

## Supporting Information

### **Porous Framework Materials for Stable Zn Anode in Aqueous Zinc-Ion Batteries**

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Table S1. Electrochemical performance of MOFs/COFs-based Zn anode

Materials	Metal	Organic ligand	Maximum pore size, <sup>a</sup> BET surface area <sup>b</sup>	Morphology	Uses	Lifespan, Voltage hysteresis	( $\tau_{Zn^{2+}}$ ), $\sigma$	Ref
ZIF-8	Zn	2-methylimidazole	12 Å, 1,879 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Coating layer	30 mV, 1200 h at 2 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>		1
ZIF-8	Zn	2-methylimidazole	12 Å, 1,879 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Electrolyte additive	55 mV, over 560 h at 1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>		2
ZIF-8-500	Zn	2-methylimidazole	12 Å, 1,635 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Zn host	30 mV, 1.0 mA cm <sup>-2</sup> , 1.0 mAh cm <sup>-2</sup>		3
ZIF-L	Zn	2-methylimidazole	12 Å, 93 m <sup>2</sup> g <sup>-1</sup>	Leaflike shaped nanoparticles	Coating layer	26 mV, 800 h, 0.25 mA cm <sup>-2</sup> and 0.25 mAh cm <sup>-2</sup>	39.1 mS m <sup>-1</sup>	4
ZIF-7	Zn	benzimidazole	4 Å, 380 m <sup>2</sup> g <sup>-1</sup>	Tetragonal nanoparticles	Coating layer	28 mV, 3000 h, 0.5 mA cm <sup>-2</sup> , 0.5 mAh cm <sup>-2</sup>		5
Zn(BTC)	Zn	1, 3, 5- benzenetricarboxylate	14 Å, 1600 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Coating layer	40 mV, 800 h, 1 mA cm <sup>-2</sup> , 1 mA cmh <sup>-2</sup>		6
Zn(TCPP)	Zn	tetra-(4-carboxyphenyl) porphyrin		Nanoplates	Coating layer	50 mV, 1880 h, 5 mA cm <sup>-2</sup> , 0.5 mAh cm <sup>-2</sup>		7
Zn-stp-bpy	Zn	monosodium 2- sulfoterephthalate (stp) 4,4'-bipyridine (bpy)		Octahedral nanoparticles	Coating layer	40 mV, 5700 h at 2 mA cm <sup>-2</sup>	0.63, 0.68 mS cm <sup>-1</sup> at 30 °C	8
Zn[Fe (CN) <sub>6</sub> ] <sub>n</sub> ·nH <sub>2</sub> O	Zn	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>		Nanocubes	Coating layer	80 mV, 2100 h, 4 mA cm <sup>-2</sup> , 4 mA cm <sup>-2</sup>	0.88	9
Cu <sub>3</sub> (BTC) <sub>2</sub>	Cu	1,3,5-benzenetricarboxylic acid	14 Å, 1600 m <sup>2</sup> g <sup>-1</sup>	Nanocubes	Coating layer	20 mV, 700 h, 0.5 mA cm <sup>-2</sup>		10

UiO-66	Zr	terephthalic acid	8 Å, 1200 m <sup>2</sup> g <sup>-1</sup>	Octahedral nanoparticles	Coating layer	50 mV, 250 h, 1 mA cm <sup>-2</sup> , 0.5 mAh cm <sup>-2</sup>		11
Defective UiO-66 (D-UiO-66)	Zr	terephthalic acid	10 Å, 1470 m <sup>2</sup> g <sup>-1</sup>	Octahedral nanoparticles	Coating layer	66 mV, 1800 h, 1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	0.60, 6.90 mS cm <sup>-1</sup>	12
UiO-66-(COOH) <sub>2</sub>	Zr	1,2,4,5-benzenetetracarboxylic acid(BTEC)	6 Å, 519 m <sup>2</sup> g <sup>-1</sup>	Spherical nanoparticles	Coating layer	61 mV at 2 mA cm <sup>-2</sup> , 2 mAh cm <sup>-2</sup>	0.55, 1.91 mS cm <sup>-1</sup>	13
UiO-66-(COOH) <sub>2</sub>	Zr	1, 2, 4, 5-benzenetetracarboxylic acid (BTEC)	6 Å, 461.6 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Coating layer	50 mV, 240 h at 10 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	0.23	14
2D UiO-67	Zr	4,4'-biphenyl dicarboxylic acid	8 Å, 424 m <sup>2</sup> g <sup>-1</sup>	Hexagonal nanoflakes	Coating layer	30 mV, 800 h, 0.5 mA cm <sup>-2</sup> , 0.5 mA h cm <sup>-2</sup>	0.84, 2.65 mS cm <sup>-1</sup>	15
EDTA grafted MOF-808	Zr	1,3,5-benzenetricarboxylic acid	11.8 Å, 968.01 m <sup>2</sup> g <sup>-1</sup>	Octahedron nanoparticles	Coating layer	40 mV, 900 h, 2 mA cm <sup>-2</sup> , 2 mA h cm <sup>-2</sup> ; 30 mV, 300 h at 1 mA cm <sup>-2</sup> at 10 mA h cm <sup>-2</sup>	0.53	16
MOF-808	Zr	1,3,5-benzenetricarboxylic acid	18.4 Å, 1820 m <sup>2</sup> g <sup>-1</sup>	Octahedron nanoparticles	Solid electrolyte	100 mV, 360 h, 0.1mA cm <sup>-2</sup>	0.93, 2.1×10 <sup>-1</sup> mS cm <sup>-1</sup>	17
F-COF		2, 3, 5,6-tetrafluoroterephthaldehyde (TFTA)	20 Å, 723 m <sup>2</sup> g <sup>-1</sup> ,	Film	Coating layer	60 mV, 1700 h, 5 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	0.75, 24.19 mS cm <sup>-1</sup>	18
flexible DIP D COF films		1, 3, 5-tris (4-amino-phenyl) benzene (TAPB)	217.5 m <sup>2</sup> g <sup>-1</sup>	Film	Coating layer	36 mV, 420 h at 1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	0.56	19
		1,3,5-triphloroglucinol (TFP), 2,6-diaminoanthraquinone (DAAQ)						

