Supporting information

Zr-Based-MOF Composite Electrode Design Enabling Uniform and Dense Lithium Deposition through Tuned Conductivity

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Experimental Section

Material characterization

The morphologies of the samples were examined via scanning electron microscopy (SEM, TESCAN, VEGA3). For a more detailed analysis of the microstructure, transmission electron microscopy TEM (JEOL, JM-2100F) was performed at the Korea Basic Science Institute (KBSI), Daegu Center. The crystallographic structure of the synthesized materials was analyzed using X-ray diffraction (XRD, X's pert Pro MPD) at KBSI Daegu center, employing Cu-K radiation ($\lambda = 1.54$ Å). Thermogravimetric analysis (TGA, Pyris 1, PerkinElmer) was conducted for carbonized derivative of MOF-808 (C-MOF-808) under air from 0 to 800 °C. X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo U.K), with a monochromatic Al K_α X-ray source, was utilized at Yonsei center for Research Facilities (YCRF) to investigate surface chemical states. Raman spectroscopy (LabRAM HR Evolution Visible_NIR, HORIBA) with a 633 nm He-Ne laser was used to analyze the vibrational modes of the samples at the KAIST Analysis Center for Research Advancement (KARA). The specific surface area and pore size distribution were determined from N_2 adsorption-desorption isotherms using the Brunauer–Emmett–Teller (BET, ASAP2460, Micromeritics) method. Finally, the electrical conductivity of the electrodes was measured using a four-point probe (AiT, CMT-SR2000N) in the range of 5 μS cm^{-1} to 100 kS cm^{-1}.

Electrochemical measurement

All CR2032 type coin cells were assembled in an Ar-filled glove box. Electrochemical measurements were performed using a battery analyzer (WonATech, WBCS-3000s cycler). To prepare the lithium metal host electrodes, a slurry was formed by mixing sample powders of MOF-808 and C-MOF-808 in particular ratios with polyvinylidene fluoride (PVDF) in a mass ratio of 9:1, using N-methyl-2-pyrrolidone (NMP) as the solvent. The slurry was then uniformly coated onto Cu foil using a doctor blade, followed by drying overnight at 50 °C. Circular electrodes with a diameter of 1.4 cm were punched, with the active material loading controlled in the range of 1.3-1.6 mg cm^{-2}. The electrolyte used in both asymmetrical and symmetrical cell tests consisted of 1.0 M lithium bis (trifluoromethane) sulfonamide (LiTFSI) dissolved in a 1:1 (v/v) mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL), supplemented with 0.3 M $LiNO_3$. For SEI stabilization and removal of surface contaminants, two initial cycles were conducted at 1.0 mA cm^{-2} within a potential range of 0.0-1.0 V at 1.0 mA cm^{-2} prior to the asymmetric cell tests. For symmetric and full cell tests, 5.0 mAh cm^{-2} amount of lithium was pre-deposited onto the electrodes at a current density of 2.0 mA cm^{-2}. For full-cell assembly,

$LiFePO_4$ (LFP) cathodes were prepared by blending LFP powder, PVDF, and Super-P conductive agent at a weight ratio of 90:5:5 and dispersing them in NMP. The slurry was coated onto Al foil, dried at 60 °C, and punched into a circle with a diameter of 1.4 cm. The electrolyte for the full cells consisted of 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) in a 1:2:1 (v/v/v) ratio. Additional full cell cycling tests were conducted using ether-based electrolytes identical to those employed in the asymmetrical and symmetrical cell experiments. The LFP cathode loading was maintained between 5.8 – 6.5 mg cm^{-2}, and the N/P ratio of the full cells were calculated to range from 4.5 to 5.0, based on the theoretical capacity of LFP (1.0 C = 170.0 mAh g^{-1}). For full cells utilizing ether-based electrolytes, N/P ratio was adjusted to approximately 4.1. The full cells were cycled between 2.5 and 3.7 V at various current densities.

