# Supporting information

## Synergistic dual sites of Zn-Mg on hierarchical porous carbon as an

## advanced oxygen reduction electrocatalyst for Zn-air batteries

Mincong Liu, <sup>a</sup> Jing Zhang, <sup>b</sup> Yan Peng <sup>a</sup> and Shiyou Guan \*<sup>a</sup>

a. Department of Chemistry, College of Science, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China; Email: syquan@shu.edu.cn

b. College of Sciences&Institute for Sustainable Energy, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China.

#### 1. Materials characterizations

The morphologies and structures were conducted with scanning electron microscopy (SEM, ZEISS Gemini 300), transmission electron microscopy (TEM, JEOL-2100F) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) with energy dispersive spectrometry (EDS) (Tecnai G2 F20 electron microscope). X-ray diffraction (XRD) was analyzed by using a Bruker D8 advanced X-ray diffractometer with Cu Ka (40 kV, 40 mA). Raman spectrum was obtained on the Horiba Evolution laser Raman spectrometer (under excitation at 532 nm). X-ray photoelectron spectroscopy (XPS) was measured by using Thermo Scientific K-Alpha spectrometer. Brunauer–Emmett–Teller (BET) specific surface areas was collected nitrogen adsorption–desorption analyses by using an ASAP 2460 instrument at 77 K.

#### 2. Electrochemical measurements

ORR catalytic activity was performed on a CHI760E electrochemical workstation analyzer (Cheng Hua Instruments, Inc., Shanghai, China) with a standard three-electrode system. The reference electrode and the counter electrode are Ag/AgCl electrode and graphite rod, respectively. The catalyst coated glassy carbon (GC, 5.0 mm diameter) electrodes served as the working electrodes. To prepare a homogeneous catalytic ink, 5 mg of the catalyst was mixed with Nafion solution (40  $\mu$ L), DI water (480  $\mu$ L) and ethanol (480  $\mu$ L) using dispersed ultrasonically for 60 min. Then, 10 $\mu$ L catalytic ink was cast onto the glassy carbon disk electrode and dried at room temperature. Cyclic voltammetry (CV) curves were recorded with a sweep rate of 50mV s<sup>-1</sup> in N<sub>2</sub>/O<sub>2</sub>-saturated 0.1 M KOH. A series of Linear sweep voltammetry (LSV) tests were performed at rotating speed from 400 to 2025 rpm with a scan rate of 10 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.1 M KOH.

The electron transfer number (n) and kinetic current density  $(J_k)$  were calculated based on the Koutechy-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{J_{K}} \frac{1}{J_{K}} \frac{1}{B\omega} \frac{1}{2} \frac{1}{M} \frac$$

 $B = 0.2nFC_0D_0^{2/3}v^{-1/6}$ #(2)<sub>where J</sub> is the measured current density, J<sub>K</sub> and J<sub>L</sub> are the kinetic and diffusionlimiting current densities,  $\omega$  is the rotating speed of the disk, F is the Faraday constant (96485 C·mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> (1.9 × 10-5cm<sup>2</sup> s<sup>-1</sup>), and u is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).s

The hydrogen peroxide yield ( $^{8}H_{2}O_{2}$ ) and electron transfer number (n) were determined by rotating ring disk electrode (RRDE, Pine) measurements based on the following two equations:

$$H_2 O_2(\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \#(3)$$
  
$$n = 4 \times \frac{I_d}{M} \#(4)$$

 $I_d + \frac{I_r}{N}$  where I<sub>d</sub> is the disk current, I<sub>r</sub> is the ring current, and N=0.37 is the current collection efficiency of the Pt ring.

### 3. Zn-air battery test

A homemade Zn–air battery was assembled with a Zn/Mg-N-C catalyst-coated carbon paper as the air cathode with a loading density of 0.52 mg cm<sup>-2</sup>, a Zn plate anode and 6 M KOH + 0.1 M ZnCl<sub>2</sub> aqueous electrolyte. The catalyst ink includes 5 mg of catalyst, 5 mg of RuO<sub>2</sub>, containing 40  $\mu$ L of Nafion, 480  $\mu$ L of DI water and 480  $\mu$ L ethanol. The ZABs equipped with Pt/C was also fabricated and measured under the same conditions for comparison for comparison.

