Supporting Information

Nickle-based metal-organic framework as a new cathode for chloride ion

battery with superior cycling stability

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Experimental Section

Synthesis of $[Ni(dpip)] \cdot 2.5DMF \cdot H_2O$, HKUST-1, $[Ni_3(btc)_2(bipy)_3(H_2O)_2] \cdot xDMF$ and $[Ni-(4Pyc)_2 \cdot DMF]$

The synthesis of [Ni(dpip)]·2.5DMF·H₂O was followed by our reported work.[S1] Typically, a mixture of NiSO₄·6H₂O (0.1 mmol, 26.2 mg), H₂dpip (0.05 mmol, 15.0 mg), N, N-dimethylformamide (DMF) (4 mL), CH₃CN (4 mL) and one drop of HCl (6 M) was sealed in a Teflon-lined (25 mL) at 130 °C for 72 h and cooled to 35 °C (8 h) .The green prism crystals obtained were isolated by filtration (45% yield based on nickel, Fig. S2), washed with DMF, and dried in air (30 min); crystal data: C₁₈H₁₀N₂NiO₄; Mr=376.99; Tetragonal; *I-4c2*; a=22.9846(9), b=22.9846(9), c=23.4908(12); V=12410.0(12) Å³; D_{calcd} =0.807 g·cm⁻³; μ =0.639 mm⁻¹; 31579 total reflections, 5600 unique; T=158(2) K; GOF=1.036. The synthesis of HKUST-1, [Ni₃(btc)₂(bipy)₃(H₂O)₂]·*x*DMF and [Ni-(4Pyc)₂·DMF]by reported methods.[S2–S4]

Preparation of MOFs electrodes and electrochemical characterizations

The MOF material was mixed with 30 wt.% Super P 60 conductive agent and 10 wt.% polyvinylidene fluoride (PVDF) binder in a mortar for 60 min with N-Methylpyrrolidone (NMP) solvent. Then, the resulting homogenous slurry was coated on graphite paper collector (with negligible Cl storage capacity in Fig. S4) followed by drying in vacuum at 100 °C for 24 h before assembling and the mass loading of active materials was approximately 1.5 mg cm⁻². CIBs in this work based on CR2032 type coin cells were composed of Li-metal anode and ionic liquid electrolyte of 0.5 M 1-butyl-1-methylpiperidinium chloride (BPy14Cl, 99 %) in the propylene carbonate. The electrochemical measurements were carried out on the LANHE CT3002AU battery testing devices and CHI 760e electrochemical workstation.

Materials characterization

X-ray diffraction (XRD) of [Ni(dpip)]·2.5DMF·H₂O was recorded using a Bruker diffractometer in the range between 5° and 45° at a scanning rate of 10° min⁻¹ with Cu K α radiation (λ =0.154 nm). The morphology of the Ni-MOF sample was obtained by field scanning electron microscopy (SEM) instrument (Zeiss SUPRA 55) with an operating voltage of 20 kV. The transmission electron microscopy (TEM) images were acquired through a FEI TalosF200S microscope at an acceleration voltage of 200 kV, equipped with an energy dispersive X-ray attachment. Thermogravimetric analyzer (TGA) was carried out on a PCT-1A thermal analysis system at nitrogen atmosphere a range from 25 °C to 800 °C (heating rate: 10 °C min⁻¹). X-ray photoelectron spectra (XPS) were carried out by a Thermo VG Escalab 250 X-ray photoelectron spectrometer at a pressure of about 2×10⁻⁹ Pa with Al K α (1486.6 eV) X-rays as the excitation source. X-ray absorption spectroscopy (XAS) measurements of Ni K-edge was obtained at the beam line 1W1B of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). And the IFFEFIT data analysis package (Athena, Artemis, Atoms, and FEFF6) was used for data analysis. In the *ex-situ* XAS measurement, the Ni k-edge cathodes were charged or discharged until a specified voltage at a low current density of 50 mA g^{-1} . The electrode samples were removed from the cell in the glovebox and dipped in PC for 2 min to remove the residual electrolyte. To avoid contamination of moisture or oxygen, samples were wrapped with Kapton in glovebox before testing. For the *ex-situ* XRD and XPS study for electrodes, the cells ended at the specified voltages are disassembled in the glovebox and the needed cathodes were washed three times with PC and acetone to remove the residual electrolyte and glass fiber separator. Then, the cathode materials were scraped off the current collector and sealed in stainless-steel bottles in glovebox to avoid contamination by moisture or oxygen before testing.

