Electronic Supplementary Information

An attempt to confirm the contribution to ORR activity of different N-species in M-NC (M=Fe, Co, Ni) catalysts with XPS analysis

Zhuxin Li, [a] Hongquan Yu, [b] Yong Zhang, [a] Danyang Wu, [b] Yunxiang Bai, [a] Shuhong Liu, [a] and Hong Zhao *[a]

[a] Key laboratory of metal-air new energy batteries of Liaoning province, Dalian Jiaotong University, Dalian 116028, China

[b] Department of Physics, Dalian Maritime University, Dalian 116026, Liaoning, China

*Corresponding author.

E-mail address: zhaohong@djtu.edu.cn (Hong Zhao)

Materials

The specific preparation process of Co-NC and Ni-NC catalysts is as follows: Take the mass of $C_4H_6CoO_4$ and $Ni(NO_3)_2$ to be 1.5 g and 2.0 g respectively, dissolve the medicine in 40 mL N,N-dimethylformamide respectively. Add 100 mg of highly conductive graphene. Add 4.8 g of PVP. Strong stirring to prepare viscous and drawable precursor solution; the distance between the control nozzle and the receiving plate is between 10~15 cm. The applied voltage is about 18~22 KV. The angle between the nozzle and the horizontal is adjusted to 15 °. The precursors with 3D sponge-like nanofibrous structures were prepared and then dried at 80 °C for 8 h. The dried fibers were transferred to a tube furnace for pre-oxidation experiments. The fibers are calcined in air to 300 °C and cooled to room temperature. Then they were transferred to ammonia gas and heated to 600 °C, 700 °C, 800 °C, and 900 °C for heat treatment. They are respectively recorded as Co-NC600, Co-NC700, Co-NC800, Co-

NC900; Ni-NC600, Ni-NC700, Ni-NC800, Ni-NC900.

Material characterization

Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S-4800, Japan) with an acceleration voltage of 30 kV was used to characterize the morphology of a catalyst. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 (Thermo Electron Corp, MA) X-ray photoelectron spectrometer with a vacuum of 10^{-7} Pa to remove a large number of impurity species adsorbed on the surface of the sample. The excitation source of XPS was Al Kα rays and spectral data were corrected with C 1s binding energy.

Electrochemical characterization

All electrochemical measurements were performed in a three-electrode system of an electrochemical workstation (PGSTAT302 N, Ecochemie Co, Netherlands) at 25 ^{o}C with a loading the catalyst of 0.2 mg cm^{-2} . In the measurements, the glassy carbon electrode with a diameter of 5 mm was used as the working electrode, the saturated calomel electrode was used as the reference electrode, and the platinum mesh electrode with a side length of 2 cm was used as the auxiliary electrode. High-purity nitrogen and oxygen with a purity of 99.5% were used as the test gas conditions. ORR stability was investigated by cyclic voltammetry at a scan rate of 50 mV s^{-1} in a 0.1 M KOH electrolyte solution over a potential range between -1 and 0.2 V and linear sweep voltammetry (LSV) curves were recorded at a scan rate of 10 mV s^{-1} in an O_2 saturated electrolyte solution at rotation rates of 1600 rpm.

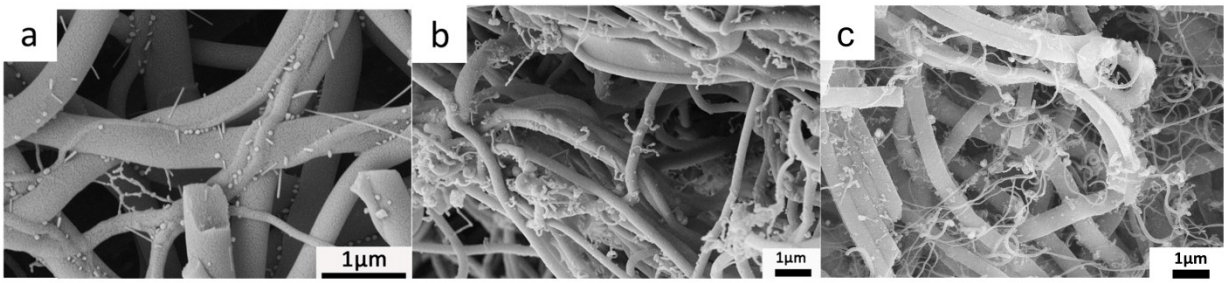

Fig. S1. SEM images of the (a) Fe-NC600 catalysts; (b) Fe-NC700 catalysts; (c) Fe-NC900 catalysts.

