

## Electronic Supplementary Information

### Well-Defined Dual Mn-Sites based Metal-Organic Framework to Promote CO<sub>2</sub> Reduction / Evolution in Li-CO<sub>2</sub> Batteries

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## Experimental Procedures

### Materials

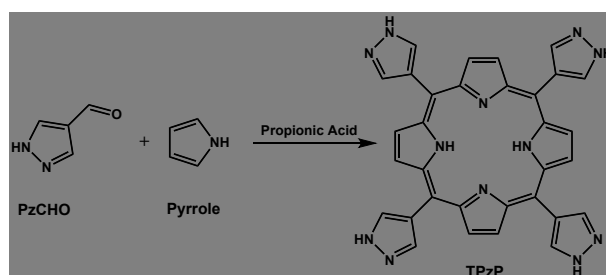
All chemicals, solvents, and gases were commercially available and used without further purification. Manganese sulfate tetrahydrate ( $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ), Manganese acetate tetrahydrate ( $\text{MnOAc}_2 \cdot 4\text{H}_2\text{O}$ ), cobalt sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), methane dichloride ( $\text{CH}_2\text{Cl}_2$ ), Triethylamine ( $\text{Et}_3\text{N}$ ), hydrochloric acid ( $\text{HCl}$ ) were purchased from China National Medicines Corporation LTD. Propionic acid was purchased from Alfa Aesar. Methanol ( $\text{MeOH}$ ), *N,N*-dimethylformamide (DMF), anhydrous *N*-methylpyrrolidone (NMP), 1*H*-Pyrazole-4-carboxaldehyde (PzCHO) were purchased from Adamas-beta. Pyrrole, Tritylchloride ( $\text{TrtCl}$ ) were purchased from TCI chemicals. High purity gas of  $\text{CO}_2$  (99.9995%) and Ar (99.9995%) were purchased by Nanjing Yehao.

### Instrumentation

Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku SmartLab diffractometer equipped with graphite monochromatized Cu  $K\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) at 40 kV and 150 mA. Fourier transform infrared spectroscopy (IR) was measured on alpha II (Bruker). Thermogravimetric analyses (TGA) were carried out on a Diamond DSC Pyris analyzer (Perkin-Elmer). 273K, 298K  $\text{CO}_2$  adsorption-desorption isotherms were determined by Autosorb IQ2 (Quantachrome Instruments). The electrochemical test was carried out with and CHI 660E (CHI Instruments). Nuclear magnetic resonance (NMR) data were collected on an ADVANCE III 400 MHz spectrometer (Bruker). Field emission scanning electron microscopy (SEM) was applied to investigate the morphology (JSM-7600F, JEOL). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out on an UltrafleXtreme MALDI-TOF (Bruker). The in-situ differential electrochemical mass spectrometry (DEMS) was performed using a commercial quadrupole mass spectrometer (Pfeiffer Vacuum, ThermoStar) and a customized Swagelok-type DEMS cell. The DEMS system was purged with 2 mL/min pure Ar for 10 h before charge, and the current density of charge reaction during DEMS tests is 50  $\mu\text{A}$ .

### Synthesis Method

#### Synthesis of 5,10,15,20-Tetra(1*H*-pyrazol-4-yl)porphyrin (TPzP).

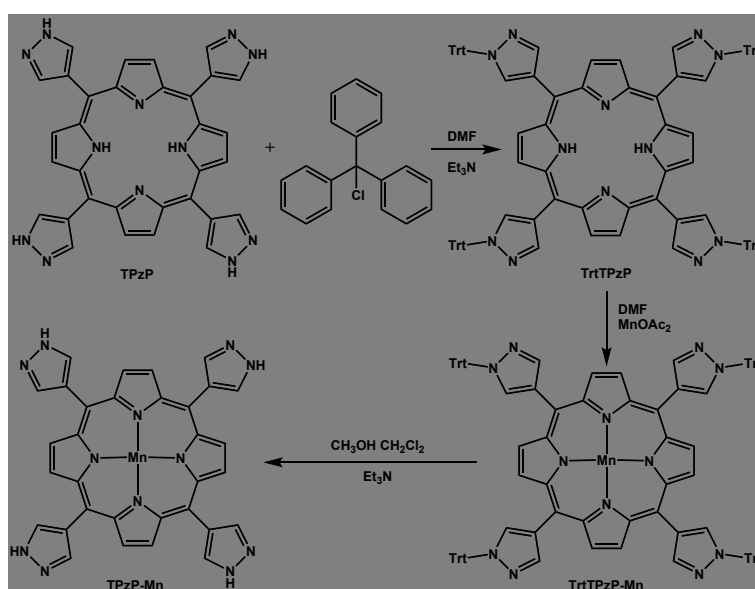


**Scheme S1.** Synthesis procedure for TPzP

TPzP was synthesized according to the slightly modified reported method.<sup>1</sup> In detail, PzCHO (4.8 g, 50 mmol) and propionic acid were added in the two-neck round bottom flask. After degassing and purification with high-purity Ar gas three times, pyrrole (3.5 mL, 50 mmol) was added into

the flask under Ar atmosphere. Then the flask was heated at 150 °C with reflux and keep stirring overnight in darkness. After the reaction mixture was cooled to room temperature and stand 5 hours, the product was collected by filtration and washed with acetone (1.25 g, 2.19 mmol, 17.5% yield). <sup>1</sup>H NMR (400 MHz, DMSO) δ (ppm) 13.63 (s, 4H), 9.11 (s, 8H), 8.70 (s, 4H), 8.38 (s, 4H), -2.71 (s, 2H).

### Synthesis of 5,10,15,20-Tetra(1H-pyrazol-4-yl)porphyrin-Mn (TPzP-Mn).



**Scheme S2.** Synthesis procedure for TPzP-Mn

#### A. Synthesis of 5,10,15,20-Tetra(1-trityl-pyrazol-4-yl)porphyrin (TrtTPzP)

TPzP (0.574 g, 1 mmol) was dissolved in 100 mL of DMF, and the mixture was added to a dried 250 mL two-neck round bottom flask. Et<sub>3</sub>N (2.0 mL) was then added dropwise to the reaction mixture, and a water condenser was attached to the flask. The mixture was heated to reflux and cautiously stirred for 10 min. TrtCl (1.2 g, 4.3 mmol) was added to the reaction mixture and kept reflux for another 12 h. The reaction system was cooled to room temperature and then poured over 300 mL of ice water in a 1 L beaker. The dark purple powder was collected by filtration and dried at 60 °C under vacuum. Then it dissolved the dark purple powder in CH<sub>2</sub>Cl<sub>2</sub> and ultrasonic for 30 min. After that, the dispersion is filtered under reduced pressure to collect the filtrate, and the solvent was removed by rotary evaporation to obtain the crude purple product. Finally, the crude product is purified by flash column chromatography (1:9 v/v, MeOH: CH<sub>2</sub>Cl<sub>2</sub>) to give TrtTPzP (1.2 g, 78.0% yield based on TPzP). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.10 (s, 8H), 8.51 (s, 4H), 8.20 (s, 4H), 7.3-7.6 (m, 60H), -2.75 (s, 2H).

#### B. Synthesis of 5,10,15,20-Tetra(1-trityl-pyrazol-4-yl)porphyrin-Mn (TrtTPzP-Mn)

TrtTPzP (1.543 g, 1.0 mmol) and MnOAc·4H<sub>2</sub>O (2.45 g, 10 mmol) were dissolved in 100 mL of DMF in a 250 mL two-necked round-bottom flask. The solution was heated to reflux and stirred for 16 h. After the reaction system was cooled to room temperature, the solvent was removed by rotary evaporation to obtain a dark green solid. Then dispersed the green solid in 300 mL CH<sub>2</sub>Cl<sub>2</sub>

and washed it three times with water ( $3 \times 100$  mL). The organic layer was dried over  $\text{MgSO}_4$  for 10 min and evaporated to afford **TrtTPzP-Mn** (1.09 g, 69% yield based on **TrtTPzP**). MS (MALDI-TOF) calcd for  $\text{C}_{108}\text{H}_{76}\text{MnN}_{12}$  m/z: 1596.57 (100.0%), 1595.57 (85.6%), 1597.58 (57.9%), 1598.58 (12.1%); found : 1596.59 (100.0%), 1595.59 (74.2%), 1597.61 (33.2%), 1598.58 (3.9%).

#### C. Synthesis of 5,10,15,20-Tetra(1H-pyrazol-4-yl)porphyrin-Mn (**TPzP-Mn**).

**TrtTPzP-Mn** (1.597g, 1.0 mmol) was suspended in 100 mL of  $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH}$  (1:1) mixed solvent in a 250 mL round-bottom flask. 25 mL of 2 M HCl was slowly added to the suspension, and the mixture was stirred at 50 °C overnight. The reaction mixture was cooled to room temperature, and the solvents were removed by rotary evaporation. The crude product was washed successively with deionized water (~70 mL), methanol (~20 mL), and chloroform (~70 mL). The resulting dark green solid was dried under vacuum to afford **TPzP-Mn** (0.40 g, 63.7% yield based on **TrtTPzP-Mn**). MS (MALDI-TOF) calcd for  $\text{C}_{32}\text{H}_{20}\text{MnN}_{12}$  m/z: 627.13 (100.0%), 628.13 (34.6%), 629.14 (5.8%); found : 627.17 (100%), 628.16 (17.9%), 629.17 (1.5%).

