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Supproting Information

Designing Highly Efficient Dual-Metal Single-Atom Electrocatalysts for Oxygen Reduction Reaction Inspired by Biological Enzyme System

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1. Experimental Section

1.1 Reagents

2-Methylimidazole (99%), Zinc nitrate hexahydrate (Zn(NO)₃•6H₂O, 99%), Iron (II) sulfate heptahydrate (FeSO4•7H2O, 99%), potassium hydroxide (KOH) and methanol were all purchased from Sinopharm Chemical Reagent Co. Ltd (AR grade, China). Manganese (II) 2, 4-pentanedionate (C10H14MnO4) was purchased from Alfa Aesar. Nafion® perfluorinated ion-exchange resin solution (5% w/w) was purchased from Sigma-Aldrich. All chemicals were used directly without further purification.

1.2 Preparation of zeolitic imidazolate framework, ZIF-8

The synthetic methods of ZIF-8 had been reported before.¹ In a typical synthesis, 4 g of 2-methylimidazole was dissolved in 60 mL of methanol (MeOH) to form a clear solution. 1.68 g of Zn(NO3)2•6H2O in 20 mL MeOH was poured into above solution quickly followed by vigorous stirring for 1 h. The mixture was then incubated at room temperature without stirring. After 12 h, the product was isolated as a white powder by centrifugation and washed several times with MeOH, and finally dried overnight in oven at 60°C

1.3 Synthesis of Fe-ZIF-8, Mn-ZIF-8, Fe, Mn-ZIF-8

Firstly, we prepared three kinds of solution containing Fe²⁺, Mn²⁺, and both Fe²⁺ and Mn²⁺ respectively, and the concentration is 5wt% for each metal salt. To prepare Fe, Mn-ZIF-8, 100mg ZIF-8 powder was dissolved in 20ml MeOH to form a clear solution, and then 1ml solution containing 5mg Fe and 5mg Mn metal salt was injected into above solution followed by vigorous stirring for 12h. The product was filtered and washed one time with MeOH and finally dried in oven at 60°C. Fe-ZIF-8 and Mn-ZIF-8 were prepared in a similar method by using corresponding metal salt solution.

1.4 Synthesis of Fe-N/C, Mn-N/C, Fe, Mn-N/C, N/C

The powder of Fe, Mn-ZIF-8 was transferred into a ceramic boat and placed in a tube furnace. The sample was heated to 800°C, 900°C, 1000°C with a heating rate of 5 °C min⁻¹ and kept for 3h under flowing argon gas and then naturally cooled to room temperature. The obtained material was named Fe, Mn-N/C-800, Fe, Mn-N/C-900, Fe, Mn-N/C-1000. And Fe-N/C, Mn-N/C was synthesized by heating corresponding powder to 900°C for 3h. N/C was obtained through pyrolysis of ZIF-8 at 900°C.

1.5 Characterization

Powder XRD data were acquired on a Japan Rigaku SmartLab TM rotation anode X-ray diffractometer with Cu Ka radiation (λ =1.54178 A). FESEM images were taken on a JEOL JSM-6700 M scanning electron microscope. TEM images were collected from Hitachi H-800 transmission electron microscope using an accelerating voltage of 200 kV, and a HRTEM (JEOL-2011) was operated at an accelerating voltage of 200 kV. The HAADF-STEM images were imaged by using a FEI, Talos F200X scanning/transmission

electron microscope operated at 200 kV, equipped with a probe spherical aberration corrector. XPS was performed on an ESCALAB 250 X-ray photoelectron spectrometer using Al Ka radiation. C and N XANES were obtained at soft x-ray magnetic circular dichroism station in national synchrotron radiation laboratory in USTC, Hefei. Fe L-edge XANES was operated at BL08U1A in Shanghai synchrotron radiation facility. Raman spectra were obtained using a LabRAM HR Raman spectrometer. Inductively coupled plasma (ICP) data were obtained by using an Optima 7300 DV instrument. The specific surface area was evaluated at 77 K (Autosorb iQ Station 2) using the Brunauer–Emmett–Teller (BET) method applied to the adsorption branch.

