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Supporting Information

Atomic scale enhancement of metal-support interactions between Pt and ZrC for highly stable electrocatalysts

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Experimental

ALD synthesis of Pt on Zirconium carbide (ZrC)

Zirconium carbide (ZrC) was purchased from Kaier Nanometer Energy & Technology Co., Ltd , China. Before Pt ALD on ZrC, the ZrC support was heat-treated at 600°C for 30 mins under N₂ atmosphere. Platinum was deposited on ZrC supports by ALD (Savannah 100, Cambridge Nanotechnology Inc., USA) with a procedure similar to the one reported previously¹. MeCpPtMe₃ was used as precursor to deposited Pt on ZrC. High purity O₂ (99.999%) was used as the counter reactant, and high-purity N₂ (99.9995%)was used as both a purging gas and carrier gas. The container for powder ZrC support was placed inside the chamber of reactor of ALD. The deposition temperature was 250°C, while the container for the Pt precursor was kept at 65°C to provide a steady state flux of MeCpPtMe₃ to the reactor (~800 m Torr at 65°C). Gas lines were held at 100°C to avoid precursor condensation. In each ALD cycle, 1 s of MeCpPtMe₃pulse and 5s of O₂ pulse were separated by 20 s of N₂ purge. The Pt loading on ZrC was accurately controlled by the number of ALD cycles. In this work, 150 cycles ALD Pt on ZrC was prepared. For comparison, Pt nanoparticles were deposited on ZrC by ethylene glycol reduction method (conventional wet method)².

Physical characterization

The morphology and microstructures of samples were characterized by transmission electron microscope (TEM, Hitachi H-7000) and high-resolution TEM (HRTEM, JEOL 2010FEG).

X-ray Absorption Spectroscopy

XANES measurements of Pt L_2 edge and Pt L_3 edge were conducted on the 06ID superconducting wiggler sourced hard X-ray microanalysis (HXMA) beamline at the Canadian Light Source. The spectra were collected in fluorescence yield using a solid state

detector, and the spectra of high purity metal Pt foil were collected in transmission mode for comparison and mono energy calibration. WL intensity analysis was conducted as follows based on the previous researches. ^{3, 4} In this method, the Pt L₃ edge WL intensity is obtained by subtracting the Pt L₃ edge XANES from the corresponding XANES of Au. The area under the difference curve was integrated between the two vertical bars, and ΔA_3 and ΔA_2 were calculated using the following expressions.

$$\Delta A_3 = \int \mu(Pt)_{L_3WL} - \mu(Au)_{L_3WL}$$
$$\Delta A_2 = \int \mu(Pt)_{L_2WL} - \mu(Au)_{L_2WL}$$

and according to Sham et al⁴, these value were able to be calculated from the following theoretical expressions.

$$\Delta A_3 = C_0 N_0 E_3 (R_d^{2p_2/3})^2 \left[\frac{6h_{5/2} + h_{3/2}}{15} \right]$$
$$\Delta A_2 = C_0 N_0 E_2 (R_d^{2p_1/2})^2 \left(\frac{1}{3} h_{3/2} \right)$$

where $C_{0=} 4\pi r^2 \alpha/3$ (α is the fine structure constant), N_0 is the density of Pt atoms, h_j are the 5d hole counts, and E_2 and E_3 are the corresponding edge thresholds, E_o , for the L₂ and L₃ edges, respectively. The R term is the radial transition matrix element. By assuming R terms are similar for both edges

$$C = C_0 N_0 R^2$$

and with this approximation

$$h_{\frac{5}{2}} = \frac{1}{2C} \left[5\frac{E_2}{E_3} \Delta A_3 - \Delta A_2 \right]$$
$$h_{3/2} = \left[\frac{3\Delta A_2}{C} \right]$$

C value of 7.484×10^4 cm⁻¹ was derived previously for Pt metal⁵.

Electrochemical Characterization

A three-compartment cell was employed for the electrochemical measurements. Hg/Hg_2SO_4 electrode and Platinum wire were used as the reference electrode and the counter, respectively.

