# **Supplementary Materials**

Co-Mn spinel supported self-catalysis induced N-doped carbon nanotubes with high efficiency electron transport channels for Zincair batteries

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#### **1.1 Preparation Methods**

Chemicals. All the raw materials and reagents used were not further purified after purchase. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%, AR), Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (99%, AR), NH<sub>3</sub>·H<sub>2</sub>O (25%, AR) were bought from Guangzhou Chemical Reagent Factory. Melamine (99.5%, AR), anhydrous ethanol (99.7%, AR) were obtained from Tianjin Damao Chemical Reagent Factory, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (99.5%, AR), glucose (99%, AR) were gained from Tianjin Fuchen Chemical Reagent Factory, Polyvinylpyrrolidone (99%, AR) from Aladdin. Commercial CNTs (99%, AR) bought from Shenzhen Nanotech Port Co. Ltd. Commercial Pt/C (Pt 20 wt.%) and commercial IrO<sub>2</sub> (IrO<sub>2</sub> 85%, Ar) was obtained from Shanghai Hesen Electric Co. Ltd. and Shanghai Hansi Chemical Industry Co., Ltd., respectively.

#### 1.2 Synthesis of catalysts

#### 1.2.1 Synthesis of NCNTs@Ni.

NCNTs@Ni was prepared by a simple self-catalytic process with known program-controlled temperature pyrolysis, with melamine, glucose and nickel nitrate serve as raw materials.

**1.2.2** Synthesis of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, CoMn<sub>2</sub>O<sub>4</sub>/CNTs and pure CoMn<sub>2</sub>O<sub>4</sub>.

 $Co(OAc)_2 \cdot 4H_2O$  (0.50 mmol), Mn(OAc)\_2 \cdot 4H\_2O (1.00 mmol), and 0.05 g of PVP were placed in a round bottom flask, and absolute ethanol and distilled water were added for 100 mL. After ultrasonic dissolution, 60 mg of NCNTs@Ni synthesized by self-catalysis process and 0.7 mL of  $NH_3 H_2O$  were added, and ultrasonic dispersion dissolution is accelerated. After stirring in a water bath for 20 h at 80°C, the solution in a round bottom flask was poured into a 50 mL reaction kettle, and a hydrothermal reaction was carried out at a temperature of 150°C, then the reaction kettle was removed from the oven and cooled to room temperature. The unwanted reaction residue was then drained and removed, the final black powder sample was obtained after being placed in the drying box at 70 °C for 0.5 h. CoMn<sub>2</sub>O<sub>4</sub>/CNTs, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, and pure CoMn<sub>2</sub>O<sub>4</sub> all follow the same synthesis steps above. As a comparative sample to prove the existence of electron-transfer channels, the conductive substrate of CoMn<sub>2</sub>O<sub>4</sub>/CNTs was commercial CNTs without Ni-NCNTs structure. Only single metal salts Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O of 1.50 mmol was added in the synthesis of Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, in order to avoid the influence of N and Ni when commercial CNTs was used instead of autocatalytic NCNTs@Ni in the synthesis of pure  $CoMn_2O_4$ . Finally, the obtained  $CoMn_2O_4/CNTs$  needs to be calcined for a second time (400°C), and the pure CoMn<sub>2</sub>O<sub>4</sub> was finally obtained by removing CNTs.

#### **1.3 Physicochemical Characterizations**

Field emission scanning electron microscopy (SEM, JEOL-6700F) for observing NCNTs surface morphology and Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) for observing skeleton morphology. Transmission electron microscopy (TEM, 300 kV, Tecnai<sup>M</sup> G2 F30) operated at 200 kV accelerating voltage. The qualitative analysis, element composition and chemical state analysis information of the catalyst was obtained by X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi instrument). X-ray diffraction (XRD) patterns with crystal structure information are obtained by X-ray diffraction measurement on a MiniFlex II diffractometer, and the specific surface area and pore size information of the materials was calculated using Brunauer-Emmett-Teller (BET) model. Raman spectra were taken under the wavelength of 532 nm.

#### **1.4 Electrochemical measurements**

#### **1.4.1** Electrode preparation.

The 4.3 mg catalyst was dissolved in a mixture of 1 mL ethanol and water, then dissolved in a uniform black solution by ultrasonic wave, and then after Nafion<sup>®</sup> solution (5.0 wt%) was added, continue ultrasound for 5 min to get catalyst ink. The 6.5  $\mu$ L of the catalyst ink was then transferred onto glassy carbon rotating ring disk electrode (RRDE, 0.196 cm<sup>-2</sup>) and working electrode dried at room temperature for the next step.