1.6 Electrocatalytic measurements

The electrochemical tests were carried out in a three-electrode system on an electrochemical workstation (CHI 760E). The catalysts dispersed onto a glassy carbon rotating disk electrode (PINE, PA, USA) were used as a working electrode, while 3M Ag/AgCl and a platinum foil served as the reference and counter electrodes, respectively. The GC RDE has a diameter of 5 mm and a geometric area of 0.196 cm². All of the potentials were calibrated to the reversible hydrogen electrode (RHE) according to Nernst equation. To prepare the working electrode, 4 mg catalysts mixed with 30 µl Nafion solution (Sigma Aldrich, 5wt %) were dispersed in 1 ml ethanol solution by sonicating for at least 60 min to form a homogeneous ink. A certain volume of catalyst ink was then drop-casted onto the glassy carbon electrode with a 0.204 mg cm⁻² loading for all samples. Before ORR catalytic activity testing, oxygen was used to purge the 0.1 M KOH solution for 30 min to keep the solution oxygen saturation. Before Cyclic voltammetry (CV) and Linear sweep voltammetry (LSV) tests, the working electrodes were activated using CV test at a scan rate of 50 mV s⁻¹ for several times. During the test in stability, the scan rate of CV was 100 mv s⁻¹. The linear sweep voltammetry (LSV) were applied at a scan rate of 10 mV s⁻¹. The polarization curves of the ORR were measured from 0.2 to 1.1 V (vs. RHE) at a scan rate of 10 mV s⁻¹ with a series of rotating electrode speeds (400, 625, 900, 1225, 1600 and 2025 rpm). The Pt/C (20 wt% Pt) catalyst which is considered to be one of the best ORR electrocatalysts was used as the reference material.

For the ORR at a RDE, the electron transfer numbers can be calculated with Koutecky– Levich equations

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{Bw^{1/2}} + \frac{1}{j_k}$$
$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6}$$
$$j_k = nFkC_0$$

where *j* is the measured current density; $j_{\rm K}$ and $j_{\rm L}$ are the kinetic and diffusion-limiting current densities, respectively; ω is the angular velocity of the disk (= 2π N, N is the linear rotation speed); n represents the overall number of electrons transferred in oxygen reduction; F is the Faraday constant (F = 96485 C mol⁻¹); C₀ is the bulk concentration of

 O_2 (1.2×10⁻⁶ mol cm⁻³); D_0 is the diffusion coefficient of O_2 in 0.1 M KOH electrolyte (1.9 × 10⁻⁵ cm² s⁻¹); v is the kinematics viscosity for electrolyte, and k is the electron-transferred rate constant.

1.7 Fabrication of Zn-air battery

The home-made Zn-air battery was fabricated by catalyst-coated carbon cloth as the air cathode and Zn foil as anode, 6 M KOH as electrolyte. Typically, 4 mg Fe, Mn-N/C catalysts was dispersed in 1 ml ethanol solution mixed with 30 μ l Nafion by sonicating for at least 60 min to form a homogeneous ink. Then a certain volume of catalyst ink was then brushed onto a 1 cm² carbon paper with a catalyst loading of 1.5 mg cm⁻². A polished zinc plate was used as the anode. As a reference material, 20 wt% Pt/C catalysts were prepared as the same procedure.

2 Supplementary Figures and Tables



Figure S1. Representative SEM images of (a) N/C (c) Fe-N/C (e) Mn-N/C (g) Fe, Mn-N/C-800 (i) Fe, Mn-N/C-1000. TEM images of (b) N/C (d) Fe-N/C (f) Mn-N/C (h) Fe, Mn-N/C-800 (j) Fe, Mn-N/C-1000.



Figure S2. XRD pattern of ZIF-8 precursor.



Figure S3. (a) N2 adsorption/desorption isotherm curves of N/C and Fe, Mn-N/C-900 (b) and the corresponding pore distribution.



Figure S4. Fe 2p XPS spectra of Fe, Mn-N/C-900



Figure S5. (a) C 1s XPS spectra (b) Mn 2p_{3/2} spectra of Fe, Mn-N/C-900



Figure S6. (a) C 1s (b) N 1s (c) Fe 2p XPS spectra of Fe-N/C. (d) C 1s (e) N 1s (f) Mn $2p_{3/2}$ XPS spectra of Mn-N/C



Figure S7. EDX spectra of Fe, Mn-N/C-900.



Figure S8. Tafel slope of Fe, Mn-N/C-900 and 20% Pt/C



Figure S9. The home-made Zn-air battery.

