

Electronic Supporting Information (ESI)

High Pressure Pyrolyzed Non-precious Oxygen Reduction Catalysts for Alkaline  
Polymer Electrolyte Membrane Fuel Cells

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## Characterization:

The N<sub>2</sub> adsorption–desorption measurements were carried out using ‘Micromeritics’ (ASAP 2020) at 77 K. Bruner–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH) models and the t-plot method (Harkins and Jura formula) were used to determine the specific surface area, the microporous (0.5-2 nm) and mesoporous (2-50 nm) pore size distributions and microporous information for the cobalt embedded carbon nanorods samples, respectively. Before the measurements, the samples were degassed at 200 °C under vacuum for 4 hours. The amount of nitrogen and carbon in samples were accurately determined by elemental analyzer (C, H, N analysis).

The kinetics of ORR on M-N-C catalyst evaluated by Koutecky-Levich plots were determined by follow equation.

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$
$$B = 0.62 n F C_0 D_0^{\frac{2}{3}} \nu^{-\frac{1}{6}}$$

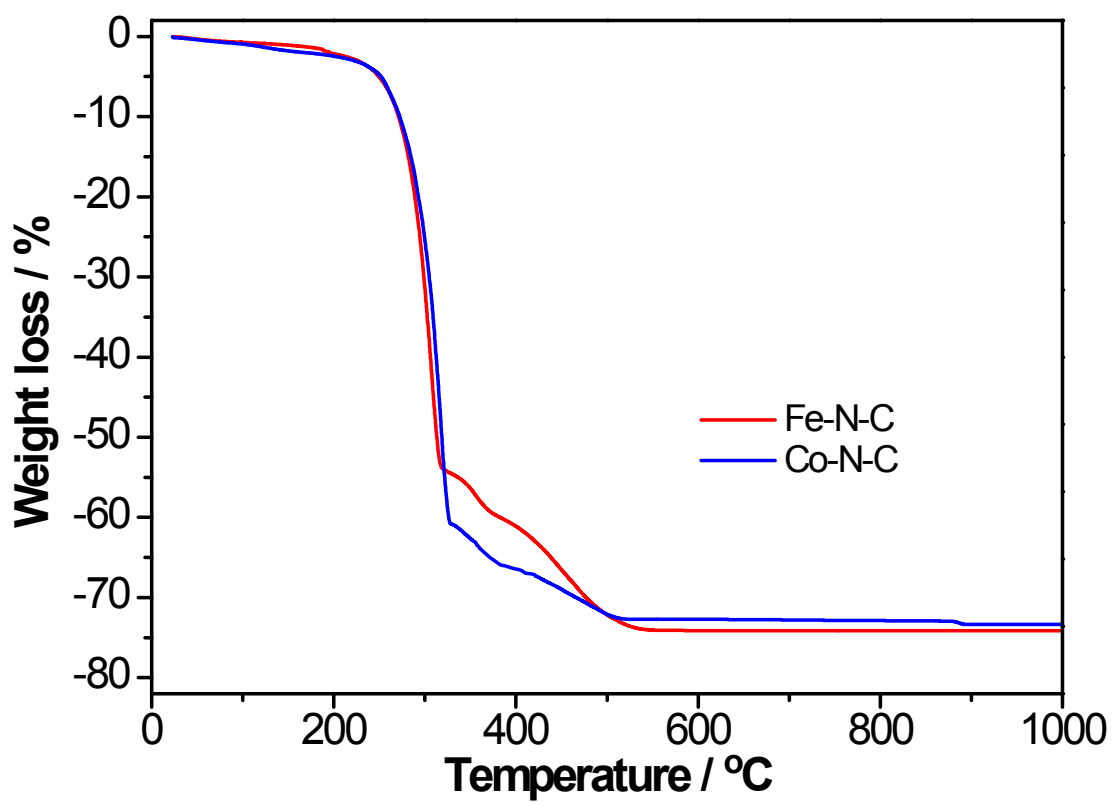
Where, J is the experimentally measured current, J<sub>L</sub> is the diffusion-limiting current, J<sub>K</sub> is the kinetic current, ω is the angular velocity, F is the Faraday constant, C<sub>0</sub> is the saturated concentration of O<sub>2</sub> in 0.1M KOH (1.2 x 10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> in 0.1M KOH (1.9 x 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and ν is the kinematic viscosity of the electrolyte. “n” can calculate from slop by under plot of J<sup>-1</sup> vs ω<sup>-1/2</sup> and J<sub>k</sub> is calculated from inverse of intercept.

