Breaking Sabatier's vertex via switching the oxygen adsorption configuration and reaction pathway on dual active sites for acidic oxygen reduction

Pan Guo,^{‡a} Bo Liu,^{‡a} Fengdi Tu,^a Yunkun Dai,^a Ziyu Zhang,^a Yunfei Xia,^a Miao Ma,^a Yunlong Zhang,^{a*} Lei Zhao,^{a*} Zhenbo Wang^{a*}

^a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Space Power-Sources, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China.
E-mail: 20220123@hit.edu.cn, leizhao@hit.edu.cn, wangzhb@hit.edu.cn
‡ These authors contributed equally to this work.

Table of contents

- 1. Experimental section
- 2. Supplementary Figures S1-S34
- 3. Supplementary Tables S1-S14

1. Experimental section

1.1. Chemicals

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 2-methylimidazole (2-MeIm), Ruthenium(III) chloride hydrate (RuCl₃·nH₂O), methanol (CH₃OH), ethanol (C₂H₅OH), isopropanol, 2,2'-Bipyridine (bpy), iron sulfate heptahydrate (FeSO₄·7H₂O) and perchloric acid (HClO₄) were purchased from Aladdin. Nafion (5 wt %) was purchased from Dupont. The commercial Pt/C (20 wt%) was purchased from Suzhou Sinero Technology Co., Ltd. The distilled deionized water (18.2 M Ω ·cm⁻¹) applied in all experiments was obtained through an ultra-pure water system. All chemicals were employed directly without further purification.

1.2. Fabrication of catalysts

Firstly, solution A: 3.30 g Zn(NO₃)₂·6H₂O was solubilized in 350 mL methanol with stirring uniformly, followed by the addition of 370 μ L 1.0 M RuCl₃/CH₃OH into the above solution. Solution B: 7.30 g 2-methylimidazole (2-MeIm) was solubilized in 350 mL methanol and mixed homogeneously. Afterward, the A and B solutions were thoroughly combined and stirred at 25°C for 24 h. Next, separate the samples and wash them three times with methanol via centrifugation at 10 000 r min⁻¹. After drying at 60°C for 6 h, the precursors were obtained and named as Ru-ZIF-8.

The Ru-ZIF-8 and ZIF-8 precursors were heated at 950°C for 1 h under 10% H_2/Ar . The resultant derived from Ru-ZIF-8 was labeled as Ru-NC SAS and the other was designated as NC. In detail, Ru-NC SAS was dispersed as the carbon precursor in the mixed solution containing water/ethanol and $[Fe(bi-py)_3]^{2+}$. The mixture was subsequently ultrasonicated at 25°C for 1 h. Afterward, the sample was rinsed thoroughly using deionized water and then gathered through filtration. The black powder was dried in a vacuum oven at 60°C for 6 h and then annealed under an Ar atmosphere at 950°C for 1 h. Finally, the Ru,Fe-NC DAS was acquired. Fe-NC SAS was produced in the same way, except that the carbon precursor was replaced by NC.

1.3. Characterizations

To determine the crystal phase of catalysts, the powder X-ray diffraction (XRD) was performed using a Bruker D8 diffractometer with Cu K_{α 1} X-rays. The morphology and the nanoparticle size distribution Ru-NC SAS were analyzed via scanning electron microscopy (SEM) Merlin Compact (Carl Zeiss AG). More accurate morphologies were obtained by transmission electron microscopy (TEM) and aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) via the Tecnai G2 F30 (FEI Company) the Themis G2 300 (FEI Company), respectively. The N₂ isothermal adsorption/desorption was collected by Quantachrome Autosorb IQ. Thermo Scientific K-Alpha was utilized for conducting X-ray photoelectron spectroscopy (XPS), and the binding energy data were meticulously calibrated utilizing C 1s (284.6 eV). Raman spectra were obtained via the inVia-Reflex system at a wavelength of 532 nm. The contents of Ru and Fe were detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 7400).

