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Electronic supplementary information (ESI)

Capacity control of the ferric coordination polymers by zinc nitrate for lithium-ion battery

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Characterization of materials

A Rigaku Ultima IV X-ray Diffractometer with Cu-Kα radiation (V = 35 kV, I = 25 mA, λ=1.5418 Å) was used to analyze the crystal phase of the as-prepared materials in the 2θ range 5°–50° at a scanning rate of 15° min^{-1}. N_2 sorption isotherms and BET surface area were measured at 77 K with an ASAP 2020 system (Microeritics, Norcross, GA). SEM images and *EDX spectra* were taken by a Hitachi S-4800 scanning electron microscope (Japan) and before thses tests, the samples were mounted on aluminum stubs, sputtered with gold. TG curves that range from room temperature to 800°C were recorded on a STA 449 F3 Jupiter® simultaneous thermo-analyzer at a heating rate of 10°C min^{-1}. A Nicolet-Nexus 670 infrared spectrometer was used to perform flourier transform infrared spectroscopy (FTIR) analysis in the wavenumber range of 2500–400 cm^{-1} in transmission mode. ICP test was performed on a Thermo IRIS Intrepid II XSP Spectrometer.

Electrochemical testing

All the electrochemical measurements were carried out at room temperature. To active the materials and remove the coordinated waters, we dry the materials at 300°C for 12h before the electrochemical testing. The active material (weight ratio: 80%), conducting additive (Super-P carbon black, weight ratio: 10%) and the binder (carboxymethyl cellulose sodium or CMC, weight ratio: 10%) were homogenously mixed in deionized water (solvent) for at least 3 h to produce a slurry. Then, the obtained slurry was coated onto Cu foil and dried at 70°C in vacuum oven for 12 h. The electrodes were punched into round plates (diameter of 14.0 mm). The loading of the as-prepared electrodes is about 1.5 mg cm^{-2}. 1M LiPF6 in EC-DMC-EMC (ethyl carbonate: dimethyl carbonate: ethyl methyl carbonate = 1:1:1 in volume) was used as the electrolyte. Finally, a coin cell (CR2032) was assembled by the as-prepared anode, a Celgard 2325 separator (diameter of 19.0 mm), a pure lithium wafer (counter electrode), and electrolyte in an argon filled glove box with oxygen and water less than 0.1 ppm. The galvanostatic charge and discharge and rate tests were performed on a multichannel LAND CT2001A battery test system (Wuhan Kingnuo Electronic Co., China) in the voltage range of 0.01-3 V. Cyclic voltammetry (CV) testing and electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (CHI660e, ChenHua Instruments Co., China) at a scan rate of 0.2mV s^{-1} in the voltage range of 0.01-3 V.