	Fe, Mn-N/C-800	Fe, Mn-N/C-900	Fe, Mn-N/C-1000
Pyridinic N	48.2%	38.4%	35.2%
Fe-N _x	13.2%	12.8%	12.3%
Pyrrolic N	14%	10%	9.4%
Graphitic N	24.6%	38.8%	43.1%
Total N	15.32%	8.08%	8.11%
С	84.36%	91.49%	91.55%

Table S1. The contents of pyridinic N, Fe-N_x, pyrrolic N, graphitic N and total N and C of Fe, Mn-N/C-800, 900, 1000.

Electrocatalysts	<i>E</i> _{1/2} (V vs. RHE)	Kinetic Current Density J _k (mA/cm²)	Loding(mg/c m²)	Ref
Fe, Mn-N/C-900	0.904	33.33 at 0.85 V	0.204	This work
BCNFNHs	0.861	7.0 at 0.8 V	1.2	J. Am. Chem. Soc. 2015, 137, 1436.
Fe-N _x /C	0.837	10.3 at 0.8 V	0.1	J. Am. Chem. Soc. 2013, 135, 15443.
Fe/NMC-11	0.862	-	0.51	Adv.Energy.Mater. 2017 , 7, 1701154
Fe-ISAs/CN	0.900	37.83 at 0.85 V	0.408	Angew. Chem. Int. Ed. 2017 , 56, 6937
Fe@C-FeNCs-2	0.899	41.6 at 0.8 V	0.7	J. Am. Chem. Soc. 2016, 138, 3570.

Fe/N-gCB	0.82	-	0.2	Chem.Commun. 20 15 ,51,7516
Fe ₃ C/C-800	0.86	0.8 at 0.9 V	0.6	Angew. Chem. Int. Ed. 2014, 53,3675.
S,N-Fe/N/C-CNT	0.85	-	0.6	Angew. Chem. Int. Ed. 2016, 55, 1.
FePhen@MOF-ArN H₃	0.86	2.1 at 0.9 V	0.6	Nat. Commun. 2015, 6, 7343.
Co SAs/N-C(900)	0.881	21.2 at 0.8 V	0.408	Angew. Chem. Int. Ed. 2016, 55,10800
NCNTFs	0.87	-	0.2	Nature Energy 2016, 1, 15006.

Table S2. Comparison of ORR performance between Fe, Mn-N/C-900 and other iron- and non-iron-based metal catalysts in the reported literatures in 0.1 M O_2 -saturated KOH.

3 DFT calculation.

All the calculations have been carried out through the spin-polarized density functional theory as implemented in the Vienna ab-initio simulation package (VASP).² The generalized gradient approximation (GGA) of Perdew-Becke-Ernzerhof (PBE) was used for the exchange-correlation functional.^{3, 4} The projector augmented wave was applied to describe the electron-ion interaction and the plane-wave energy cutoff was set to 400 eV. All structures were optimized with a convergence criterion of 1×10^{-5} eV for the energy and 0.02eV/Å for the forces. Brillouin zone sampling was employed using a Monkhorst-Packing grid with $3 \times 3 \times 1$. The free energy diagrams of the oxygen reduction reactions (ORR) have been calculated according to the method developed by Nørskov *et al.*⁵ The free energies of the intermediates at 298.15 K were obtained according to previous work using Equation $1.^{6}$

 $\triangle G = \triangle E + \triangle ZPE - T \triangle S + eU$

Eq. 1

where ΔE is the binding energy of adsorption species OH*, O* and OOH*, ΔZPE , ΔS and U are the zero point energy changes, entropy changes and applied potentials, respectively.

The charge density difference on Fe, Mn-N/C was calculated following Equation 2. $\rho_{diff} = \rho(Fe, Mn-N/C) - \rho(N/C) - \rho(Fe) - \rho(Mn)$ Eq. 2



Figure S10. Optimized Fe, Mn-N/C structure



Figure S11. Optimized Fe-N/C structure with ORR intermediates (a) O*, (b) OH* and (C) OOH*. (d) Free energy diagram of ORR on Fe-N/C under 0.33V overpotential.



Figure S12. Optimized Mn-N/C structure with ORR intermediates (a) O*, (b) OH* and (C) OOH*. (d) Free energy diagram of ORR on Mn-N/C under 0.33V overpotential.



Figure S13. DFT calculated electronic structures. (a) Differential charge density illustrates the increase (olive color) and decrease (cyan color) of electron distributions. (b) Bader charge.

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