Supplementary Information for

Bimetallic Coordination Polymer as a Promising Anode

Material for Lithium-Ion Batteries

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Experimental details

Synthesis of Co-Zn-MOF and BiCP: The Co-Zn-MOF was synthesized through a modified hydrothermal method according to a literature method.¹ Typically, 2.578 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 1.289 mmol Zn $(NO_3)_2 \cdot 6H_2O$, 3.867 mmol of terephthalic acid were dissolved in a 60 mL mixed solvent (dimethyl formamide/ ethanol = 4 : 1). After thoroughly mixing, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and placed in an oven at 105 °C for 20 h. After the autoclave was cooled down naturally to room temperature in the fumehood, the resultant crystal was collected by centrifugation, washed with DMF and EtOH for several times. The purple powder of Co-Zn-MOF was obtained after drying in a vacuum oven at 110 °C for 12 h. Subsequently, the as-formed Co-Zn-MOF was soaked with distilled water for 12 h, and the final product of BiCP was obtained after dried at 110 °C for 4 h.

Synthesis of Co-MOF-71: Typically, $Co(NO_3)_2 \cdot 6H_2O$ (3.867 mmol) and terephtalic acid (3.867 mmol) were dissolved in 60 mL mixed solvent (dimethyl formamide/ ethanol = 4 : 1). After thoroughly mixing, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and placed in an oven at 105 °C for 20 h. After the autoclave was cooled down naturally to room temperature in a fumehood, the resultant crystal was collected by centrifugation, washed thoroughly with DMF and EtOH. Finally, the purple powder of Co-MOF-71 was obtained after drying in a vacuum oven at 110 °C for 12 h.

Synthesis of Zn-MOF-5: Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (3.867 mmol) and terephtalic acid (3.867 mmol) were dissolved in 60 mL mixed solvent (dimethyl formamide/ ethanol = 4 : 1). After thoroughly mixing, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and placed in an oven at 105 °C for 20 h. After the autoclave was cooled down naturally to room temperature in a fumehood, the resultant crystal was collected by centrifugation, washed thoroughly with DMF and EtOH. Finally, the white powder of Zn-MOF-5 was obtained after drying in a vacuum oven at 110 °C for 12 h.

Materials Characterization: XRD patterns were collected using a Holland Panalytical PRO PW3040/60 Diffractometer with high-density Cu-K α radiation (V = 30 kV, I = 25 mA, λ =1.5418 Å). Internal structures of the samples were studied using TEM (JEOL JEM-2100F). XPS measurements were performed on a Perkin-Elmer PHI 5000C

ESCA spectrometer. The nitrogen adsorption isotherm was measured at 77 K with an ASAP 2020 Accelerated Surface Area and Porosimetry System (Microeritics, Norcross, GA) and the specific surface area was determined by the Brunauer–Emmett–Teller (BET) method. ICP test was performed on Thermo IRIS Intrepid II XSP Spectrometer. Solid-state NMR (ssNMR) experiments were performed on a Bruker AVANCE III spectrometer equipped with 9.40 T widebore supercoducting magnet, at Larmor frequencies of 400.1 MHz and 100.6 MHz for ¹H and ¹³C, respectively. Commercial Bruker double-resonance 4-mm MAS probes and 4 mm ZrO₂ rotors were used for all experiments. The ¹³C chemical shifts were determined from the carbonyl carbon signal ($\delta_{iso} = 176.03$ ppm) of glycine relative to tetramethylsilane (TMS).

Electrochemical measurements: Firstly, to keep the same water immersion time, Co-Zn-MOF, Super-P carbon black (CB, conducting additive) and carboxymethyl cellulose (CMC, binder), with a weight ratio of 80:15:5, were homogenously mixed in distilled water to produce slurry. Co-Zn-MOF was transformed to BiCP after water immersion for 12 h with CB and CMC. Secondly, the obtained slurry was coated onto a piece of copper foil using a doctor blading method, dried at 110 °C in vacuum oven for 4 h, and then punched into round plates (diameter of 14.0 mm) as the anode electrodes. The loading density of the active materials is calculated as $2.0 \sim 2.5 \text{ mg/cm}^2$. Finally, the asprepared anode, a Celgard 2325 separator (diameter of 19.0 mm), a pure lithium counter electrode, electrolyte of 1M LiPF₆ in EC-DEC-EMC (1:1:1 vol %), and the other components of the coin-type cell were assembled into a coin cell (CR2032) in an argon filled glove box with oxygen and water less than 1 ppm. The assembled coin-type cells were aged for at least 12 h before electrochemical test. Galvanostatic charge-discharge cycles were performed using a LAND 2001A battery test system in the voltage range of 0.01-3 V (vs. Li/Li⁺). Cyclic voltammetry (CV) was performed using an electrochemical workstation (AUTOLAB PGSTAT302N) between the voltage ranges of 0.01-3 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (ESI) measurements tests were also carried out on an electrochemical workstation (AUTOLAB PGSTAT302N) with the frequency range of 10^4 Hz to 10^{-2} Hz.



