Title:

Optimizing Oxygen Reduction Reaction Performance in Pt-based Catalysts through Fe/Ce Dual-Component Interface Engineering on Nitrogen-Doped Carbon

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# **1. Experimental and Characterization**

#### 1.1 Chemicals

Carbon (ECP-600jd), O-phenanthroline, ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), cerium nitrate hexahydrate (Ce (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), methanol, ethanol, isopropanol, ethylene glycol, perchloric acid (HClO<sub>4</sub>) were purchased from Aladdin Commercial Pt/C (Suzhou Sinero Technology Co., Ltd, 20wt%) was purchased from JM (Johnson Matthey). Nafion (5 wt %) was purchased from Dupon. The ultrapure water (18.2 MΩ·cm) used in all experiments was obtained through an ultra-pure water system. All chemicals were used as received without further purification.

# **1.2 Experimental**

# 1.2.1 The synthesis of Fe-NC

Initially, 120 mg of carbon (C) was dissolved in 40 mL of methanol, sonicated for 1 hour, and stirred for 12 hours to ensure uniform dispersion of C. 56 mg of FeSO<sub>4</sub> and 108 mg of 1,10-phenanthroline were separately dissolved in 10 mL of methanol, sonicated for 0.5 hours, and stirred until completely dissolved. Subsequently, the two solutions were dropwise added to the dispersed C in methanol, stirring for 1 hour. The resulting mixture was then evaporated in a water bath at 60°C to obtain the precursor of Fe-NC. Finally, the precursor was subjected to high-temperature treatment at 900°C under an Ar atmosphere for 3 hours to obtain Fe-NC, which will support the reference catalyst.

# 1.2.2 The synthesis of Pt/Fe-NC

A 40 mg Fe-NC support was dissolved in a mixed solution of 60 mL of ethanol

and isopropanol (v: v = 4: 1). After sonication for 1 hour, a solution of chloroplatinic acid in ethanol (0.0486 mmol/mL-1055 uL) was added and sonicated for another hour followed by overnight stirring to achieve uniform dispersion. A measured amount of NaOH-ethanol solution (adjusted to pH=12) was then added to the mixed solution, followed by the introduction of N<sub>2</sub> gas for 0.5 hours. The mixture was then microwaveheated for 100 seconds, cooled, and slowly titrated with dilute nitric acid to adjust the pH to 2. After stirring for 12 hours, the solution was filtered and dried, and the resulting product was placed in a tube furnace and treated at 200°C under an Ar atmosphere for 2 hours to obtain the Pt/Fe-NC catalyst.

#### 1.2.3 The synthesis of Ce-NC

Initially, 120 mg of carbon was dissolved in 40 mL of methanol, sonicated for 1 h, and stirred for 12 h to ensure uniform dispersion. 43 mg Ce(NO<sub>3</sub>)<sub>3</sub> and 108 mg 1-10 phenanthroline were separately dissolved in 10 mL of methanol, sonicated for 0.5 h, and stirred until fully dissolved. The two solutions were then added dropwise to the dispersed carbon in methanol and stirred for 1 h. Subsequently, the mixed solution was evaporated in a water bath at 60°C to obtain the precursor of Ce-NC, which was further subjected to high-temperature treatment at 900°C for 3 h under an Ar atmosphere to yield Ce-NC, serving as the carrier for comparative catalysis.

#### 1.2.4 The synthesis of Pt/Ce-NC

A total of 40 mg of Ce-NC carrier was dissolved in a mixed solution of 60 mL of ethanol and isopropanol (v: v=4:1). The mixed solution was sonicated for 1 hour, followed by the addition of chloroplatinic acid-ethanol solution (0.0486 mmol/mL-

1055 uL), which was then sonicated for another hour and stirred overnight to achieve uniform dispersion. A measured amount of NaOH-ethanol solution (adjusted to pH=12) was added to the mixed solution, followed by the introduction of N2 into the solution. After maintaining this state for 0.5 hours, the mixed solution was microwave-heated for 100 seconds. Upon cooling, a dilute nitric acid solution (adjusted to pH=2) was slowly added to the mixture, which was then stirred for 12 hours, filtered, dried, and placed in a tube furnace. The product was treated at 200°C for 2 hours under an Ar atmosphere to obtain Pt/Ce-NC catalyst.

