

Electronic Supplementary Information (ESI)

Fe–N/C catalysts with tunable mesoporous structure and carbon layer number reveal the role of interlayer O₂ activation

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1. Supplementary Figures and Tables

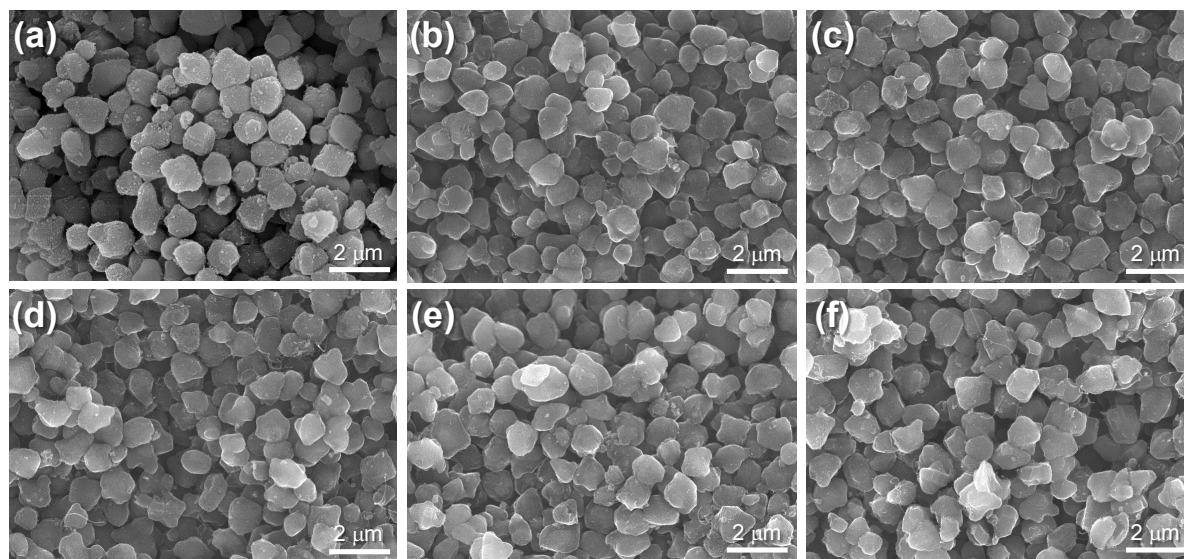


Fig. S1 SEM images of (a) SBA-15 silica template, (b) Meso-Fe-N/C_1.0, (c) Meso-Fe-N/C_1.25, (d) Meso-Fe-N/C_1.5, (e) Meso-Fe-N/C_1.75, and (f) Meso-Fe-N/C_2.0.