The BL14W1 beam line at Shanghai Synchrotron Radiation Facility (SSRF) was explicitly utilized to conduct experiments on X-ray absorption spectroscopy (XAS), focusing on the Ru K-edge and Fe K-edge. The Si(311) double-crystal monochromator was employed, and the results were obtained using a Lytle detector filled with Argon gas in fluorescence mode. Ru foil and Fe foil were adopted as comparison samples. The collected data were manipulated via the Demeter software package, including Athena, Artemis, and Hephaestus.

In situ attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed on a Nicolet 6700 spectrometer equipped with the MCT detector. The catalysts were loaded onto a silicon wafer working electrode coated with a thin layer of gold nanoparticles. The electrochemical tests were conducted in O_2 -saturated 0.1 M HClO₄, adopting the Hg/Hg₂SO₄ electrode as RE. In situ Raman was carried out via the inVia-Reflex system with 532 nm.

1.4. Electrochemical measurements

The electrocatalytic performance of each catalyst was measured via the rotating ring-disk electrode (RRDE) measurements (CHI760e, Shanghai Chenhua Instrument,

China) with three-electrode system in 0.1 M HClO₄ at room temperature, in which the catalyst-coated glassy-carbon electrode as the working electrode (WE), the home-made RHE as the RE, and the carbon rod as the counter electrode. Firstly, 2.5 mg catalysts were dispersed in 500 μ L mixed solution (*V*(DI-water): *V*(ethanol): *V*(5% Nafion solution) = 5:5:0.3) and ultrasonicated for 1 h. Afterward, a certain amount of ink was added dropwise to the glassy-carbon electrode (GCE, 5.61 mm inner diameter, 0.2472 cm²) and dried naturally at 25°C. The mass loading of as-prepared catalysts was 0.6 mg cm⁻², and the loading of Pt for the Pt/C was 40 μ g_{Pt} cm⁻². Next, the catalysts were activated via cyclic voltammetry (CV). Subsequently, the electrocatalytic ORR performance was tested by steady-state measurement through the staircase voltammetry (SCV) tests. The test techniques were as follows: Quiet time 30 s, 1.10 - 0.05 V, Incre E 50 mV, Step period 30 s, 900 rpm. The chronoamperometric tests (*I-t*) were conducted at 0.6 V in O₂-saturated 0.1 M HClO₄ with a rotation rate of 900 rpm for 30 000 s. The stability of catalysts was also assessed by cycling the potential from 0.6 to 1.0 V (vs. RHE) at a scan rate of 100 mV s⁻¹ in O₂-saturated 0.10 M HClO₄.

The H₂O₂ yield, electron-transfer number (n), the kinetic current density (j_k) at 0.85 V and Tafel slope were calculated according to the following equations:

$$\% H_2 O_2 = 200 \times \frac{I_r / N}{I_d + I_r / N}$$
(1)
$$n = \frac{4I_d}{I_d + I_r / N}$$
(2)
$$\frac{1}{j} = \frac{1}{jk} + \frac{1}{jd}$$
(3)
$$\eta = a + b \log |jk|$$
(4)

Notes: I_r and I_d stand for the ring and the disk current, respectively. N is the ring current collection efficiency (37%), respectively. j, j_k , and j_d are the measured, kinetic, and diffusion-limiting current densities, respectively. η represents the overpotential.

1.5. Fuel cell tests

The Scribner 850e fuel cell test system was employed to measure the performance of various catalysts in PEMFC. The membrane electrode assembly (MEA) with the geometric size of 5 cm² was prepared via Gas Diffusion Electrode method (GDE). The catalyst ink was obtained by mixing the catalyst powder with Nafion ionomer solution and isopropanol/water, followed by ultrasonicating for 1 h (As for Ru,Fe-NC DAS, Ru-