 δ_{13C} (ppm) Figure S1. ¹³C CP MAS NMR spectra (9.40 T, 8 kHz MAS) of (a) Zn-MOF and (b) Co-MOF, Co-Zn-MOF, BiCP, acquired with a contact time of 2 ms. Spectrum (a) was acquired with signal averaging over 2048 transients using a 3 s recycle interval. Asterisks denote spinning sidebands. Spectra (b) were acquired with signal averaging over 81920 transients using a 0.8 s recycle interval. Due to the interactions between ¹³C nuclei and unpaired electrons in paramagnetic Co²⁺, the ¹³C CP MAS NMR spectra of Co²⁺-bearing MOF show wider lines compared with Zn-MOF. Besides, the line shape of BiCP is different from Co-Zn-MOF, from which different structures were determined.



Figure S2. (a) High-resolution Co 2p and (d) Zn 2p XPS spectra of Co-Zn-MOF, from which the existence form of Co^{2+} and Zn^{2+} were also determined.



Figure S3. (a and b) EDS spectra and corresponding element analysis of Co-Zn-MOF, BiCP. (c-f) EDX mapping images of Co-Zn-MOF from selected region. The two samples were composed of Co, Zn, O and C. The signal of Cu came from the conducting layer of Cu used.



Figure S4. Nitrogen adsorption/desorption isotherms of (a) Co-Zn-MOF and (b) BiCP.



Figure S5. Cyclic voltammetry (CV) curves for the BiCP electrode at a scan rate of 0.1 mV s⁻¹ in the voltage window of 0.01V-3.0V vs Li/Li⁺. The CV curves for the BiCP particles exhibit two well-defined cathodic peaks, one of them may be attributable to Co^{2+} reduction, and the other may be associated with Zn²⁺ reduction. For the anodic scan, a sharp peak is observed around 1.16V vs Li/Li⁺, also containing two shoulders at lower (~0.55V) and higher (~1.92V) voltages, suggesting multistep processes. The observation is consistent with galvanostatic charge-discharge profiles.



Figure S6. (a) Cyclic voltammetry (CV) curves for Co-Zn-MOF at a scan rate of 0.1 mV s⁻¹ in the voltage window of 0.01 V-2.0 V vs Li/Li⁺. (b) Cycle performance of Co-Zn-MOF at a current rate of 100 mA g⁻¹ in the voltage window of 0.01 V-3.0 V vs Li/Li⁺. Samples of electrochemically active materials were mixed with carbon black (Super P) and polyacrylic acid (PAA) in a 7:2:1 weight ratio, N-methyl-2-pyrrolidone (NMP) was used as the solvent. The CV curves for the Co-Zn-MOF only exhibit one broad cathodic peak (~0.64V for the 1st scan and ~0.75V for the 2nd scan), suggesting different electrochemical reaction kinetics from BiCP. Besides, after 100 cycles, the Co-Zn-MOF electrode only maintained a charge capacity of 760 mAh g⁻¹, which is much lower than BiCP.



Figure S7. (a) The charge-discharge curves of BiCP half cells at different current densities. (b) EIS spectra for Co-Zn-MOF and BiCP at 100th cycles with a current desity of 100 mA g⁻¹. It is clear that the impedance associated charge-transfer resistance in BiCP is lower than that of Co-Zn-MOF, demonstrating a better conductive capability of the BiCP electrode.

References

1 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O. M. Yaghi, J. Am. Chem. Soc., 2005, 127, 1504–1518.