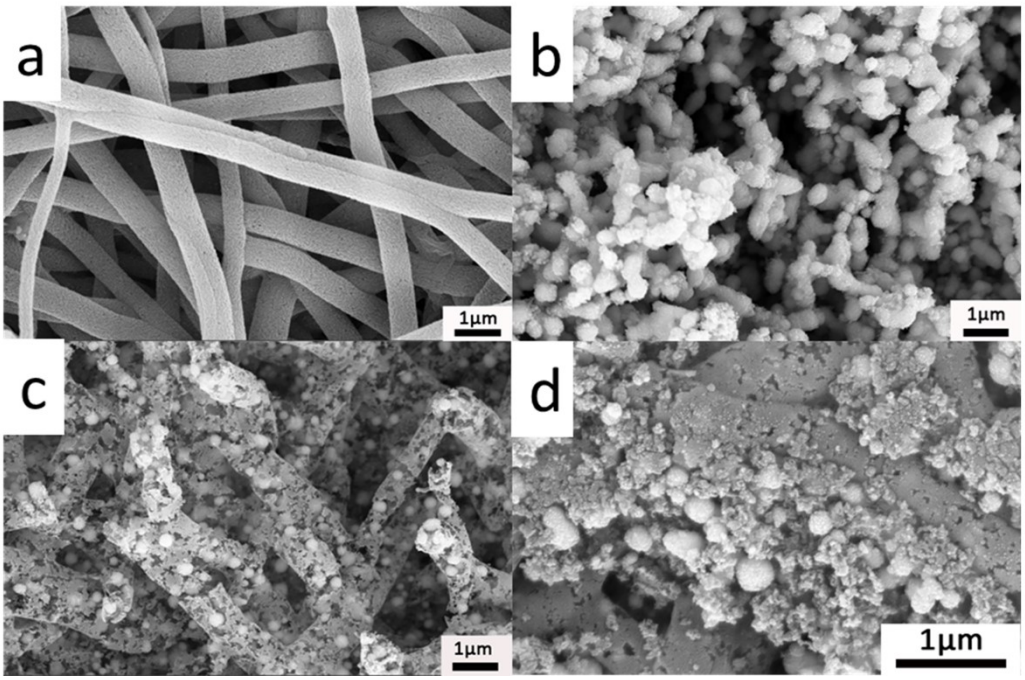

Fig. S2. SEM images of the (a) Co-NC600 catalysts; (b) Co-NC700 catalysts; (c) Co-NC800 catalysts; (d) Co-NC900 catalysts.

