Supplementary Information (SI) for Dalton Transactions.

Supporting Information

An iron and lanthanide heterobimetallic coordination polymer derived electrocatalyst showing Enhanced activity and stability for oxygen reduction reaction

Xin Liu,[a] Peng-Peng Guo,[a] Kun-Zu Yang,[a] Yong-Zhi Su,[a] Chao Xu,[b]* and Jin-Gang Liu[a]*

[a] Key Lab for Advanced Materials, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Shanghai, 200237, P. R. China. E-mail: liujingang@ecust.edu.cn

[b] State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, P. R. China. E-mail: chaoxu@ecust.edu.cn

Chemicals and Materials

All reagents and solvents used in this paper were obtained from commercial suppliers and were utilized directly without further purification. High-purity water (≥18.25 MΩ·cm) and methanol were used to prepare the solutions. The 1,1'-Ferrocenedicarboxylic acid was obtained from Shanghai Boer Chemical Reagent CO., Ltd.

Characterizations

The FTIR spectra were recorded using a Shimadzu Fourier transform infrared spectrometer (IR Prestige-21). The morphologies of catalysts were investigated using Transmission electron microscopy (ThermoFisher Talos F200X). X-ray Diffraction (XRD) patterns were performed on an X-ray powder diffractometer (D/max2550 V, Rigaku Japan). High angle annular dark field (HAADF)-STEM images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. N_2 adsorption-desorption data were obtained at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2010 M apparatus. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific TM K-Alpha TM+ spectrometer with a monochromatic Al Kα X-ray source (hν =1486.6 eV) and the binding energies was referenced to the C1s peak (284.8 eV) corresponding to the adventitious carbon. The Brunauer-Emmett-Teller (BET) method was used to calculate the catalyst surface areas. Raman spectra were obtained on a Renishaw 2000 instrument with a 532 nm excitation wavelength. UV-vis diffuse reflectance spectra were obtained on a Shimadzu UV-vis spectrophotometer (UV-2600). The metal contents of the catalysts were measured by ICP OES (Perkin Elmer Ltd., USA).

Materials Synthesis

Preparation of carbonized ZIF-8

3.0 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 6.5 g of 2-Methylimidazole were dissolved in 80 mL methanol and 160 mL methanol, respectively. The zinc nitrate solution was poured into 2-Methylimidazole solution and was stirred for 6 h at room temperature. After stirring, the product was collected by centrifuging and washed with methanol, and dried overnight at room temperature to obtain ZIF-8. The ZIF-8 was pyrolyzed at 900 °C in nitrogen atmosphere for 60 min at a heating rate of 5 °C min^{-1}. After cooling to room temperature the samples was etched by 0.5 M H_2SO_4 at 80 °C for 8 h and washed to neutral with high-purity water. Finally, the carbonized ZIF-8 was dried overnight at 80 °C.

Preparation of $[La_2L_3(CH_3OH)_4]_\infty$

0.08 g of 1,1′-ferrocenedicarboxylic acid and 0.02 g of NaOH were dissolved in 10 mL methanol to form solution A. 0.07 g of $La(NO_3)_3$ was dissolved in 10 mL water to form solution B. Solution A was pour into solution B and stirred for 4 h at room temperature. After stirring, the product was collected by centrifuging and washed with methanol, and dried overnight at room temperature to obtain $[La_2L_3(CH_3OH)_4]_\infty$.

Preparation of FeLaNC

200 mg of carbonized ZIF-8 was mixed with 60 mg of $[La_2L_3(CH_3OH)_4]_\infty$ by ball milling and subsequently pyrolyzed at 900 °C in nitrogen atmosphere for 60 min at a heating rate of 5 °C min^{-1}. After cooling to room temperature, the samples were etched by 0.5 M H_2SO_4 at 80 °C for 8 h and washed to neutral with high-purity water to obtain FeLaNC. The FeLaNC-0.5 and FeLaNC-1.5 were prepared in a similar procedure for preparing FeLaNC by replacing 60 mg of $[La_2L_3(CH_3OH)_4]_\infty$ with 30 mg of $[La_2L_3(CH_3OH)_4]_\infty$ and 90 mg of $[La_2L_3(CH_3OH)_4]_\infty$, respectively.