4. Theoretical calculation

The first principle calculations are performed by Vienna Ab initio Simulation Package(VASP)<sup>1</sup> with the projector augmented wave (PAW) method<sup>2</sup>. The exchange-functional is treated using the Perdew-Burke-Ernzerhof (PBE)<sup>3</sup> functional, in combination with the DFT-D3 correction<sup>4</sup>. The cut-off energy of the plane-wave basis is set at 450 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration is performed with 2\*2\*1 Monkhorts-Pack<sup>5</sup> kpoint sampling. The self-consistent calculations apply a convergence energy threshold of 10-5 eV. The equilibrium geometries and lattice constances are optimized with maximum stress on each atom within 0.02 eV/Å.



Fig. S1. SEM images of (a) Zn-N-C and (b) Mg-N-C.



Fig. S2. HRTEM of Zn/Mg-N-C.



Fig. S3. XRD pattern of Mg-N-C and Zn-N-C.



Fig. S4. Raman spectra of Zn/Mg-N-C, Zn-N-C and Mg-N-C.



Fig. S5. CV curves for Zn/Mg-N-C, and Pt/C in  $N_2/O_2$ -saturated solution at a scan rate of 50 mV s<sup>-1</sup>.



Fig. S6. RDE curves recorded in 0.1 M KOH before and after 5,000 cycles for Zn/Mg-N-C (a) and Pt/C (b).



S7. Discharge and charge polarization curves of  $Zn/Mg-N-C+RuO_2$ -based ZABs, and  $Pt/C+RuO_2$ -based ZABs for Zn-air battery.



Fig. S8. Cycling tests of batteries for  $Pt/C+RuO_2$ -based ZABs at a current density of 5 mA cm<sup>-2</sup>.



Fig. S9 Optimized geometry of Zn-N-C.



Fig. S10 Optimized geometry of Mg-N-C.



Fig. S11 The models of  $*O_2$ , \*OOH, \*O, \*OH intermediate adsorbed on the active site of Zn -N-C.



Fig. S12 The models of  $*O_2$ , \*OOH, \*O, \*OH intermediate adsorbed on the active site of Mg-N-C.



# **Reaction Coordinate**

Fig. S13 The Gibbs free energy diagram of the ORR on Zn/Mg-N-C, Zn-N-C and Mg-N-C obtained from DFT

calculations (U=0 V).

Tabl	e S1. The Content of Zn and Mg in Zn/N	1g-N-C
Catalyst	Zn content (wt%)	Mg content (wt%)
Zn/Mg-N-C	0.57	0.21

Table S2.	Comparison of	f electrocatalytic OF	R activity as well a	s ZABs performanc	e of recently reported metal
-----------	---------------	-----------------------	----------------------	-------------------	------------------------------