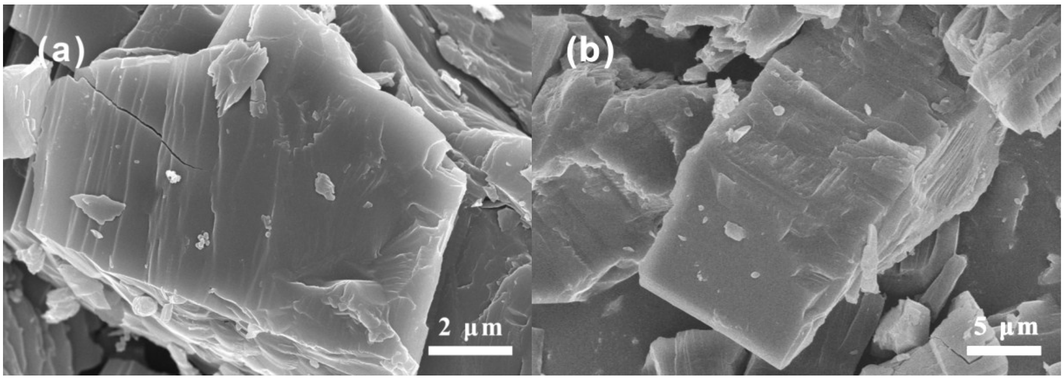

Fig. S1 SEM of (a) Fe(Zn)-BDC and (b) Fe-BDC

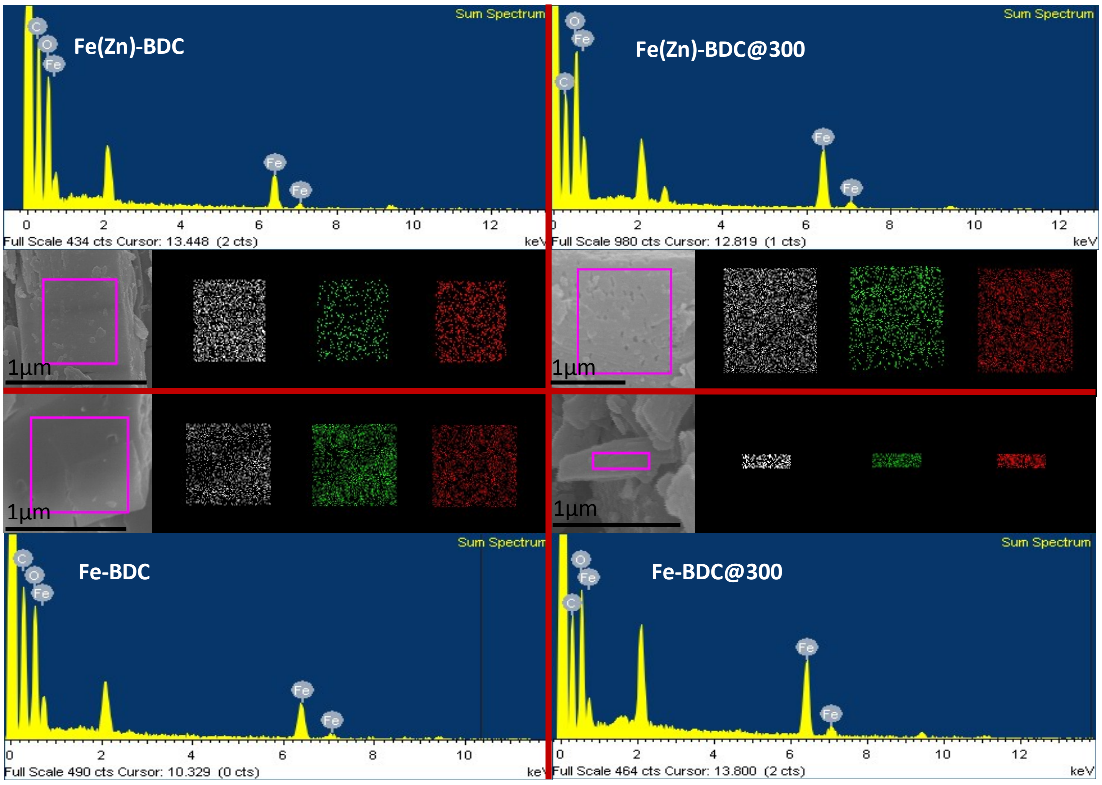

Fig. S2 EDX-elemental mapping (white. C, green. O red. Fe) and whole energy spectra of Fe(Zn)-BDC, Fe-BDC, Fe(Zn)-BDC@300 and Fe-BDC@300 from the selected region. Before test, the samples were mounted on aluminum stubs, sputtered with gold resulting in the remaining peaks (approx. 2 keV) on the EDX spectrum.