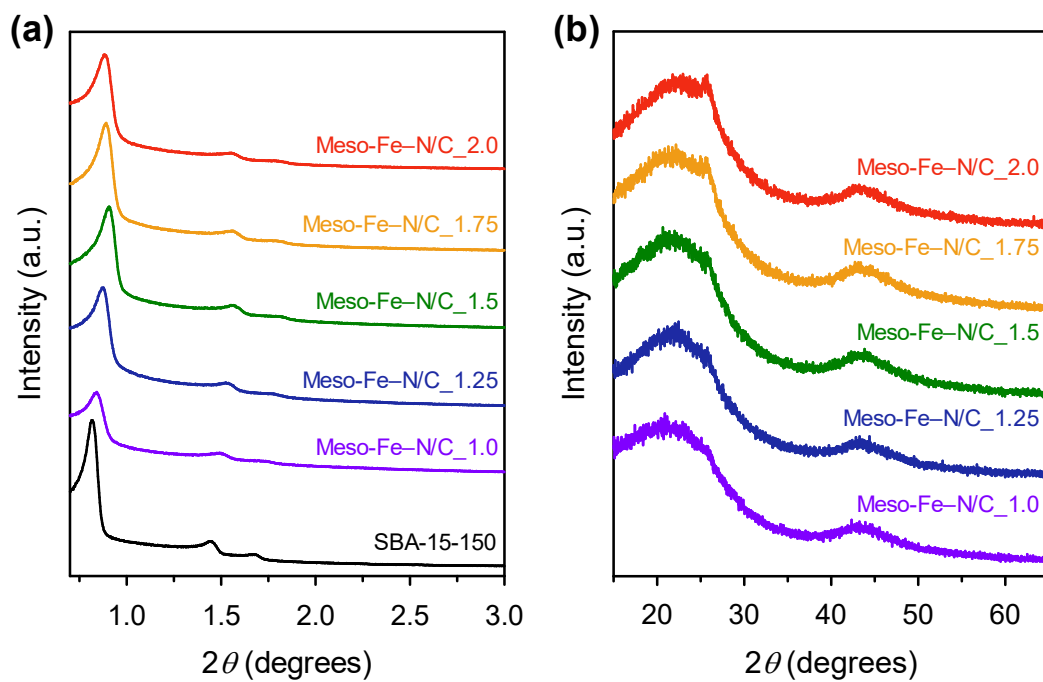


Fig. S2 (a) Small-angle and (b) wide-angle XRD patterns of the Meso-Fe-N/C_X catalysts.

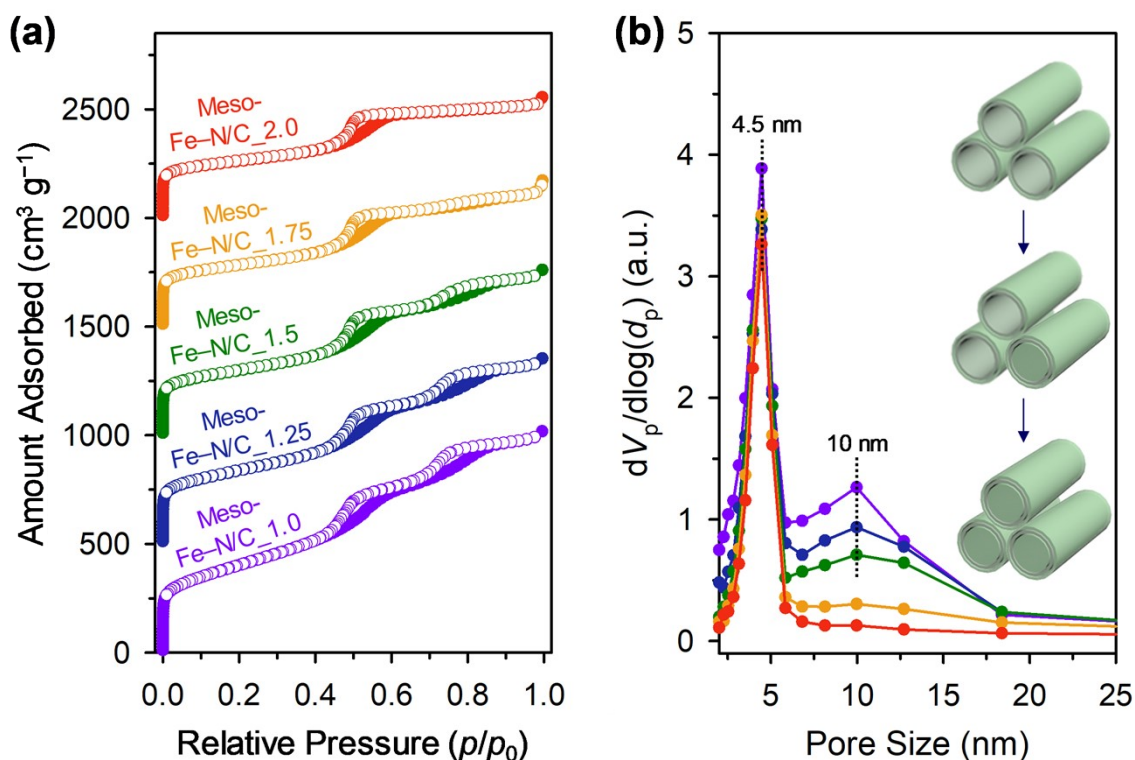


Fig. S3 (a) N₂ adsorption-desorption isotherms of the Meso-Fe-N/C_X catalysts. The isotherms of Meso-Fe-N/C_{1.25}, Meso-Fe-N/C_{1.5}, Meso-Fe-N/C_{1.75}, and Meso-Fe-N/C_{2.0} are offset by 500, 1000, 1500, and 2000 cm³ g⁻¹, respectively, for clarity. (b) Pore size distribution curves obtained from the adsorption branches of the corresponding isotherms. Structural models in inset illustrate the evolution of mesopore filling with gradual increase of Fe and N precursor loading.

Table S1. Textural properties of the Meso-Fe–N/C_X catalysts.

