Supporting information

Titanium-based Metal-Organic Framework as an Ultralong Cycle-Life

Anode for PIBs

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1 Experimental sections

1.1 Synthesis of MIL-125(Ti)

The MIL-125(Ti) was synthesized by a solvothermal method in methanol (MeOH)-N,N-dimethylformamide (DMF) mixed solvent with terephthalic acid (H₂BDC) and tetra-n-butyl titanate (Ti(OC4H₉)₄) as organic linker and metal root. In a typical process of experiment, 0.5 g (3 mmol) of H₂BDC and 0.26 ml (0.75 mmol) Ti(OC4H₉)₄ were added into 9 ml of DMF and 1 ml of MeOH to compose a well-distributed solution under magnetic stirring for 1 h at a room temperature. Then the solution was transferred to a 50 ml autoclave and heated at 150 °C for 20 h. After reaction, the resultant precipitate was filtered, washed several times with DMF and MeOH, dried in the vacuum oven at 60 °C for 10 h and calcined at 200 °C for 5h to obtain the white product.(as shown in Scheme S2)^{30,31}

1.2 Characterization Methods

Crystallographic phases of the as-synthesized MIL-125(Ti) were characterized by power X-ray diffraction (XRD) on a Rigaku Dmaxrc diffractometer using Cu K α radiation at a scanning rate of 10 °C min⁻¹ from 5 °C to 90 °C. The morphology of the prepared samples was measured by SU-70 field emission scanning electron microscopy (FESEM) and JEOL JEM-2100 high resolution transmission electron microscopy (HRTEM). The thermal stability of MIL-125(Ti) was investigated by thermogravimetric analysis (TGA, TG-209C) at a heating rate of 5 °C min⁻¹ from 30 °C to 800 °C in oxygen. The porous property of the as-synthesized samples based on N₂ sorption isotherm was estimated by Brunauer-Emmett-Teller theory (BET, ASAP 2020). The Fourier transformation infrared (FTIR) pectroscopy was obtained on a NICOLET AVATAR 360 FT-IR spectrometer from 400 cm⁻¹ to 4000 cm⁻¹.

1.3 Electrochemical Measurements

The slurry was arranged by mixing 75 wt% MIL-125(Ti), 15 wt% Super P carbon and 10 wt% sodium carboxymethylmellulose (CMC) binder. Then the obtained slurry was pasted onto a Cu foil and dried in a vacuum oven at 80 °C for 24 h. The mass loading of active materials was about 0.8-1.2 mg. The electrode of terephthalic acid was also prepared through the above steps. The potassium metal was used as the counter electrode and reference electrode. Glassy-fiber was employed as the separator. The electrolyte was 1 M KFSI in ethylene carbonate/diethyl carbonate (EC/DEC, v/v=1:1). All the cells were assembled in a glovebox filled with argon and measured in a room temperature. Galvanostatic charge/discharge was tested on a galvanostatic programmable

battery charger in the voltage range of 0.01-3 V (vs. K/K⁺). Cyclic voltammetry (CV) was carried out with an electrochemical workstation between 0.01 V and 3 V at the rate of 0.1 mV s⁻¹. Ex situ XRD and IR were checked out after certain cycles. The electrode was taken out and washed with DEC to remove the residual electrolyte in the glovebox and then dried at 50 °C for 10 h before testing.



Scheme S1. Schematic illustration of electrochemical mechanism of MIL-125(Ti) in potassium-ion batteries



Scheme S2. Schematic of the synthesis of MIL-125(Ti).



Fig. S1 Electrochemical performance of terephthalic acid as anode for PIBs. (a) Galvanostatic charge-discharge voltage profiles at 50 mA g^{-1} . (b) Cycling performance at 50 mA g^{-1} .



Fig. S2 (a) The ex-situ XRD patterns for MIL-125(Ti) at the different status during the 1st cycle in potassium-ion batteries. (b) The ex-situ IR spectra of MIL-125(Ti) at the different status during the 1st cycle in potassium-ion batteries.



Fig. S3 Ex situ SEM images of MIL-125(Ti) electrode (a) before (b) after 2000 cycels and EIS spectra of MIL-125(Ti) electrode before, and after 10, 100cycles.