Preparation of FeNC ,LaNC and NC

The FeNC and LaNC were prepared in a similar procedure for preparing FeLaNC by replacing 60 mg of $[La_2L_3(CH_3OH)_4]_\infty$ with 40 mg of $Fe(NO_3)_3 \cdot 9H_2O$ and 40 mg of $La(NO_3)_3 \cdot 6H_2O$, respectively. The NC was prepared in a similar procedure for preparing FeLaNC but without adding precursor before pyrolyzing.

Electrochemical Measurement

2.0 mg of catalyst was added to a 100 μL of mixture solution in a centrifuge tube with 5 wt% Nafion dispersion (Aldrich) and isopropanol in a volume ratio of 1:9. Then, catalyst was dispersed by ultrasonic for 30 min to form an even catalyst ink. 5 μL of catalyst ink was dropped onto the surface of glassy carbon disk (area: 0.196 cm^2), and dried naturally to form an even film with a catalyst mass loading of 0.5 mg cm^{-2}.

For RRDE measurement: The H_2O_2 yield and electron transfer number (n) were calculated from the RRDE data by the following equations:

$$H_2O_2(\%) = \frac{200 \times I_r}{I_r + N + I_d}$$

$$n = \frac{4 \times N \times I_d}{I_r + N + I_d}$$

where N is the collection coefficient, and the value is 0.26.

RHE (Reversible Hydrogen Electrode) calibration: The calibration of the reference electrode was conducted in a H_2-saturated electrolyte with Pt wire as the working electrode. The potential at which the current crossed zero was regarded as the thermodynamic potential for the hydrogen electrode reactions.

ABTS Radical Scavenging Assay.

First, catalysts (4.0 mg) were dispersed in 5.0 mL of 0.1 M H_2SO_4 solution by ultrasonication to obtain a homogeneous suspension. ABTS (5.5 mg) and H_2O_2 (5 μL) were added to 5.0 mL of H_2SO_4 (0.1 M) solution to obtain concentrations of 2.0 and 10.0 mM, respectively. Subsequently, 5.0 mL of an ABTS (2.0 mM) solution and 5.0 mL of an H_2O_2 (10.0 mM) solution were mixed for 10 min. Then, the mixture was diluted with a 0.1 M H_2SO_4 solution (1:50). The catalyst suspension (0, 5, 10, 15, 20, and 25 μL of catalyst) were added to 2.0 mL of dilution solution for 7 min, respectively. The obtained solution was characterized by UV-vis spectrophotometer. The absorbance of the catalyst at 417 nm was detected to evaluate the radical scavenging activity

Zn-air battery test

The carbon fiber paper (1.0 cm^2) loaded catalyst ink was conducted as the cathode and the zinc plate was conducted as the anode, and mixed solution of $Zn(Ac)_2$ (0.2 M) and KOH (6.0 M) as the electrolyte. The loading amount of all tested sample was 1.0 mg cm^{-2}.