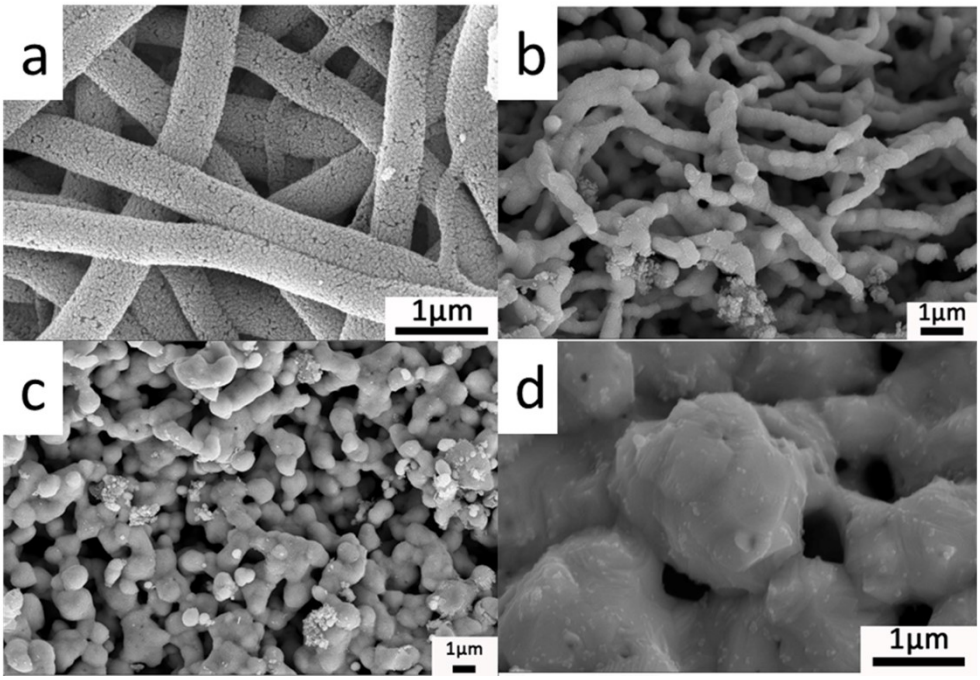

Fig. S3. SEM images of the (a) Ni-NC600 catalysts; (b) Ni-NC700 catalysts; (c) Ni-NC800 catalysts; (d) Ni-NC900 catalysts.

Table S1. Linear fitting equation between the content of different N-species in M-NC(M=Co, Ni) catalysts and the corresponding ORR half-wave potential.

Catalysts	Equation	Solution
Co-NC600	15%x+49%h+36%i=0.66	x=0.91
Co-NC700	30%x+13%y+57%z=0.86	y=1.04
Co-NC800	30%x+17%y+53%z=0.87	z=0.79
		h=0.44
Co-NC900	32%x+20%y+48%z=0.88	i=0.85
Ni-NC600	33%x+16%y+51%h=0.66	x=0.84
Ni-NC700	34%x+15%y+51%z=0.81	y=1.18
Ni-NC800	51%x+49%z=0.76	z=0.68
Ni-NC900	45%x+55%z=0.75	h=0.38

Table S2. The influence coefficient of different N-species in the M-NC catalysts on the ORR performance of the catalysts and the statistical table of the highest half-wave potential value.

	pyridinic-N(x)	M-N_x(y)	graphitic-N(z)	pyrrolic-N(h)	$E_{1/2}$(highest)
Fe-NC	0.92	1.09	0.83	0.46	0.89
Co-NC	0.91	1.04	0.79	0.44	0.88
Ni-NC	0.84	1.18	0.68	0.38	0.81

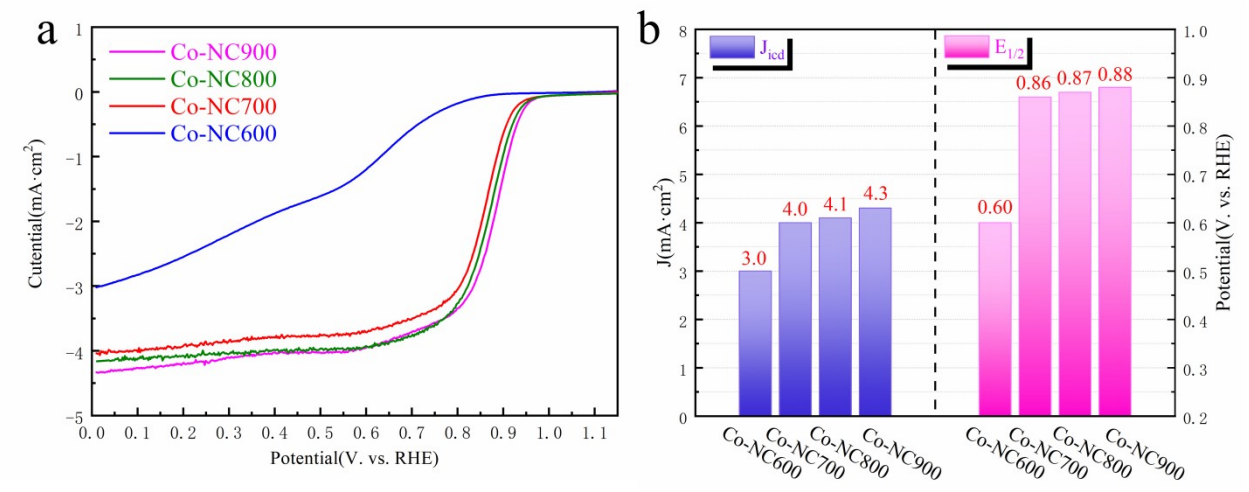

Fig. S4. (a) LSV curve and (b) corresponding half-wave potential and current density of Co-NC catalysts at different calcination temperatures.