$ \begin{array}{c c c c c } & \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $									
$\begin{array}{c c c c c c c } \hline ({\rm W \ V \ V \ V \ V \ V \ V \ V \ V \ V \$	Sample	Half-wave potential	Power dendity	Pef					
$\begin{array}{c c c c c } & 29.8,7 & This work \\ \hline Pr(Co NPs & 0.82 & 124.9 & Nano-Micro Lett, 2023, 15, 26. & 15, 26. & 2023, 24, 203, 22, 24, 203, 22, 24, 203, 22, $	Sample	(V vs. RHE)	(mW cm <sup>-2</sup> )	Kei.					
Fe/Co NPs         0.82         124.9         Nano-Micro Lett., 2023, 15, 26. $2nCo,@NCNTs-800$ 0.85         194.3         Chem. Eng. J., 2022, 429, 132199.           Mg-N-C@800         0.80         N.A.         Appl. Mater. Today, 2020, 21, 100846.           P-Fe-N-CNTs         0.88         145         Appl. Catal, B, 2023, 327, 122469.           NC-Co_3O,/CC         0.87         82         Adv. Mater., 2017, 29, 1704117.           Cn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFs-NH         0.89         255.84         2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           Fe-NSDC         0.84         225.1         Small, 2019, 15, 100007.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 2105887.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-ISAC         0.802         137.1         Small 2021, 18, 2107141           SA Fe@ZrO_/NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           ZnCo-Sse_@rGO         0.802         137.1<	Zn/Mg-N-C	0.89	298.7	This work					
Fe/CO Nrs         0.82         124.3         15, 26.           ZnCo,@NKNTS-800         0.85         194.3         Chem. Eng. J., 2022, 429, 132199.           Mg-N-C@800         0.80         N.A.         Appl. Mater. Today, 2020, 21, 100846.           P-Fe-N-CNTs         0.88         145         Appl. Catal, B, 2023, 2020, 21, 100846.           P-Fe-N-CNTs         0.88         145         Appl. Catal, B, 2023, 2020, 21, 100846.           NC-Co_3O_4/CC         0.87         82         Adv. Mater., 2017, 29, 1704117.           Zn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFs-NH         0.89         255.84         2105410.           SSM/Co4N/CoNC         0.83         105         2105887.           SSM/Co4N/CoNC         0.83         NA.         Angew. Chem. 2021, 60, 2105887.           Fe-NSDC         0.84         225.1         Small, 2019, 15, 1900307.           Gu/Zn-NC         0.83         N.A.         Angew. Chem. Ap, 2021, 9, 25160-25167.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.802         137.1         Smal		0.83	124.9	Nano-Micro Lett., 2023,					
$2nCo_2@NCNTs-800$ $Mg-N-C@800$ $0.80$ $194.3$ Chem. Eng. J., 2022, 429, 132199. Appl. Mater. Today, 2020, 21, 10846. 327, 122469. 327, 120417. 327, 122469. 327, 120417. 327, 120417. 328, 1205410. 328, 1205410. 328, 1205410. 328, 1205410. 328, 1205410. 328, 1205410. 328, 1205410. 329, 1205410. 329, 1205410.SSM/Co4N/CoNC CoU/Zn-NC $0.89$ $255.84$ 210587. 3181Adv. Mater., 2022, 18, 1209, 15, 1300307. 3181, 2022, 18, 20141 300307.Fe-NSDC Cu/Zn-NC $0.86$ $152.8$ 2022, 45, 805-813. 2022, 45, 805-813.Co/CNT_10 Mg/Ni Co7C $0.75$ $181$ J. Mater. Chem. A 2021, 9, 215160-25167. 2021, 9, 21660. 2021, 9, 21660.Co/CNT_10 Mg/Ni Co2C/MoC/Co@CNTS $0.802$ 137.1Small 2023, 19, 220704. 313, 1SA Fe@270_/NC Mo2C/MoC/Co@CNTS $0.89$ $137.1$ Small 2023, 19, 220704. 314.1Mo2C/MoC/Co@CNTS FeSA-N-C $0.905$ $126$ Angew. Chem., 2018, 57, 355.2529. 	Fe/Co NPs	0.82		15, 26.					
Line         134.3         429, 132199.           Mg-N-C@800         0.80         N.A.         Appl. Mater. Today, 2020, 21, 100846.           P-Fe-N-CNTs         0.88         145         Appl. Catal., 8, 2023, 327, 122469.           NC-Co <sub>3</sub> O <sub>4</sub> /CC         0.87         82         Adv. Mater., 2017, 29, 1704117.           Zn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFs-NH         0.89         255.84         Adv. Mater., 2022, 34, 2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           Fe-NSDC         0.84         225.1         1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         2152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         I. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HINC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_2/NC         0.86         250         12938           ZnCo-HINC         0.82         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTS         0.82         137.1         Small 2023, 19, 2207096		0.95	194.3	Chem. Eng. J., 2022,					
$\begin{array}{c c c c c c } & & & & & & & & & & & & & & & & & & &$	ZnCo <sub>2</sub> @NCNTs-800	0.85		429, 132199.					
Mg-N-Legisto         0.80         N.A.         2020, 21, 100846.           P-Fe-N-CNTs         0.88         145         Appl. Catal, 8, 2023, 327, 122469.           NC-Co <sub>3</sub> O <sub>4</sub> /CC         0.87         82         Adv. Mater., 2017, 29, 1704117.           Zn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFS-NH         0.89         255.84         7035-7039           Fe/SNCFS-NH         0.89         255.84         703540.           SSM/Co4N/CONC         0.83         105         Small, 2022, 13, 2105887.           Fe-NSDC         0.84         225.1         1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         137.1         Small 2021, 82, 107141           SA Fe@ZrO <sub>2</sub> /NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           ZnCo <sub>2</sub> Sea,@FGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063		0.80	N.A.	Appl. Mater. Today,					