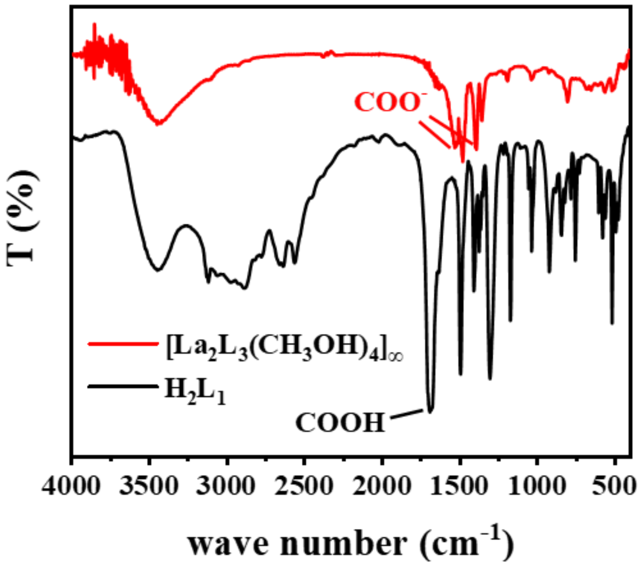

Figure S1. FT-IR spectra of $[La_2L_3(CH_3OH)_4]_\infty$ and H_2L_1

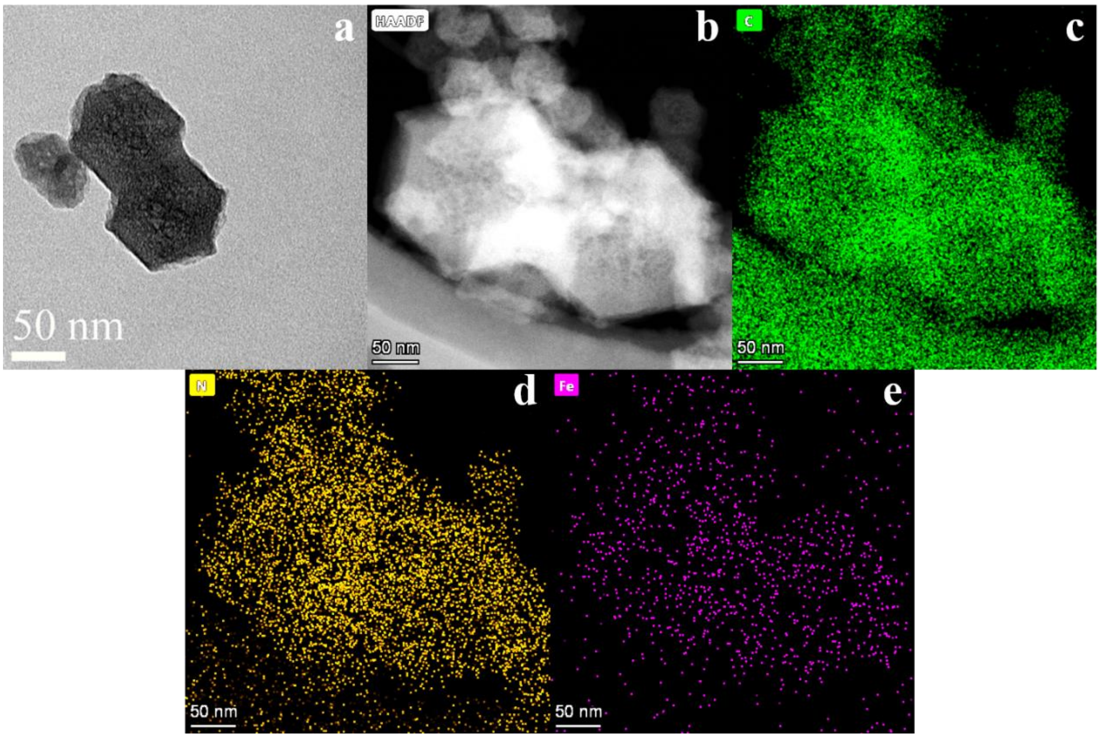

Figure S2. (a) The HR-TEM, (b) HADDF-STEM images, and (c, d, e) element mapping patterns of FeNC.