#### 1.4.2 Electrochemical testing.

In addition to the performance of Zinc-air batteries obtained on the CHI600e electrochemical workstation, other electrochemical tests were carried out on the Princeton electrochemical workstation. A general three-electrode system was used, platinum foil as electrode, saturated calomel electrode (SCE) as reference electrode and glass carbon electrode loaded with catalyst as working electrode in  $O_2$ -saturated 0.1 M KOH solution. The cyclic voltammetry (CV) curve was

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tested repeatedly at a scanning rate of 10 mV s<sup>-1</sup> until the curve was stable before data were collected. Then linear sweep voltammograms (LSV) of ORR at different rotational speeds were obtained in oxygen saturated  $0.1 \text{ }_{M}$  KOH solution, the sweep rate was 10 mV s<sup>-1</sup> and the rotational speeds were 400, 625, 900, 1225, 1600 and 2025 rpm, respectively.

The kinetics of ORR and electron transfer number (*n*) were calculated by koutech-Levich (K-L) equation:

$J^{-1} = J_{k}^{-1} + (B\omega^{1/2})^{-1}$	(1)
$B = 0.62 (D_0)^{2/3} v^{-1/6} C_0$	(2)
$J_k = nFkC_0$	(3)

where J and J<sub>k</sub> represent current density and kinetic current density,  $\omega$  represents the electrode rotating angular velocity, B is the slope of K-L plots, n represents the electron transfer number, F is the Faraday constant (96485 C mol<sup>-1</sup>), D<sub>0</sub> means the diffusion coefficient of O<sub>2</sub> (1.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), v is the kinetic viscosity (0.01 cm<sup>2</sup> s<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-3</sup> mol L<sup>-1</sup>).

Under the condition of rotating speed of 1600 rpm, the RRDE data are obtained by scanning the voltage window from -0.8 V to 0.2 V (*vs.* SCE) at speed of 10 mV s<sup>-1</sup>. The apparent electron transfer number and  $H_2O_2$  yield are calculated by equation (4), (5):

$$\mathbf{n} = \frac{4J_D}{J_D + (J_R/N)} \tag{4}$$

$$H_2 O_2 \% = 100 \frac{2(J_R / N)}{J_D + (J_R / N)}$$
(5)

where  $J_D$  and  $J_R$  represent disk current and ring current, N (0.37) is collection coefficient of H<sub>2</sub>O<sub>2</sub> on the ring electrode.

Based on the CV measurements at different scanning rates (10, 15, 20, 25, 30 mV s<sup>-1</sup>) to get the electrochemical capacitance ( $C_{dl}$ ) of the catalyst, the electrochemical active surface area (ECSA) was obtained according to the following equation:

$$ECSA = C_{dl}/C_s \tag{6}$$

where  $C_s$  represents the specific capacitanc. EIS was measured at a bias potential of -0.6 V (*vs.* SCE) and in a frequency range from 0.1 to  $10^6$  Hz. The stability of ORR was characterized by the chronoamperometry at -0.6 V for 24 h.

#### **1.4.3** Zn-air Battery Assembly.

Zn air battery performances in aqueous electrolyte ( $6 \le KOH$ ) with CoMn<sub>2</sub>O<sub>4</sub>@NCNT@Ni acting as the air cathode in comparison with the coupled noble metal Pt/C (Pt/C:IrO<sub>2</sub> mass ratio is 1:1) catalyst, and the loading of catalyst is ~9 mg cm<sup>-2</sup>, The discharge-charge performance and cycle reversibility of the battery were tested on CHI760E electrochemical workstation.

#### **1.5 Computational studies**

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP).<sup>1,2</sup> The Perdew-Burke-Ernzerhof (PBE) functional for the exchange correlation term was used with the projector augmented wave method and a cutoff energy of 400 eV. <sup>3</sup> The model used in the calculation was shown in Figure 6 and Figure S20, which consists of CoMn<sub>2</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub>

adsorbing on the outer surface of CNT (6, 6), respectively. To investigate the effect of nitrogen doping, the CNT doped with the graphitic nitrogen was used as the calculated model. In Figure 6, CNT is omitted in order to simplify the expression. Spin-polarization was considered in all calculations. The convergence of energy and forces were set to  $1 \times 10^{-4}$  eV and 0.05 eV/Å, respectively. The free energies of the intermediates were obtained by  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ , where  $\Delta E$ ,  $\Delta ZPE$  and  $\Delta S$  is the binding energy, zero point energy change and entropy change, respectively. The  $\Delta ZPE$  and  $\Delta S$  were obtained according to the NIST (https://janaf.nist.gov/). The extra pH effect ( $\Delta G_{pH}$ ) and electrode effect ( $\Delta G_{U}$ ) are not considered in this manuscript.