NC SAS, and Fe-NC SAS catalysts, solid content = 7%, $m_{\text{Nafion ionomer}}/m_{\text{C}} = 0.6$, and $V_{\text{isopropanol}}/V_{\text{water}} = 10$. As for Pt/C, solid content = 4.5%, $m_{\text{Nafion ionomer}}/m_{\text{C}} = 0.7$, and $V_{\text{isopropanol}}/V_{\text{water}} = 5$). Subsequently, the catalyst ink was applied uniformly onto the gas diffusion layer (AvCarb MB30) using a brush. The loading of cathode catalysts (Ru,Fe-NC DAS, Ru-NC SAS, Fe-NC SAS) was 3.5 mg cm⁻² and anode Pt loading of 0.1 mg cm⁻². As for Pt/C, the cathodic Pt loading was 0.3 mg cm⁻². Afterward, the as-obtained cathode and anode electrodes were placed on each side of a Nafion NC700 membrane (DuPont) to produce the final MEA. During the MEA test, the fuel cell MEA testing process rigorously followed the U.S. Department of Energy (DOE). The temperature of the cell and H₂/O₂ gas is programmed to increase to 80°C, and the MEA test was measured under 80°C, 100% relative humidity (RH), and 1 bar back pressure for H_2/O_2 and H₂/Air. The polarization and the power density curves of all catalysts were tested under $H_2(500 \text{ sccm})/O_2(500 \text{ sccm})$ and $H_2(500 \text{ sccm})/Air(2000 \text{ sccm})$ conditions. Electrochemical impedance spectroscopy (EIS) tests were performed at H₂/O₂ and H_2/Air operating conditions in the frequency range of 10^5 to 10^{-1} Hz at 0.65 V. The durability tests of catalysts were performed in H₂ (200 sccm)/N₂ (75 sccm) condition via square wave cycling protocol (0.6 V: 3 s, 0.95 V: 3 s, 80 °C, 100% RH, and 0 bar).

1.6. DFT calculations

The density functional theory (DFT) calculations were implemented via the Vienna Ab Initio Simulation Package (VASP). In this calculation, to characterize the core electrons, the Projector Augmented Wave (PAW) pseudopotential was utilized. The electronic exchange-correlation energy was then depicted using the Perdew-Burke-Ernzerhof (PBE) functionals model with the generalized gradient approximation (GGA). To avoid any interaction between adjacent surfaces, a vacuum layer was created at a distance of 15 Å in the z-direction. A cut-off energy for plane-wave expansion was defined as 400 eV. The Brillouin zone was sampled employing the Monkhorst-Pack with $4 \times 4 \times 1$ *k*-point mesh. In the self-consistent-field (SCF) calculation, the convergence threshold for iteration was set at 10^{-6} eV, and the maximum atomic forces were kept below 0.01 eV Å⁻¹.

The calculation for the change in Gibbs free energy (G) is determined by the following equations:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}$$
$$\Delta G_U = -eU$$

Notes: ΔE is called the reaction energy change. ΔZPE represents the change of the zeropoint energy (ZPE). ΔS indicates the difference in entropy between reactants and products at 298.15 K. The contribution of the applied electrode potential (U) to ΔG is referred to as ΔG_U . The ΔG_{pH} is a critical indicator of how variations in the concentration of H⁺ impact free energy. Numerous studies have shown that pH has no impact on the rate-determining step as the free energy of the elementary reactions remains unaffected by pH. Therefore, the ΔG_{pH} is ignored in this work.

The scaling relationships were obtained through the following methods: Firstly, the ΔG_{*OOH} , ΔG_{*O} , and ΔG_{*OH} were obtained from the Gibbs free energy diagram (U = 0 V). Then, the relationships between $\Delta G_{*OOH} / \Delta G_{*O}$ and ΔG_{*OH} were obtained by linear fitting as follows: $\Delta G_{*OOH} = k_1 \Delta G_{*OH} + b_1$, $\Delta G_{*O} = k_2 \Delta G_{*OH} + b_2$. Finally, the thermodynamic limiting potential is obtained by the following function: $U_{onset} = 1.23 - \max (\{1.23 - \Delta G_{*OH}\}, \{1.23 - (k_2 \Delta G_{*OH} + b_2) + \Delta G_{*OH}\}, \{1.23 - (k_1 \Delta G_{*OH} + b_1) + (k_2 \Delta G_{*OH} + b_2)\}, \{(k_1 \Delta G_{*OH} + b_1) - 3.69\}).$

The projected density of states (pDOS), and the crystal orbital Hamilton population (COHP) analyses including integrated COHP (ICOHP) were calculated with the LOBSTER 4.0.0 package^{1, 2}.

2. Supplementary Figures S1-S34



Figure S1. Schematic of Griffiths model on single-active sites.