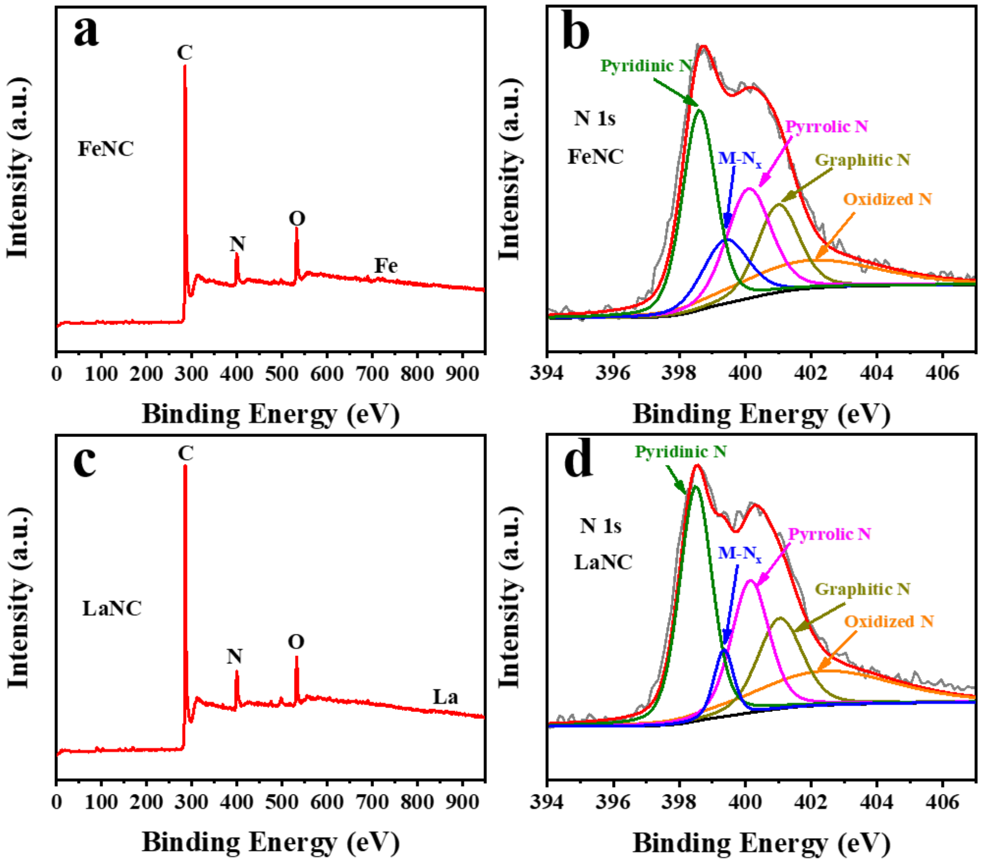

Figure S3. (a) XPS survey and (b) High-resolution N 1s XPS spectra of FeNC. (c) XPS survey and (d) High-resolution N 1s XPS spectra of LaNC.

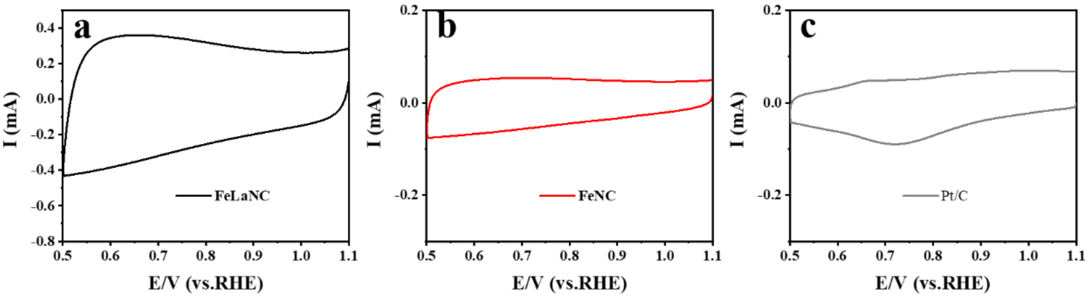

Figure S4. CV curves of FeLaNC (a), FeNC (b), and Pt/C (c) in N_2-saturated 0.1 M KOH solution.

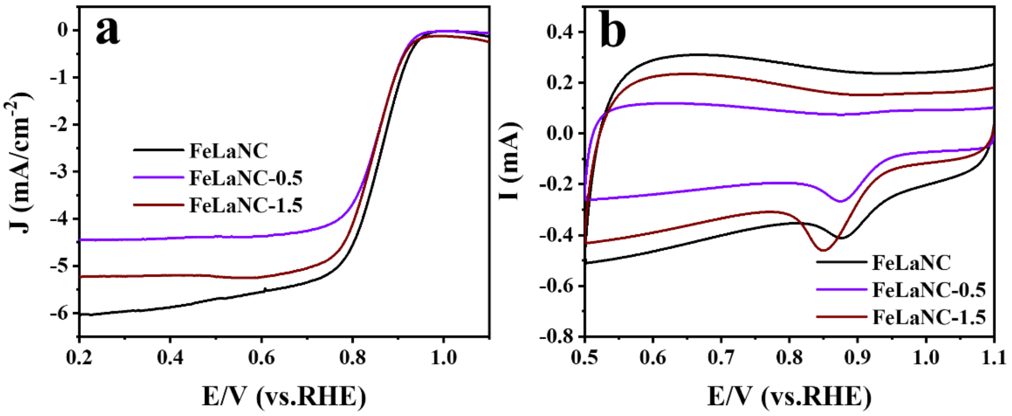

Figure S5. (a) LSV curves and (b) CV curves of FeLaNC , FeLaNC-0.5 and FeLaNC-1.5 in O_2-saturated 0.1 M KOH solution.