Computational Methods

First-principles calculations were performed by DFT calculations implemented in the Vienna ab initio simulation Package (VASP),[S5] with plane wave basis set with an energy cutoff of 400 eV, projector augmented wave (PAW) pseudopotentials[S6] and the generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof (GGA-PBE) for exchange-correlation functional,[S7] Grimme's semiempirical DFT-D3 scheme for the dispersion correction.[S8] The model structures were fully optimized for the cell and ionic degrees of freedom using the convergence criteria of 10^{-5} eV for electronic energy and 10^{-2} eV/Å for the forces on each atom. The Brillouin zones were sampled at Gamma point only. The transition states were determined with the climbing image nudged elastic band (Cl-NEB) method.[S9] Seven images were generated between the initial state and the final state by a linear interpolation of the coordinates. The other atoms were frozen in MOF structures during the migration of chlorine in order to reduce the computational cost.



Fig. S1 TG curve of the $[Ni(dpip)] \cdot 2.5DMF \cdot H_2O$.



Fig. S2. The digital photograph of $[Ni(dpip)] \cdot 2.5DMF \cdot H_2O$.



Fig. S3. XPS survey spectrum of [Ni(dpip)]·2.5DMF·H₂O.



Fig. S4. Cycling performance of graphite paper current collector in CIB at the similar surface current density as Ni(dpip) cathode.



Fig. S5. CV curves of the Ni(dpip) cathode with the pseudocapacitive fraction shown by the orange area at scan rates of (a) 0.1 mV s⁻¹, (b) 0.2 mV s⁻¹, (c) 0.3 mV s⁻¹, (d) 0.5 mV s⁻¹ and (e) 0.8 mV s⁻¹.



Fig. S6. Charge/discharge curves of the Ni(dpip) electrode at different cycles.



Fig. S7. Electrochemical performance of the Li/LiPF₆-EC-DMC-PC/Ni(dpip) cell at current density of 150 mA g^{-1} .



Fig. S8. Charge/discharge curves of Ni(dpip) electrode in the LIB at current density of 150 mA g⁻¹.



Fig. S9. Electrochemical performance of the $Li/NiSO_4$ LDH cell at current density of 150 mA g⁻¹.



Fig. S10. Electrochemical performance of the Li/4,6-di(pyridin-4-yl) isophthalic acid ligand cell at current density of 150 mA g^{-1} .



Fig. S11. SEM images of Li anode after 100 charge-discharge cycles.



Fig. S12. PXRD patterns of the Ni(dpip) cathode at different charge-discharge depths.



Fig. S13. Normalized XANES spectra of Ni k-edge in Ni(dpip) electrode at different voltage states.



Fig. S14. PXRD patterns of the Li anode at fully (a) charged and (b) discharge state.



Fig. S15. PXRD pattern of Ni(dpip) electrode material after 200th cycles.



Fig. S16. (a) The structure and (b) CIB electrochemical performance of HKUST-1 at current density of 150 mA g^{-1} .



Fig. S17. (a) The structure and (b) CIB electrochemical performance of $[Ni_3(btc)_2(bipy)_3(H_2O)_2] \cdot xDMF$ at current density of 150 mA g⁻¹.



Fig. S18. (a) The structure and (b) CIB electrochemical performance of $[Ni-(4Pyc)_2 \cdot DMF]$ at current density of 150 mA g⁻¹.



Fig. S19. Schematic illustration for a single charge step in GITT measurement.

Galvanostatic intermittent titration technique (GITT) measurement was carried out to calculate the diffusion coefficient of bromide ions ($D_{CI^{-}}$) in Ni(dpip) cathode based on the following equation:

$$D_{Cl^{-}} = \frac{4}{\pi\tau} \frac{mV}{(MA)^2} (\frac{\Delta Es}{\Delta Et})^2$$
(1)

where *m* (g) and *M* (g mol⁻¹) are assigned to the loading mass and molecular weight of Ni(dpip); *V* (cm³ mol⁻¹) represents the molar volume of materials deduced from crystallographic data; τ (s) is constant current pulse time; *A* (cm²) is the surface area of electrode; ΔE_s (V) and ΔE_t (V) denote the change of steady-state voltage and the total change of the voltage during a constant pulse *t* for a single-step GITT curve, respectively. In this work, the charge and rest time was 10 mins and 60 mins, respectively, and the applied current is 25 mA g⁻¹.

Cathode	Current density (mA g ⁻¹)	Stable discharge capacity (mAh g ⁻¹)	Cycling life	Capacity decay ratio (%/cycle)	Reference
Ni(dpip) MOF	150	155	500	0.026	This work 1
Ni(dpip) MOF	300	123	200	0.176	This work 2
CoFe-Cl LDH	100	160	100	0.357	[10]
BiCl ₃	3	74	3	19.37	[11]
FeOC1	10	58	30	2.125	[12]
PPy/CNT	10	90	40	0.593	[13]
PANI/CNT	10	70	50	0.087	[14]
NiFe-Cl LDH	100	101	800	0.091	[15]
FeOOH	100	122	100	0.684	[16]
FeOC1-PPy	10	155	30	0.570	[17]

Table S1. The electrochemical performance of reported CIBs cathodes.

$Sb_4O_5Cl_2$ 10	60	120	1.002	[18]
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