#### Synthesis of **MnTPzP-Mn**.

$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  (8 mg), **TPzP** (8 mg), and 5 mL DMF add into a 10 mL glass vial was ultrasonically dissolved, then HCl (16  $\mu\text{L}$ ) was added into the solution. This glass vial heat at 423 K 48 hours under autogenous pressure. After cooling down to room temperature, dark greenish-purple crystals were collected by filtration and washed with DMF. Then those crystals dried under a vacuum. Yield: 43%.

#### Synthesis of **CoTPzP-Mn**.

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (12 mg), **TPzP** (8 mg), and 4 mL DMF add into a 10 mL glass vial was ultrasonically dissolved, then HCl (20  $\mu\text{L}$ ) was added into the solution. This glass vial heat at 423 K 48 hours under autogenous pressure. After cooling down to room temperature, dark purple crystals were collected by filtration and washed with DMF. Then dried those crystals under a vacuum. Yield: 66%.

#### Synthesis of **MnTPzP-Mn**.

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (10 mg), **TPzP-Mn** (8.5 mg), and 4 mL DMF add into a 10 mL glass vial was ultrasonically dissolved, then HCl (20  $\mu\text{L}$ ) was added into the solution. This glass vial heat at 423 K 48 hours under autogenous pressure. After cooling down to room temperature, dark purple crystals were collected by filtration and washed with DMF. Then dried those crystals under a vacuum. Yield: 86%.

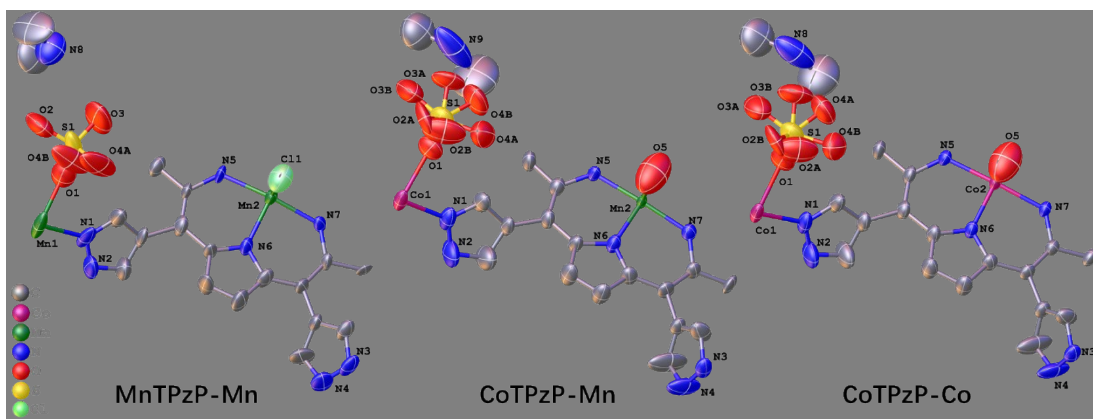
#### Single-Crystal X-ray Analyses.

The diffraction data of **MTPzP-M** (**M** = **Co**, **Mn**) mounted on a Hampton Research cryoloop in light oil for data collection at 296 K. Indexing and data collection of the single crystals were measured on Bruker APEX Duo II equipment CCD area detector. The X-ray generator was operated at 50 kV and 35 mA using Mo  $\text{K}\alpha$  ( $\lambda = 0.71073$  Å) radiation. Data integration was performed using SAINT<sup>2</sup>. Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using SADABS<sup>2</sup>. Using Olex<sup>2,3</sup> those structures were

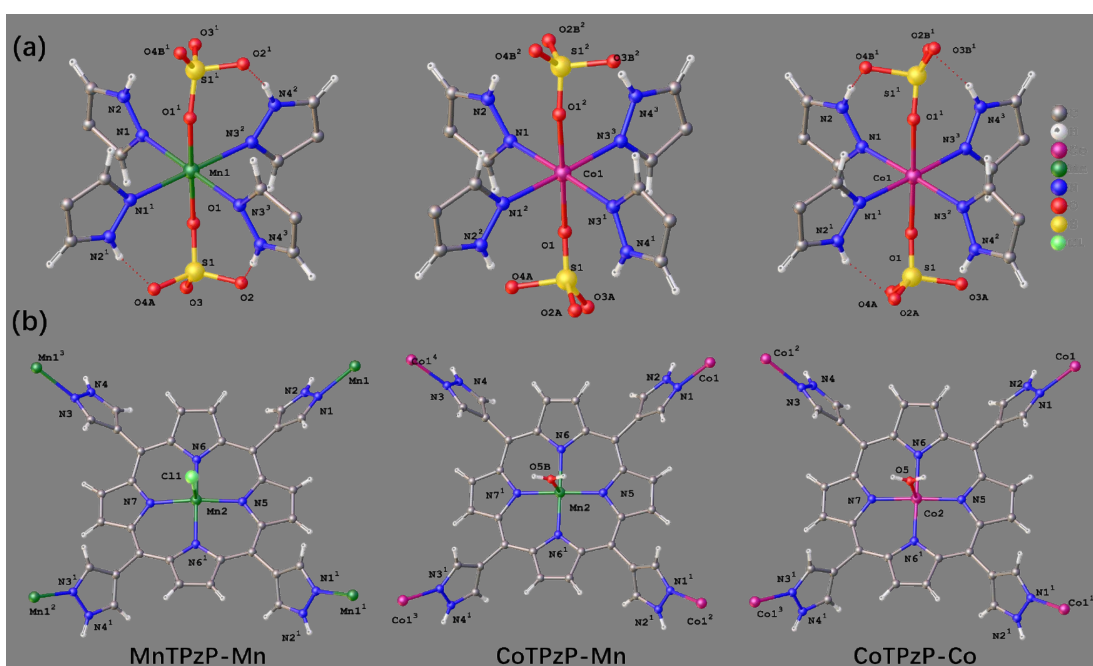
solved with the ShelXT<sup>4</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL-2018<sup>5</sup> refinement package using Least Squares minimization. All the solvent molecules that are highly disordered and unable to be modeled were treated by the SQUEEZE routine in PLATON<sup>6</sup>. The detailed structure determination parameters and crystallographic data are shown in **Table S1**. CCDC 2087766-2087768 (**CoTPzP-Mn, MnTPzP-Mn and CoTPzP-Co**) contains the supplementary crystallographic data for the paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

### **Electrochemical Measurements**

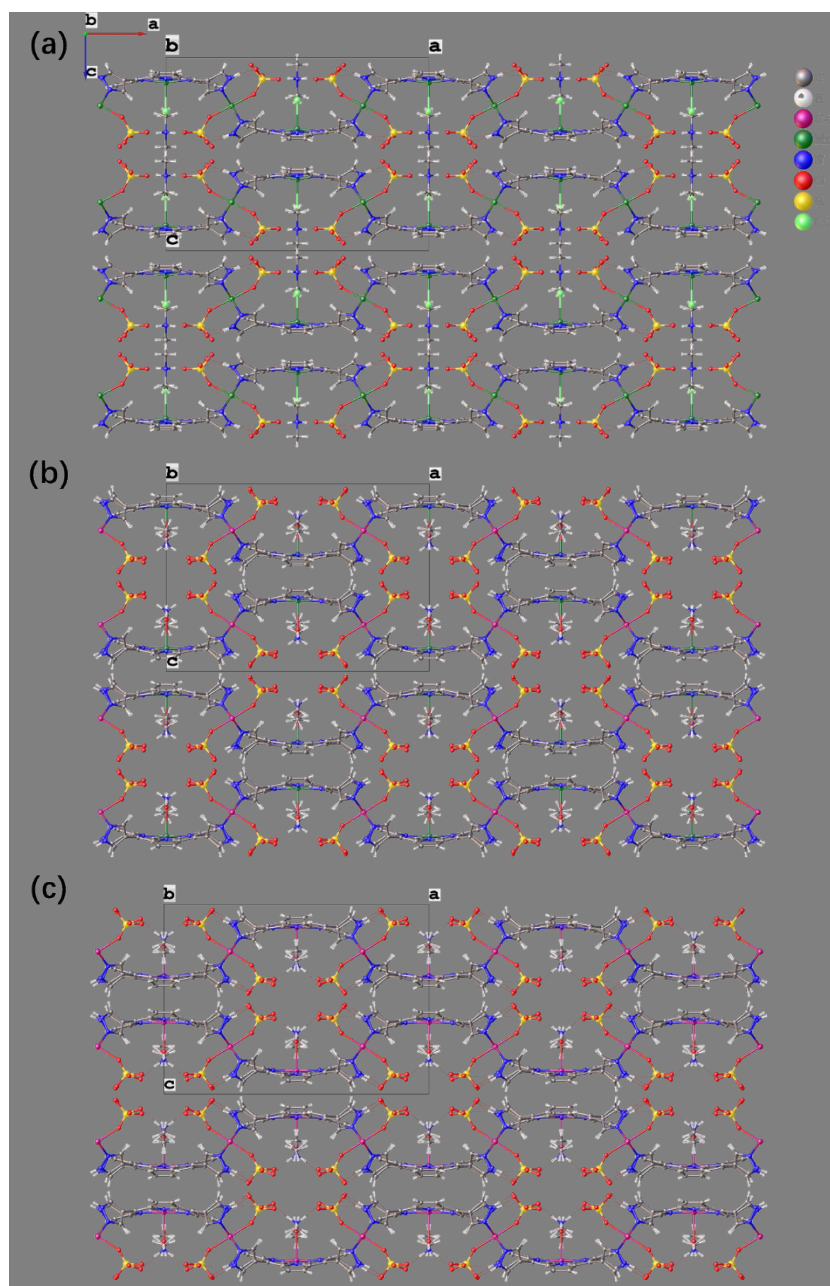
The electrochemical performance of Li-CO<sub>2</sub> batteries was tested using 2032 coin-type cells with holes on the cathode side. The cells were composed of a lithium metal tablet anode, one slice of glass microfiber separator (Whatman), 0.2 mL of electrolyte, and a carbon paper coated with cathode material as the cathode (12 mm diameter). The batteries were assembled in an argon-filled glove box and then installed in a homemade chamber. Before the measurements, the chambers were purged with pure CO<sub>2</sub>. Each measurement was begun after a 12 h open circuit potential step to ensure the equilibrium in the cell. The electrochemical measurements were carried out using a LAND cyler (CT2001A) and an electrochemical workstation (CHI660E; Shanghai Chenhua). A mixture containing 60 wt% of cathode material, 30 wt% of KB as the conductive agent, and 10 wt% of polyvinylidene fluoride as the binder was well mixed in anhydrous NMP solvent by grinding. The as-obtained suspension was then dropped onto carbon paper, which served as a current collector. The cathodes were dried at 80 °C under vacuum for 12 h before use. The active material is both cathode material and KB. The mass loading of the active material (KB + catalyst) was controlled to be approximately 0.1-0.13 mg cm<sup>-2</sup>, with the gravimetric current density and capacity normalized to the total cathode material. 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in tetraethylene glycol dimethyl ether was employed as the electrolyte prepared in an argon-filled glove box with water and oxygen contents below 0.1 ppm.