## 2. Supplementary Figures



Figure S1. (a-b) SEM image of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni with different magnifications.



**Figure S2**. (a)  $N_2$  sorption isotherms of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, and (b) the corresponding pore-size distributions calculated by the BJH method.



**Figure S3**. Photographs of (a) CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni and (b) commercial CNTs distributed in the aqueous solution.



**Figure S4**. Raman spectra of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni and NCNTs@Ni.



Figure S5. (a-b) SEM image of commercial CNTs with different magnifications.



Figure S6. (a-b) SEM image of NCNTs@Ni with different magnifications, (c) XRD pattern.



Figure S7. (a-b) SEM image of Pure CoMn<sub>2</sub>O<sub>4</sub> with different magnifications, (c) XRD pattern.



Figure S8. (a-b) SEM image of Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni with different magnifications, (c) XRD pattern.



Figure S9. (a-b) SEM image of CoMn<sub>2</sub>O<sub>4</sub>/CNTs with different magnifications, (c) XRD pattern.



Figure S10. XPS survey scan of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni and CoMn<sub>2</sub>O<sub>4</sub>/CNTs.



**Figure S11.** Co 2p core level of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni and CoMn<sub>2</sub>O<sub>4</sub>/CNTs. The Co 2p spectrum was deconvoluted into four singlets ascribed to Co<sup>2+</sup> (780.20/795.27 eV), and Co<sup>3+</sup> (781.88/796.53 eV).



Figure S12. Ni 2p core level of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni and NCNTs@Ni.



**Figure S13**. CV curves of pure CoMn<sub>2</sub>O<sub>4</sub>, NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni and CoMn<sub>2</sub>O<sub>4</sub>/CNTs in an O<sub>2</sub>-saturated and N<sub>2</sub>-saturated 0.1 <sub>M</sub> KOH solution at the scan rate of 10 mV s<sup>-1</sup>.



**Figure S14**. LSV curves of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni and Pt/C in 0.1  $_{M}$  KOH solution at the scan rate of 10 mV s<sup>-1</sup> with 1600 rpm.



**Figure S15a**. LSVs with different scanning rates (400 to 2025 rpm) of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni and pure CoMn<sub>2</sub>O<sub>4</sub>, and the corresponding Koutecky-Levich plots at different potentials.



**Figure S15b**. LSVs with different scanning rates (400 to 2025 rpm) of NCNTs@Ni, Pt/C and CoMn<sub>2</sub>O<sub>4</sub>/CNTs, and the corresponding Koutecky-Levich plots at different potentials.



**Figure S16a**. The CVs measured at different scan rates of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, pure CoMn<sub>2</sub>O<sub>4</sub>.



Figure S16b. The CVs measured at different scan rates of NCNTs@Ni, Pt/C and CoMn<sub>2</sub>O<sub>4</sub>/CNTs.



**Figure S17**. The EIS measured at -0.6 V *vs.* SCE of CoMn<sub>2</sub>O<sub>4</sub>/NCNTs@Ni, Mn<sub>3</sub>O<sub>4</sub>/NCNTs@Ni, CoMn<sub>2</sub>O<sub>4</sub>/CNTs, pure CoMn<sub>2</sub>O<sub>4</sub>, NCNTs@Ni, and Pt/C.



**Figure S18**. A working homemade zinc-air battery, the magnification chart shows that the supported area of the catalyst is about  $1 \text{ cm}^{-2}$ .



**Figure S19**. (a) SEM image and (b) XRD of CoMn<sub>2</sub>O<sub>4</sub>/NCNT@Ni which acting as the air cathode after stability charge-discharge for 238 h.



**Figure S20**. The model of DFT calculation: (a)  $Mn_3O_4$  and (b)  $CoMn_2O_4$  adsorbing on the outer surface of CNT (6, 6). The red circles, purple circles and blue circles represent O atom, Mn and Co atom, respectively.

**Table S1.** Contents of elements in different catalysts, the data was acquired from the fitted XPSspectra by the software of XPSPEAK41.