Figure S2. Structure of (a) RuN₄, (b) FeN₄, and (c) RuFeN₆.



Figure S3. ORR Gibbs free energy diagrams of RuN₄, FeN₄, and RuFeN₆.



Figure S4. The conversion of the ORR process from an associative pathway on singleactive sites to a dissociative pathway on dual-active sites.



Figure S5. Optimized configurations of O₂ adsorbed on the (a) RuN₄ and (b) FeN₄.



Figure S6. Optimized configurations of O_2 adsorbed on the (a) RuFeN₆-Ru, (b) RuFeN₆-Fe, and (c) RuFeN₆-RuFe.



Figure S7. Top/side views of the differential charge density for O_2 adsorbed on the (a) RuN₄, (b) FeN₄, and (c) RuFeN₆. The yellow and cyan iso-surfaces represent electron accumulation and depletion, respectively.



Figure S8. The Crystal Orbital Hamilton Population (COHP) of O1-Ru (left) and O2-Fe (right) for HO-RuFe-OH intermediate.



Figure S9. Computed structural models of the (a) $RuCrN_6$, (b) $RuMnN_6$, (c) $RuCoN_6$, (d) $RuCuN_6$, and (e) $RuNiN_6$. The brown, white, grey, purple, navy, blue, and green balls represent C, N, Ru, Mn, Co, Cu, and Ni atoms, respectively.



Figure S10. ORR Gibbs free energy diagrams of various catalysts.



Figure S11. ORR Gibbs free energy diagrams of CoN₄, MnN₄, CuN₄, and NiN₄.



Figure S12. The procedure of fabricating Ru,Fe-NC DAS catalysts.



Figure S13. XRD patterns of ZIF-8 and Ru-ZIF-8.



Figure S14. (a) SEM image and (b) the nanoparticle size distribution of Ru-NC SAS.



Figure S15. (a) TEM, (b) HR-TEM, and (c) AC-HAADF-STEM images of Ru-NC SAS.



Figure S16. (a) The N_2 adsorption/desorption isothermal physisorption curves and (b) pore size distribution plots of different catalysts.



Figure S17. XRD patterns of Ru, Fe-NC DAS, Ru-NC SAS, Fe-NC SAS, and NC.



Figure S18. XPS survey spectra of Ru,Fe-NC DAS, Ru-NC SAS, and Fe-NC SAS.



Figure S19. The deconvoluted high-resolution N 1*s* spectra of (a) Ru,Fe-NC DAS, (b) Ru-NC SAS, and (c) Fe-NC SAS.



Figure S20. Raman spectra of Ru, Fe-NC DAS, Ru-NC SAS, and Fe-NC SAS.



Figure S21. The linear relationship between the valence state and absorption edge energy of (a) Ru and (b) Fe.



Figure S22. The wavelet transform of (a) RuO_2 and (b) Fe_2O_3 .



Figure S23. Ru *K*-edge EXAFS data and fitting results in (a) *R*-space and (b) *k*-space for Ru,Fe-NC DAS. Fe *K*-edge EXAFS data and fitting results in (c) *R*-space and (d) *k*-space for Ru,Fe-NC DAS.



Figure S24. Cyclic voltammetry curves of Ru,Fe-NC DAS, Ru-NC SAS, and Fe-NC SAS in N₂-saturated and O₂-saturated 0.1 M HClO₄.



Figure S25. The lower Tafel slope of Ru,Fe-NC DAS, Ru-NC SAS, Fe-NC SAS, and Pt/C.



Figure S26. The polarization curves of Ru,Fe-NC DAS with different heating temperatures (a) and times (b).



Figure S27. ORR polarization curves of different catalysts: (a) Ru,Fe-NC DAS, (b) Ru-NC SAS, (c) Fe-NC SAS, and (d) Pt/C before and after 5 000 cycles in O₂-saturated 0.1 M HClO₄.



Figure S28. Anti-methanol toxicity tests of Ru,Fe-NC DAS and Pt/C.



Figure S29. Fuel cell polarization and power density plots of before (solid sphere) and after 5 000 potential cycles (hollow sphere) for (a) Pt/C, (b) Ru-NC SAS, and (c) Fe-NC SAS in H_2/O_2 (blue) and H_2/Air (pink) conditions.