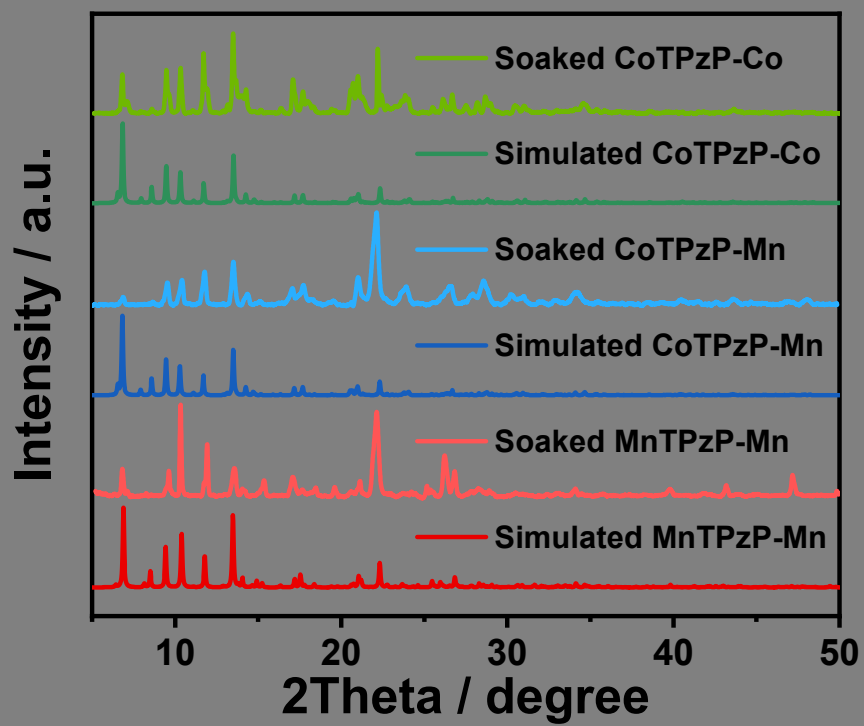
**Figure S1** Asymmetric units of MnTPzP-Mn, CoTPzP-Mn and CoTPzP-Co.



**Figure S2** (a) Coordinated environment of Mn1 or Co1 for MnTPzP-Mn, CoTPzP-Mn and CoTPzP-Co; (b) Coordinated environment of TPzP for MnTPzP-Mn, CoTPzP-Mn and CoTPzP-Co.



**Figure S3** Stacked structure for MnTPzP-Mn (a), CoTPzP-Mn (b) and CoTPzP-Co (c) at b-axis.



**Figure S4** PXRD patterns of MTPzP-M after soaked in electrolyte for 72 hours.



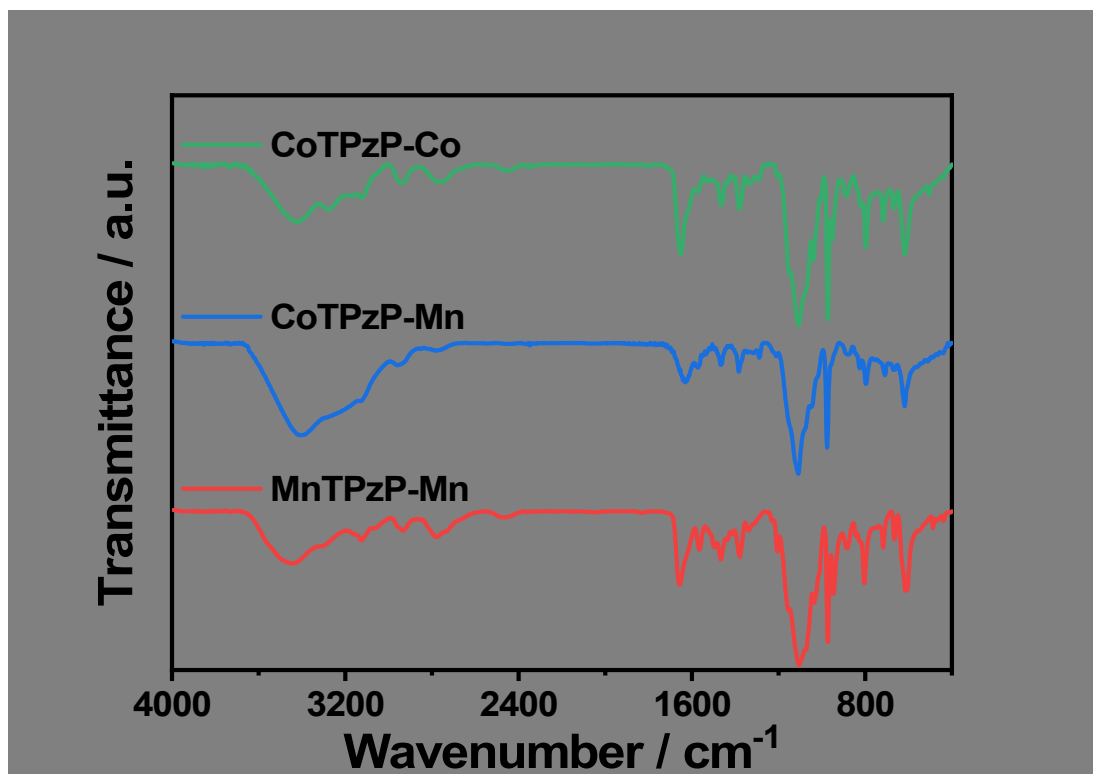


Figure S5 FTIR spectra of MnTPzP-Mn, CoTPzP-Mn and CoTPzP-Co.