Sample	BET surface area (m ² g ⁻¹) ^a	Pore volume (cm ³ g ⁻¹) ^b	Pore size (nm) ^c
Meso-Fe–N/C_1.0	1350	1.56	4.5, 10.0
Meso-Fe–N/C_1.25	1200	1.31	4.5, 8.0–12.5
Meso-Fe–N/C_1.5	1070	1.16	4.5, 8.0–12.5
Meso-Fe–N/C_1.75	1030	1.00	4.5, 8.0–12.5
Meso-Fe–N/C_2.0	950	0.84	4.5

^a Calculated in the relative pressure range of 0.05–0.3.

^b Calculated at the relative pressure of 0.98–0.99.

^c Calculated from the adsorption branch of the corresponding isotherm using the BJH method.

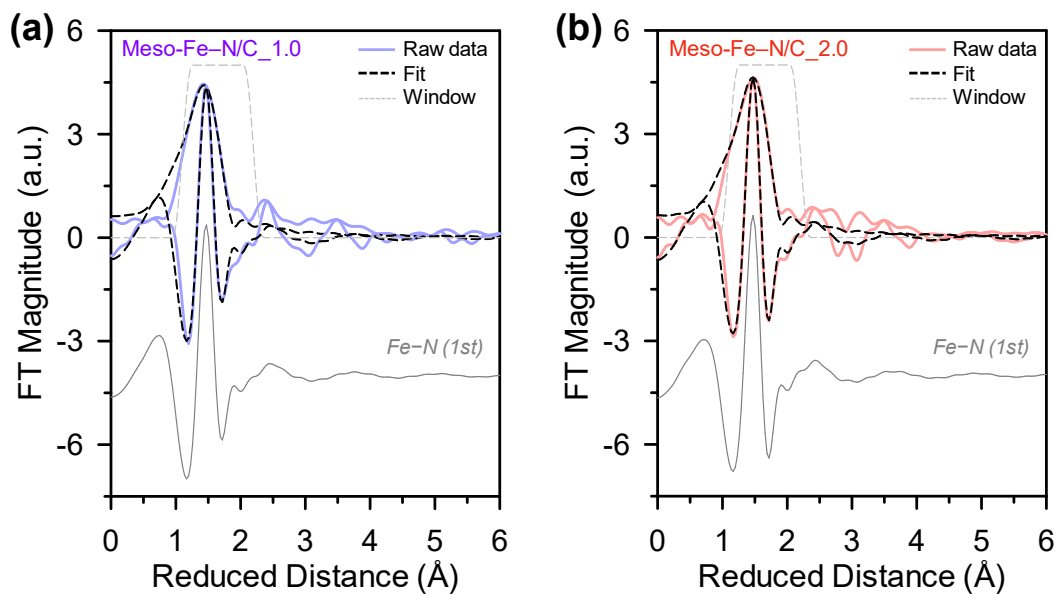


Fig. S4 EXAFS fitting curves of (a) Meso-Fe-N/C_1.0 and (b) Meso-Fe-N/C_2.0 in R space.

Table S2. EXAFS curve fitting results of Meso-Fe–N/C_1.0 and Meso-Fe–N/C_2.0.

Sample	k range (\AA^{-1})	R range (\AA)	Shell ^a	CN ^b	R (\AA)	σ^2 (10^{-3}\AA^{-2}) ^c	ΔE_0 (eV)
Meso-Fe–N/C_1.0	2.5–11.5	1.1–2.2	Fe–N (1st)	5.6 (± 1.2)	1.96 (± 0.02)	13.25 (± 2.8)	–5.64 (± 1.20)
Meso-Fe–N/C_2.0	2.5–11.5	1.1–2.2	Fe–N (1st)	5.3 (± 0.6)	1.98 (± 0.01)	12.21 (± 1.59)	–2.42 (± 1.41)

^a k^3 -weighted fitting shell of single scattering path was noted in parentheses.

^b Coordination number; the amplitude reduction factor ($S_0^2 = 0.87$, PAL 8C) was obtained from EXAFS fitting of Fe foil reference.

^c Debye-Waller factor.