A glassy carbon electrode was applied as the working electrode. The potentials presented in this study are referred with respect to reversible hydrogen electrode (RHE). The working electrodes were prepared as follows. Typically, the catalyst dispersions were prepared by mixing catalysts in 3 mL aqueous solution containing 1 mL of isopropyl alcohol and then ultrasonicated to form a uniform black ink. For ALD-Pt/ZrC and CW-Pt/ZrC catalysts, in order to improve the conductivity, about 20% Wt carbon black was added to the ink. The uniform black ink was then pipetted on the electrode with area of 0.196 cm⁻². After dying at room temperature, 5 uL of 0.05 wt% Nafion solution was applied onto the surface of the catalyst layer to form a layer protecting catalyst particles from detaching. The final Pt loading of all catalysts was 11.5 ug cm⁻². Prior to measurements, working electrodes were first activated with cyclic voltammetry (CV) (0.05-1.2 V, 50mV/s) in a N₂-saturated 0.5M H₂SO₄ on the rotating-disk electrode system (Pine Instruments).

The electrochemically active surface area (ECSA) was calculated by integrating the double layer corrected H_{upd} charge in the cathodic scan and dividing by a value of 210 μ C/cm² for the adsorption of a hydrogen monolayer on polycrystalline Pt. The specific value of the ECSA based on Pt mass for ALD-Pt/ZrC, CW-Pt/ZrC and commercial Pt/C are estimated to be 51, 45 and 43 m²/g, respectively. The kinetic current was calculated from the ORR polarization curves by using mass-transport correction and normalized to the loading amount of Pt, in order to compare the mass activity of different catalysts. According to the Levich–Koutecky equation⁶:

$$1/i = 1/i_k + 1/i_d$$

Where i_k is the kinetic current and i_d is the diffusion-limiting current.



Figure S1. CV curves of ZrC (a) and carbon black (Vulcan XC-72) (b) by held at 1.20V for different durations ($0.5M H_2SO_4$, scan rate: $50 mVs^{-1}$).



Figure S2. TEM image of CW-Pt/ZrC nanocomposties (a) before and (b) after ADT.



Figure S3. Cyclic voltammogram of ALD-Pt/ZrC catalyst in 0.5 M H_2SO_4 solution at scan rate of 50 mVs⁻¹ (a) with and (b) without carbon black.



Figure S4. (a) Cyclic voltammogram of ALD-Pt/ZrC nanocomposties in 0.5 M H_2SO_4 solution at scan rate of 50 mVs⁻¹ before and after ADT. (b) ORR curves of electrodes made from ALD-Pt/ZrC nanocomposties in an O₂-saturated 0.5 M H_2SO_4 solution at room temperature (1600rpm, sweep rate: 10 mVs⁻¹) before and after ADT.



Figure S5. (a) Cyclic voltammogram of CW-Pt/ZrC nanocomposties in 0.5 M H₂SO₄ solution at scan rate of 50 mVs⁻¹ before and after ADT. (b) ORR curves of electrodes made from CW-Pt/ZrC nanocomposties in an O₂-saturated 0.5 M H₂SO₄ solution at room temperature (1600 rpm, sweep rate :10 mVs⁻¹) before and after ADT.



Figure S6. Cyclic voltammogram of (a) CW-Pt/ZrC nanocomposties and (c) Pt/C catalysts in 0.5 M H_2SO_4 solution at scan rate of 50 mVs⁻¹ before and after ADT. ORR curves of electrodes made from (b) CW-Pt/ZrC nanocomposties and (d) Pt/C catalysts in an O₂-saturated 0.5 M H_2SO_4 solution at room temperature (1600 rpm, sweep rate :10 mVs⁻¹) before and after ADT.



Figure S7. Comparison of stability of different ceramic supported Pt catalysts compared with our ALD-Pt/ZrC catalyst: Pt/TiN@ND⁷, Pt/TiO_xN_y⁸, Pt/TiO₂@CNT⁹, Pt/TiB₂¹⁰ and Pt/SnO₂¹¹.



Figure S8. TEM images of Pt/C catalyst before (a) and after (b) ADT.



Figure S9. TEM images of ALD-Pt/ZrC catalyst after ADT.

Supplementary Reference

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