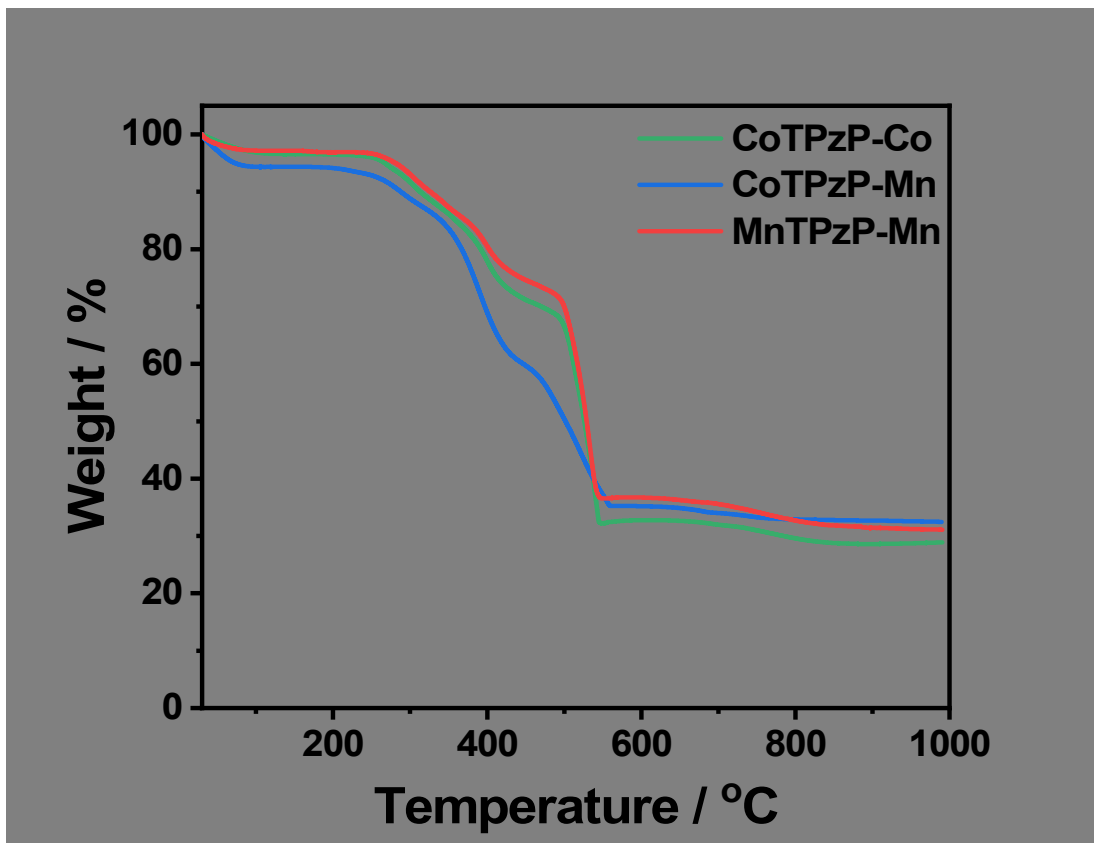
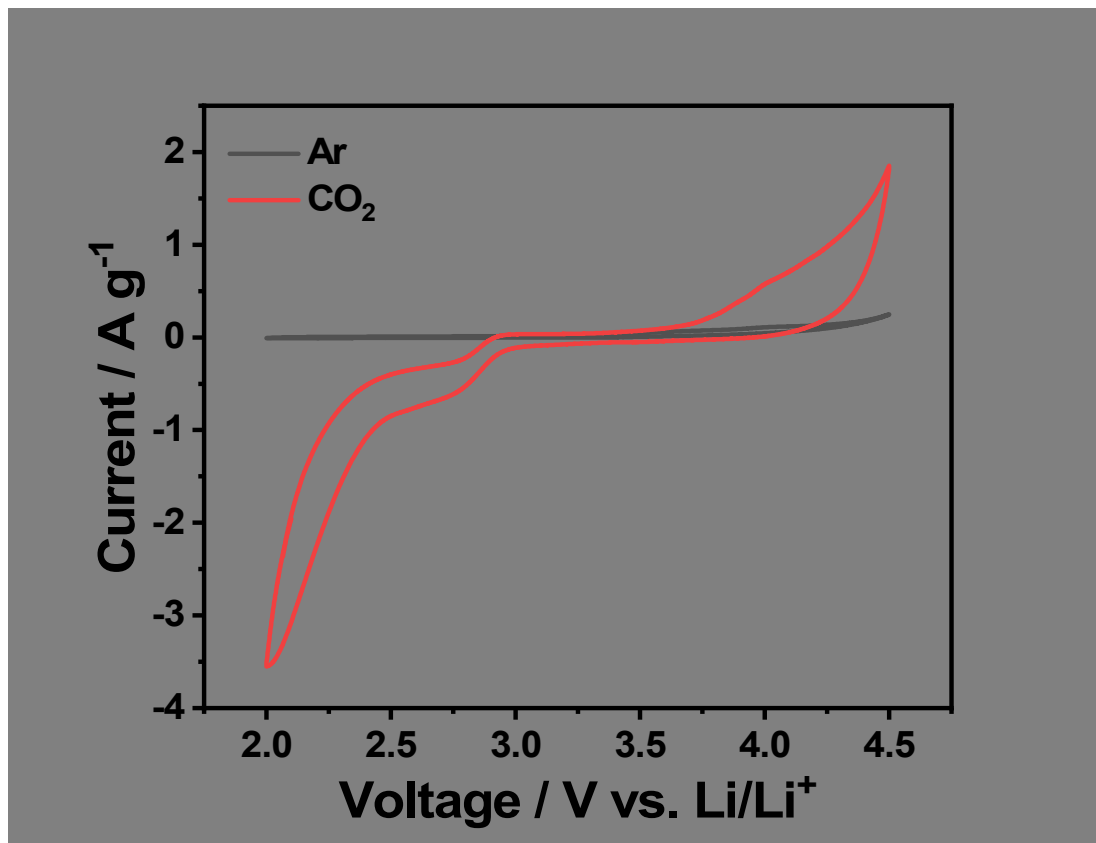
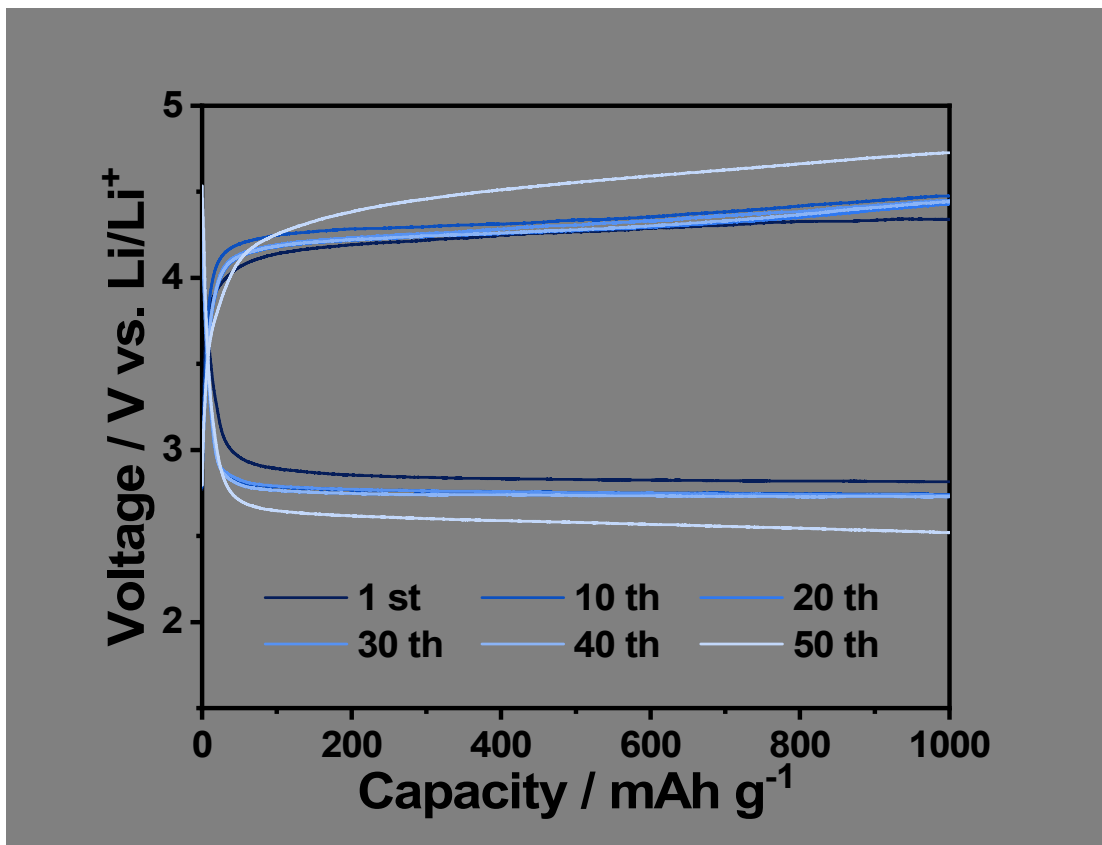


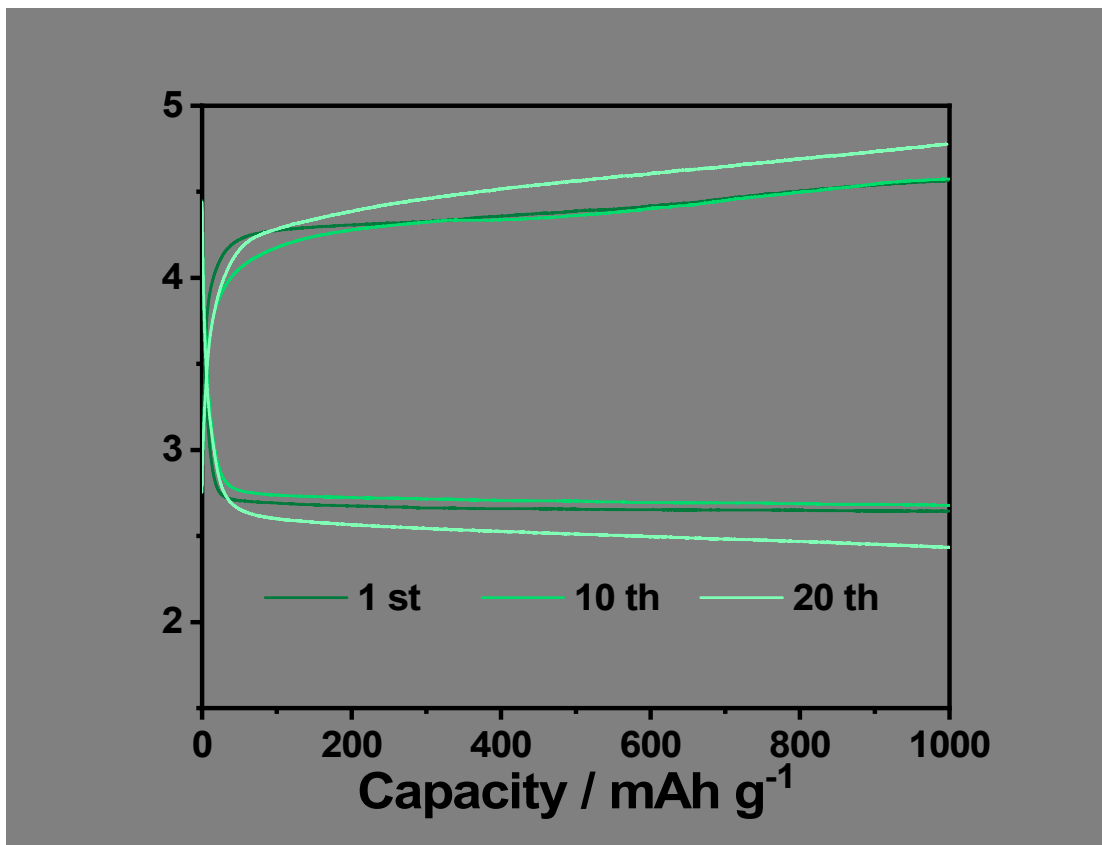
Figure S6 TGA curve of MnTPzP-Mn, CoTPzP-Mn and CoTPzP-Co