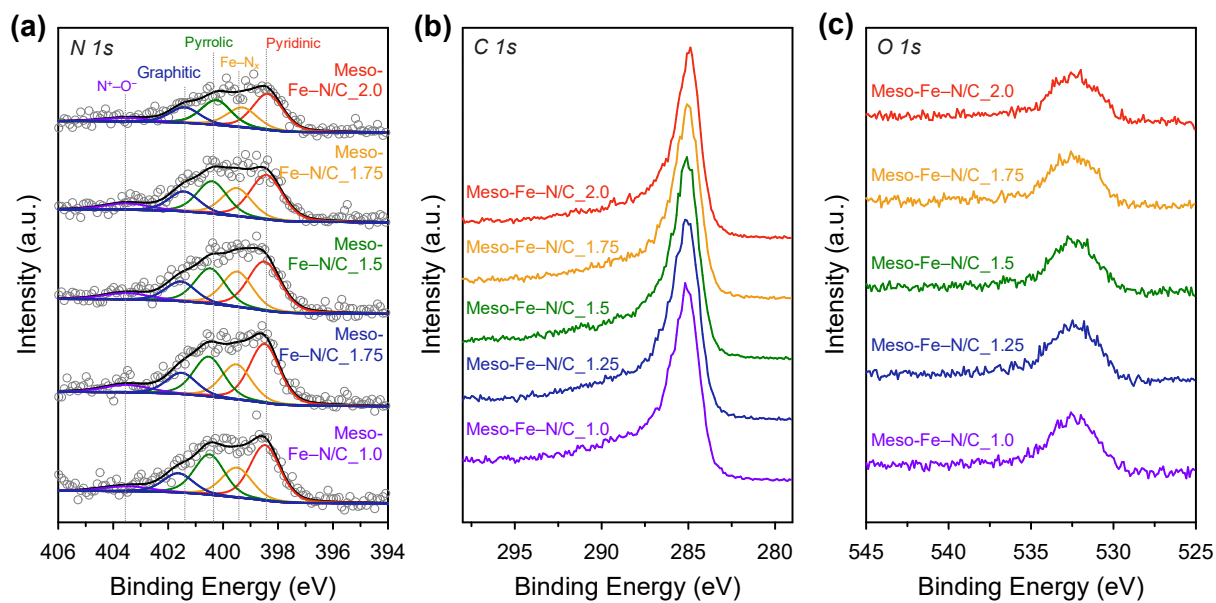


Fig. S5 (a) Deconvoluted N 1s, (b) C 1s, and (c) O 1s XPS spectra of the Meso-Fe-N/C_X catalysts.

Table S3. Relative peak areas for the deconvoluted N 1s XPS spectra of the Meso-Fe-N/C_*X* catalysts.

Sample	Relative peak area (%)				
	Pyridinic	Fe-N _x	Pyrrolic	Graphitic	N ⁺ -O ⁻
Meso-Fe-N/C_1.0	36.3	19.6	26.4	12.6	5.1
Meso-Fe-N/C_1.25	35.3	21.0	23.8	12.8	7.1
Meso-Fe-N/C_1.5	34.5	23.1	23.0	12.9	6.5
Meso-Fe-N/C_1.75	34.6	20.4	23.5	14.5	7.1
Meso-Fe-N/C_2.0	35.4	19.5	24.4	15.2	5.6

Table S4. Elemental analysis results of the Meso-Fe–N/C_*X* catalysts.

Sample	Content (wt%)				
	Fe ^a	C ^b	H ^b	N ^b	O ^b
Meso-Fe–N/C_1.0	1.9	70.0	1.3	9.1	8.8
Meso-Fe–N/C_1.25	1.9	70.8	1.5	8.6	10.0
Meso-Fe–N/C_1.5	2.0	72.7	1.4	8.3	9.1
Meso-Fe–N/C_1.75	1.9	73.6	1.7	8.0	9.2
Meso-Fe–N/C_2.0	2.0	73.9	1.6	7.2	7.9

^a Obtained by an inductively coupled plasma optical emission spectrometer.

^b Obtained by a combustion element analyzer.