Figure S30. The electrochemical impedance spectroscopy (EIS) of different catalysts at 0.65 V in (a) H_2/O_2 and (b) H_2/Air .



Figure S31. The density-of-states calculations (DOS) of Ru in Ru,Fe-NC DAS and Ru-NC SAS.



Figure S32. The projected density of states (pDOS) of Fe in Ru,Fe-NC DAS.



Figure S33. The total COHP of Ru-O for (a) HO-RuFeN₆ and (b) HO-RuN₄.



Figure S34. (a) The projected COHP (pCOHP) analysis of HO-RuN₄ for Ru-O. (b) pDOS of Ru 4*d* and O 2*p* for HO-RuN₄.

3. Supplementary Tables S1-S14

	Bond length (Å)
RuN ₄	1.304
FeN ₄	1.296

Table S1. The O-O bond length of O₂ adsorbed on the RuN₄ and FeN₄

Table S2. The O-O bond length/adsorption energy of O₂ adsorbed on the RuFeN₆

	Bond length (Å)	Adsorption energy (eV)
RuFeN ₆ -Ru	1.302	-0.31
RuFeN ₆ -Fe	1.293	-0.21
RuFeN ₆ -RuFe	1.376	-0.52

Table S3. The ICOHP between O-O bonds of O_2 , RuN_4 - O_2 , and $RuFeN_6$ - O_2

	O_2	RuN ₄ -O ₂	RuFeN ₆ -O ₂
Total $(p-p)$	-6.986	-6.479	-5.576
π	-3.370	-2.108	-1.233
σ	-3.616	-4.375	-4.346

Table S4. BET surface areas and pore distribution of different catalysts

	S _{BET}	S _{BET} V _{micro}		V _{meso}		V _{total}	•
	m ² g ⁻¹	cm ³ g ⁻¹	%	$cm^3 g^{-1}$	%	cm ³ g ⁻¹	
Ru-ZIF-8	1699.55	0.564	45.23	0.683	54.77	1.247	
Ru-NC SAS	1211.49	0.388	28.2	0.988	71.8	1.376	
Ru,Fe-NC DAS	1259.30	0.404	27.6	1.060	72.4	1.464	

Table S5. The contents of different types of N in as-prepared catalysts (%)

	Metal-N	Oxidized-N	Graphitic-N	Pyridinic-N
Ru,Fe-NC DAS	21.6	6.9	49.6	21.9
Ru-NC SAS	15.9	11.4	30.3	42.4
Fe-NC SAS	15.2	14.8	33.2	36.8

Sample	Path	CNs	R (Å)	$\sigma^2(\text{\AA}^2)$	ΔE_0 (eV)	R factor
	Fe-Fe	8.0	2.47±0.01	$0.006 {\pm} 0.001$	6.05±2.12	
Fe foil	Fe-Fe	6.0	$2.84{\pm}0.01$	$0.005{\pm}0.001$	6.05±2.12	0.009
	Fe-Fe	12.0	4.00 ± 0.02	$0.009 {\pm} 0.001$	-0.49±2.33	
Ru foil	Ru-Ru	6.5	2.66±0.01	$0.001 {\pm} 0.001$	-5.15±0.92	0.006
	Fe-N	4.0	2.06±0.01	0.003±0.001	7.49±1.41	0.019
Du Es NC DAS	Fe-Ru	1.0	2.45±0.03	$0.007{\pm}0.003$	7.49±1.41	0.018
Ru, re-INC DAS	Ru-N	4.5	2.04 ± 0.02	$0.004{\pm}0.001$	-2.96±3.12	0.024
	Ru-Fe	0.9	2.55±0.03	$0.007 {\pm} 0.004$	2.96±3.12	0.024

Table S6. The least-squares EXAFS fitting results of Ru K-edge and Fe K-edge

Note: $S_0^{2=} 1.0$ for Ru *K*-edge and $S_0^{2=} 0.8$ for Fe *K*-edge; CNs: coordination numbers; *R*: bond distance between absorber and backscatter atoms; σ^2 : Debye-Waller factor; ΔE_0 : the inner potential correction; R factor demonstrates the goodness of curve-fitting.