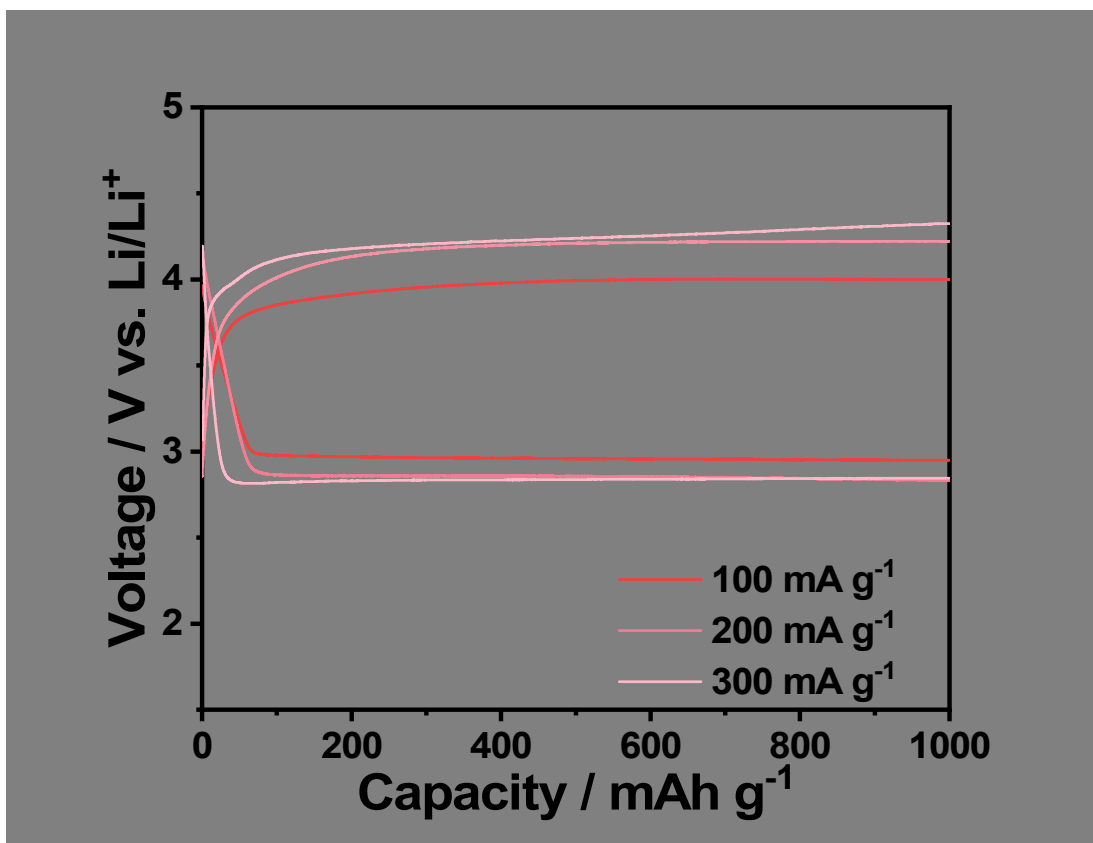
**Figure S7** CV curves of the Li-CO<sub>2</sub> batteries with MnTPzP-Mn cathode at 1 mV s<sup>-1</sup> under CO<sub>2</sub> and Ar atmosphere.



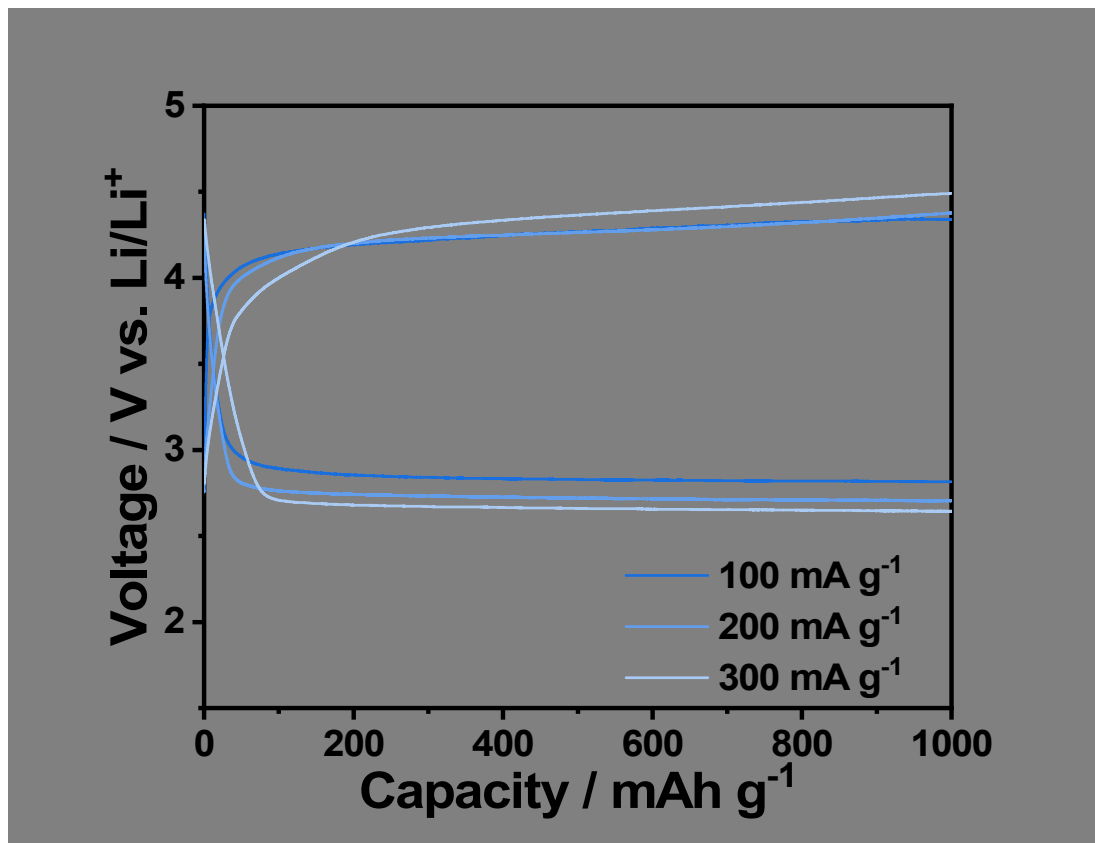
**Figure S8** Discharge/charge curves of CoTPzP-Mn cathode catalysts with the limited capacity of 1000 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>:



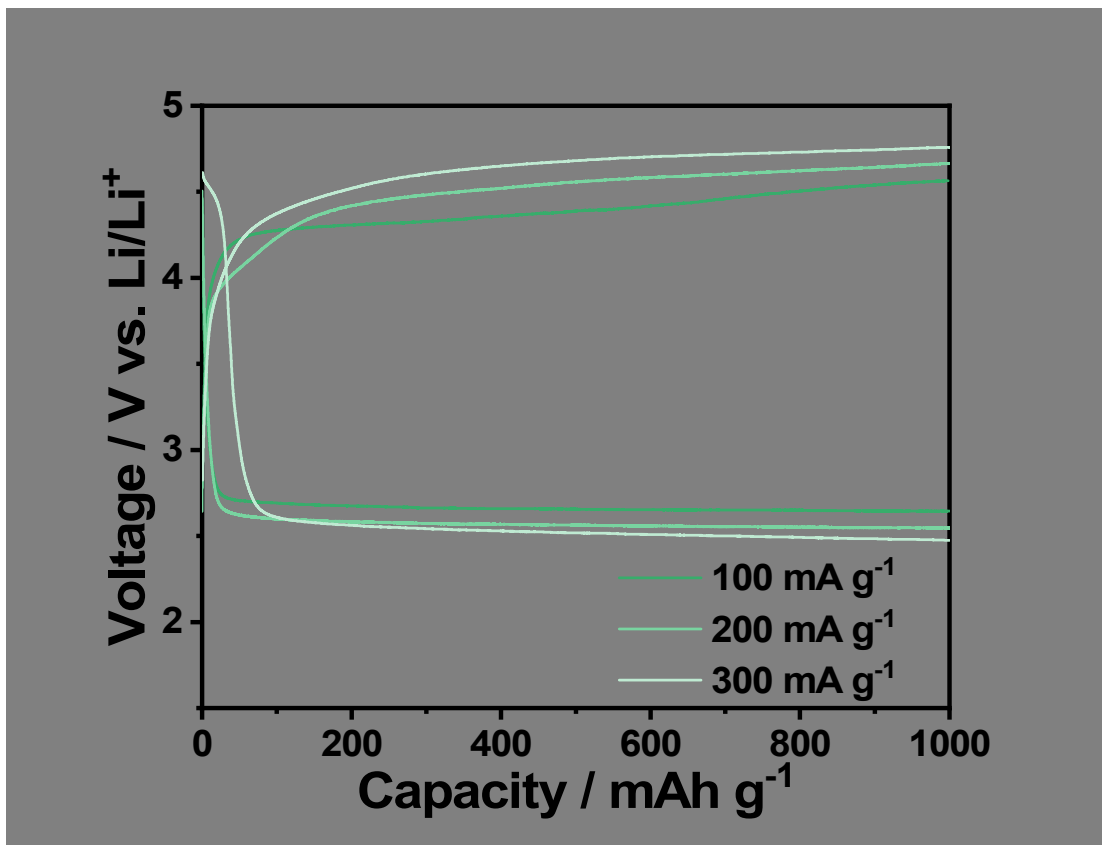
**Figure S9** Discharge/charge curves of CoTPzP-Co cathode catalysts with the limited capacity of 1000 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>:



**Figure S10** Discharge/charge curves of MnTPzP-Mn cathodes at different current densities of 100 mA g<sup>-1</sup>, 200 mA g<sup>-1</sup>, and 300 mA g<sup>-1</sup>

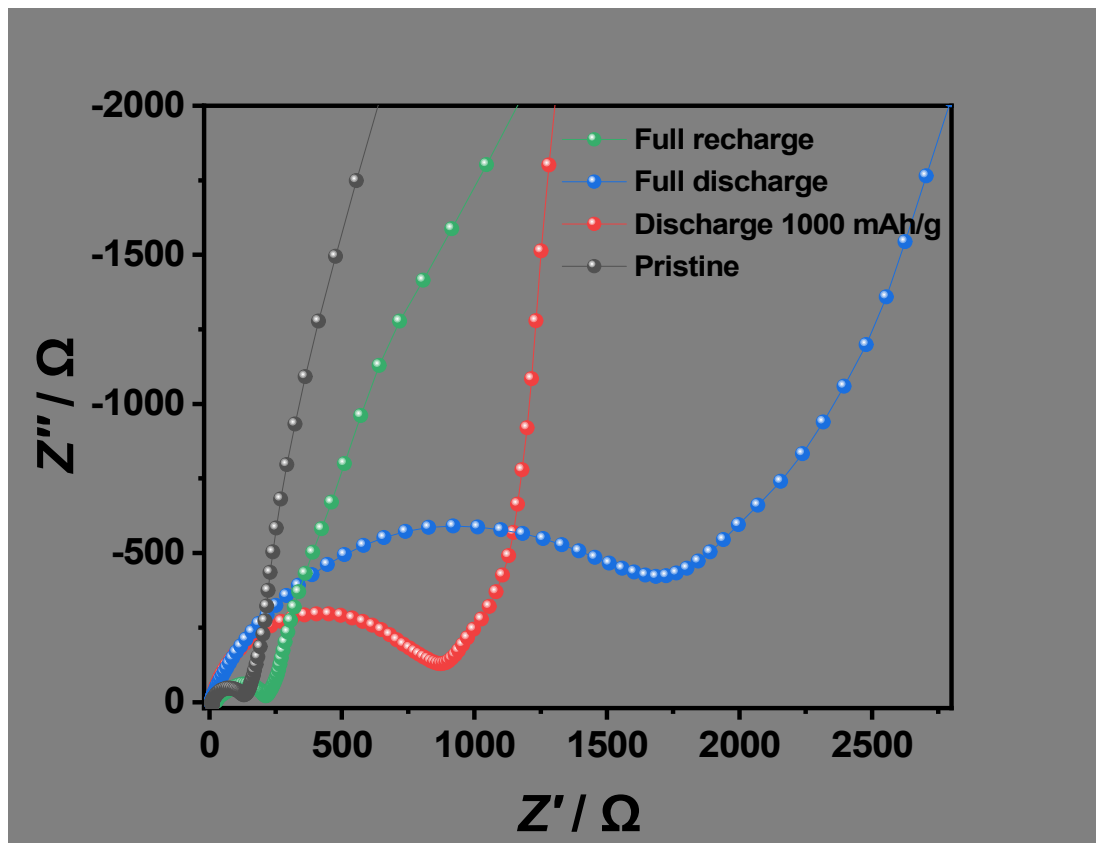


**Figure S11** Discharge/charge curves of CoTPzP-Mn cathodes at different current densities of 100 mA g<sup>-1</sup>, 200 mA g<sup>-1</sup>, and 300 mA g<sup>-1</sup>

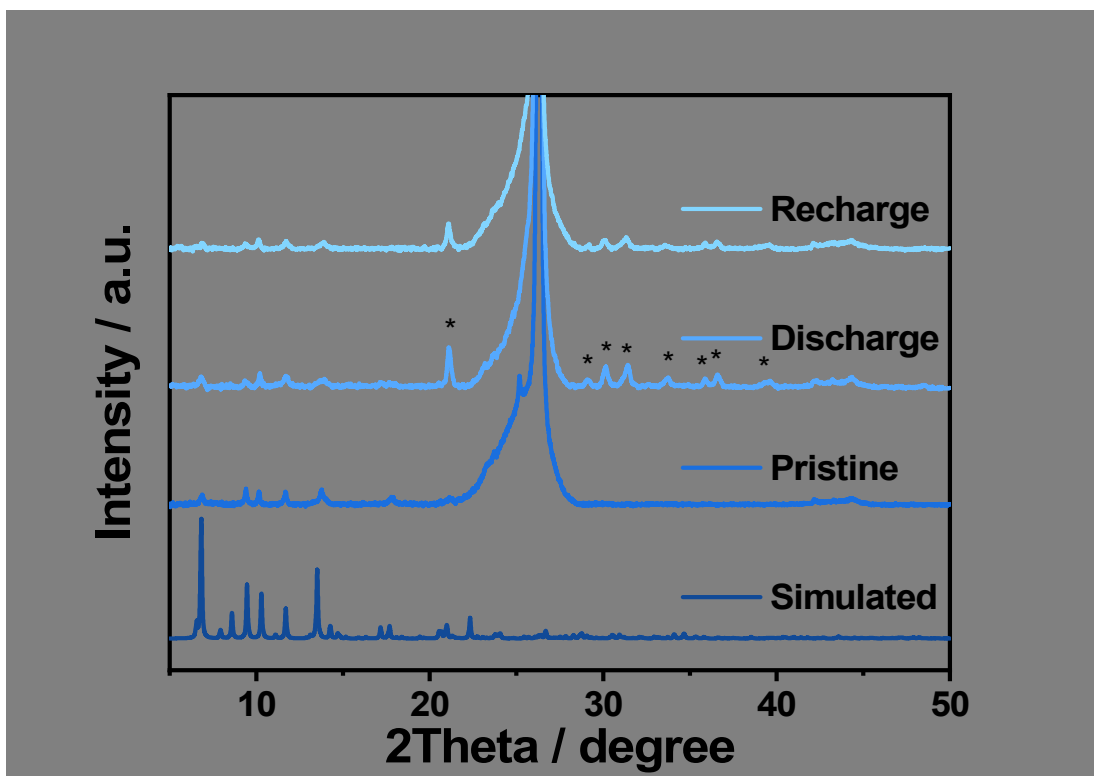


**Figure S12** Discharge/charge curves of CoTPzP-Co cathodes at different current densities of 100 mA g<sup>-1</sup>, 200 mA g<sup>-1</sup>, and 300 mA g<sup>-1</sup>