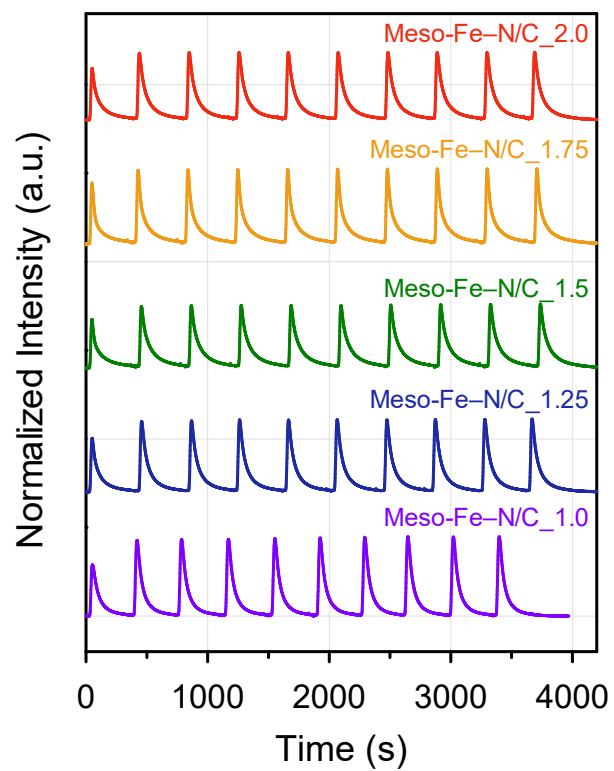


Fig. S6 CO pulse cryo-adsorption profiles of the Meso-Fe-N/C_*X* catalysts measured at -80 °C.

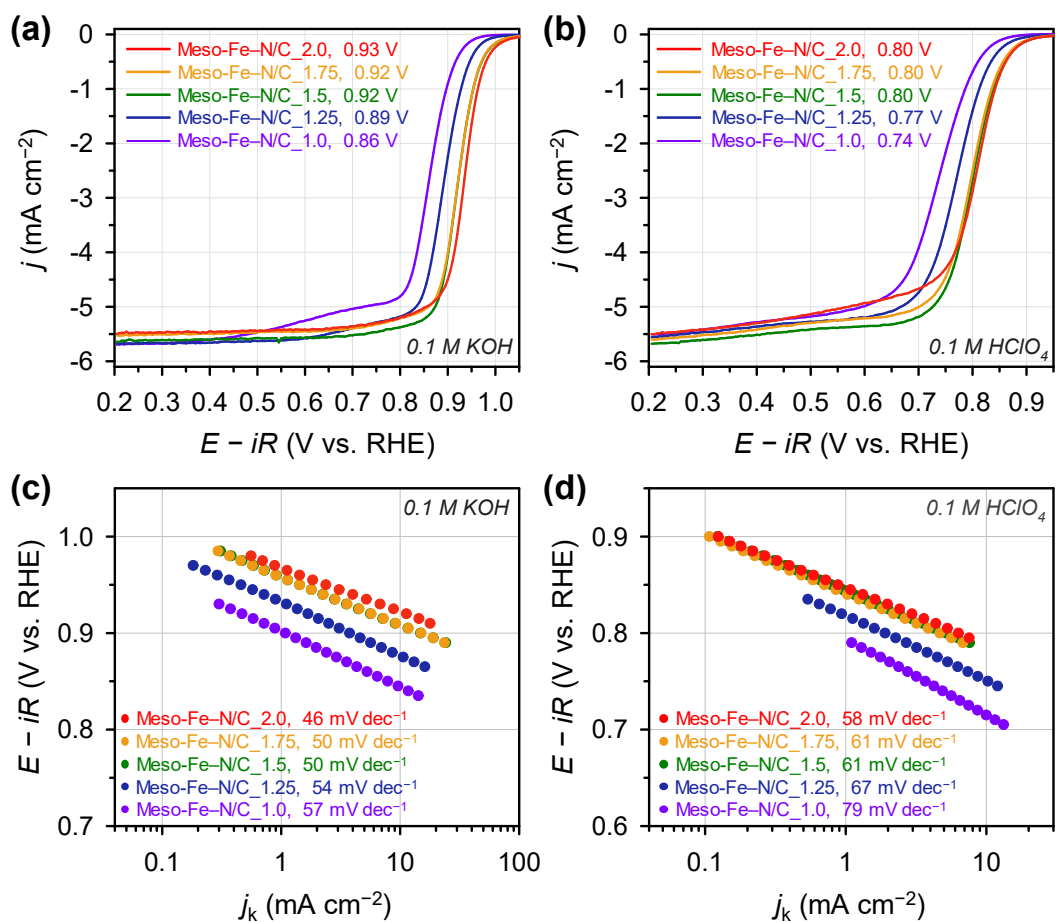


Fig. S7 ORR polarization curves of the Meso-Fe-N/C_X catalysts in (a) 0.1 M KOH and (b) 0.1 M HClO₄ electrolytes. Tafel slopes of the Meso-Fe-N/C_X catalysts in (c) 0.1 M KOH and (d) 0.1 M HClO₄ electrolytes.

Table S5. Site density and ORR activity parameters of the Meso-Fe–N/C_*X* catalysts in 0.1 M KOH.

