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Supporting Information

Hierarchical pore-in-pore and wire-in-wire catalysts for rechargeable Zn- and Li-air batteries with ultra-long cycle life and high cell efficiency

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Experimental Section

Synthesis: The macro/meso-NC-NH₃ was synthesized by using a 400 nm SiO₂ sphere monolith template (SiO₂-400) and Ludox[®] HS40 silica colloid solution (SiO₂-12, Sigma Aldrich). SiO₂-400 was synthesized by a modified Stöber method.^{S1} In a typical experiment, ethanol (61.75 mL), of deionized (DI) water (24.75 mL), and concentrated ammonia (28.89 %, Fisher Scientific, 9.0 mL) were well mixed by stirring at room temperature. Then tetraethylorthosilicate (TEOS, 98 %, Sigma Aldrich, 4.5 mL) was quickly added into the above mixture. After stirring for 2 h, the white precipitate was collected by washing and centrifuging with ethanol for three times. After drying at 50 °C overnight, the white monolith was fired at 550 °C for 5 h in air.

In a typical synthesis of the resol ethanol solution,^{S2} phenol (99+ %, Fisher Scientific, 12 g) was molten in a round-bottom flask at 65 °C, and NaOH solution (20 wt. %, 2.5 g) was added dropwise into the above solution. Afterwards, formaldehyde solution (37 % W/W, Fisher Scientific, 21 g) was added into the solution slowly, and the mixture was kept at 65 °C for 50 min. The obtained precursor solution was then neutralized with HCl solution (2 mol/L, Fisher Scientific). Next, the residual water in the precursor was removed by vacuum evaporation to obtain resol. Finally, equal weight of ethanol was mixed with the resol to form the resol ethanol solution (50 wt. %).

To prepare the hierarchical porous carbon, resol ethanol solution (50 wt. %, 1 g) was mixed with cyanamide (nitrogen source, Acros Organics, 0.5 g) and SiO₂-12 (3 mL) under sonication for about 10 min. Afterwards, the obtained transparent yellowish solution was casted into the SiO₂-400 monolith template. After drying at 50 °C overnight and thermopolymerization at 100 °C for 24 h, the monolith was carbonized at 800 °C for 2 h in Ar, with a heating and cooling rate of 2 °C min⁻¹. To etch away the SiO₂ templates, the obtained black monolith was ground into

powder and immersed in 20 wt. % HF (Acros Organics) for 24 h. After washing with large quantity of DI water, the N-doped macro- and meso-porous carbon (macro/meso-NC) were finally obtained by drying at 50 °C overnight. NH₃ activation was carried out in anhydrous NH₃ atmosphere at 900 °C for 15 min. The heating and cooling rates were 5 °C min⁻¹ in Ar atmosphere. The obtained catalyst is called macro/meso-NC-NH₃. In a similar procedure, meso-NC and meso-NC-NH₃ were synthesized without adding the macropore template (SiO₂-400). Macro/meso-C was synthesized without adding cyanamide as the nitrogen source.

COMT@Ni was synthesized by a hydrothermal method. In a typical experiment, cobalt nitrate hexahydrate (Co(NO₃)₂· $6H_2O$, 99+%, Acros Organics) and urea (Certified ACS, Fisher Scientific) were dissolved and mixed in DI water with concentrations of 0.096 M and 0.48 M, respectively. Then, the mixed solution (40 mL) was transferred to a Teflon-lined stainless stain autoclave. A piece of commercial Ni foam (MTI Inc.), rolled to 200 µm in thickness, was loaded into the autoclave. After reacting at 95 °C for 6 h, the reacted Ni foam was taken out from the solution, rinsed with DI water carefully, and annealed at 400 °C for 4 h in air. As a result, large arrays of Co₃O₄ microtrepangs were grown uniformly onto the Ni foam.

Characterizations: The X-ray diffraction experiment was carried out with a Philips X-ray diffractometer equipped with CuK α radiation from 10 - 70° at a scan rate of 0.03° s⁻¹. The observation of morphology and elemental distribution was carried out with a Hitachi S-5500 STEM. The TEM images and SAED patterns were collected with JEOL 2010F TEM at 200 keV. The elemental compositions at the surface were analyzed by X-ray photoelectron spectroscopy (XPS) with a Kratos Analytical spectrometer with monochromatic Al K α X-ray source. The standard Brunauer–Emmett–Teller (BET) method was applied to obtain the specific surface area

(AutoSorb iQ2, Quantachrome). The pore size distribution curves were calculated based on the Barrett-Joyner-Halenda (BJH) method.