# **1.3 Electrochemical measurement**

#### **1.3.1 Electrochemical half-cell measurements**

2.5 mg of Pt/FeCe-NC catalyst was ultrasonically dispersed in the 500 µL dispersion, which consisted of DI-water, ethanol, and 5% Nafion solution(v/v/v=5:5:0.3). Then 10 µL of the ink was drop-casted on the surface of a prepolished glassy-carbon electrode and dried at the room temperature. The method of preparing Pt/Fe-NC, Pt/Ce-NC, and Pt/C working electrodes was the same as Pt/FeCe-NC. The Pt loading of Pt/FeCe-NC, Pt/Fe-NC, Pt/Ce-NC, and 20% Pt/C was 10 µg, 10 µg, 10 µg, and 10 µg (theoretical calculation value), respectively. A reversible hydrogen electrode (RHE) was chosen as the reference electrode. 0.1 M HClO<sub>4</sub> was injected into the semi-closed cavity of the quartz capillary of RHE, and then 0.1 M HClO<sub>4</sub> was used as an electrolyte. The RHE was used as the anode, and the Pt mesh electrode was used as the cathode and reference electrode. The potential of RHE was set at -4 V~ -5 V vs. Pt mesh electrode to produce a coherent H<sub>2</sub> cylinder inside the RHE quartz capillary, and then it sat for a while.

Electrochemical measurements were carried out using an electrochemical

workstation (CHI 760e) coupled with a rotating-ring disk electrode (RRDE, Pine). The RRDE experiments were performed in 0.1 M HClO<sub>4</sub> electrolyte at room temperature with a standard three-electrode cell. The glassy carbon disk of 5.61 mm in diameter was used as the working electrode, and the carbon rod and the RHE (homemade) were used as the counter electrode and reference electrode, respectively. Before testing, N<sub>2</sub> was aerated for about 30 mins to remove O<sub>2</sub>. A cyclic voltammetry (CV) test was performed within a potential range of 0.05 V-1.05 V in an N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte at a scan rate of 100 mV s<sup>-1</sup> which was used to activate the catalysts and then recorded CV within a potential range of 0.05 V-1.0 V with a scan rate of 50 mV s<sup>-1</sup>. The ORR activity was evaluated by staircase voltammetry (LSV) tests in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte. The test techniques were as follows: 0.05-1.1 V, 1600 rpm. Catalyst stability was studied by potential cycling from 0.6 to 1.0 V (200 mV/s) in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte. Moreover, the kinetic current density J<sub>K</sub> was calculated from the Koutecky-Levich equation (1). the MA was calculated from equation (2).

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_d}$$
(1)  
$$MA = \frac{J_k}{mPt}$$
(2)

In the first equation, J is the measured current density,  $J_k$  and  $J_d$  represent the kinetic and diffusion- limiting current density.

#### **1.3.2 Electrochemical PEMFC Single-Cell Measurements**

The Pt/FeCe-NC was mixed with perfluoro sulfonic acid ionomer (Nafion D520) (23% ionomer content in the mixture) and sonicated in isopropanol and deionized water (3:2, v: v) to prepare a slurry with 5.5% solids (catalyst and dry ionomer). The membrane electrode assembly (MEA) was prepared by the CCM. The active area of

the as-prepared MEA was 5 cm<sup>2</sup>. The catalysts are loaded with 0.1 mg<sub>Pt</sub>·cm<sup>-2</sup> for the cathode and 0.1 mg<sub>Pt</sub>·cm<sup>-2</sup> for the anode in the MEA prepared from commercial 20% Pt/C. The catalysts are loaded with 0.1 mg<sub>Pt</sub>·cm<sup>-2</sup> for the cathode and 0.1 mg<sub>Pt</sub>·cm<sup>-2</sup> for the anode in the MEA prepared from Pt/FeCe-NC. The MEA of the commercial 20% Pt/C catalyst is prepared in the same way as a comparison. This study performed the MEA test using the Scribner 850e fuel cell test system. After sufficient activation, the H<sub>2</sub> (500 sccm)-O<sub>2</sub> (500 sccm)/H<sub>2</sub> (500 sccm)-Air (2000 sccm) polarization (I-V) versus power density (I-P) curves were measured from open circuit voltage to 0.3 V at 80°C and 100% RH test conditions with a back pressure of 100 kPa/200kPa.