Sample	Site density (sites g ⁻¹) ^a	<i>j</i> _k (mA cm ⁻²) ^b	<i>MA</i> (mA mg ⁻¹) ^c	TOF (e ⁻ site ⁻¹ s ⁻¹) ^d
Meso-Fe–N/C_1.0	4.7 × 10 ¹⁹	1.1	1.83	0.25
Meso-Fe–N/C_1.25	3.5 × 10 ¹⁹	3.8	6.33	1.12
Meso-Fe–N/C_1.5	4.5 × 10 ¹⁹	14.8	24.7	3.44
Meso-Fe–N/C_1.75	3.7 × 10 ¹⁹	15.0	25.0	4.23
Meso-Fe–N/C_2.0	3.5 × 10 ¹⁹	25.9	43.2	7.77

^a Derived from CO cryo chemisorption.

^b Kinetic current density calculated at 0.9 V.

^c Mass activity calculated at 0.9 V.

^d Turnover frequency calculated at 0.9 V.

Table S6. Benchmarking TOF of Meso-Fe–N/C_2.0 in alkaline media with those of previously reported Fe–N/C catalysts.

Sample	Site density (sites g ⁻¹) ^a	TOF (e ⁻ site ⁻¹ s ⁻¹) ^b	Ref
Meso-Fe–N/C_2.0	3.5 × 10¹⁹	7.77	This work
Fe _{0.5} NC-800	3.99 × 10 ¹⁹	0.46	1
ZIF-Fe	4.39 × 10 ¹⁹	1.21	2

^a Determined by CO cryo-chemisorption.

^b Turnover frequency calculated at 0.9 V.

Table S7. Site density and ORR activity parameters of the Meso-Fe–N/C_*X* catalysts in 0.1 M HClO₄.

Sample	Site density (sites g ⁻¹) ^a	<i>j</i> _k (mA cm ⁻²) ^b	<i>MA</i> (mA mg ⁻¹) ^c	TOF (e ⁻ site ⁻¹ s ⁻¹) ^d
Meso-Fe–N/C_1.0	4.7 × 10 ¹⁹	0.8	1.33	0.18
Meso-Fe–N/C_1.25	3.5 × 10 ¹⁹	1.9	3.17	0.56
Meso-Fe–N/C_1.5	4.5 × 10 ¹⁹	5.2	8.67	1.21
Meso-Fe–N/C_1.75	3.7 × 10 ¹⁹	4.7	7.83	1.32
Meso-Fe–N/C_2.0	3.5 × 10 ¹⁹	6.3	10.5	1.89

^a Active surface site density derived from CO chemisorption.

^b Kinetic current density calculated at 0.9 V.

^c Mass activity calculated at 0.9 V.

^d Turnover frequency calculated at 0.8 V.

Table S8. Benchmarking TOF of Meso-Fe-N/C_2.0 in acidic media with those of previously reported Fe-N/C catalysts.

Sample	Site density (sites g ⁻¹) ^a	TOF (e ⁻ site ⁻¹ s ⁻¹) ^b	Ref
Meso-Fe-N/C_2.0	3.5 × 10¹⁹	1.89	This work
Fe _{0.5} NC-800	3.99 × 10 ¹⁹	0.45	1
ZIF-Fe	4.39 × 10 ¹⁹	0.49	2
FeMn~RP	6.7 × 10 ¹⁹	1.6	3,5
FeRP c	0.72 × 10 ¹⁹	1.55	4,5
PANI-CM	3.79 × 10 ¹⁹	1.18	6,7
FeNC	9.76 × 10 ¹⁹	0.156	8
PAJ	2.02 × 10 ¹⁹	0.71	9

^a Derived from CO cryo-chemisorption.

^b Turnover frequency calculated at 0.8 V.