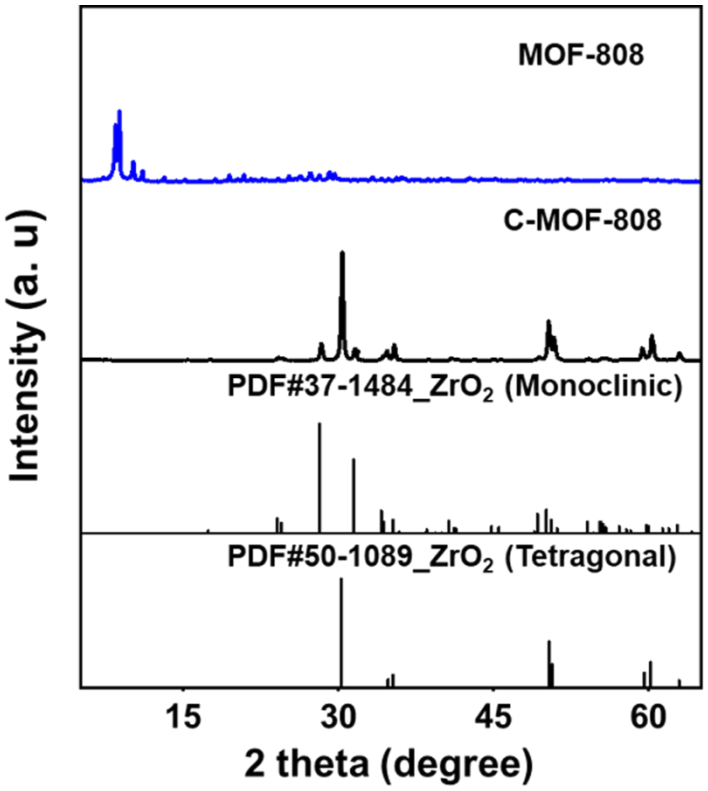

Fig. S1. XRD patterns of MOF-808 and C-MOF-808 powders.

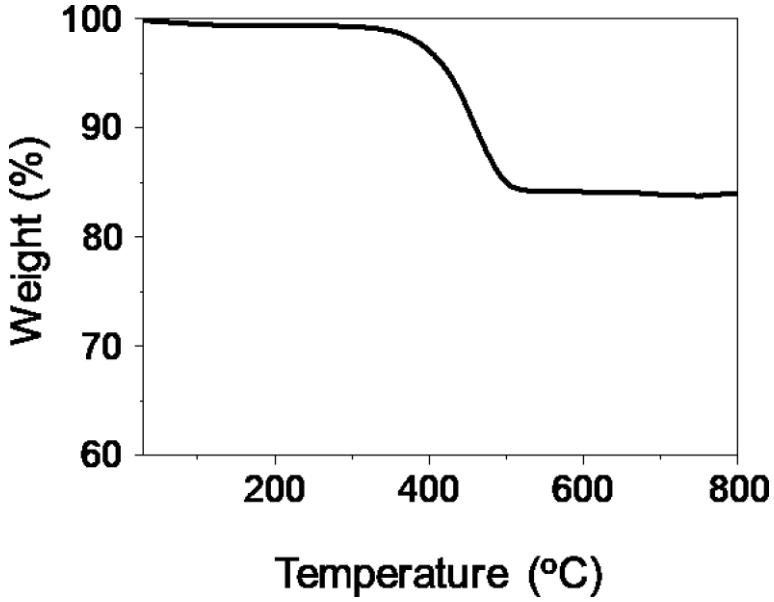

Fig. S2. TGA curve of C-MOF-808 under air atmosphere.

