Supporting Information

Fe$_3$C cluster-promoted single-atom Fe, N doped carbon for oxygen-reduction reaction

Mengyao Lv$^{a,b,c}$, Haichuan Guo$^{a,c}$, Hangjia Shen$^{a,c,*}$, Jun Wang$^b$, Jiacheng Wang$^{a,d,*}$, Yuichi Shimakawa$^{e,f}$, Minghui Yang$^{a,c,*}$

$^a$ Institute of New Energy Technology, Ningbo Institute of Industrial Technology, Chinese Academy of Sciences, Ningbo 315201, China

$^b$ College of Chemistry, Liaoning University, Shenyang 110036, China

$^c$ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

$^d$ State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.

$^e$ Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

$^f$ Integrated Research Consortium on Chemical Sciences, Uji, Kyoto 611-0011, Japan

*Corresponding author.

E-mail address: H. S. (hjshen@nimte.ac.cn); J. W. (jiacheng.wang@mail.sic.ac.cn); M. Y. (myang@nimte.ac.cn)
Electrochemical details

The catalyst inks were prepared by dispersing the catalyst in 1 mL mixture of water and isopropanol with a volume ratio of 1:4 with another 0.5 μL Nafion (5 wt%). The prepared catalysts were characterized as thin films drop-casted on a GC collector electrode. The 10 μL as-prepared ink with catalysts concentration of 10 mg/mL was dropped on the glassy carbon (GC) electrode to lead the catalyst loading of 0.5 mg cm$^{-2}$. All the linear sweep voltammetry (LSV) tests were conducted in 0.5 M H$_2$SO$_4$ or 0.1 M KOH electrolytes with a rotation speed of 1600 rpm at a scan rate of 10 mV s$^{-1}$. The RDE polarization curves were recorded at different speeds and the background current measured in the N$_2$ saturated electrolyte. Tafel analysis was performed by plotting log $j_k$ versus potential in the kinetically controlled region. In order to evaluate the durability of the as-prepared catalysts, the cycle voltammetry was carried out at the potential ranging from 0.6 to 1.0 V (vs. RHE)$^{1,2}$. After 8000 cycles, the LSV at 1600 rpm was measured for comparison. The measurement was performed in both N$_2$ and O$_2$ saturated electrolyte solution.

The electron transfer number for the ORR is determined from the fitting of the Koutecky-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}}$$

where $J$ and $J_K$ are the measured current density and kinetic current density and $\omega$ is the rotation speed. And the B can be expressed as

$$B = 0.62nFC_0D^{2/3}v^{-1/6}$$

where n is the electron transfer number, F (96,485 C mol$^{-1}$) is the Faraday constant, $v$ (0.01 cm$^2$ S$^{-1}$) is the viscosity of the electrolyte solution, $C_0$ (1.2 × 10$^{-6}$ mol cm$^{-3}$) is concentration of oxygen and $D$ (1.9 × 10$^{-5}$ cm$^2$ s$^{-1}$) is the diffusion coefficient.

In the Test of rotating Ring-disk electrode, the disk electrode was scanned cathodically at a rate of 10 mV s$^{-1}$ and the ring potential was constant at 1.14 V versus RHE. The yield of HO- 2 and the electron transfer number (n) from RRDE measurements were calculated with the following equations:
\[ H_2O_2(%) = 200 \times \frac{|J_R/N|}{|J_D| + |J_R/N|} \]

\[ n = 4 \times \frac{|J_D|}{|J_D| + |J_R/N|} \]

where \( J_R \) is the ring current density, \( J_D \) is the disk current density, \( N \) is the current collection efficiency of the Pt ring (\( N = 37\% \)).

The TOF for each catalyst was calculated by following equation:

\[ TOF = \frac{J_K \times N_A}{nF \times ECSA} \]

where \( J_K \) is the current during linear sweep measurement, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)) and \( n \) is 4 of electron transfer number for oxygen reduction. \( N_A \) is Avogadro's constant, and ECSA is electrochemically active surface area.

**Reversible nitrite poisoning experiment**

To determine the active sites, it is necessary to perform a series of experiments with the catalyst. In the range of 0.4~0.3V (vs. RHE), charge stripping will occur in the buffer solution of the sample, and the nitrite ligand may be converted to the nitroso ligand during the cycle. After the reaction, charge stripping was carried out again in the buffer solution, and the sample was reduced to Fe-N\(_4\) structure.

A 0.5 M acetate buffer at pH 5.2 was used as an electrolyte to improve reproducibility because the reduction of nitrite was sufficiently easy at this pH, while the nitrite anion was sufficiently stable. The reversible nitrite poisioning process was carried out according to Kucernak et al\(^3\).
Supplementary Figures and Tables

Figure S1 Raman spectra of FeNC and A-FeNC.

Figure S2 SEM of A-FeNC (a) and FeNC (b).

Figure S3. (a). Wide band XPS survey of FeNC and Fe$_3$C/FeNC. (b) High resolution C1s of A-FeNC
Figure S4. CV curves of A-FeNC in O$_2$ (black line) or N$_2$ (red line) saturated 0.1 M KOH electrolyte.

Figure S5. The mass activity of A-FeNC, FeNC and Pt/C.
Figure S6. RDE polarization curves of (a) A-FeNC and (b) Pt/C with different rotation rates in O$_2$-saturated 0.1 M KOH solution at a scan rate of 10 mV s$^{-1}$
Koutecky-Levich plots of (c) A-FeNC and (d) Pt/C at different potentials

Figure S7. HO- 2 yield (left) and Electron transfer number (n) (right) vs. potential of A-FeNC with the RRDE test at 1600 rpm
**Figure S8.** (a) The cycle voltammetry with different scan rate of FeNC and (b) A-FeNC

**Figure S9.** ORR performance of catalyst layer before, during and after nitrite adsorption
Table S1. Mössbauer parameters of A-FeNC. Isomer shift (IS), quadrupole splitting (QS), hyperfine field (HF) and relative spectral area % of each component

<table>
<thead>
<tr>
<th>Component</th>
<th>IS (mm s(^{-1}))</th>
<th>QS (mm s(^{-1}))</th>
<th>HF (T)</th>
<th>Area(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doublet</td>
<td>0.20</td>
<td>0.73</td>
<td>-</td>
<td>41.6</td>
</tr>
<tr>
<td>sextet</td>
<td>0.21</td>
<td>-0.03</td>
<td>20.70</td>
<td>58.4</td>
</tr>
</tbody>
</table>
Supplementary references