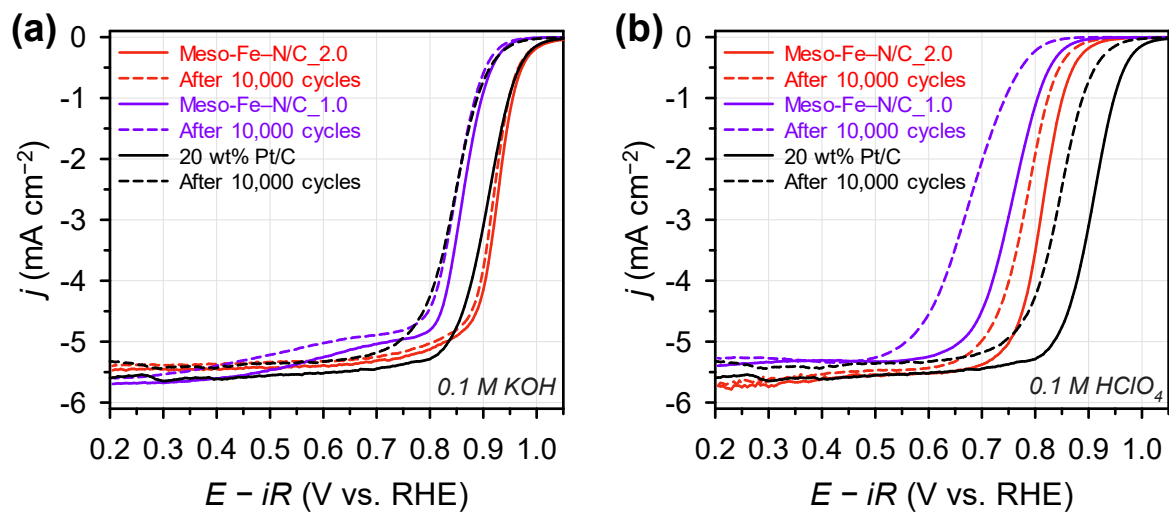


Fig. S8 ORR polarization curves for the ORR activity of the Meso-Fe-N/C_1.0, Meso-Fe-N/C_2.0, and Pt/C before and after 10,000 potential cycles in a) 0.1 M KOH and b) 0.1 M HClO₄.

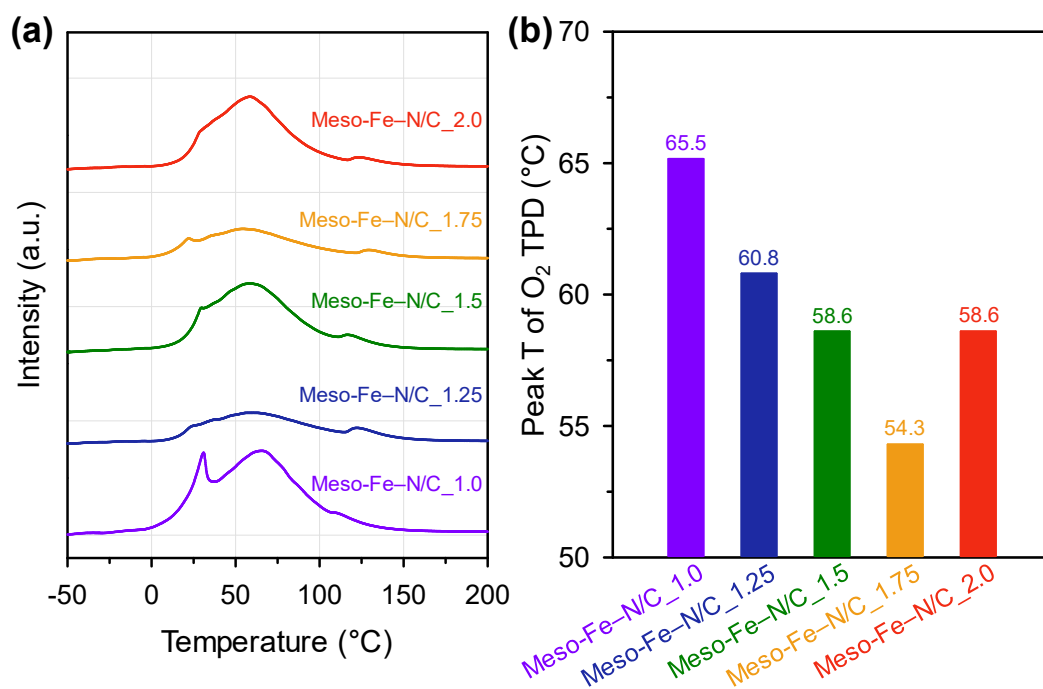


Fig. S9 (a) O₂ TPD profiles and (b) second O₂ desorption peak temperatures of the Meso-Fe-N/C_X catalysts.