The formation of  $\text{HO}_2^-$  and the electron transfer number from RRDE experiment were determined by follow equation;

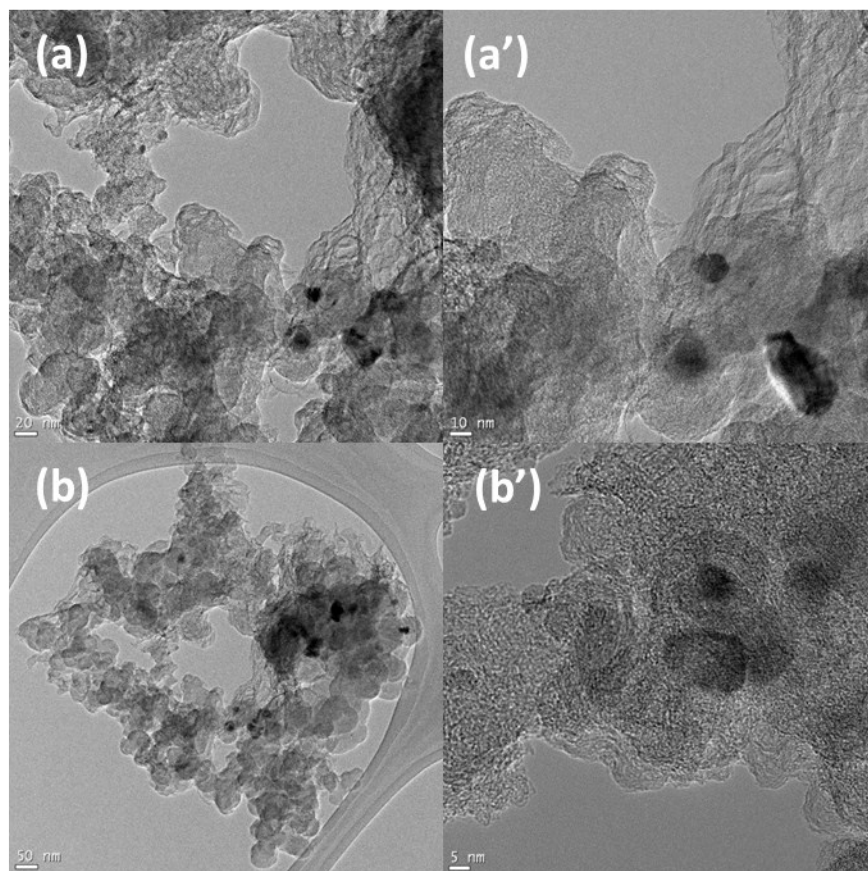
$$\text{H}_2\text{O}_2(\%) = 200 \times \frac{I_R/N}{I_D + (I_R/N)}$$