3D-COOH-COF; OH-COF	succinic anhydride, OH-COF; tetra(4-formylphenyl) methane (TFPM), 3,3'-dihydroxybenzidine (DHBD)	13 Å, 121 m <sup>2</sup> g <sup>-1</sup> ; 16 Å 107.4 m <sup>2</sup> g <sup>-1</sup>	Film	Coating layer	50 mV, 2000 h, 1 mA cm <sup>-2</sup> , 1 mA h cm <sup>-2</sup> ; 60 mV, 1272 h, 1 mA cm <sup>-2</sup> , 1 mA h cm <sup>-2</sup>	0.82; 0.69, 0.26 mS cm <sup>-1</sup> ; 0.2 mS cm <sup>-1</sup>	20
AAn-COF	1,5-fiaminoanthraquinone	12 Å, 321 m <sup>2</sup> g <sup>-1</sup>	Nanofiber	Coating layer	20 mV, 1 mA cm <sup>-2</sup> , 1 mA h cm <sup>-2</sup>		21
MCOF-Ti <sub>6</sub> Cu <sub>3</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O H-pyrazole-4-carbaldehyde	23 Å, 152 m <sup>2</sup> g <sup>-1</sup>	Nanosheet	Coating layer	25 mV, at 1 mA h cm <sup>-2</sup> with 1 mA cm <sup>-2</sup>		22
2D alkynyl-based COF (COF-H)	1,3,5-tris(arylethynyl)benzene; 2,4,6-triformylphloroglucinol	12 Å, 984.2 m <sup>2</sup> g <sup>-1</sup>	Petal-like nanosheets	Coating layer	22.9 mV, 900 h at 3 mA cm <sup>-2</sup> , 1 mA h cm <sup>-2</sup>		23
TpPa-SO <sub>3</sub> H	2,5-diaminobenzenesulfonic acid; p-toluenesulfonic acid; 2,4,6-Triformylphloroglucinol		Film	Coating layer	25 mV, 900 h at 1 mA cm <sup>-2</sup> , 5 mA cm <sup>-2</sup>	18.56 mS cm <sup>-1</sup>	24
2D PI COF	tris (4-aminophenyl) amine(TAPA), 1,4,5,8-naphthalene tetracarboxylic dianhydride(NTCDA)		Film	Coating layer	92 mAh g <sup>-1</sup> ) at 0.7 A g <sup>-1</sup> , capacity remained 85% after 4000 <sup>th</sup> charge/discharge		25
TpPa-SO <sub>3</sub> Zn <sub>0.5</sub>	1,3,5-triformylphloroglucinol (Tp), 1,4-phenylenediamine-2-sulfonic acid	13 Å, 472 m <sup>2</sup> g <sup>-1</sup>	Nanoparticles	Solid electrolyte	500 h, 60 mV at 0.1 mA cm <sup>-2</sup> , 0.1 mA h cm <sup>-2</sup>	0.91, 22 mS cm <sup>-1</sup>	26