$\begin{array}{c c c c c c } & & & & & & & & & & & & & & & & & & &$				2020, 21, 100846.					
P-Fe-N-CNTS         0.88         145         327, 122469.           NC-Co <sub>3</sub> O <sub>4</sub> /CC         0.87         82         Adv. Mater., 2017, 29, 1704117.           Zn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFS-NH         0.89         255.84         Adv. Mater., 2022, 34, 2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           Fe-NSDC         0.83         105         Small, 2019, 15, 1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805–813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160–25167.           ZnCo-HNC         0.86         250         Chem. Eng. J., 2021, 420, 12938           AFe@ZrO_J/NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.89         N.A.         S52, 234063           FeSA-N-C         0.89         N.A.         S525, 8529.           Chem Eng J., 2024, 481, 555, 234063         S525, 8529.         Chem Eng J., 2024, 48			145	Appl. Catal., B, 2023,					
$\begin{array}{ccccccc} & & & & & & & & & & & & & & & &$	P-Fe-N-CNTS	0.88		327, 122469.					
NC-Co <sub>3</sub> O <sub>3</sub> /CC         0.87         82         1704117.           Zn-N-C         0.873         N.A.         Angew. Chem. 2019, 58, 7035-7039           Fe/SNCFs-NH         0.89         255.84         7035-7039           Fe/SNCFs-NH         0.89         255.84         2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           Fe-NSDC         0.84         225.1         Small, 2019, 15, 1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-O DSAC         0.83         N.A.         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_J/NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo_Sea@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           Fee/Zn-N-C         0.905         126         Chem Eng J, 2024, 481, 148598.		0.07		Adv. Mater., 2017, 29,					
$ \begin{array}{c c c c c c } & & & & & & & & & & & & & & & & & & &$	NC-Co <sub>3</sub> O <sub>4</sub> /CC	0.87	82	1704117.					
Zh-N-L         0.89         N.A.         7035-7039           Fe/SNCF5-NH         0.89         255.84         Adv. Mater., 2022, 34, 2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           SSM/Co4N/CoNC         0.83         105         2105887.           Fe-NSDC         0.84         225.1         1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.86         250         Chem. Eng. J., 2021, 420, 12938           SA Fe@ZrO_2/NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.89         N.A.         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         Angew. Chem., 2018, 57, 8525-8529.         8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022,	7- 11 0	0.070		Angew. Chem. 2019, 58,					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Zn-N-C	0.873	N.A.	7035-7039					
Fe/SNCFS-NH         0.89         255.84         2105410.           SSM/Co4N/CoNC         0.83         105         Small, 2022, 18, 2105887.           SSM/Co4N/CoNC         0.83         225.1         Small, 2019, 15, 1900307.           Fe-NSDC         0.84         225.1         Small, 2019, 15, 1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_/NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           M02C/MOC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           M02C/MOC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A. <t< td=""><td rowspan="2">Fe/SNCFs-NH</td><td></td><td></td><td>Adv. Mater., 2022, 34,</td></t<>	Fe/SNCFs-NH			Adv. Mater., 2022, 34,					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.89	255.84	2105410.					
SSM/C64N/C6AL         0.83         105         2105887.           Fe-NSDC         0.84         225.1         Small, 2019, 15, 1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.83         152.8         Energy storage Mater., 2022, 45, 805-813.           Fe-Co DSAC         0.86         152.8         Energy storage Mater., 2021, 9, 25160-25167.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_/NC         0.86         250         Chem. Eng. J., 2021, 420, 12938           ZnCo_Sea,@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           FeSA-N-C         0.89         N.A.         Sp5, 234063           FeSA-N-C         0.89         N.A.         8255-8529.           ZnSe@PNC         0.905         126         Chem Eng. J, 2024, 481, 148598.           Ferge Environ Sci, 2022, 15, 1601-1610.         148598.         148598.		0.83	105	Small, 2022, 18,					
$\begin{array}{cccc} & & & & & & & & & & & & & & & & & $	SSM/Co4N/CoNC			2105887.					
Fe-NSDC         0.84         225.1         1900307.           Cu/Zn-NC         0.83         N.A.         Angew. Chem., 2021, 60, 14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO2/NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo-Zse4@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           FeSA-N-C         0.89         N.A.         I. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         S525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	5 1/000	0.84	225.1	Small, 2019, 15,					