#### **1.4 Physical Characterization**

High-resolution transmission electron microscopy (HRTEM), High-angle annular dark-field - scanning transmission electron microscope (HAADF-STEM), and STEM energy dispersive X-ray spectroscopy (STEM-EDS) images were obtained using Tecnai G2 F20 TEM (Thermo Fisher Scientific). Aberration-corrected HAADF-STEM (AC-HAADF-STEM) images were acquired with Themis G2 300 (FEI Company)

The powder X-ray diffraction (XRD) spectra were obtained by a D2 PHASER XE-T diffractometer (Bruker Corporation) with a Cu K $\alpha$  X-ray source operating at 30 kV and 10 mA, scanning at a rate of 6° min<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo Scientific K-Alpha (Thermo Fisher Scientific). Monochromatic X-rays were generated by an Al K $\alpha$  source (1486.7 eV), and all binding energies were calibrated by the peak position of C 1s peak (284.8 eV). Raman spectra measurements were performed on an in Via-Reflex confocal Raman microscope (in Via-Reflex, Renishaw Instruments), excited with a 532 nm laser.

#### **1.5 DFT calculation**

The first-principles density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP). The electronic exchangecorrelation was described by generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) functional. A kinetic energy cutoff of 400 eV was used for the plane-wave expansion of the electronic wave functions, and the convergence criterion of force and energy was set to 0.01 eV·Å-1 and 10–5 eV, respectively. A model was established for the loading of Pt nanoparticles on FeCe-NC, Fe-NC, Ce-NC, and C (Figure 5a, S14). A Gaussian smearing of 0.05 eV width with a  $1 \times 1 \times 1$  k-points mesh was applied for structural optimizations, while a  $3 \times 3 \times 1$ Gamma-centered mesh was used for density of states (DOS) calculations. The VASPKIT code was used to post-process the results of the VASP calculations. All the reported free energies (G) are defined as:

$$G = E_{DFT} + E_{ZPE} - TS$$
$$G = E_{DFT} + E_{ZPE} - TS$$

Where  $E_{DFT}$  represents the calculated intermediate's energy, and  $E_{ZPE}$  represents zero-point energy. T and S denote the temperature (298 K) and entropy, respectively. According to the mechanism of oxygen reduction reaction (ORR), the free energy of each step can be calculated as:

initial: 
$$G_* + G_{O2} + 2 \times G_{H2} - 4 \times |e|U$$
  
 $1^{st} e^-: G_{*OOH} + 1.5 \times G_{H2} - E(H^+/H_2) \times e^- 3 \times |e|U$   
 $2^{nd} e^-: G_{*O} + G_{H2O} + G_{H2} - 2 \times E(H^+/H_2) \times e^- 2 \times |e|U$   
 $3^{rd} e^-: G_{*OH} + G_{H2O} + 0.5 \times G_{H2} - 3 \times E(H^+/H_2) \times e^- 1 \times |e|U$   
 $4^{th} e^-: G_* + 2 \times G_{H2O} - 4 \times E(H^+/H_2) \times e$ 

Where the value of  $E(H^+/H_2)$  is 0 V (pH=0), and *e* stands for elementary charge. The overpotential ( $\eta$ ) is calculated by:

$$\eta = \max\left(\Delta G_i\right)/e + E(O_2/H_2O)$$

The vacancy formation energy, Evac was defined as:

$$E_{vac} = E_{[vac]} + E_{[M]} - E_{[no vac]}$$

Where  $E_{\text{[vac]}}$  is the energy of the slab with a vacancy,  $E_{\text{[M]}}$  is the energy of a single M

atom in bulk, and  $E_{\text{[no vac]}}$  is the energy of the vacancy-free slab.



# 2. Supplementary Figures and Tables

Fig S1. The TEM image (a) and HAADF-STEM image (b) of FeCe-NC.







Fig S3. The TEM images of Pt/FeCe-NC (a), Pt/Fe-NC (b), Pt/Ce-NC (c), and Pt/C (d).



Fig S4. The size and distribution of Pt nanoparticles: Pt/FeCe-NC (a), Pt/Fe-NC(b), Pt/Ce-NC (c), and Pt/C (d).



Fig S5. XRD pattern of C, Fe-NC, FeCe-NC (a), Pt/Fe-NC, Pt/Ce-NC, and Pt/FeCe-NC (b).



Fig S6. (a) The XPS spectra of Pt/FeCe-NC with different Fe/Ce atomic ratios: (b) Pt 4f.



Fig S7. Electrochemical testing of catalysts. (a) ECSA and SA of Pt/FeCe-NC and comparison samples. (d) ECSA and SA of Pt/FeCe-NC with different Fe/Ce atomic ratios.