Catalyst	Element content (At.%)					
	С	0	N	Mn	Со	Ni
CoMn <sub>2</sub> O <sub>4</sub> /NCNTs@Ni	57.61	25.47	3.41	7.32	4.91	1.28
Mn <sub>3</sub> O <sub>4</sub> /NCNTs@Ni	70.52	17.50	4.90	6.06	-	1.01
CoMn <sub>2</sub> O <sub>4</sub> /CNTs	63.80	24.64	-	6.70	4.86	-
NCNTs@Ni	89.46	3.96	5.08	-	_	1.50

**Table S2.** Valence data of Mn obtained from XPS peak area, the areas of the peaks were acquired from the fitted XPS spectra (Figure. 3a) by the software of XPSPEAK41.

Catalyst	Mn state				
	Mn <sup>2+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>	<sup>2+/3+</sup> Mn	<sup>3+/4+</sup> Mn
CoMn <sub>2</sub> O <sub>4</sub> /NCNTs@Ni	23176.29	22484.26	14957.63	2.49	3.40
Mn <sub>3</sub> O <sub>4</sub> /NCNTs@Ni	16182.29	34512.28	12708.47	2.68	3.26
CoMn <sub>2</sub> O <sub>4</sub> /CNTs	22007.42	24688.55	13237.77	2.52	3.33

**Table S3.** Contents of N in different catalysts, the data were acquired from the fitted XPS spectra by the software of XPSPEAK41.

Catalyst	Content (At.%)					
	Pyridine N	Pyrrolic N	Graphite N			
CoMn <sub>2</sub> O <sub>4</sub> /NCNTs@Ni	24.96	48.17	26.87			
Mn <sub>3</sub> O <sub>4</sub> /NCNTs@Ni	26.12	52.95	20.93			
NCNTs@Ni	41.94	35.30	22.76			

**Table S4.** Comparison of ORR performance of catalysts in this work and other reported transitionmetal electrocatalysts in alkaline media.

Catalyst	Current density	Tafel	E <sub>1/2</sub> (V)	n	Catalyst Ioading	Ref.
					$(mg cm^{-2})$	
CoMn <sub>2</sub> O <sub>4</sub> /NCNTs@Ni ( <i>vs.</i> SCE)	5.51	64	-0.21	3.92	0.028	This work
Mn <sub>3</sub> O <sub>4</sub> /NCNTs@Ni ( <i>vs.</i> SCE)	5.35	94	-0.31	3.80	0.028	This work
CoMn <sub>2</sub> O <sub>4</sub> /CNTs ( <i>vs</i> .SCE)	4.06	157	-0.31	2.98	0.028	This work
Pure CoMn <sub>2</sub> O <sub>4</sub> (vs.SCE)	3.73	202	-0.39	3.82	0.028	This work
NCNTs@Ni ( <i>vs.</i> SCE)	3.56	87	-0.33	3.44	0.028	This work
Pt/C ( <i>vs</i> .SCE)	4.62	75	-0.18	3.94	0.028	This work
MnCo <sub>2</sub> O <sub>4</sub> -900 ( <i>vs</i> .RHE)	5.5	-	-	-	-	4
A-MnO <sub>2</sub> ( <i>vs</i> .RHE)	4.70	105	-	4.20	0.19	5
D-AC@2Mn-4Co ( <i>vs</i> .RHE)	4.72	-	0.803	3.83	0.08	6
ZnMnCoO <sub>4</sub> ( <i>vs</i> .RHE)	6.2	72	0.82	-	0.25	7
Mn/C-NO ( <i>vs</i> .RHE)	~5.7	-	0.86	3.95	0.3	8
MnCo <sub>2</sub> O <sub>4</sub> ( <i>vs</i> .RHE)	~6.0	-	-	3.94	0.04	9
MCO/CNFs@NC ( <i>vs</i> .RHE)	5.12	70	0.76	4.0	0.025	10

**Table S5.** Comparative summary of the performance of Zn-air battery with the present work.

Catalyst	Catalyst loading (mg cm <sup>-2</sup> )	Electrolyte	OCP (V)	Stability	Ref.
CoMn <sub>2</sub> O <sub>4</sub> /NCNTs@Ni	9	6 М КОН	1.46	238 h	This work
Ni-doped CoO NSs	0.5	6 М КОН	1.45	400 h	11
NCNT/Co <sub>x</sub> Mn <sub>1-x</sub> O	0.53	6 M KOH +0.2 M Zn <sup>2+</sup>	-	40000 s	12
ZnCo <sub>2</sub> O <sub>4</sub> /NCNTs	2	6 М КОН	1.47	~10 h	13
ND-CFs	1.0	6 M KOH +0.2 M Zn <sup>2+</sup>	1.46	800 min	14
MCO/CNFs@NC	-	-	1.55	220 cycles	10

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