Electrochemistry: The half-cell tests were carried out with a home-made three-electrode cell with a Hg/HgO reference electrode (filled with 1 M NaOH) and a Pt flag counter electrode. The working electrode is COMT@Ni or pure nickel foam (0.76 cm \times 0.76 cm) connected with a nickel wire, which acted as the current collector. The rotating ring-disk electrode (RRDE) experiments were done in a three-electrode cell controlled by a potentiostat (Autolab PGSTAT302N) and rotation control device (Pine Research Intrumentation). The reference and counter electrodes are, respectively, saturated calomel electrode (SCE) and a Pt flag. The reported potentials are relative to SCE and converted to RHE based on the equation RHE = SCE+ 0.2412 V + 0.059 V \times pH (13). The RRDE electrode possessed a glassy carbon (GC) disk (5 mm in diameter) and a Pt ring. In a typical procedure of preparing the catalyst ink, 10 mg of catalyst powder was dispersed in a mixture of isopropanol (IPA, 2 mL) and 5 wt. % Nafion (50 µL) solution. In the case of Pt/C, the solution was made of 0.2 mL of water and 1.8 mL of isopropanol due to the need to wet Pt/C by water to avoid fire. Then 10 µL of the catalyst ink was dropped onto the GC disk of the RRDE electrode, leading to a mass loading of 255 µg cm⁻². The linear sweep voltammetry (LSV) was collected at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm in O₂-saturated 0.1 M KOH solution within the potential range of 0 - 0.8 V vs. SCE. At the same time, the potential of the Pt ring was set at 0.45 V vs. SCE. In order to deduct double layer capacitance, the LSVs were measured again in N₂-saturated 0.1 M KOH solution and the obtained current densities were deducted from the LSVs in O2-satured electrolyte. The percentage of H₂O₂ yield and number of electrons transferred (n) were calculated based on the following equations:

$$H_{2}O_{2}(\%) = 200 \times \frac{I_{R}/N}{(I_{R}/N) + I_{D}} (1)$$
$$n = \frac{4 \times I_{D}}{(I_{R}/N) + I_{D}} (2)$$

In both equations, I_D represents the disk current and I_R is the ring current. N is the ring collection efficiency (0.37, determined by $Fe(CN)_6^{3-/4-}$ redox couple).

The hybrid Li-air full-cell tests were carried out with a layered battery mould shown in our previous reports with details on the air-electrode making and cell assembly.⁴¹ The anode side of the cell consisted of a nickel foam current collector, a lithium metal foil, and the organic carbonate electrolyte (1 M LiPF₆ in ethylene carbonate (EC) / diethylcarbonate (DEC) (1:1 v/v)) absorbed by two layers of Celgard® polypropylene, which were assembled inside the glove box. The assembled anode was taken out of the glove box and combined with 2 mL of aqueous catholyte (0.5 M LiOH + 1 M LiNO₃) and an air electrode. The catalyst layer on the air electrode was made of 80 wt. % catalyst powder and 20 wt. % LITHion binder as described in a previous report.¹⁹ The solid electrolyte used is a LTAP (Li_{1+x+y}Ti_{2-x}Al_xP_{3-y}Si_yO₁₂) membrane (0.15 mm thick, = 1×10^{-4} S cm⁻¹) purchased from OHARA Inc., Japan. The conventional bifunctional air electrode consisted of a mixture of 1 mg cm⁻² Pt/C (20 wt. %, Johnson Matthey) and 1 mg cm⁻² IrO₂ nanopowder. In the cell with decoupled bifunctional air electrodes, the OER electrode is made of 1 mg cm⁻² Co₃O₄ microtrepangs grown onto nickel foam. The cell was fed with humidified air to suppress water evaporation.