$$n = 4 \times \frac{I_D}{I_D + (I_R/N)}$$

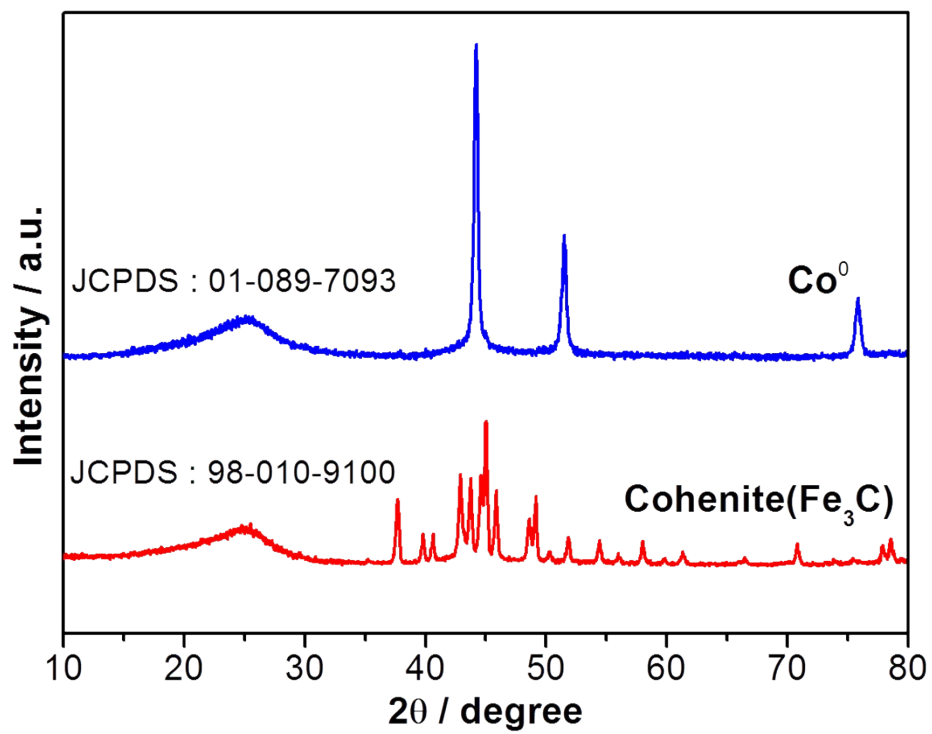
where,  $I_D$  is the disk current,  $I_R$  is the ring current, and  $N$  is the ring correction coefficient in RRDE experiment was determine to be 0.37 from the reduction of  $\text{Fe}(\text{CN})_6^{4-/3-}$  redox couple. The ring potential was held at 1.3 vs. RHE.



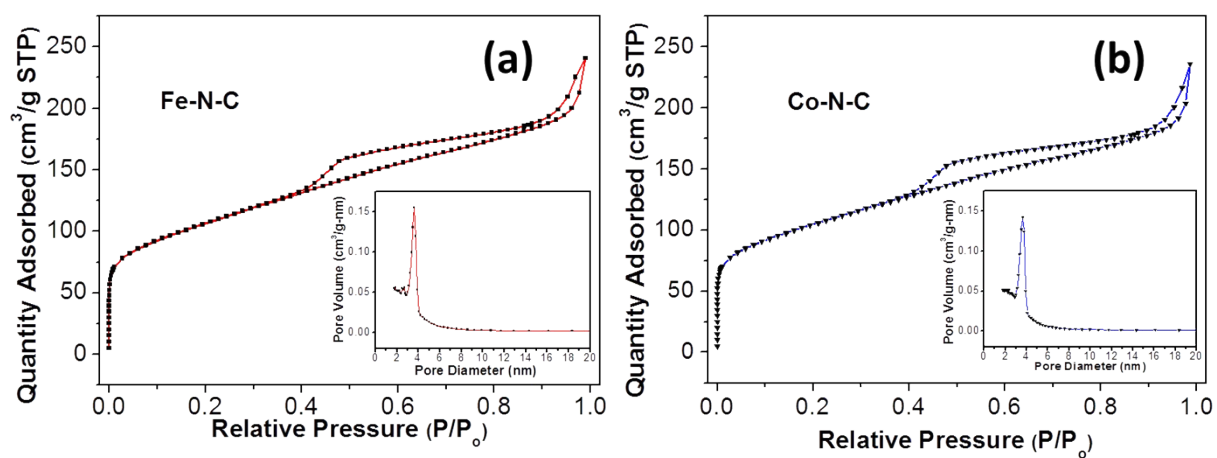
**Figure S1.** Thermograms of Fe-N-C and Co-N-C precursors carried out in an air atmosphere with a heating rate of  $10^{\circ}\text{C min}^{-1}$