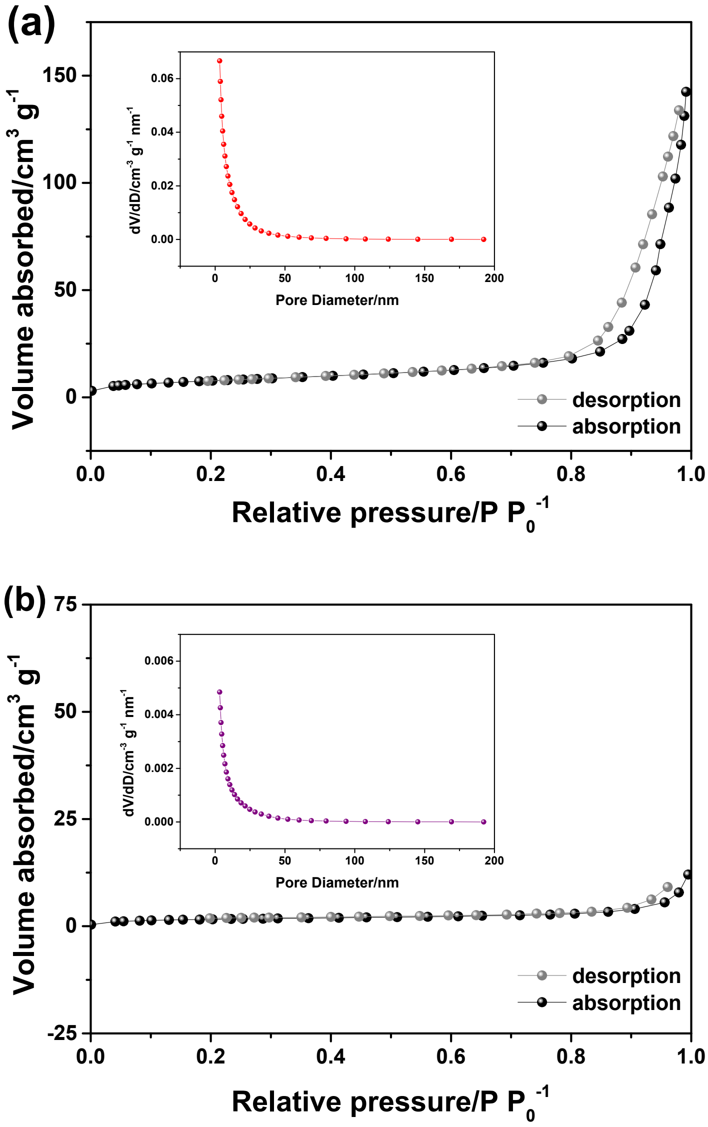

Fig. S3 Nitrogen adsorption/desorption isotherm of (a) Fe(Zn)-BDC@300 and (b) Fe-BDC@300. Inset: the pore-size distribution calculated based on the desorption branch of the corresponding isotherm.