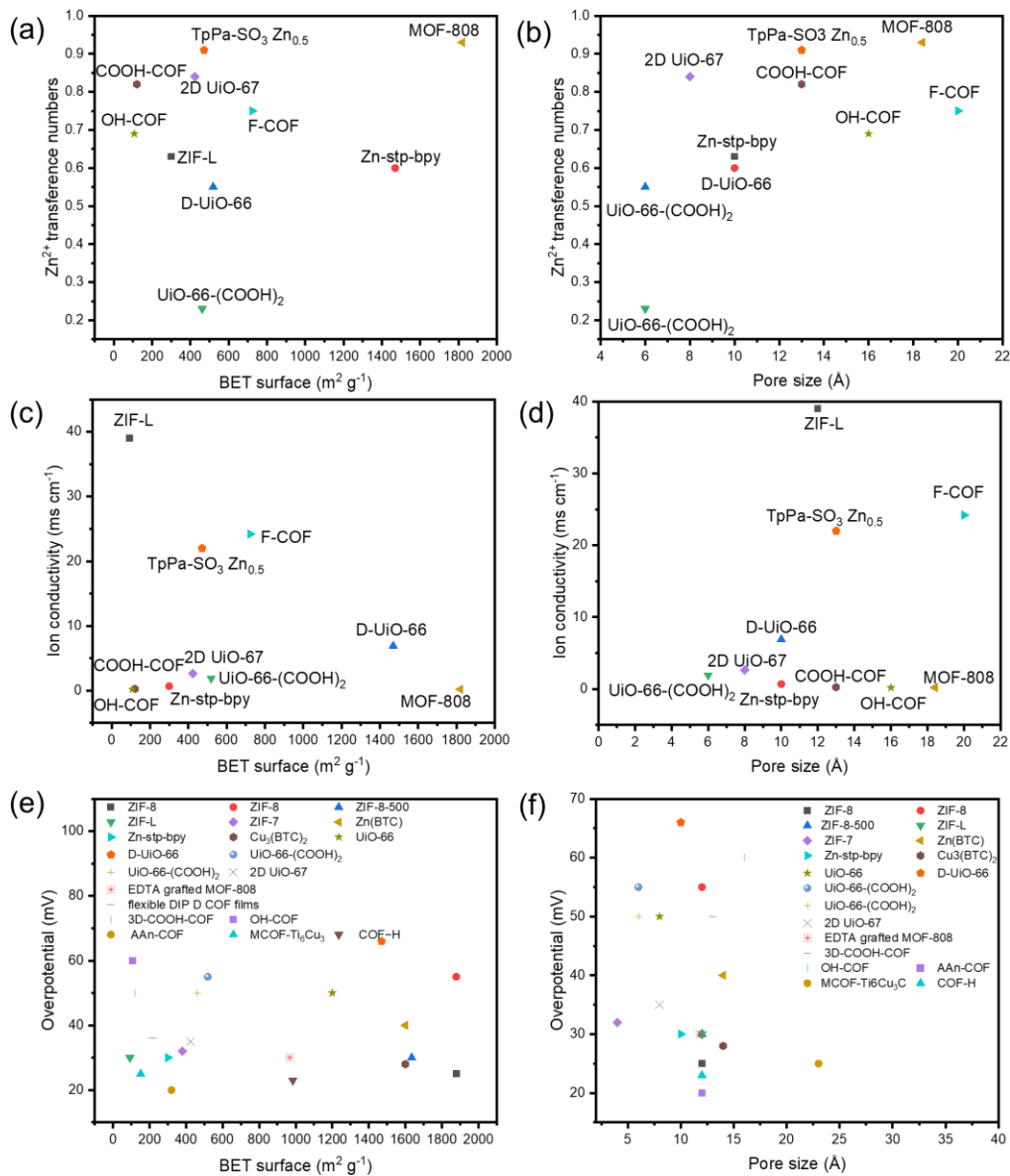
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HqTpCOF		SEI	700 h, 35 mV at 1 mA cm <sup>-2</sup> , 1 mAh cm <sup>-2</sup>	27
	2,5-diaminohydroquinone dihydrochloride (Hq),2,4,6- triformylphloroglucinol (Tp)			

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<sup>a</sup> Pore sizes of MOFs and COFs were estimated based on their crystal structures.

<sup>b</sup> BET surface areas of MOFs and COFs were calculated from N<sub>2</sub> adsorption measurements of the cited reference. If the BET surface area was not reported in the cited reference of ZIBs, the BET data were taken from other literature reporting the same MOFs/COFs.



**Fig. S1** (a) Relationship of BET surface and  $Zn^{2+}$  transference numbers. (b) Relationship of pore size and  $Zn^{2+}$  transference numbers. (c) Relationship of BET surface and  $Zn^{2+}$  conductivity. (d) Relationship of pore size and  $Zn^{2+}$  conductivity. (e) Relationship between BET surface of MOFs/COFs and overpotential of assembled symmetric cell with these MOFs/COFs protected Zn at a current density of 1 mA cm<sup>-2</sup>. (f) Relationship between pore size of MOFs/COFs and overpotential of assembled symmetric cell with these MOFs/COFs protected Zn at a current density of 1 mA cm<sup>-2</sup>.

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