Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

Amorphization and disordering of metal–organic framework materials for rechargeable batteries by thermal treatment

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Experimental

Synthesis of MOF-Co: $Co_3(BTC)_2\cdot 12H_2O$ was prepared based on a reported Procedure.[30] Typically, 10 mmol $Co(NO_3)_2\cdot 6H_2O$ and 5 mmol 1, 3, 5-benzenetricarboxylic acid were introduced into 60 mL mixed solvent (N,N-dimethylformamide : deionized water : ethanol = 1:1:1, v/v/v). After two min of stirring, the resulting suspension was transferred into a 100 mL Teflon-lined stainless steel autoclave and placed in an oven at 85 ℃ for 20 h. After that, the reactor was taken out and gradually cooled down to room temperature. The resulting large rod-like red single crystals were collected by filtration, washed with deionized water and ethanol, then air-dried, and finally grinded into powders for further use. The evacuated MOF-Co was prepared by a heat post-treatment of the pristine sample at 200 ℃ under laboratory air for 4 h with a ramp rate of 5 ℃ min^{-1}. The red color which appeared initially was changed to blue after activation.

Materials Characterization: XRD patterns were collected using a Holland Panalytical PRO PW3040/60 Diffractometer with high-density Cu-Kα radiation (V = 30kV, I = 25 mA, λ=1.5418 Å). Thermogravimetric analysis (TGA) was carried out using STA 449 F3 Jupiter® simultaneous thermo-analyzer at a ramping rate of 10 ℃min^{-1} from room temperature to 800 ℃. N_2 sorption isotherms were measured at 77 K using an ASAP 2020 Accelerated Surface Area and Porosimetry System (Microeritics, Norcross, GA). The XPS measurements were performed on a Kratos Axis Ultra DLD spectrometer. Field-emission scanning electron microscopy (FESEM) images were taken o on a Hitachi S-4800 system (HITACHI, Japan) operating at 10 kV, 100 μA.

Electrochemical measurements: For energy storage studies, Coin-type cells (CR2032) were assembled in the configuration of Li/separator/MOF-Co in an argon filled glove box with oxygen and moisture level less than 0.1 ppm. The Li metal foil was used as the counter electrode and reference electrode and 1M $LiPF_6$ in ethylene carbonate (EC) / diethylene carbonate (DEC) / ethyl-methyl carbonate (EMC) (1 : 1 : 1 (V:V:V)) as the electrolyte. The Celgard 2325 membrane (diameter of 19.0 mm) was used as a separator between the electrodes. Working electrodes were prepared by homogenously mixing a power sample, Super-P carbon black and polyacrylic acid (PAA) binder in N-methyl-2-pyrrolidone (NMP) at a 70:20:10 weight ratio. Then, the resultant lurry was spread onto a copper foil using a doctor blading method, dried at 65 ℃ in a vacuum oven for at least 24h, and finally punched into round plates with 14.0 mm in diameter. The active material content in the electrode was around 2.0 mg. The assembled coin-type cells were aged for ~ 24 h before electrochemical testing. Galvanostatic charge-discharge cycles were was recorded on a multichannel LAND cycler (Wuhan Kingnuo Electronic Co., China) in the voltage range of 0.01-3 V. CV measurement was performed using a CHI 660a electrochemical workstation (ChenHua Instruments Co., China) within the voltage range of 0.001-3 V at a scan rate of 0.2 mV s^{-1}. Electrochemical impedance spectroscopy (ESI) measurements were also carried out on an electrochemical workstation (ChenHua Instruments Co., China) with the frequency range of 1×10^5 Hz to 1×10^{-2} Hz.

Table S1. MOF [a] designed with the consideration of improving structure stability and [b] those without degassing as LIB anodes