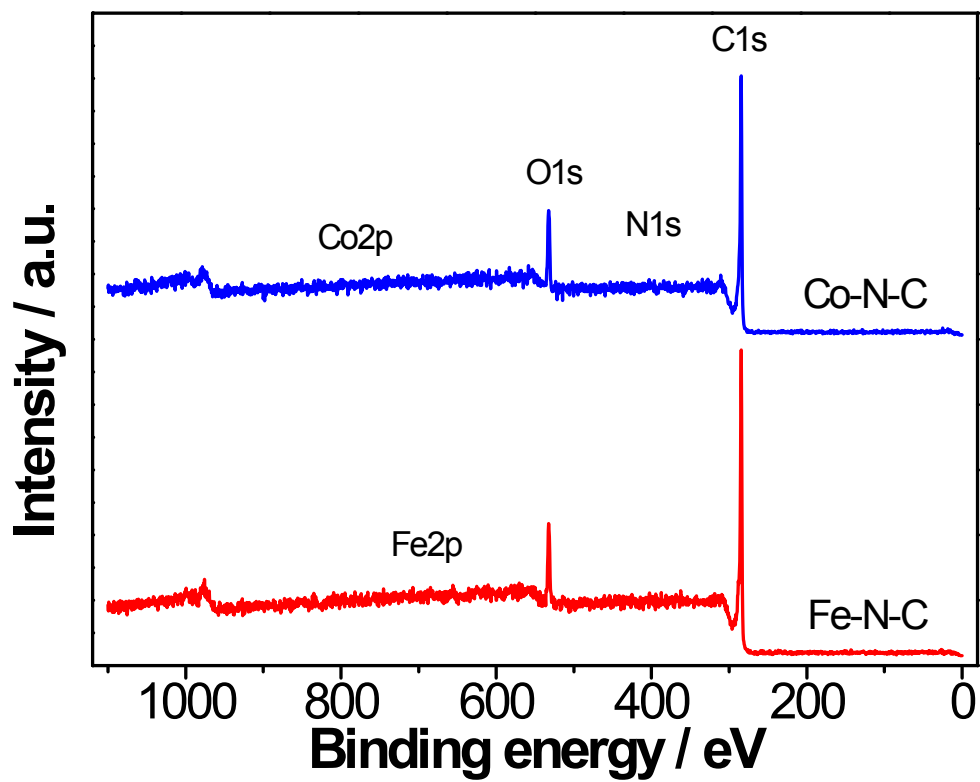
**Figure S2.** TEM images of (a, a') Fe-N-C (b, b') Co-N-C catalyst