	H ₂ /O ₂ (W cm ⁻²)			H ₂ /Air (W cm ⁻²)		
	Initial	5000	Degradation	Initial	5000	Degradation
		cycles			cycles	
Ru,Fe-NC DAS	1.152	1.085	5.7%	0.520	0.486	6.46%
Ru-NC SAS	0.888	0.798	10.1%	0.477	0.416	12.8%
Fe-NC SAS	0.493	0.428	13.2%	0.260	0.228	12.2%
Pt/C	1.431	1.330	7.07%	0.860	0.808	6.1%

Table S7. The activity and stability of as-prepared catalysts and Pt/C in MEA

Table S8. The comparison of ORR performance between Ru,Fe-NC DAS and

		Half-wave	Peak power		
Catalysts	electrolyte	potential	density	Test conditions for M	IEA Reference
		(V vs. RHE)	(mW cm ⁻²)		
Ru,Fe-NC		0.042	1151 (80°C, 100% RH	
DAS	0.1 M HCIO ₄	0.843	1151.0	under 1 bar H ₂ /O ₂	This work
(Au-Co) DP-		0.020	400	80°C, 100% RH	Applied Catalysis B: Environmental,
NPAs	0.1 M HClO ₄	0.820	490	under 1 bar H_2/O_2	2022, 301: 120782 ³ .
		0.07	010	,	Journal of the American Chemical
FeCoN5-OH	0.1 M HClO ₄	0.86	819	1	Society, 2019, 141(44): 17763-17770.4
planar-like		0.84	945	80°C, 100% RH	Matter 2020 2(2), 500 521 5
Fe2N6	0.1 M HCIO ₄	0.84	845	under 1.5 bar H_2/O_2	Matter, 2020, 3(2): 509-521. ³
	0.5 M U SO	0.80	075	80°C, 100% RH	Energy Storage Materials, 2023, 54:
re, cu DAs-NC	$0.5 \text{ M} \text{ H}_2 \text{ S} \text{ O}_4$	0.80	873	under 2 bar H_2/O_2	533-542. ⁶
Eaco NC 2		0.842	800	80°C, 100% RH	Journal of Materials Chemistry A, 2022,
FeCo-INC-3	0.1 M HCIO4	0.842	800	under 30 PSIG H_2/O_2	10(18): 9886-9891.7
Zn/CoN C		0 706	705	1	Angewandte Chemie International
ZI/CON-C	0.1 WI HCIO4	0.790	705	I	Edition, 2019, 131(9): 2648-2652.8
FoMo N6 C		0.84	460	350 K, 100% RH	Nano Letters, 2022, 22(23): 9507-
remo-no-c	0.1 WI HCIO4	0.84	400	under 2 bar H_2/O_2	9515. ⁹
FeNi N6 C	0.1 M HClO	0.78	216	80°C, /	The Journal of Physical Chemistry
T CIVI-INO-C	0.1 W HClO4	0.78	210	under 20 PSIG $\rm H_2\!/\rm O_2$	Letters, 2020, 11(4): 1404-1410. ¹⁰
FeNC 1100	0.1 M HClO	0 795	687	80°C, 100% RH	Advanced Materials, 2023, 35(5):
renc-1100	0.1 WINCIO ₄	0.795	087	under 1 bar H_2/O_2	2204474.11
E. N. C/Dd		0.85	020	80°C, /	Cham 2022 0(1), 181 107 12
re-n-C/ra _{NC}	0.1 M HCIO ₄	0.85	920	under 20 PSIG H_2/O_2	Chem, 2023, 9(1): 181-1972
E-NIACI		0.010	840	80°C, 100% RH	ACS Nano, 2022, 16(9): 15165-
Fen4CI	0.1 M HCIO4	0.818	840	under 1 bar H_2/O_2	15174.13
E-Ny SAC		0 905	220	80°C, 100% RH	ACS Nano, 2022, 16(9): 15165-
renx SAC	0.1 M HCIO ₄	0.803	550	under 1 bar H_2/O_2	15174.13
Co(mIm)–	0.5 M H SO	0.82	640	80°C, 100% RH	Nature Catalysis, 2020, 3(12): 1044-
NC(1.0)	$0.5 \text{ M} \text{ H}_2 \text{ S} \text{ O}_4$	0.82	040	under 1 bar H_2/O_2	1054.14
20Mn-NC-	0.5 M U SO	0.80	460	80°C, 100% RH	Nature Catalysis, 2018, 1(12): 935-
second	$0.5 \text{ M} \text{ H}_2 \text{ S} \text{ O}_4$	0.80	400	under 1 bar H_2/O_2	945. ¹⁵
20C- NC 1100		0.90	5(0)	80°C, 100% RH	Advanced Materials, 2018, 30(11):
20C0-NC-1100	0.1 M HCIO4	0.80	560	under 275 kPa $\rm H_2/\rm O_2$	1706758.16
DON A GEARA		0.70	514	80°C, 100% RH	Journal of Energy Chemistry, 2021, 59:
rUN-A@fe SA	0.1 M HCIO ₄	0.79	514	under 2 atm $\mathrm{H_2/O_2}$	388-395.17
60° N C 050		0.0	520	80°C, 100% RH	Journal of Colloid and Interface
000-14-0-930	0.1 WI HCIO ₄	0.8	550	under 30 PSIG H_2/O_2	Science, 2023, 634: 940-948. ¹⁸