The Zn-air full cells were assembled with a layered battery mold similar to that used with the hybrid Li-air batteries. The major cell parts and the assembled full cell are shown in Fig. S14. The decoupled ORR and OER electrodes were mounted on each side of the cathode chamber to avoid contact. The Li-metal anode was replaced by a polished Zn foil. The solid electrolyte and

aprotic anode electrolyte were not necessary in Zn-air batteries, so they were replaced with 6 M $KOH + 0.2 M ZnCl_2$. The air electrodes were the same as those in hybrid Li-air batteries.

An Arbin BT 2000 battery cycler was used to carry out the cycling test with a five-minute rest time between each discharge and charge at a current density of 0.5 mA cm⁻² for hybrid Li-air batteries and 10 mA cm⁻² for Zn-air batteries. Each discharge and charge period was set to be 2 h. For the decoupled cell configuration, the discharge and charge voltage profiles were collected by two independent Arbin channels alternatively.

Sample	C wt. %	0 wt. %	N wt. %
meso-NC	84.3	3.7	12.0
meso-NC-NH ₃	92.3	1.5	6.2
macro/meso-NC	85.6	9.1	5.3
macro/meso-NC-NH ₃	91.5	2.5	6.0

 Table S1. Surface elemental contents based on the peaks in the XPS spectra

Sample	Pyridinic atom%	Pyridone/pyrrolic atom%	Quaternary atom%	Pyridinic N-O atom%
meso-NC	44.0	27.4	22.7	5.9
meso-NC-NH ₃	52.6	5.9	38.1	3.4
macro/meso-NC	34.2	32.1	28.6	5.1
macro/meso-NC-NH ₃	47.3	12.9	36.3	3.5

 Table S2.
 The N1s compositional analysis

Sample	S _{bet} (m ² g ⁻¹)	S _{micro} (m ² g ⁻¹)	S _{meso} (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)
meso-NC	677	179	498	1.24	0.14	1.1
meso-NC-NH ₃	1024	201	823	2.06	0.22	1.84
macro/meso-NC	728	270	458	1.75	0.31	1.44
macro/meso-NC-NH ₃	1462	307	1155	4.21	0.62	3.59
macro/meso-C	876	226	650	2.12	0.34	1.78

Table S3. The contribution of micropores and mesopores to the surface area and pore volume

Table S4. Comparison of the performances of the state-of-art metal-free catalysts in O_2 -saturated 0.1 M KOH

No.	Catalyst	Diffusion limited current density (-0.4 V vs SCE or 0.61 V vs. RHE)	Scan rate (mV s ⁻¹)	Rotating speed (rpm)	Reference ^a
1	N-meso/microporous carbon	5.8 mA cm ⁻²	10	1600	32
2	Polyelectrolyte/carbon nanotube	4.5 mA cm ⁻²	10	1600	S3
4	N-nanoporous carbon	4.2 mA cm ⁻²	20	1600	S4
5	N-carbon nanocages	40 mA mg ⁻¹ (4.1 mA cm ⁻²)	10	2500	S5
6	N-holey graphitic carbon	4.5 mA cm ⁻²	5	1600	S 6
7	N-meso carbon	5.2 mA cm ⁻²	10	1600	S7
8	Nanoporous-graphitic C ₃ N ₄ @C	3.8 mA cm ⁻²	n/a	1500	S8
9	P-mesoporous carbon	4.0 mA cm ⁻²	10	1600	S9
10	N- and O-mesoporous carbon	3.5 mA cm ⁻²	5	1600	24
11	Macro/meso-NC-NH ₃	6.6 mA cm ⁻²	10	1600	This work

^aThe reference numbers listed here are same as those in the manuscript.

No.	Catalysts	Catholyte	Working Environment	Current Density	Total cycling time(h)	Reference ^a
1	Heat-treated graphene nanosheets	0.5 M LiOH + 1 M LiNO ₃	air	0.5 mA cm ⁻²	200	S10
2	Stainless steel + commercial ORR electrode (decoupled)	LiOH	air	2 mAh cm ⁻²	<200 (Li- water)	22
3	Co ₃ O ₄ /graphene	0.01 M LiOH	air	160 mA g ⁻¹ (0.05 mA cm ⁻²)	125	S11
4	N-CNT grown on carbon fiber paper	0.5 M LiOH + 0.5 M LiNO ₃	air	0.5 mA cm ⁻²	65	17
5	Ketjen black + RuO ₂ @Ti (decoupled)	Saturated LiOH + 10 M LiCl	oxygen	0.64 mAcm ⁻²	~430 h	21
6	Meso-NC+NiCo ₂ O ₄ @Ni (decoupled)	0.5 M LiOH + 1 M LiNO ₃	air	0.5 mA cm ⁻²	400 h	41
7	Macro/meso-NC- NH ₃ +COMT@Ni (decoupled)	0.5 M LiOH + 1 M LiNO ₃	air	0.5 mA cm ⁻²	1200 h	This work