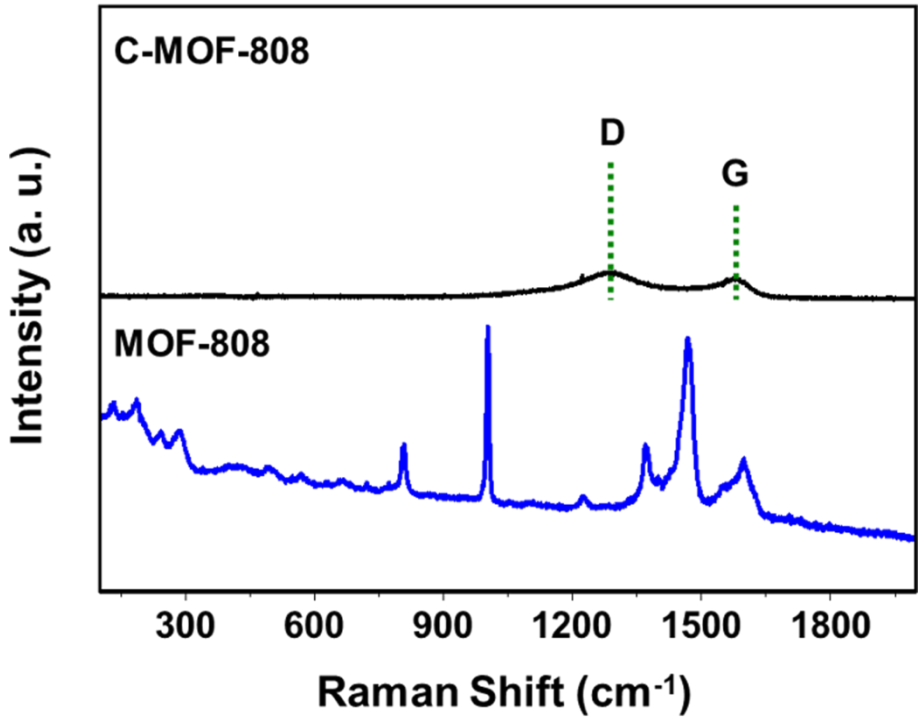

Fig. S3. Raman spectra of MOF-808 and C-MOF-808 powders.