previously reported single-site and dual-site electrocatalysts



	H_2/O_2	H ₂ /Air
	(mA cm ⁻²)	(mA cm ⁻²)
Ru,Fe-NC DAS	0.917	0.433
Ru-NC SAS	0.765	0.379
Fe-NC SAS	0.256	0.109
Pt/C	1.632	1.132

Table S10. The charge transfer impedance at 0.65 V of as-prepared catalysts and Pt/C

	H_2/O_2	H ₂ /Air
	$(\Omega \ \mathrm{cm}^2)$	$(\Omega \text{ cm}^2)$
Ru,Fe-NC DAS	0.12	0.34
Ru-NC SAS	0.18	0.35
Fe-NC SAS	0.41	1.03
Pt/C	0.1	0.2

Table S11. The ICOHP of Ru 4d - O 2p for HO-RuFeN₆ and HO-RuN₄

	HO-RuFeN ₆	HO-RuN ₄
Spin-up	-1.00	-1.11
Spin-down	-0.87	-1.09

Table S12. The component of atomic orbital of Ru–O for HO-RuFeN $_6$ and HO-RuN $_4$

	HO-RuFeN ₆	HO-RuN ₄
Ru(5 <i>s</i>)-O(2 <i>s</i>)	8.23%	8.69%
Ru(5 <i>s</i>)-O(2 <i>p</i>)	4.68%	5.42%
Ru(4 <i>d</i>)-O(2 <i>s</i>)	16.47%	16.81%
$\operatorname{Ru}(4d_{xy})$ -O(2 p)	0.63%	0.00%
$\operatorname{Ru}(4d_{yz})$ -O(2 p)	15.54%	20.95%
$\operatorname{Ru}(4d_{z^2})$ -O(2 <i>p</i>)	37.13%	37.25%
$\operatorname{Ru}(4d_{xz})$ -O(2 p)	15.27%	10.81%
$\mathrm{Ru}(4d_{x^2-y^2})-\mathrm{O}(2p)$	2.05%	0.07%

Table S13. The ICOHP of Ru 4d - O 2p for HO-RuFeN₆

	$d_{ m yz}$	d_{z^2}	d _{xz}
Spin-up	-0.157	-0.717	-0.119
Spin-down	-0.153	-0.685	-0.050

Table S14. The ICOHP of Ru 4d - O 2p for HO-RuN₄

	$d_{ m yz}$	d_{z^2}	d _{xz}
Spin-up	-0.136	-0.888	-0.077
Spin-down	-0.136	-0.888	-0.077

Reference

1. S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, J. Comput. Chem., 2013, 34, 2557-2567.

2. S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, J. Comput. Chem., 2016, 37, 1030-1035.

3. F. Kong, R. Si, N. Chen, Q. Wang, J. Li, G. Yin, M. Gu, J. Wang, L.-M. Liu and X. Sun, *Applied Catalysis B: Environmental*, 2022, **301**.