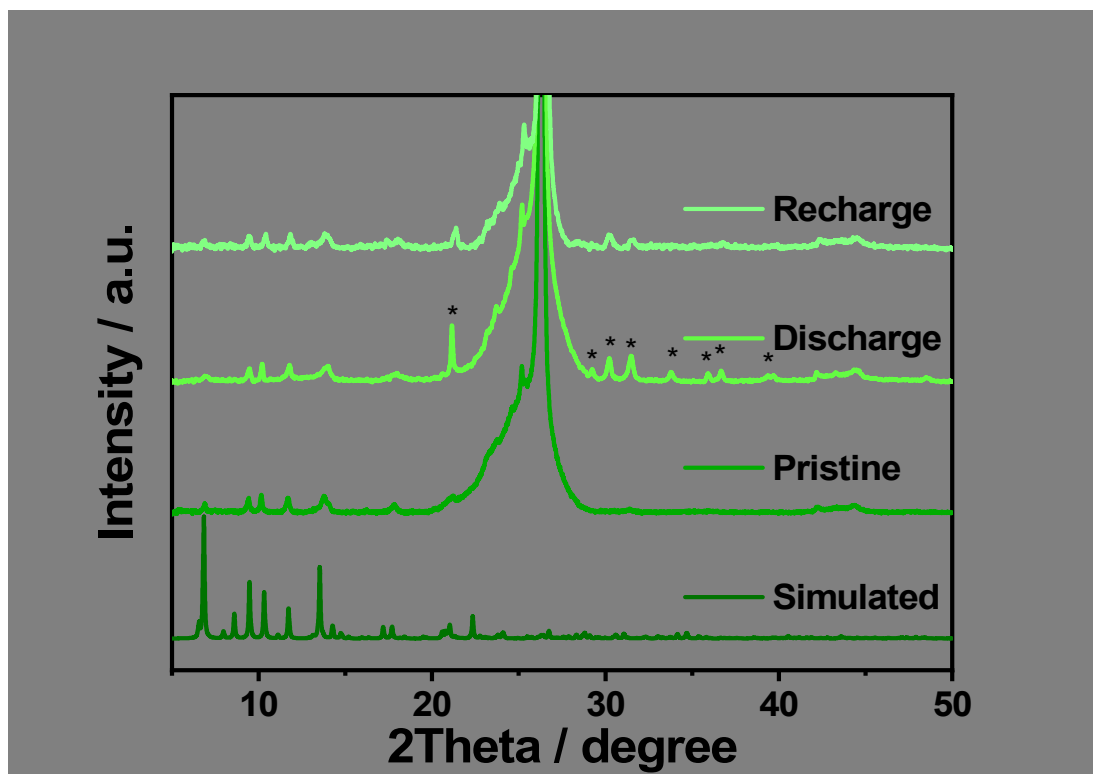




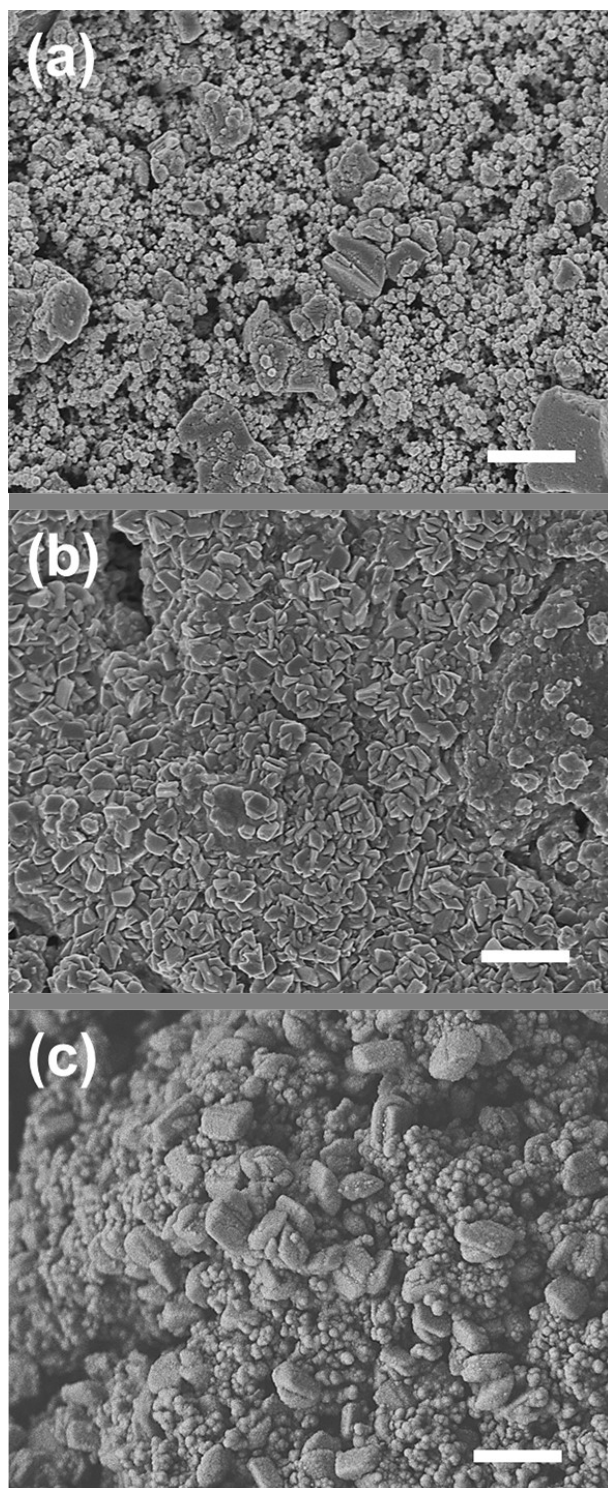
**Figure S13** Electrochemical impedance spectroscopy (EIS) of MnTPzP-Mn based Li-CO<sub>2</sub> battery at pristine, discharged to 1000 mAh g<sup>-1</sup>, full discharge and full recharged back states.



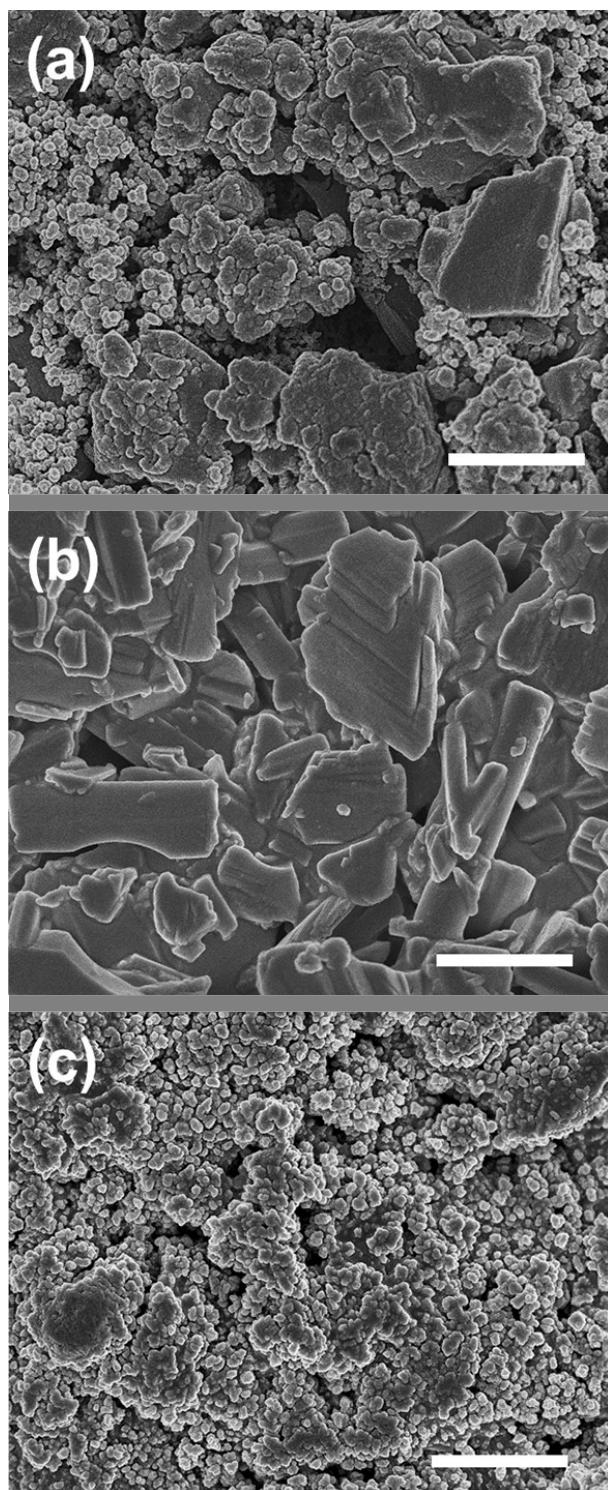
**Figure S14.** PXRd patterns of CoTPzP-Mn cathode catalysts at different stages. (The PXRd signal of Li<sub>2</sub>CO<sub>3</sub> is marked with \*)



**Figure S15** PXRD patterns of CoTPzP-Co cathode catalysts at different stages. (The PXRD signal of Li<sub>2</sub>CO<sub>3</sub> is marked with \*)



**Figure S16** SEM images of CoTPzP-Mn in three stages: pristine, discharge, and recharge. All scale bars represent 2  $\mu\text{m}$ .



**Figure S17** SEM images of CoTPzP-Co in three stages: pristine, discharge, and recharge. All scale bars represent 2 μm.

**Table S1** Crystal data and structure refinement for **MnTPzP-Mn**, **CoTPzP-Mn**, and **CoTPzP-Co**.

<b>Compounds</b>	<b>MnTPzP-Mn</b>	<b>CoTPzP-Mn</b>	<b>CoTPzP-Co</b>
Formula	$C_{34}H_{28}ClMn_2N_{13}O_8S_2$	$C_{34}H_{30}CoMnN_{13}O_9S_2$	$C_{34}H_{30}Co_2N_{13}O_9S_2$
Formula Weight	956.14	942.70	946.69
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space Group	<i>Pmna</i>	<i>Pmna</i>	<i>Pmna</i>
<i>a</i> /Å	21.678(6)	22.29(2)	22.1875(12)
<i>b</i> /Å	13.712(4)	13.477(12)	13.4774(7)
<i>c</i> /Å	15.918(5)	15.919(16)	15.9045(9)
$\alpha$ /°	90	90	90
$\beta$ /°	90	90	90
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	4732(2)	4782(8)	4755.9(4)
<i>Z</i>	4	4	4
Wavelength/Å	0.71073	0.71073	0.71073
Radiation type	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$
$\mu$ /mm <sup>-1</sup>	0.736	0.757	0.845
<i>F</i> (000)	1944.0	1924.0	1932.0
<i>D</i> <sub>calc</sub> /g cm <sup>-3</sup>	1.342	1.309	1.322
<i>R</i> <sub>int</sub>	0.0334	0.0604	0.0275
Goof	1.066	1.015	1.033
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.1289	0.0778	0.0602
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.2663	0.2087	0.1626
<i>R</i> <sub>1</sub> (all data)	0.1537	0.1198	0.0886
<i>wR</i> <sub>2</sub> (all data)	0.2820	0.2480	0.1829

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c||/|F_o|$ . <sup>b</sup> $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$