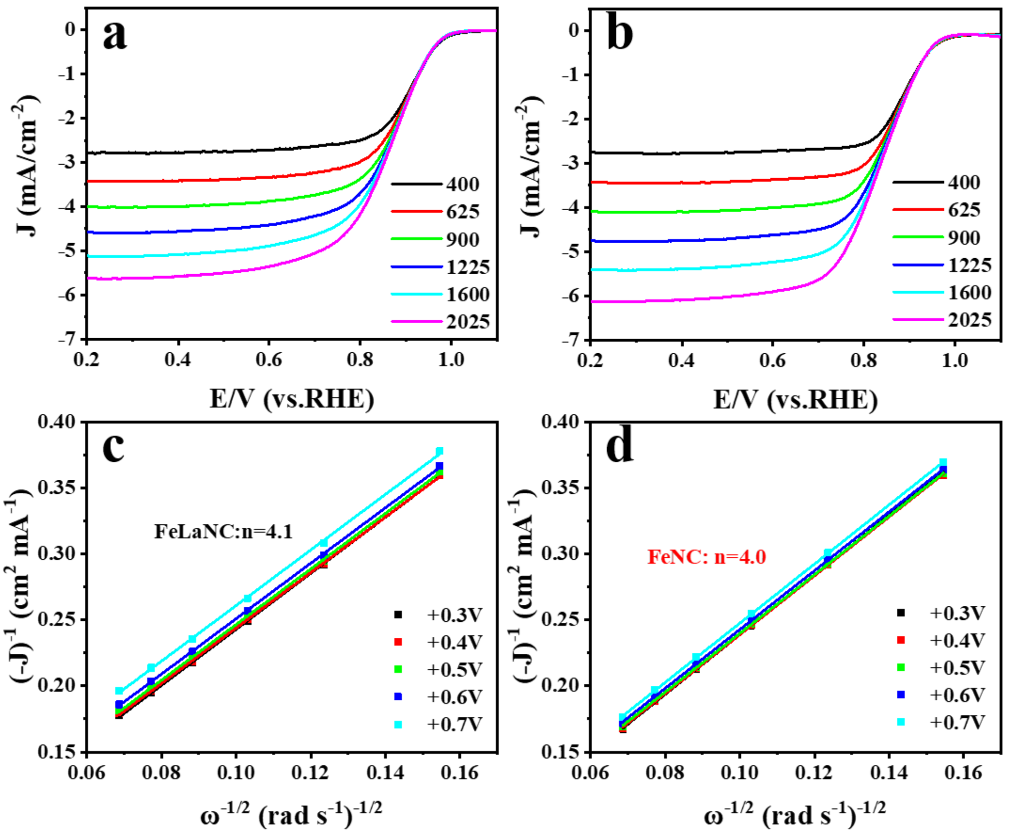

Figure S6. (a-b) LSV plots at 400-2025 rpm of FeLaNC (a) and FeNC (b). (c-d) K-L plots of FeLaNC and FeNC in O_2-saturated 0.1 M KOH solution.

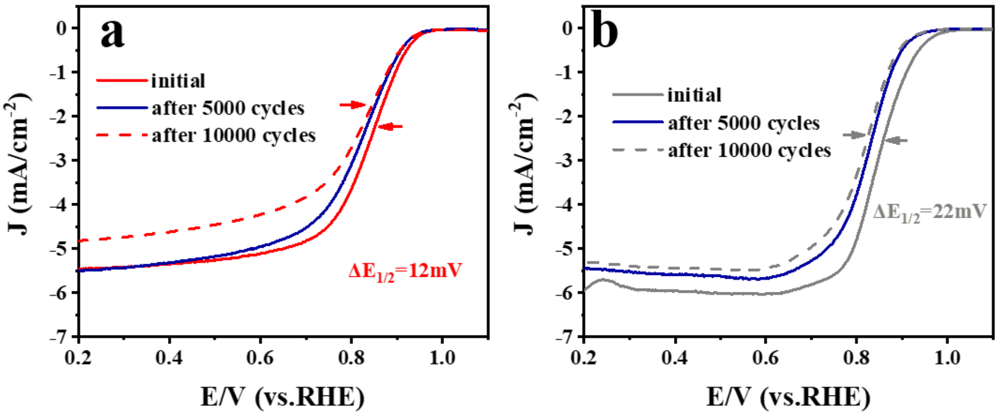

Figure S7. LSV curves of FeNC (a) and Pt/C (b) at 1600 rpm before and after ADT in O_2-saturated 0.1 M KOH solution.