**Figure S3.** XRD patterns of as-synthesized products after first heat-treated (before acid treatment)

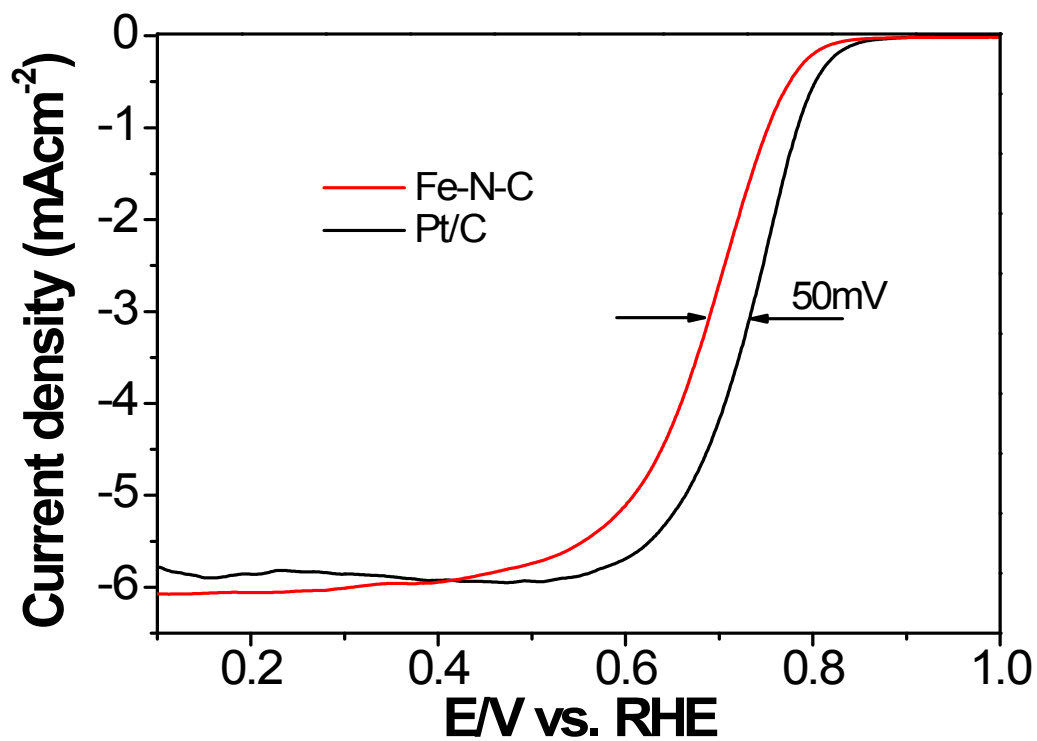


**Figure S4.** BET surface area analysis of (a) Fe-N-C (b) Co-N-C catalysts; insets show BJH pore-size distribution.

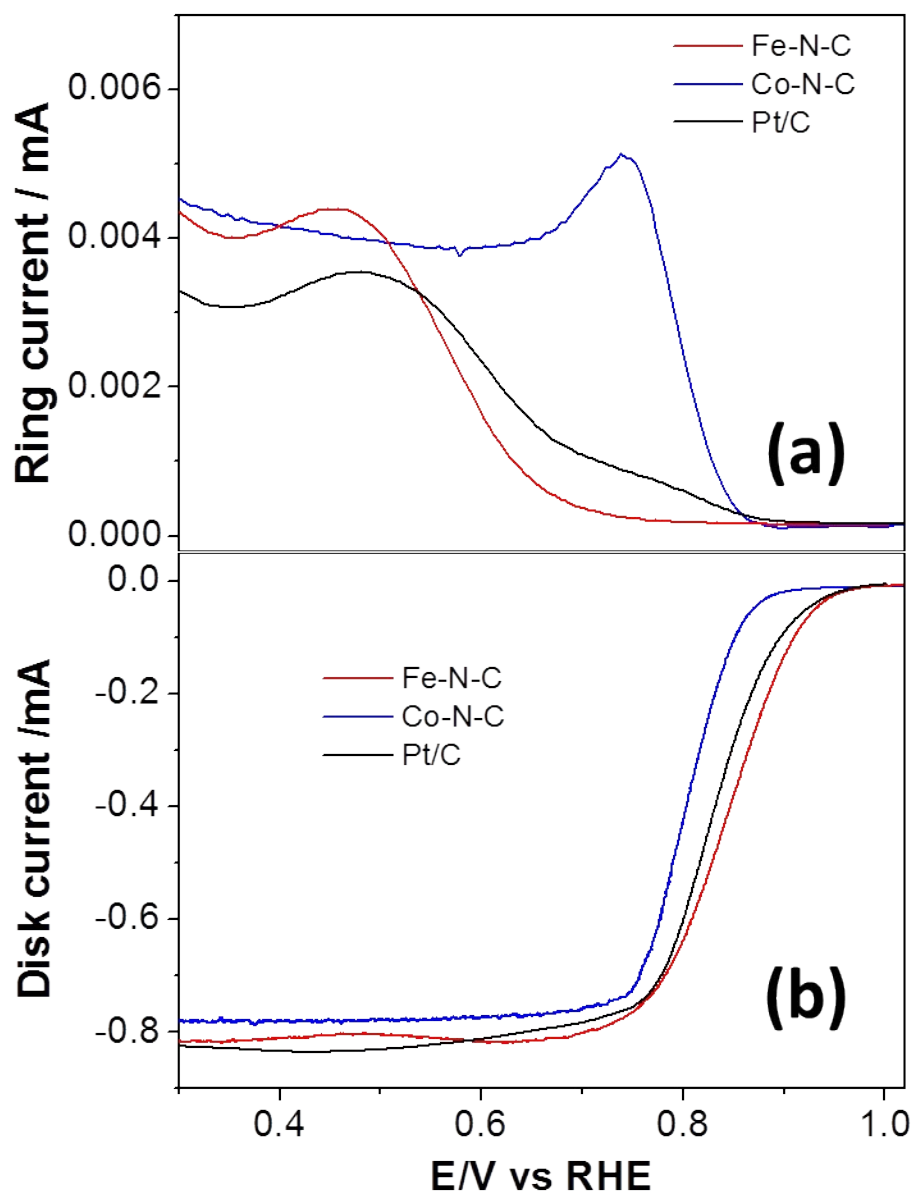


**Figure S5.** XPS survey spectra of Fe-N-C and Co-N-C catalyst.





**Figure S6.** RDE traces of Fe-N-C ( $0.6 \text{ mg cm}^{-2}$ ) and Pt/C ( $30 \mu\text{g cm}^{-2}$ ) catalysts obtained at 1,600 rpm in  $\text{O}_2$ -saturated  $0.5\text{M H}_2\text{SO}_4$  (cathodic scan direction) in  $0.5\text{M H}_2\text{SO}_4$  electrolyte, All potential were converted to RHE scale by adding  $0.26\text{V}$ .



**Figure S7.** RRDE response of Fe-N-C, Co-N-C and Pt/C catalysts obtained at 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH. (catalyst loading- 0.4 mg cm<sup>-2</sup> ; Pt/C -30 μg cm<sup>-2</sup> )

**Table S1.** The XPS data of Fe-N-C and Co-N-C catalysts.

Catalyst	N1s Distribution (%)			Total N content (%)	Fe2p <sub>3/2</sub> Distribution (%)		Total Fe content (%)	Co2p <sub>3/2</sub> distribution (%)		Total Co Content (%)	N/C ratio (%)