**Table S2** Selected bond distance (Å) of MTPzP-M.

MnTPzP-Mn			CoTPzP-Mn			CoTPzP-Co		
Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O1	2.058(13)	Co1	O1	2.110(7)	Co1	O1	2.128(4)
Mn1	N1	2.269(12)	Co1	N1	2.153(6)	Co1	N1	2.162(4)
Mn1	N3 <sup>1</sup>	2.258(10)	Co1	N3 <sup>1</sup>	2.150(6)	Co1	N3 <sup>1</sup>	2.156(3)
Mn2	N5	1.997(10)	Mn2	N5	1.949(7)	Co2	N5	1.959(4)
Mn2	N6	2.011(8)	Mn2	N6	1.976(6)	Co2	N6	1.968(3)
Mn2	N7	2.002(11)	Mn2	N7	1.959(8)	Co2	N7	1.968(4)
Mn2	Cl1	2.381(8)	Mn2	O5	2.475(14)	Co2	O5	2.473(9)

Symmetry transformations used to generate equivalent atoms: <sup>1</sup>+X,1+Y,+Z;

**Table S3** Selected bond angle (°) of MTPzP-M.

<b>MnTPzP-Mn</b>				<b>CoTPzP-Mn</b>				<b>CoTPzP-Co</b>			
<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle/°</b>	<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle/°</b>	<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle/°</b>
N5	Mn2	Cl1	98.2(5)	N7	Mn2	N6	90.02(14)	N3 <sup>1</sup>	Co1	N3 <sup>2</sup>	90.20(18)
N5	Mn2	N7	165.3(6)	N7	Mn2	O5	93.0(4)	N3 <sup>2</sup>	Co1	N1	91.27(13)
N5	Mn2	N6	89.4(2)	N5	Mn2	N7	173.9(3)	O1	Co1	N3 <sup>1</sup>	92.01(14)
N7	Mn2	Cl1	96.5(4)	N5	Mn2	N6	90.18(14)	N3 <sup>1</sup>	Co1	N1	178.39(15)
N7	Mn2	N6	88.9(2)	N5	Mn2	O5	93.1(4)	O1	Co1	N3 <sup>2</sup>	89.01(15)
N6	Mn2	Cl1	96.4(3)	N6	Mn2	N6 <sup>1</sup>	176.2(3)	O1 <sup>3</sup>	Co1	O1	178.6(2)
N6	Mn2	N6 <sup>1</sup>	167.2(6)	N6	Mn2	O5	88.12(17)	O1	Co1	N1	87.35(15)
O1 <sup>2</sup>	Mn1	O1	179.1(6)	N3 <sup>2</sup>	Co1	N3 <sup>3</sup>	90.5(3)	O1	Co1	N1 <sup>3</sup>	91.61(16)
O1	Mn1	N1	87.6(5)	N3 <sup>2</sup>	Co1	N1	91.2(2)	N1 <sup>3</sup>	Co1	N1	87.28(19)
O1	Mn1	N1 <sup>2</sup>	93.0(5)	N3 <sup>3</sup>	Co1	N1	178.2(2)	C12	N7	Co2	127.47(19)
O1	Mn1	N3 <sup>3</sup>	93.0(4)	O1	Co1	N3 <sup>2</sup>	88.3(3)	C5	N5	Co2	127.1(2)
O1	Mn1	N3 <sup>4</sup>	86.4(4)	O1	Co1	N3 <sup>3</sup>	92.3(3)	C10	N6	Co2	126.8(2)
N1 <sup>2</sup>	Mn1	N1	87.9(6)	O1	Co1	O1 <sup>4</sup>	179.1(3)	C7	N6	Co2	126.6(2)
N3 <sup>3</sup>	Mn1	N1	179.3(4)	O1	Co1	N1 <sup>4</sup>	92.2(3)	N4	N3	Co1 <sup>5</sup>	125.9(3)
N3 <sup>4</sup>	Mn1	N1	91.8(4)	O1	Co1	N1	87.1(3)	C14	N3	Co1 <sup>5</sup>	129.8(3)
N3 <sup>3</sup>	Mn1	N3 <sup>4</sup>	88.5(5)	C5	N7	Mn2	127.8(4)	S1	O1	Co1	150.2(2)
S1	O1	Mn1	146.7(7)	C12	N5	Mn2	127.2(4)	N2	N1	Co1	125.2(3)
C5	N5	Mn2	127.0(5)	C7	N6	Mn2	126.8(4)	C1	N1	Co1	129.2(4)
C12	N7	Mn2	126.8(5)	C10	N6	Mn2	126.7(4)	N7	Co2	N6	89.93(8)
C10	N6	Mn2	125.0(7)	C3	N3	Co1 <sup>5</sup>	130.3(6)	N7	Co2	O5	93.2(2)
C7	N6	Mn2	125.3(7)	N4	N3	Co1 <sup>5</sup>	125.9(5)	N5	Co2	N7	173.73(19)
N2	N1	Mn1	126.9(8)	S1	O1	Co1	149.7(4)	N5	Co2	N6	90.29(8)
C1	N1	Mn1	126.5(13)	N2	N1	Co1	125.1(5)	N5	Co2	O5	93.0(2)
N4	N3	Mn1 <sup>5</sup>	125.0(8)	C16	N1	Co1	129.6(7)	N6	Co2	N6 <sup>4</sup>	175.99(19)
C14	N3	Mn1 <sup>5</sup>	129.5(10)					N6	Co2	O5	88.00(10)

Symmetry transformations used to generate equivalent atoms:

**MnTPzP-Mn:** (<sup>1</sup>1-x,+y,+z; <sup>2</sup>1/2-x,+y,3/2-z; <sup>3</sup>1/2-x,1+y,3/2-z; <sup>4</sup>+x,1+y,+z; <sup>5</sup>+x,-1+y,+z)**CoTPzP-Mn:** (<sup>1</sup>1-x,+y,+z; <sup>2</sup>+x,1+y,+z; <sup>3</sup>3/2-x,1+y,1/2-z; <sup>4</sup>3/2-x,+y,1/2-z; <sup>5</sup>+x,-1+y,+z)**CoTPzP-Co:** (<sup>1</sup>1/2-x,1+y,1/2-z; <sup>2</sup>+x,1+y,+z; <sup>3</sup>1/2-x,+y,1/2-z; <sup>4</sup>1-x,+y,+z; <sup>5</sup>+x,-1+y,+z)



**Table S4** The Li-CO<sub>2</sub> battery performance of some reported cathode catalysts, including crystalline-based materials and transition metals based materials.

Cathode catalyst	Overpotential of 1 <sup>st</sup> cycle	Discharge capacity / Current density	Cycle performance (current density/cut-off condition)	Ref
MnTPzP-Mn	1.05 V/100 mA g <sup>-1</sup>	14025 mAh g <sup>-1</sup> /100 mA g <sup>-1</sup>	90 cycles (200 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	This work
Mn <sub>2</sub> (dobdc)	1.40 V/50 mA g <sup>-1</sup>	18022 mAh g <sup>-1</sup> /50 mA g <sup>-1</sup>	50 cycles (200 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	7
TTCOF-Mn	1.07 V/100 mA g <sup>-1</sup>	13018 mAh g <sup>-1</sup> /100 mA g <sup>-1</sup>	180 cycles (300 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	8
MnO@NC-G	1.18 V/100 mA g <sup>-1</sup>	50 mA g <sup>-1</sup> /25021 mAh g <sup>-1</sup>	206 cycles (1000 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	9
CoPPc	1.50 V/0.05 mA cm <sup>-2</sup>	13.6 mAh cm <sup>-2</sup> /0.1 mA cm <sup>-2</sup>	50 cycles (0.05 mA cm <sup>-2</sup> /limited capacity of 1 mAh cm <sup>-2</sup> )	10
Bi-CoPc-GPE	1.14 V/200 mA g <sup>-1</sup>	27 196 mAh g <sup>-1</sup> /100 mA g <sup>-1</sup>	120 cycles (200 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	11
Fe-ISA/N,SHG	1.17 V/100 mA g <sup>-1</sup>	23 174 mAh g <sup>-1</sup> /100 mA g <sup>-1</sup>	100 cycles (1000 mA g <sup>-1</sup> / limited capacity of 1000 mAh g <sup>-1</sup> )	12
NiO-CNT	1.79 V/100 mA g <sup>-1</sup>	100 mA g <sup>-1</sup> /9000 mAh g <sup>-1</sup>	25 cycles (100 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	13
Ni-NG	1.43 V/100 mA g <sup>-1</sup>	100 mA g <sup>-1</sup> /17625 mAh g <sup>-1</sup>	101 cycles (100 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	14
Ni/r-GO	1.05 V/100 mA g <sup>-1</sup>	0.1 mA cm <sup>-2</sup> /14.6 mAh cm <sup>-2</sup>	100 cycles (100 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	15
Cu-NG	0.77 V/200 mA g <sup>-1</sup>	200 mA g <sup>-1</sup> /13676 mAh g <sup>-1</sup>	50 cycles (200 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	16
graphene@COF	1.08 V/500 mA g <sup>-1</sup>	27833 mAh g <sup>-1</sup> /75 mA g <sup>-1</sup>	56 cycles (0.5 A g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	17
P-Mn <sub>2</sub> O <sub>3</sub> /KB	1.40 V/50 mA g <sup>-1</sup>	9434 mAh g <sup>-1</sup> (50 mA g <sup>-1</sup> )	50 cycles (50 mA g <sup>-1</sup> /limited capacity of 1000 mAh g <sup>-1</sup> )	18

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