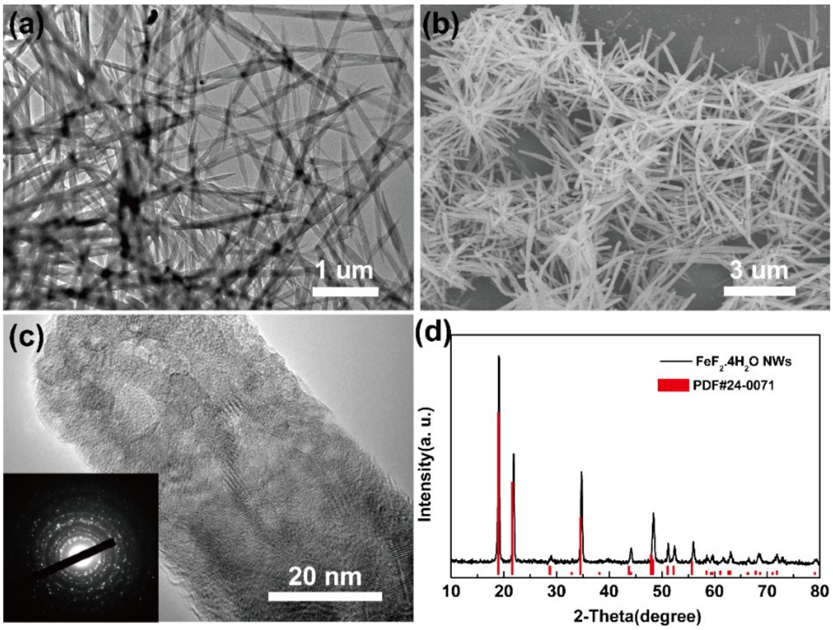

Fig. S1 (a) Typical TEM images of $FeF_2{\cdot}4H_2O$ NWs. (b) SEM image of $FeF_2{\cdot}4H_2O$ NWs. (c) HRTEM and corresponding SAED patterns for $FeF_2{\cdot}4H_2O$ NWs. (d) XRD patterns of $FeF_2{\cdot}4H_2O$ NWs.

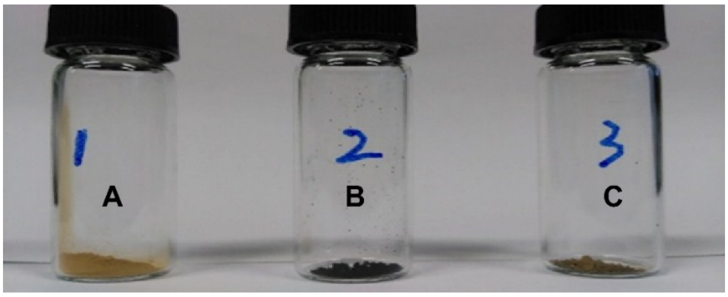

Fig. S2 Comparison of the optical images for the (a) pure FeOF, (b) PEDOT and (c) the coated FeOF powders.

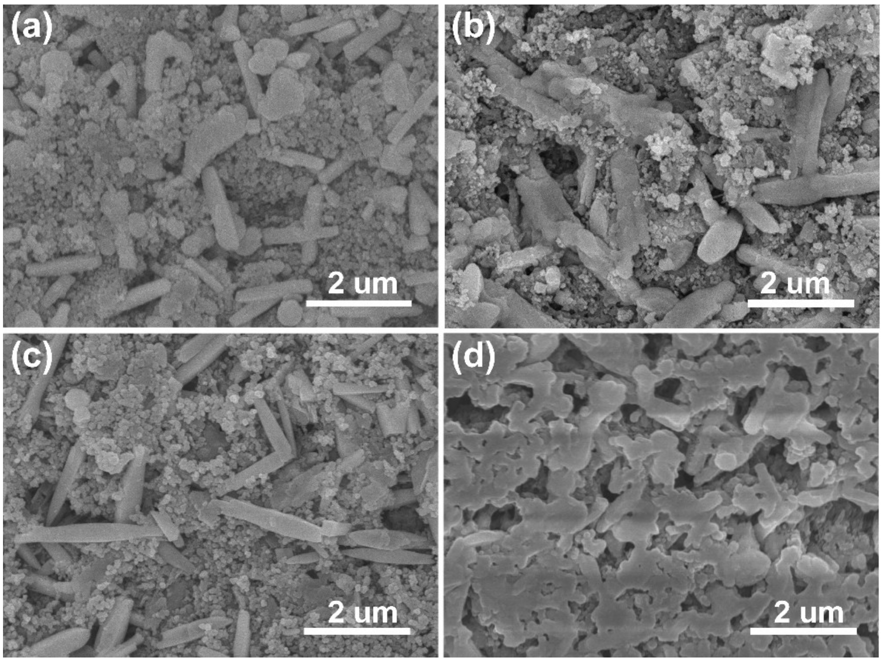

Fig. S3 Typical SEM images of cathode (the coated FeOF, super P mixture) (a) before charge/discharge; (b) after charge/discharge for 100 cycles with solid electrolyte. And cathode (pure FeOF, super P mixture) (c) before charge/discharge; (d) after charge/discharge for 100 cycles with solid electrolyte.

