Defect-driven Oxygen Reduction Reaction (ORR) of Carbon without Any Element Doping

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Detailed Experimental Section

Reagents and Materials. All chemicals purchased are reagent grade or better and are used without further purification. 2,6-Naphthalenedicarboxylic acid (2,6-NDC, 99%), zinc nitrate hexahydrate (Zn(NO₃)₃·6H₂O, 99%), platinum on graphitized carbon (Pt/C, wt 20%) and Naflon® 117 solution (5%) are purchased from Sigma-Aldrich. N, N-diethylformamide (DEF, 99%) is purchased from Alfa Aesar.

Preparation of IRMOF-8. IRMOF-8 compound was synthesized basing on the reported literature. Zn(NO₃)₂·6H₂O (0.55 g) and 2,6-NDC (0.15 g) were dissolved in 50 mL DEF and dispensed to 100 mL Teflon-lined stainless steel vessels, the reaction was carried out at 95 °C for 20 hours under autogenous pressure. After filtering and washing with 5 mL DEF for three times, the cubic crystals of IRMOF-8 were collected.¹⁻⁴

Synthesis of PC-18-950 porous carbon. Under nitrogen flow and with a heating rate of 5 °C·min⁻¹, 500mg of IRMOF-8 crystals were heating at 150 °C for 90 minutes to remove guest molecules, and then the treatment temperature raised to 550 °C and remained for 180 minutes. Finally, the sample was heated at 950 °C for 240 minutes and lower to room temperature. The black powerful product were collected directly and denoted as PC-18-950.

Instruments and characterization

The N₂ adsorption and desorption isotherm was measured on a Micromeritics Tristar II 3020 analyser. X-ray photoelectron spectroscopy (XPS) was recorded by an ESCALAB-M II 250 photoelectron spectrometer with Al-Kα X-ray radiation as the X-ray source for excitation. X-ray diffraction (XRD) pattern was recorded by a PANalytical Empyrean Diffractometer using Ag-Kα radiation, 60 kV, 30 mA with a scanning rate of 1°·min⁻¹ and the data were calibrated with respect to Cu-Kα radiation. Raman spectrum was measured on a Renishaw in Via Raman Microscopy with 514 nm laser. All electrochemical experiments were carried out with a CHI 760E electrochemical workstation (CH Instruments) in a three-electrode electrochemical cell.

Electrochemical Measurements

Electrochemical performance of PC-18-950 and Pt/C catalysts were measured in the three-electrode
The response method molecule diffusion-limiting from rate by constant J respectively. glassy electrochemical to with dispersed methanol Rotating Cyclic Voltammetry (CV). The catalyst modified working electrode was prepared by the method as above. The GC electrode as a working electrode was scanned at a rate of 50 mV s⁻¹ in the potential range from 0.20 to -1.20 V (vs. Ag/AgCl).

Rotating Disk Electrode (RDE) Measurement. The catalyst modified working electrode was prepared by the same method. The working electrode rotated with varying speed from 400 to 2500 rpm at a scanned rate of 10 mV s⁻¹.

LSV curves are investigated by Koutecky–Levich plots (J⁻¹ vs. ω⁻¹⁄₂) at different electrode potentials from -0.30 to -0.60 V (vs. Ag/AgCl). The slopes of the best linear fit lines are used to calculate the diffusion-limiting and kinetic current density (Jₖ) and the number of electrons transferred (n) per O₂ molecule from Koutecky–Levich equation:

\[ \frac{1}{J} - \frac{1}{J_d} + \frac{1}{B_0 \omega^{1/2}} + \frac{1}{J} (B = 0.2nF(D_O2)2/3(v)^{-1/6}C_{O2}) \]

J is the measured current density, Jₖ and J_d are the diffusion-limiting and kinetic current densities, and ω is the rotating speed. n represents the number of electrons transferred per O₂ molecule, F is the Faraday constant (F = 96485 C·mol⁻¹), D₀₂ is the diffusion coefficient of O₂ in 0.1 M KOH (1.9×10⁻⁵ cm²·s⁻¹), v is the kinetic viscosity of electrolyte (0.01 cm²·s⁻¹), C₀₂ is the bulk concentration of O₂ (1.2 ×10⁻⁶ mol·cm⁻³).

Methanol crossover effect response. The catalyst modified GC electrode was prepared by same method as above. At a voltage of -0.30 V (vs. Ag/AgCl), the current-time (i-t) chronoamperometric response was recorded in O₂-saturated 0.1 M KOH aqueous solution for Pt/C and PC-I8-950 catalysts. The methanol was added into the electrochemical cell with a volume rate of 1:10.

![Figure S1. CV curves of Pt/C in 0.1 M KOH solution.](image)
Figure S2. Linear sweep voltammogram (LSV) curves of PC-I8-950 catalyst in oxygen-saturated 0.1M KOH solution. The rotation speed of GC electrode is varied from 400 to 2500 rpm and the scan rate is 10 mV·s⁻¹.

Figure S3. Koutecky–Levich plot of the carbon products at a potential of -0.30 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

Figure S4. Koutecky–Levich plot of the carbon products at a potential of -0.40 V. The plots are generated from the LSV curves of PC-I8-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.
Figure S5. Koutecky–Levich plot of the carbon products at a potential of -0.50 V. The plots are generated from the LSV curves of PC-18-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

Figure S6. Koutecky–Levich plot of the carbon products at a potential of -0.60 V. The plots are generated from the LSV curves of PC-18-950 tested in oxygen-saturated 0.1 M KOH solution with different rotating speeds.

Figure S7. Nitrogen adsorption isotherms (left) and pore distribution curve (right) of XC-72.
Figure S8. XPS survey spectrum of XC-72.

Figure S9. High-resolution N 1s spectra of XC-72.

Figure S10. High-resolution C 1s spectra of XC-72.
Figure S11. CV curves of XC-72 in 0.1 M KOH solution.

Figure S12. Linear sweep voltammogram (LSV) curves of XC-72 sample in oxygen-saturated 0.1M KOH solution. The rotation speed of GC electrode is varied from 400 to 2500 rpm and the scan rate is 10 mV·s$^{-1}$. 
Table S1. Textural parameters of PC-I8-950 calculated by N\textsubscript{2} adsorption

<table>
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<th>$S_{\text{BET}}^{[a]}$ (m\textsuperscript{2}·g\textsuperscript{-1})</th>
<th>$S_{\text{micro}}^{[b]}$ (m\textsuperscript{2}·g\textsuperscript{-1})</th>
<th>$V_{\text{total}}^{[c]}$ (cm\textsuperscript{3}·g\textsuperscript{-1})</th>
<th>$V_{\text{micro}}^{[d]}$ (cm\textsuperscript{3}·g\textsuperscript{-1})</th>
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<tr>
<td>PC-I8-950</td>
<td>836</td>
<td>275</td>
<td>1.09</td>
<td>0.12</td>
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[a] $S_{\text{BET}}$ is the surface area calculated by Brunauer-Emmett-Teller equation.
[b] $S_{\text{micro}}$ is microporous surface area calculated by t-plot method.
[c] Total pore volume is calculated at a relative pressure of 0.96.
[d] Micro-pore volume is calculated by t-plot method.

Table S2. The carbon state and content of PC-I8-950 and XC-72 calculated by XPS

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<th>Peak (eV)</th>
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<th>Content (%)</th>
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<th>Content (%)</th>
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<tr>
<td>XC-72</td>
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Table S3. The number of electrons transferred (n) of Pt/C and PC-I8-950

<table>
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Supplementary Information References