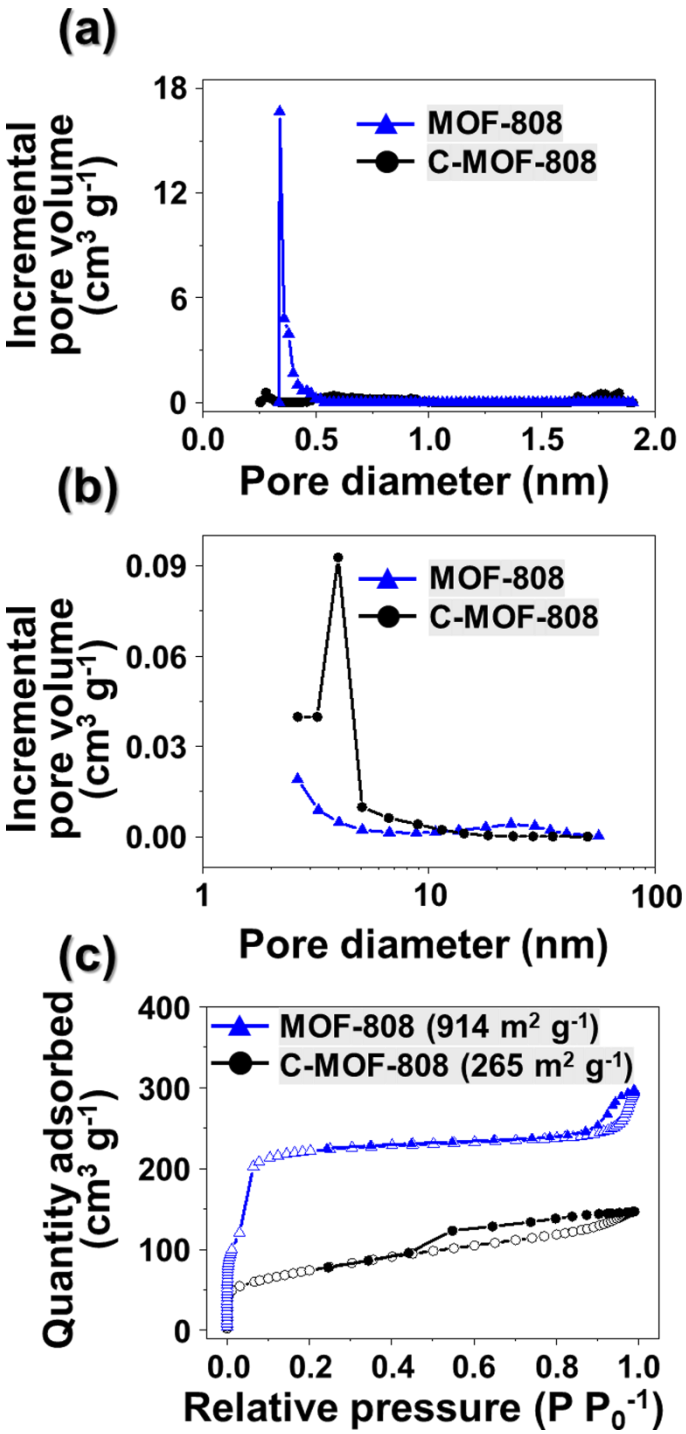

Fig. S4. Micropore and mesopore size distribution and specific surface area analysis of MOF-808 and C-MOF-808 using (a) the MP method, (b) the BJH method, and (c) N_2 adsorption-desorption isotherms, respectively.