Metal Organic frameworks	Voltage (V vs Li^+/Li)	Current Density (mA g^{-1})	Specific Capacity (mA h g^{-1})	Cycle Number	Ref.
[a]$Zn(IM)_{1.5}(abIM)_{0.5}$	0.01-3.0	100 and 400	190 and ~ 75	200 cycles	10
[a]Zn-MOF-crown	0.01-3.0	500	239	500 cycles	8
[a]$Ni\text{-}Me_4bpz$	0.01-3.0	50	120	100 cycles	11
[a,b]$Mn(3,5\text{-}PDC) \cdot 2H_2O$	0.05-3.0	300	310	115 cycles	13
[b]$[Mn_2(2,3\text{-}pdc)_2(H_2O)_3]_n \cdot 2nH_2O$	0.05-3.0	100	457.2	100 cycles	17
[b]$[Mn\text{-}(tfbdc)(4,4'\text{-}bpy)(H_2O)_2]$	0.01-2.5	50	390	50 cycles	18
[b]Mn-BTC (~ 22.28% solvents occluded inside the pores)	0.01-2.0	103 and 206	576 and ~ 400	100 cycles	9
[b]$Zn_4O(BTB)_2(DEF)_5(H_2O)_1$	0.05-1.6	50	~ 105	50 cycles	7
[b]$Li_4(H_2O)_4(BTCA)$	0.01-3.0	~ 100	93	30 cycles	19
[b]$[Li_6(pda)_3] \cdot 2EtOH$	0.2-2.0	30	160	50 cycles	20
[b]Asp-Cu (~ 20% crystal water)	0.01-3.0	50	233	200 cycles	21
[b]Ni-PTA (~ 10% solvated water molecules)	0.01-3.0	100	620	100 cycles	22

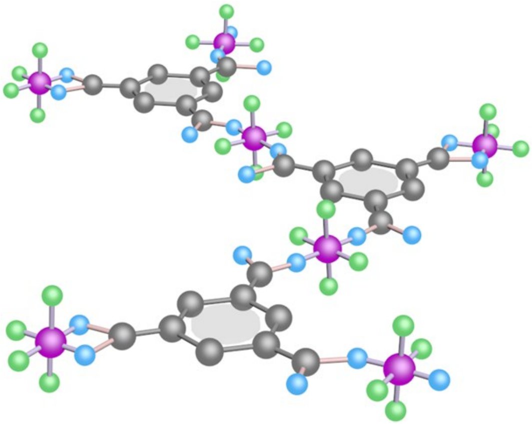

Figure S1. The Co-BTC chain, including the asymmetric unit, present as the building block in crystalline $Co_3(BTC)_2·12H_2O$. Color scheme: Co, purple; C, gray; carboxylate O, azure; water ligand O, light green (H atoms are omitted for clarity).

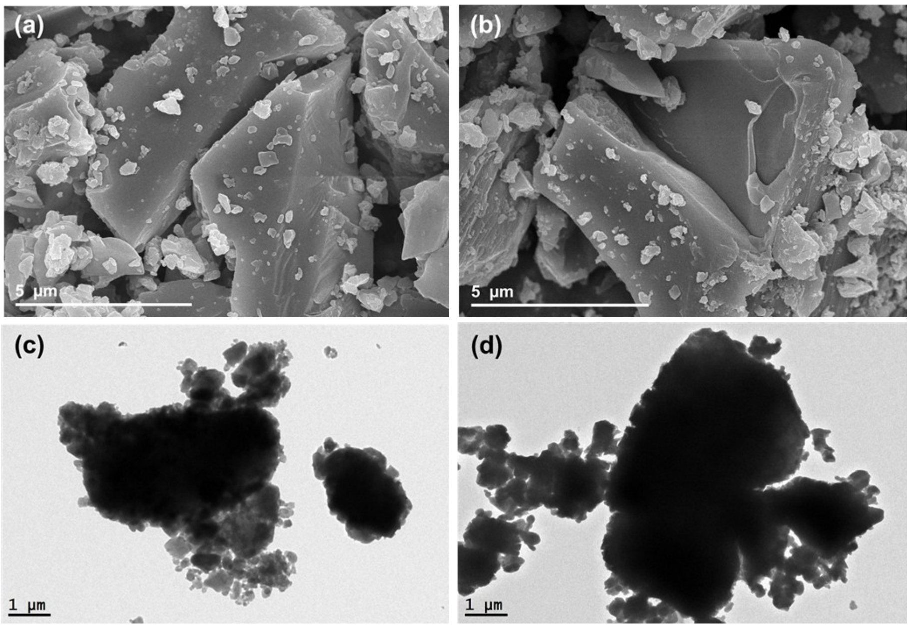

Figure S2. SEM and TEM images of the (a, c) as-synthesized and (b, d) evacuated (activated) MOF-Co powders.