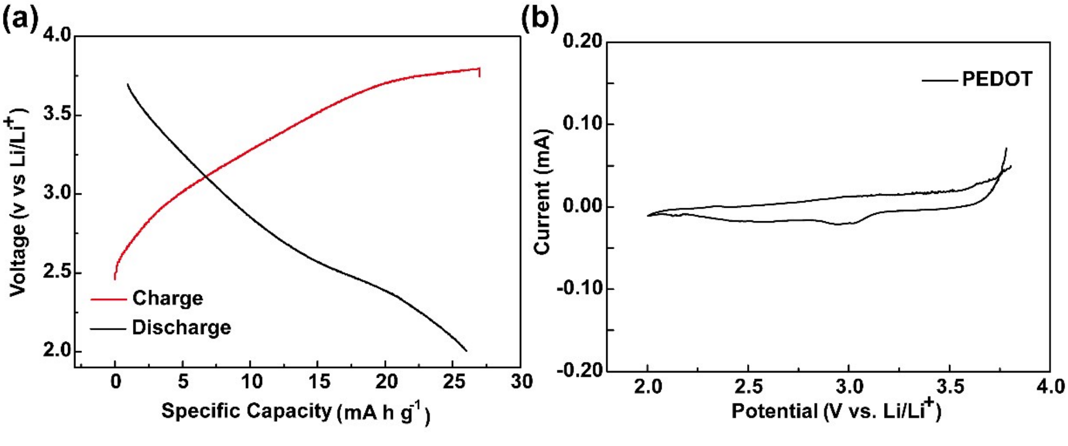

Fig. S4 (a) Galvanostatic discharge/charge voltage profiles of pure PEDOT under a current density of 20 mA $g^{-1}$. (b) CV curves of pure PEDOT in solid electrolyte measured at a scanning rate of 0.2 mV $s^{-1}$.

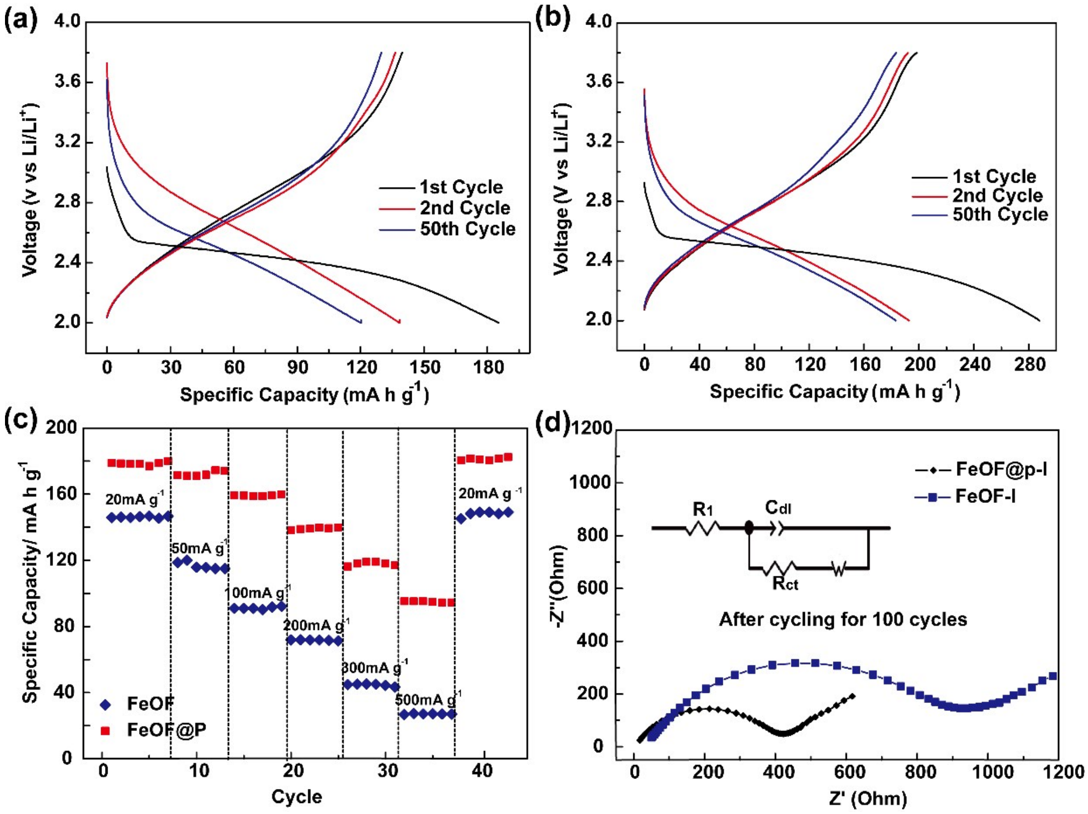

Fig. S5 Galvanostatic discharge/charge voltage profiles of (a) pure FeOF and (b) the coated FeOF under a current density of 20 mA g$^{-1}$. (c) Rate capability at the current density ranges from 100 mA g$^{-1}$ to 500 mA g$^{-1}$ under liquid electrolyte. (d) Nyquist plots of pure FeOF, the coated FeOF cathodes in the frequency range of 0.1–10 000 Hz.

## Reference

1. X. X. Zeng, Y. X. Yin, N. W. Li, W. C. Du, Y. G. Guo and L. J. Wan, *J. Am. Chem. Soc.*, 2016, **138**, 15825-15828.