Table S5. Comparison of the state-of-art hybrid Li-air batteries with alkaline catholytes

^aThe reference numbers listed here are same as those in the manuscript.

No.	Catalysts	Working Environment	Current Density	Total cycling time(h)	Reference ^a
1	N, P-doped mesoporous carbon (decoupled)	air	2 mA cm ⁻²	100	17 (Nat. Nanotech.)
2	CoO/N-CNT+NiFeLDH (decoupled)	oxygen	20 mAh cm ⁻²	200	23 (Nat. Commun.)
3	Co ₃ O ₄ NW array on SS mesh	air	17.6 mA g ⁻¹	600	2 (Adv. Energy Mater.)
4	NCNT/CoO-NiO-NiCo	air	20 mA cm ⁻²	17	S12 (Angew. Chem. Int. Ed.)
5	LaNiO ₃ /NCNT core–corona structure	oxygen	17.6 mAcm ⁻²	12.5	S13 (Nano Lett.)
6	MnO ₂ /Co ₃ O ₄	air	15 mA cm ⁻²	14	S14 (Nanoscale)
7	Macro/meso-NC-NH ₃ +COMT@Ni (decoupled)	air	10 mA cm ⁻²	800	This work

Table S6. Comparison of the state-of-art rechargeable Zn-air batteries

^aThe reference numbers listed here are same as those in the manuscript.



Figure S1. Filtration of SiO₂-400 monolith with precursor solution.





SiO₂-400 Dispersion

SiO₂-400 Monolith after centrifuge



SiO₂-400 Monolith after drying and calcination

Figure S2. The formation process of SiO_2 -400 monolith.



Figure S3. (a) The pristine SiO_2 -400 monolith template. (b) After filtration with precursor and carbonization.



Figure S4. (a) STEM image of macro/meso-NC-NH $_3$ and (b) SEM image and elemental mappings.



Figure S5. XPS survey spectra of macro/meso-NC-NH₃, macro/meso-NC, meso-NC-NH₃, and meso-NC.



Figure S6. Nyquist plots of half cells with different catalysts. The electrolyte is 0.1 M KOH, the reference electrode is SCE, and the counter electrode is a Pt flag.



Figure S7. Isotherms and pore size distribution curves of meso-NC, meso-NC-NH₃, and macro/meso-C.



Figure S8. The stability test of macro/meso-NC-NH₃ against Pt/C by chronoamperometry plots at -0.28 V and 1000 rpm.

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Figure S9. The XRD pattern of COMT@Ni.



Figure S10. XPS analysis of COMT@Ni.



Figure S11. Polarization curves of COMT@Ni at a scan rate of 1 mV s⁻¹ in 0.1 M KOH.



Figure S12. Polarization curves of COMT@Ni at a scan rate of 1 mV s⁻¹ with no iR compensation.



Figure S13. SEM images of the commercial IrO₂ nanopowder.



Figure S14. The assembly of a Zn-air battery: (a) major cell parts and (b) the assembled full cell.



Figure S15. Characterizations of $Pt/C+IrO_2$ bifunctional air electrodes before and after cycling in a hybrid Li-air battery: (a) pristine electrode, (b) after cycling and washing with DI water, (c) XRD pattern of the electrode in (b), and (d) after cycling and washing with 1 M HCl,



Figure S16. Characterizations of the decoupled ORR electrode (macro/meso-NC-NH₃) before and after cycling in a Zn-air battery: (a) pristine electrode, (b) after cycling and washing with DI water, (c) XRD pattern of the electrode in (b), and (d) after cycling and washing with 1 M HCl.

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