Support information

Insights into the synergistic catalytic mechanism on the customized dual sites of an efficient ORR catalyst

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In-situ electrochemical Raman tests are as following:

Integrating a custom cell for electrochemical test with Raman spectra to perform in situ tests, further collecting the intermediates signals on the surface of catalysts during ORR. The custom cell was a three-electrode system, and with CHI 760E for collecting electrochemical data. The glassy carbon electrode, with 4 times the area of the rotating ring disc electrode (RRDE), was the working electrode. This required that the catalyst ink be coated four times as much as for the ex-situ tests, thus ensuring that the in-situ Raman signals were captured. The Ag/AgCl (in saturated KCl), and Pt wire were reference and counter electrodes, respectively. The Raman light source with $\lambda = 532$ passed vertically through the window (quartz sheet) into the reaction cell to probe the sample surface. The acquisition time of the laser was 40 s, with the acquisition range of 0-2000 cm$^{-1}$. Each Raman spectrum was acquired at a constant voltage.
in the range of 1.05 V-0.15 V at 0.1 V intervals, while in-situ cyclic voltammetry (CV) test was performed in 0.5 M H$_2$SO$_4$ (O$_2$-saturated) at a very slow scan rate.

**All electrochemistry-related calculation equations are listed below:**

The electrochemical surface area (ECSA$_{\text{Hupd}}$) of the catalyst based on the hydrogen underpotential deposition (H$_{\text{upd}}$) peak is via Eq. S1, as follow:

$$ECSA_{(\text{Hupd})} (m^2 g^{-1}) = \frac{S}{V m_{Pt} \times 2.1(C m^{-2})}$$

Where S is the H$_{\text{upd}}$ integrated area from the CV curve. V is the scanning rate of 50 mV s$^{-1}$. $m_{Pt}$ is the actual Pt mass loadings on the WE. 2.1 is the number of charges adsorbed by Pt/unit area.

The kinetic current density ($J_K$) of the catalyst and the corresponding electron transfer number (n) are obtained through Eq. S2 (namely, Koutecky-Levich, K-L), as follow:

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

$$B = 0.2nFC_0D_0^{2/3} \nu^{-1/6}$$

$$J_K = nFkC_0$$

Where $J$, $J_K$, and $J_L$ are the measured, kinetic, and limiting current densities, respectively. $\omega$ (rad s$^{-1}$) is the angular velocity. n is electron transfer number. F is the Faraday constant (96 485 C mol$^{-1}$). C$_0$ is the O$_2$ concentration (0.5 M H$_2$SO$_4$) and D$_0$ is the diffusion coefficient. $\nu$ is the electrolyte kinetic viscosity. k is the constant of electron transfer rate.

The mass activity (MA) and specific activity (SA) of the catalyst are calculated by the following Eq. S3 and Eq. S4:

$$MA = \frac{J_K}{m_{Pt}}$$
SA = \frac{J_K}{ECSA \times m_{pt}}

Where J_K is kinetic current density, m_{pt} is the actual Pt mass loadings on the WE. ECSA is the electrochemical surface area.

The electron transfer number (n_{RRDE}) from RRDE electrode and the H_2O_2 yield derive from the following \textbf{Eq. S5} and \textbf{Eq. S6}^{6,7}:

\[
n_{RRDE} = \frac{4I_d}{I_d + \frac{I_r}{N}} \quad I_d + \frac{I_r}{N}
\]

\[
H_2O_2(\%) = 200 \times \frac{\frac{I_r}{N}}{\frac{I_r}{N} + I_d}
\]

Where \(I_d\) and \(I_r\) are the disk and ring currents, respectively. N is the current collection efficiency of 0.37 from Pt ring.
Figure S1. ICP statistical graph of PtCo/C, PtCo/PC-1, PtCo/PC-2, PtCo/PC-3.
Figure S2. SEM image of PtCo/PC-2.
Figure S3. (a) The TEM image with particle size statistical histogram, (c) the HRTEM images with IFFT images and selected stripes histograms, all for PtCo/C.
Figure S4. The XRD patterns of PtCo/C.
Figure S5. The Raman mapping map of $I_D/I_G$ in the $60 \times 60 \ \mu m^2$ region for PtCo/PC-1, PtCo/PC-2, PtCo/PC-3.
Figure S6. (a) The XPS survey scan of PtCo/PC-2. (b) The high resolution XPS spectra of Pt 4f for PtCo/C and PtCo/PC-2.
Figure S7. In-situ Raman spectra of intermediates on the surfaces for PtCo/C in O$_2$-saturated 0.5M H$_2$SO$_4$ (ORR) at different constant potentials.
**Figure S8.** (a) CV curves of PtCo/PC-2 and PtCo/C, with the statistical histograms of \( \text{ECSA}_{\text{Hupd}} \). (b) The statistical histograms of \( \text{ECSA}_{\text{Hupd}} \) for PtCo/PC-1, PtCo/PC-2, PtCo/PC-3, all in \( \text{O}_2 \)-saturated 0.5M \( \text{H}_2\text{SO}_4 \) (ORR).
Figure S9. (a) MA curve of PtCo/C in O$_2$-saturated 0.5 M H$_2$SO$_4$ (ORR).
Figure S10. (a) LSV curves at different speeds of Pt/C, and (b) the corresponding K-L curves, all in O$_2$-saturated 0.5 M H$_2$SO$_4$ (ORR).
Figure S11. LSV curves of Pt/C at 1600 rpm before and after 10000s ADT in O₂-saturated 0.5 M H₂SO₄ (ORR).