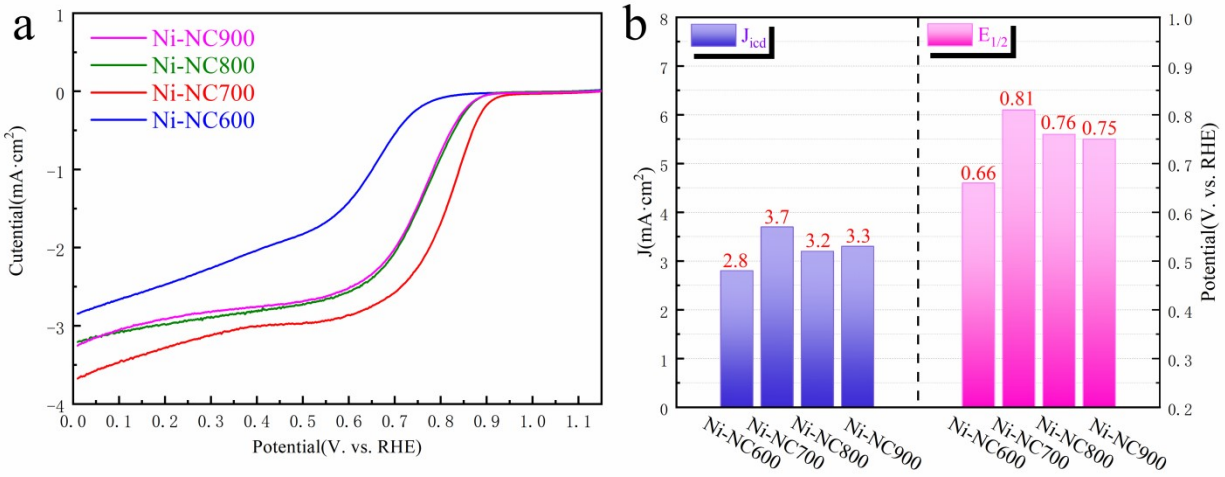

Fig. S5. (a) LSV curve and (b) corresponding half-wave potential and current density of Ni-NC catalysts at different calcination temperatures.

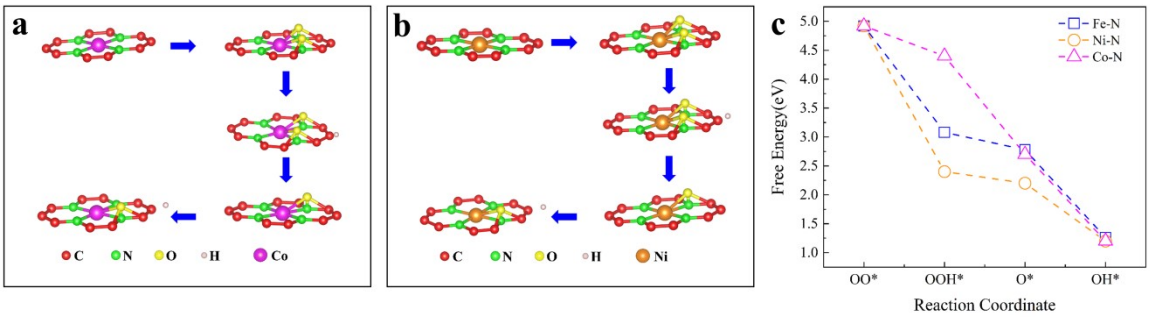

Fig. S6. (a) First-principles calculation simulation diagram of Co-Nx as an ORR activity center; (b) First-principles calculation simulation diagram of Ni-Nx as an ORR activity center; (c) First-principles calculations of free energy of Fe-Nx, Co-Nx and Ni-Nx as ORR active center.