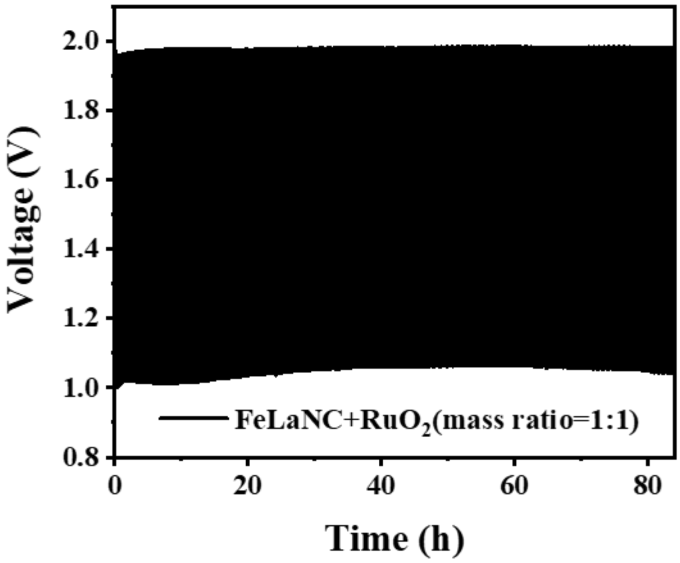

Figure S8. Charge-discharge curve of FeLaNC-loaded ZABs at 10 mA cm^{-2}.

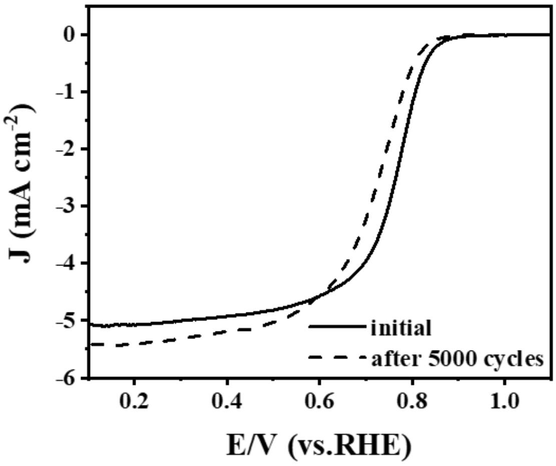

Fig. S9 LSV curves of FeLaNC at 1600 rpm before and after ADT in 0.1 M $HClO_4$.

Table S1. The content of different element for the prepared catalysts calculated from XPS.

Sample	C (at%)	N (at%)	O (at%)	Fe (at%)	La (at%)
FeLaNC	81.49	9.00	8.92	0.47	0.12
FeNC	79.43	9.84	10.26	0.48	/
LaNC	81.57	10.57	7.76	/	0.10

Table S2. The content of metal element for the prepared catalysts calculated from ICP-AES.

Sample	Fe wt%	La wt%
FeLaNC	1.33	0.77
FeNC	1.58	/
LaNC	/	0.61

Table S3. The content of different N types for the prepared catalysts calculated from XPS.

Sample	Pyridinic N	M-N_x	Pyrrolic N	Graphitic N	Oxidized N
FeLaNC	27.8%	16%	15.3%	19.7%	21.2%
FeNC	30.3%	13.3%	22.1%	16.6%	17.7%
LaNC	32.1%	4.5%	26.2%	17.2%	20.1%

Table S4. Comparison of ORR performance in 0.1 M KOH at 1600 rpm of previously reported iron-based catalysts.

Catalysts	$E_{1/2}$ (V vs. RHE)	$\Delta E_{1/2}$ (mV)	Cycles	Reference
FeLaNC	0.874	0	10000	**This work**
GO-Fe-N	0.87	10	3000	S1
Fe SA 900	0.84	9.5	10000	S2
Fe-N-C-KCl	0.877	11	2000	S3
1.3 Fe-N-C	0.84	42	10000	S4
Fe-SAC@N/CA-Cd	0.88	9	5000	S5
Fe1-HNC-500-850	0.842	0	5000	S6
FeNC@rGO-2	0.887	5	3000	S7
FeSA-NC/CNTs	0.86	1	5000	S8
Fe-ISAS/CN	0.881	2	5000	S9
Fe-N-GDY	0.89	14	5000	S10

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