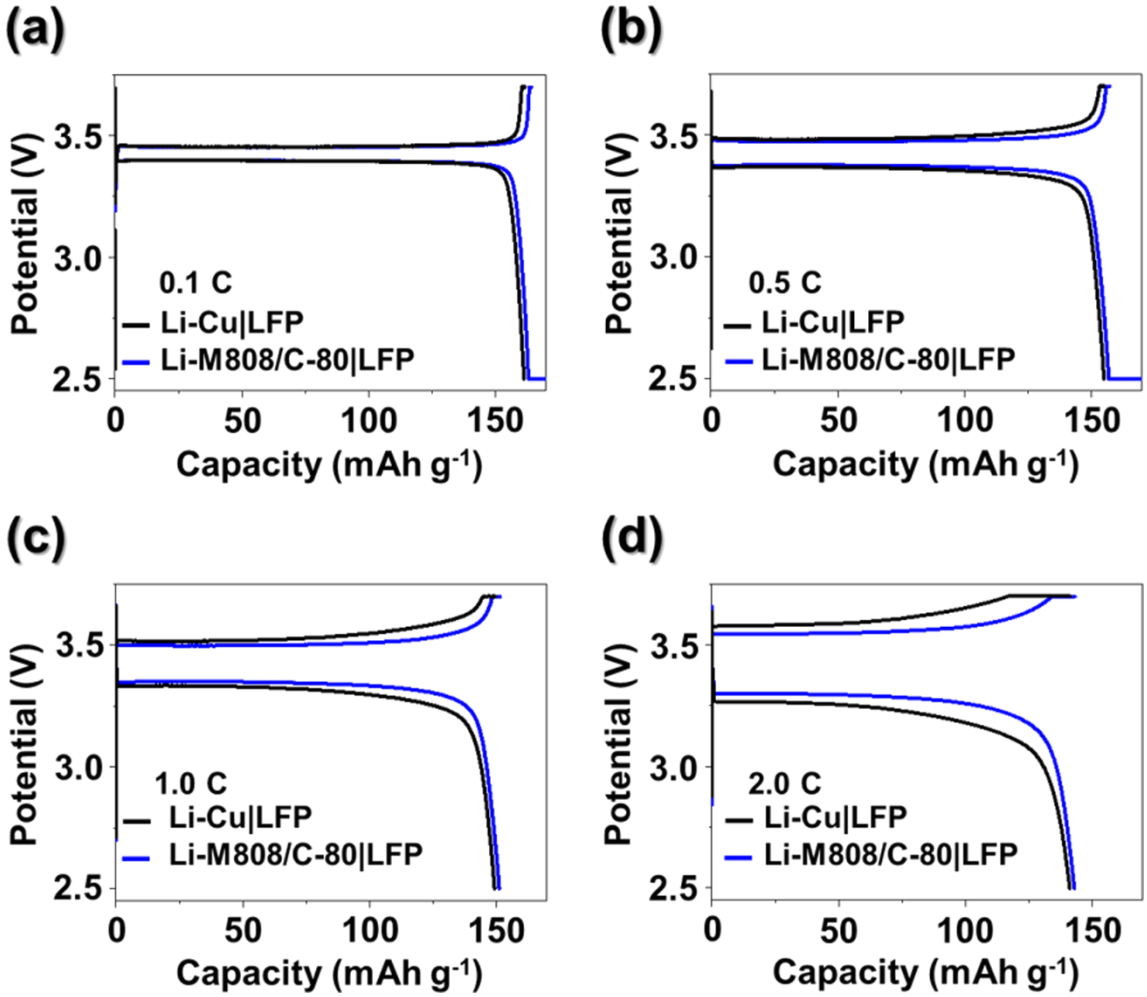

Fig. S5. Voltage profiles of Li-Cu|LFP and Li-M808/C-80|LFP full cells at current densities of (a) 0.1, (b) 0.5, (c) 1.0, and (d) 2.0 C.

Table S1. Performance comparison of asymmetric cell tests.

Samples	Asymmetric Test Capacity	Asymmetric Test Current Density	Asymmetric Test Cycle	Asymmetric Test Coulombic Efficiency	Ref
M808/C-80	**1.0 mAh cm^{-2}**	**2.0 mA cm^{-2}**	**150 cycles**	**97.0 %**	**This work**
SiC/CC	1.0 mAh cm^{-2}	2.0 mA cm^{-2}	100 cycles	90.0 %	[S1]
Cu-Au-ZnO-PAN-ZnO	1.0 mAh cm^{-2}	0.5 mA cm^{-2}	120 cycles	99.0 %	[S2]
NHCF/CN/ZnO	1.0 mAh cm^{-2}	2.0 mA cm^{-2}	100 cycles	97.5 %	[S3]
Li‖CuBIB-Gly/Cu	1.0 mAh cm^{-2}	1.0 mA cm^{-2}	100 cycles	84.7 %	[S4]
COF-LZU1	2.0 mAh cm^{-2}	1.0 mA cm^{-2}	100 cycles	84.7 %	[S5]

Table S2. Electrical conductivities of electrodes with different ratios of MOF-808 and C-MOF-808.

	MOF-808	M808/C-50	M808/C-80	C-MOF-808
Electrical conductivity ($S\ cm^{-1}$)	Out of range (Too low)	1.3	8.3	20.2

Table S3. Performance comparison of symmetric cell tests.

Samples	Cycling Capacity	Cycle Life	Voltage Hysteresis	Ref
M808/C-80	**1.0 mAh cm^{-2}**	**1250 h**	**18.5 mV**	**This work**
SiC/CC	1.0 mAh cm^{-2}	1000 h	28.0 mV	[S1]
Co_3O_4-NF	1.0 mAh cm^{-2}	1000 h	30.0 mV	[S6]
ICDL	1.0 mAh cm^{-2}	1100 h	22.0 mV	[S7]
MOF-HCF	1.0 mAh cm^{-2}	1000 h	20.0 mV	[S8]
m-MOF/PP	1.0 mAh cm^{-2}	700 h	40.0 mV	[S9]
CuO NAs/CF	1.0 mAh cm^{-2}	500 h	40.0 mV	[S10]
ZnO/Carbon	1.0 mAh cm^{-2}	388 h	28.0 mV	[S11]

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