Fig S8. CV curves of Pt/FeCe-NC (a) and Pt/C (b) before and after ASTs.







Fig S10. The size and distribution of Pt/FeCe-NC (a) before and (b) after ASTs.



Fig S11. The TEM images of Pt/C (a) before and (b) after ASTs



Fig S12. The size and distribution of Pt/C before (a) and after (b) ASTs.



Fig S13. The DFT computational structure model of Pt/Fe-NC and Pt/Ce-NC



# **Reaction Coordinate**

Fig S14. The Gibbs free energy diagram of ORR of Pt/FeCe-NC, Pt/Fe-NC, Pt/Ce-NC, and Pt/C.

based catalysts.						
Catalysts	<i>E</i> <sub>1/2</sub> (V vs. RHE)	MA@0.9V (A/mg <sub>Pt</sub> )	References			
Pt/Fe Ce-NC	0.927	0.274	This work			
Pt/Fe-NC	0.907	0.170	This work			
Pt/Ce-NC	0.901	0.146	This work			
Pt/C	0.884	0.096	This work			
Pt/Fe, N-HG	0.88	0.208	[43]			
Pt/ZnFe-N-C	0.790	0.221	[47]			
Pt/CeO <sub>2</sub> -NC	0.916	0.165	[39]			
Pt@NiNC	0.85	0.028	[45]			
Pt/Co-N-C	0.886	0.223	[44]			
Pt/Mn-N-C	0.89	0.146	[46]			
Pt/Ni-N-C	0.81	0.010	[45]			
Pt@Fe-N-OMC-2	0.844	0.53/0.85V	[7]			

Table S1. Comparison of the ORR activity of Pt/Fe Ce-NC with various recently reported Pt-

Table S2. Comparison of the ORR activity of Pt/Fe Ce-NC with various recently reported Pt-

based catalysts.					
Catalysts	E <sub>1/2</sub>	MA@0.9V	Deferences		
	(V vs. RHE)	(A/mg <sub>Pt</sub> )	References		
Pt/Fe Ce-NC	0.927	0.274	This work		
Pt/Fe-NC	0.907	0.170	This work		
Pt/Ce-NC	0.901	0.146	This work		
Pt/C	0.884	0.096	This work		
Pt/Fe, N-HG	0.88	0.208			
Pt/ZnFe-N-C	0.790	0.221	[9]		
Pt/CeO <sub>2</sub> -NC	0.916	0.165	[6]		
Pt@NiNC	0.85	0.028	[7]		
Pt/Co-N-C	0.886	0.223			
Pt/Mn-N-C	0.89	0.146			
Pt/NiNC	0.81	0.010	[8]		

Catalysts	E <sub>1/2</sub>	ECSA	MA	SA
	(V)	$(m^2 \cdot g^{-1})$	$(A \cdot mg_{Pt}^{-1})$	$(A \cdot m_{Pt}^{-2})$
Pt/C	0.885	83	0.096	1.18
Pt/Fe-NC	0.907	87	0.170	1.98
Pt/Ce-NC	0.901	84	0.146	1.86
Pt/Fe <sub>3</sub> Ce <sub>1</sub> -NC	0.907	86	0.145	1.77
Pt/Fe <sub>2</sub> Ce <sub>1</sub> -NC	0.927	92	0.274	2.97
Pt/Fe <sub>1</sub> Ce <sub>1</sub> -NC	0.919	89	0.211	2.49
Pt/Fe <sub>1</sub> Ce <sub>2</sub> -NC	0.903	82	0.140	1.65
Pt/C-30k	0.853	61	0.056	0.918
$Pt/Fe_2Ce_1$ -NC-30k	0.920	88	0.237	2.69

Table S3. Comparison of the ORR activity of different catalysts.

Sample	Pt/C	Pt/Fe-NC	Pt/Ce-NC	Pt/FeCe-NC
Binding Energy	-2.82 eV	-3.98 eV	-3.37 eV	-4.08 eV
ICOHP	-0.823	-1.041	-0.917	-1.135
Free Energy	0.776 eV	0.874 eV	0.833 eV	0.915 eV
Changes				
Theoretical	0.454 eV	0.383 eV	0.397 eV	0.315 eV
Overpotentials				
εd	-1.954 eV	-2.183 eV	-2.178 eV	-2.197 eV

Table S3. DFT calculation data of the different catalysts.