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Supporting Information

In situ growth of highly active Cu-Fe spinel materials on N-doped porous carbon spheres via an adjustable localized microenvironment

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1. Chemicals and materials

Urea ($CO(NH_2)_2$, 99%), potassium hydroxide (KOH, 85%), Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$, 99%) ware purchased from HengXing Chemical Reagent (TianJin, China), Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%) was purchased from Macklin (Shanghai, China), glucose was purchased from Sinopharm Group chemical reagents (Shanghai, China). Sodium silicate solution was purchased from Sigma Aldrich(Shanghai, China), Ethylenediaminetetraacetic acid disodium salt(EDTA-2Na,$C_{10}H_{14}N_2Na_2O_8$, 99.5%) was purchased from DaMao Chemical Reagen (TianJin, China). 5% Nafion were bought from DuPont. All chemicals were used without further purification. Deionized water (≥18.25 MΩ) used in the measurements was obtained from a Millipore System (Millipore Q).

2. Materials characterization

A field emission scanning electron microscope (FESEM) was used to study the morphology of the sample (ZEISS Gemini300). The crystal structure was measured by the X-ray diffraction of Cu Kα radiation (XRD, $\lambda = 0.15418$ nm, Bruker, D8 ADVANCE). X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB Xi+) was used to study the surface chemical composition of the catalyst.

3. Electrochemical characterization

The electrochemical tests were conducted using the CHI 760E electrochemical workstation and rotational equipment with a standard three-electrode system. A graphite rod and a 1M-KOH Hg/HgO electrode were employed as the counter and reference electrodes, respectively. The electrocatalyst inks were prepared by dispersing 5 mg electrocatalysts in a solution consisting of 20 µL 5% Nafion 117, 240 µL water, and 740 µL isopropanol. The working electrode was prepared by applying 10 µL of the electrocatalyst onto a rotating ring-disk electrode (RRDE, diameter = 4 mm) with a loading capacity of 0.5 mg per square centimeter.

Oxygen reduction reaction (ORR) tests were conducted in a 0.1 M KOH solution saturated with O_2. All potentials were calibrated to the reversible hydrogen electrode (RHE) using the equation:

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$$E\,(vs. RHE) = E\,(Hg/HgO) + 0.059 \cdot pH + 0.098$$

Linear sweep voltammetry (LSV) polarization curves were recorded at a scan rate of 5 mV per second. Long-term durability of the prepared electrocatalysts and Pt/C benchmark was assessed by performing chronoamperometry at 0.8 V and comparing LSV curves before and after thousands of cyclic voltammetry (CV) cycles. The electron transfer number (n) was calculated utilizing the Koutecký-Levich equations.

$$\frac{1}{j} = \frac{1}{j^l} + \frac{1}{j^k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j^k}$$

$$B = 0.62nFC_oD^{2/3}v^{-1/6}$$

The measured, diffusion-limited, and kinetic current density are denoted as j, j^l, and j^k respectively. The electrode's angular velocity (ω) is expressed in radians per second (rad s^{-1}), while the value of the Faraday constant (F) is 96485 C mol^{-1}. The saturated O_2 concentration (C_o) is 1.21 × 10^{-6} mol cm^{-3}, and the diffusion coefficient of O_2 in 0.1 M KOH (D) is 1.9 × 10^{-5} cm^2 s^{-1}. The kinetic viscosity (ν) is 0.01 cm^2 s^{-1}. The RRDE measurements were conducted with a ring electrode potential of 1.2 V. The H_2O_2 yield (H_2O_2%) and n of ORR were determined using the following equations:

$$n = \frac{4j^d}{j^d + j^r/N}$$

$$H_2O_2\% = \frac{200\, j^r/N}{j^d + j^r/N}$$

where N, j^d and j^r are the current collection efficiency of the Pt ring electrode (0.37), the disk current and the ring current, respectively.

4. Oxygen reduction reaction

Glassy carbon (GCE) was coated with catalyst ink using a 0.5 mg cm^2 loading quantity. The reference catalyst used was commercial Pt/C (20 wt%). The LSV curves were measured at a series of rotating electrode speeds (100, 400, 900, 1600 and 2500 rpm) at a scan rate of 2 mV s^{-1} whereas the CV curves were measured in an O_2-saturated 0.1 M KOH aqueous solution at a scan rate of 2 mV s^{-1} at a potential range of -0.8 to 0.2 V (E Hg/HgO). The reversible hydrogen electrode (RHE) was created from each potential using the formula:

$$E\,(vs.\,RHE) = E\,(Hg/HgO) + 0.059 \cdot pH + 0.098$$

In alkaline medium, the ORR could occur in the following 4 electron reaction pathway:

$$* + O_2\,(g) + H_2O\,(l) + e^- \rightarrow *OOH + OH^-$$

$$*OOH + e^- \rightarrow *O + OH^-$$

$$*O + H_2O\,(l) + e^- \rightarrow *OH + OH^-$$

$$*OH + e^- \rightarrow * + OH^-$$

5. Supplementary Tables

Table S1. Comparison of ORR parameters for recent reported electrocatalysts in 0.1M KOH.

Catalysts	E_{onset} (V)	$E_{1/2}$ (V)	Reference
Cu-Fe N-CS	0.90 V	0.83 V	This Work
N-CS	0.87 V	0.74 V	This Work
Cu-Fe ACS	0.67 V	0.59 V	This Work
Cu-Fe CS	0.8 V	0.74 V	This Work
$C\text{-}Cu_{0.7}Fe_{2.3}O_4$	0.72 V	0.65 V	1
$C-MnFe_2O_4$ NPs	0.86 V	0.81 V	1
$C\text{-}Co_{0.8}Fe_{2.2}O_4$,	0.79 V	0.72 V	1
$CuCo_2O_4$	0.89 V	0.72 V	2
$FeCo_2O_4$	0.88 V	0.7 V	2
$ZnCo_{1.4}Mn_{0.6}O_4$	0.88 V	0.8 V	3
$NiMn_2O_4$	0.81 V	0.6 V	4
Ce-CMO-18%/MWCNTs	0.93 V	0.84 V	5
$CoMn_2O_4$(0.15 M)-400	0.90 V	0.83 V	6
HEO/CoNC-3–1	0.92 V	0.85 V	7
$NiFe_{1.75}Co_{0.25}O_4$/C	0.74 V	0.68 V	8
m-ZCO-NB	0.79 V	0.75 V	9
$NiCo_2O_4\text{-}C_l$--HY	0.89 V	0.72 V	10

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