4. M. Xiao, Y. Chen, J. Zhu, H. Zhang, X. Zhao, L. Gao, X. Wang, J. Zhao, J. Ge, Z. Jiang, S. Chen, C. Liu and W. Xing, *J Am Chem Soc*, 2019, **141**, 17763-17770.

5. N. Zhang, T. Zhou, J. Ge, Y. Lin, Z. Du, C. a. Zhong, W. Wang, Q. Jiao, R. Yuan, Y. Tian, W. Chu, C. Wu and Y. Xie, *Matter*, 2020, **3**, 509-521.

6. F. Kong, M. Wang, Y. Huang, G. Meng, M. Chen, H. Tian, Y. Chen, C. Chen, Z. Chang, X. Cui and J. Shi, *Energy Storage Materials*, 2023, **54**, 533-542.

7. Y.-b. Chen, J.-j. Li, Y.-p. Zhu, J. Zou, H. Zhao, C. Chen, Q.-q. Cheng, B. Yang, L.-l. Zou, Z.-q. Zou and H. Yang, *Journal of Materials Chemistry A*, 2022, **10**, 9886-9891.

 Z. Lu, B. Wang, Y. Hu, W. Liu, Y. Zhao, R. Yang, Z. Li, J. Luo, B. Chi, Z. Jiang, M. Li, S. Mu, S. Liao, J. Zhang and X. Sun, *Angewandte Chemie International Edition*, 2019, **58**, 2622-2626.

9. P. Zhu, X. Xiong, X. Wang, C. Ye, J. Li, W. Sun, X. Sun, J. Jiang, Z. Zhuang, D. Wang and Y. Li, *Nano Lett*, 2022, **22**, 9507-9515.

10. L. Zhong and S. Li, ACS Catal., 2020, 10, 4313-4318.

11. D. Xia, X. Tang, S. Dai, R. Ge, A. Rykov, J. Wang, T. H. Huang, K. W. Wang, Y. Wei and K. Zhang, *Advanced Materials*, 2023, **35**, 2204474.

12. X. Wei, S. Song, W. Cai, X. Luo, L. Jiao, Q. Fang, X. Wang, N. Wu, Z. Luo, H. Wang, Z. Zhu, J. Li, L. Zheng, W. Gu, W. Song, S. Guo and C. Zhu, *Chem*, 2023, 9, 181-197.

13. S. Ding, J. A. Barr, Q. Shi, Y. Zeng, P. Tieu, Z. Lyu, L. Fang, T. Li, X. Pan, S. P. Beckman, D. Du, H. Lin, J.-C. Li, G. Wu and Y. Lin, *ACS Nano*, 2022, **16**, 15165-15174.

14. X. Xie, C. He, B. Li, Y. He, D. A. Cullen, E. C. Wegener, A. J. Kropf, U. Martinez,

Y. Cheng, M. H. Engelhard, M. E. Bowden, M. Song, T. Lemmon, X. S. Li, Z. Nie, J. Liu, D. J. Myers, P. Zelenay, G. Wang, G. Wu, V. Ramani and Y. Shao, *Nat. Catal.*, 2020, **3**, 1044-1054.

15. J. Li, M. Chen, D. A. Cullen, S. Hwang, M. Wang, B. Li, K. Liu, S. Karakalos, M. Lucero, H. Zhang, C. Lei, H. Xu, G. E. Sterbinsky, Z. Feng, D. Su, K. L. More, G. Wang, Z. Wang and G. Wu, *Nat. Catal.*, 2018, **1**, 935-945.

16. X. X. Wang, D. A. Cullen, Y. T. Pan, S. Hwang, M. Wang, Z. Feng, J. Wang, M. H. Engelhard, H. Zhang and Y. He, *Adv. Mater.*, 2018, **30**, 1706758.

17. X. Shi, Z. Pu, B. Chi, M. Liu, S. Yu, L. Zheng, L. Yang, T. Shu and S. Liao, *Journal of Energy Chemistry*, 2021, **59**, 388-395.

18. D. Duan, S. Zhong, J. Huo, J. Chen, X. Shi, H. Peng, X. Li and S. Liao, *Journal of Colloid and Interface Science*, 2023, **634**, 940-948.