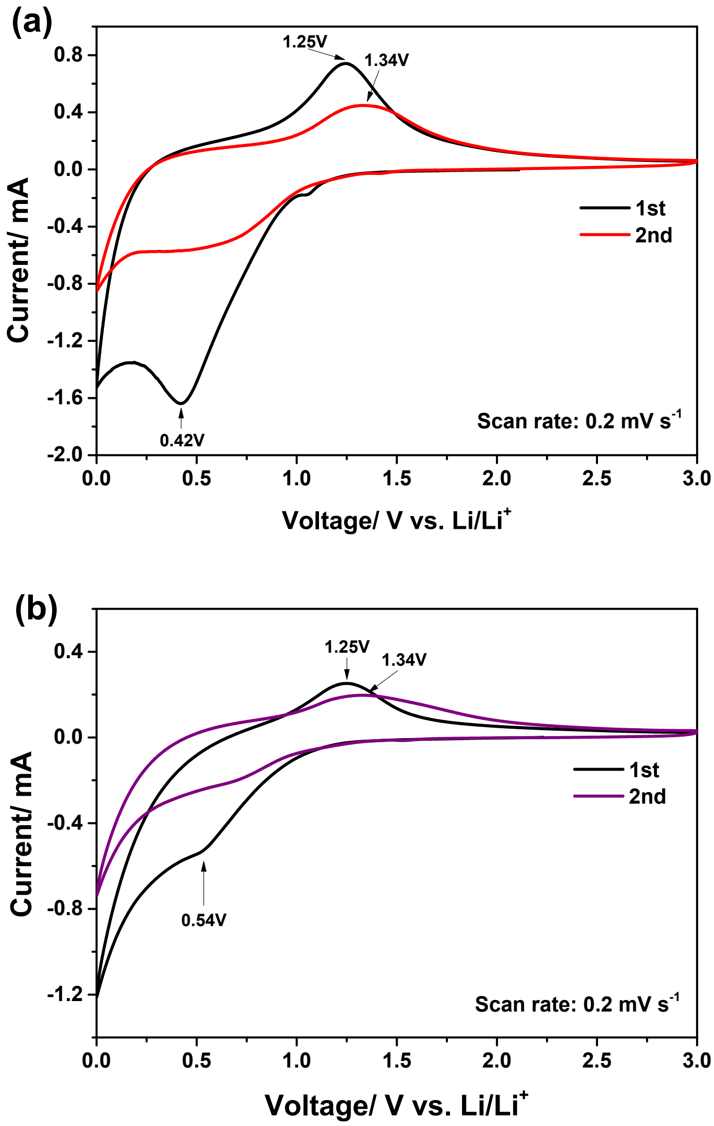

Fig. S4 Cyclic voltammograms for the initial three cycles of Fe(Zn)-BDC@300 and Fe-BDC@300 electrodes at a scan rate of 0.2 mV s^{-1} in a voltage range of 0.01V~3V.

A sharp cathodic peak is observed at ~0.42V duing to associated electrolyte decomposition and the formation of SEI film on the surface of Fe(Zn)-BDC@300 electrode. In the following anodic process, a broad peak at 1.25V can be attributed to the extraction of Li^+ from electrode. In the subsequent sweeps, the cathodic peak is too broad to measure and the anodic peak moves to ~1.34V. The peak positions in CV curves of Fe-BDC@300 are similar indicating the similar electrochemical reaction.

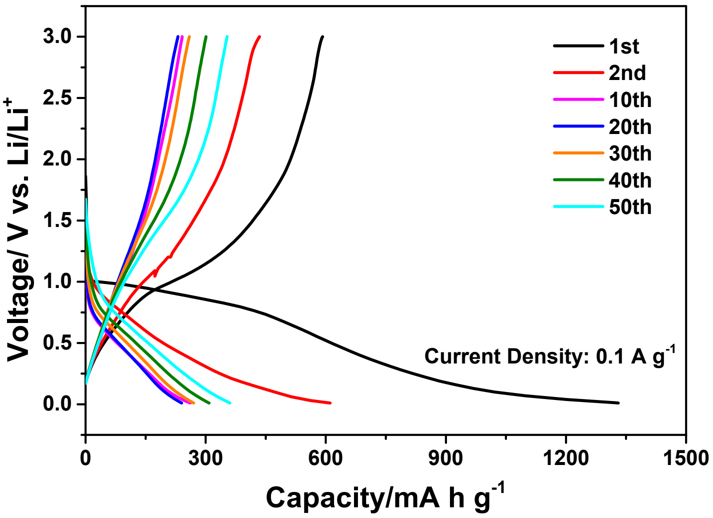

Fig. S5 Galvanostatic charge-discharge profiles of Fe-BDC@300 at 0.1 A g^{-1} in the voltage window of 0.01–3.0 V.

Table S1. Inductively coupled plasma atomic emission spectroscopy (ICP) data of Fe(Zn)-BDC and Fe-BDC

Element	Sample	100 mg/ L Fe(Zn)-BDC	100 mg/ L Fe-BDC	Blank (deionized water)
	Content (ppm)	19.53±0.05	17.80±0.01	0.02±0.01
	Standard deviation	0.070	0.018	0.008
	Relative standard deviation (%)	0.358	0.101	46.06
Zn	Content (ppm)	0.2541±0.0018	0.0410±0.0069	0.0791±0.0125
	Standard deviation	0.0025	0.0098	0.0176
	Relative standard deviation (%)	0.988	24.0	22.3

In consideration of the addition of zinc nitrate in large quantities, the trace amounts of Zn (~0.25%) could be attributed to the adsorption of zinc nitrate in the framework of Fe(Zn)-BDC.

Table S2. Surface areas, pore volumes and mean pore diameters of Fe(Zn)-BDC@300 and Fe-BDC@300.

Sample	**Fe(Zn)-BDC@300**	**Fe-BDC@300**
Surface area ($m^2\ g^{-1}$)	27.64	5.56
Pore volume ($cm^3\ g^{-1}$)	0.21	0.02
Mean pore diameter (nm)	30.6	11.9