$ \begin{array}{ccc} \label{eq:cu/Zn-NC} & 0.83 & N.A. & & & & & & & & & & & & & & & & & & $	Fe-NSDC			1900307.					
LU/ZN-NC         0.83         N.A.         14005-14012.           Fe-Co DSAC         0.86         152.8         Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_2/NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo_Sea@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.		0.83	N.A.	Angew. Chem., 2021, 60,					
Fe-Co DSAC $0.86$ $152.8$ Energy Storage Mater., 2022, 45, 805-813.           Co/CNT_10 Mg/Ni $0.75$ $181$ J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC $0.82$ 123.7         Small 2022, 18, 2107141           SA Fe@ZrO_2/NC $0.86$ $250$ Chem. Eng. J., 2021, 420, 129938           ZnCo_2Se4@rGO $0.802$ 137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs $0.82$ 137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs $0.82$ 137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs $0.82$ $134$ J. Power Sources, 2024, 595, 234063           FeSA-N-C $0.89$ N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC $0.905$ $126$ Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C $0.906$ N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	Cu/Zn-NC			14005-14012.					
Fe-Co DSAC         0.86         152.8         2022, 45, 805-813.           Co/CNT_10 Mg/Ni         0.75         181         J. Mater. Chem. A, 2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO_/NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo_2Se_4@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	5 0 0040	0.86	152.8	Energy Storage Mater.,					
$ \begin{array}{cccc} \label{eq:co/CNT_10 Mg/Ni} & \ensuremath{D.75} & \ensuremath{181} & \ensuremath{\bel{Jmatrix} J. Mater. Chem. A, 2021, 9, 25160-25167. \\ \hline \ensuremath{Z021, 9, 2107141} \\ \hline \ensuremath{Z022, 18, 2107141} \\ \hline \ensuremath{Z022, 1938} \\ \hline Z022$	Fe–Co DSAC			2022, 45, 805–813.					
CO/CNT_10 Mg/NI         0.75         181         2021, 9, 25160-25167.           ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO <sub>2</sub> /NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo_2Se4@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         137.1         Small 2023, 19, 2207096           FeSA-N-C         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 148598.		0.75	181	J. Mater. Chem. A,					
ZnCo-HNC         0.82         123.7         Small 2022, 18, 2107141           SA Fe@ZrO2/NC         0.86         250         Chem. Eng. J., 2021, 420, 129938           ZnCo2Se4@rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	CO/CNT_10 Mg/Ni	0.75		2021, 9, 25160–25167.					
$ \begin{array}{c c} SA \ Fe@ZrO_2/NC & 0.86 & 250 & Chem. \ Eng. \ J., \ 2021, \ 420, \\ 129938 & 129938 & 129938 & 12023, \ 19, \ 2207096 & 129938 & 12023, \ 19, \ 2207096 & 137.1 & Small \ 2023, \ 19, \ 2207096 & 134 & 595, \ 234063 & 148 & 595, \ 234063 & 148 & $	ZnCo-HNC	0.82	123.7	Small 2022, 18, 2107141					
SA Fe@ZrO <sub>2</sub> /NC         0.86         250         129938           ZnCo <sub>2</sub> Se <sub>4</sub> @rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	SA Fe@ZrO <sub>2</sub> /NC	0.86	250	Chem. Eng. J., 2021, 420,					
ZnCo <sub>2</sub> Se <sub>4</sub> @rGO         0.802         137.1         Small 2023, 19, 2207096           Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.				129938					
Mo2C/MoC/Co@CNTs         0.82         134         J. Power Sources, 2024, 595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn–N–C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	ZnCo <sub>2</sub> Se <sub>4</sub> @rGO	0.802	137.1	Small 2023, 19, 2207096					
Mo2C/MoC/Co@CNTs         0.82         134         595, 234063           FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn–N–C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	Mo2C/MoC/Co@CNTs	0.82	134	J. Power Sources, 2024,					
FeSA-N-C         0.89         N.A.         Angew. Chem., 2018, 57, 8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn–N–C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.				595, 234063					
FeSA-N-C         0.89         N.A.         8525-8529.           ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn-N-C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	FeSA-N-C	0.89	N.A.	Angew. Chem., 2018, 57,					
ZnSe@PNC         0.905         126         Chem Eng J, 2024, 481, 148598.           Fe/Zn–N–C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.				8525-8529.					
ZnSe@PNC         0.905         126         148598.           Fe/Zn–N–C         0.906         N.A.         Energ Environ Sci, 2022, 15, 1601-1610.	ZnSe@PNC	0.905	126	Chem Eng J, 2024, 481,					
Fe/Zn–N–C         0.906         N.A.         15, 1601-1610.				148598.					
Fe/Zn–N–C 0.906 N.A. 15, 1601-1610.	Fe/Zn–N–C		N.A.	Energ Environ Sci, 2022,					
		0.906		15, 1601-1610.					

doped carbon-based electrocatalysts

## Reference

- 1. J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- 2. G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.
- 3. J.P. Perdew, K. Burke, M. Ernzerhof, Phy. Rev. Lett. 77 (1996) 3865.
- 4. S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, J. Chem. Phys. 132, 154104 (2010).
- 5. H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188.
- 6. Z. Zhang, J. Sun, F. Wang and L. Dai, Angewandte Chemie International Edition, 2018, 57, 9038-9043.