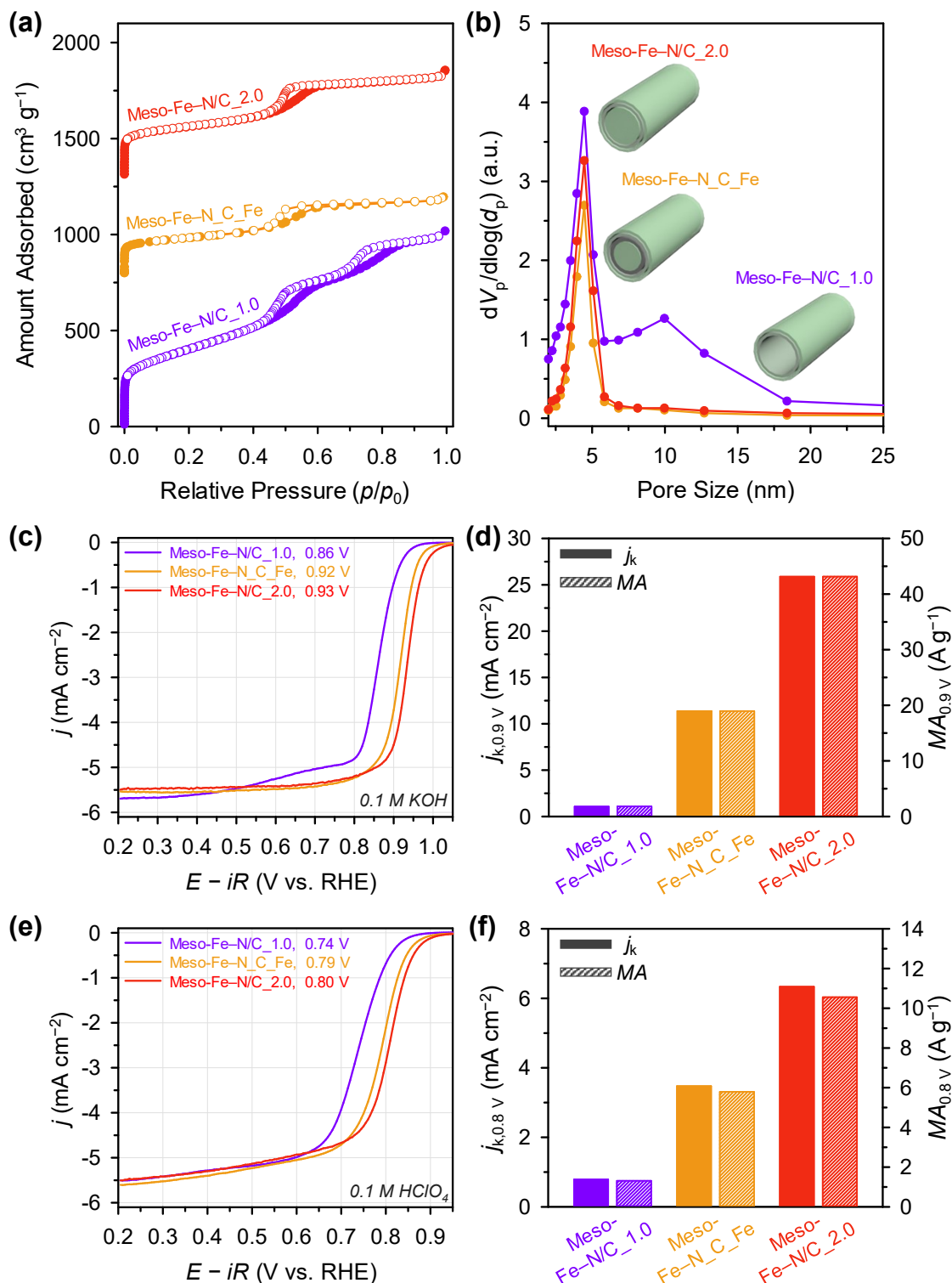


Fig. S10 (a) N₂ adsorption-desorption isotherms of Meso-Fe-N/C_1.0, Meso-Fe-N_C_Fe, and Meso-Fe-N/C_2.0. The isotherms of Meso-Fe-N_C_Fe and Meso-Fe-N/C_2.0 are offset by 800 and 1300 cm³ g⁻¹, for clarity. (b) Pore size distribution curves obtained from the adsorption branches of the corresponding isotherms with structural models for respective catalyst. (c and e) ORR polarization curves of Meso-Fe-N/C_1.0, Meso-Fe-N_C_Fe, and Meso-Fe-N/C_2.0 in (c) 0.1 M KOH and (e) 0.1 M HClO₄ electrolytes. (d and f) Bar graphs comparing ORR kinetic current density and mass activity in (d) 0.1 M KOH and (f) 0.1 M HClO₄ electrolytes.

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