	N1	N2	N3		Fe(II)	Fe(III)		Co- O	Co-N <sub>x</sub>		
Fe-N-C	1.1	1.82	0.16	3.08	0.4	0.28	0.68	-	-	-	0.033
Co-N-C	0.32	0.81	0.18	1.31	-	-	-	0.67	0.06	0.73	0.014

**Table S2.** The CHN elemental analysis of Fe-N-C and Co-N-C catalysts.

Catalyst	C(wt%)	H(wt%)	N(wt%)	N/C ratio
Fe-N-C	92.29	0.85	1.05	0.011
Co-N-C	89.37	1.04	0.68	0.007

**Table S3.** The alkaline membrane fuel cells performance data electrocatalyst with commercial membrane in H<sub>2</sub>-O<sub>2</sub> system, no added back pressurization, reported in the literature

<b>Cathode material</b>	<b>Operating Temperature (°C)</b>	<b>Maximum power density (mW cm<sup>-2</sup>)</b>	<b>Reference</b>
Fe-N-C	60	75	*
Co-N-C	60	68	
NpGr-72	50	27	1
N-CNT	50	37.3	2
MnO <sub>x</sub> -GC	70	98	3
Ag/C	25	10	4
CoPc/MWCNT	50	120	5
FePc/MWCNT	50	60	
Au/C	50	36	6
Ag/C	50	19	

\* Present study

## References

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