

Supplementary Information

Correlating the Electrocatalytic Stability of Platinum Monolayer Catalysts to Their Structural Evolution in the Oxygen Reduction Reaction

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Model analyses

Based on a cuboctahedral model with onion-like concentric atomic layers for Pd nanoparticle,¹ the number of total Pd atoms ($N_{\text{Total Pd}}$), the number of surface Pd atoms ($N_{\text{Surface Pd}}$), and the number of F-, T-, E- and V-sites (denoted as N_{F} , N_{T} , N_{E} and N_{V} , respectively) as a function of the number of layers of atoms around the central atom (v) can be calculated by the following expressions:

$$N_{\text{Total Pd}}(v) = 10 \frac{v^3}{3} + 5v^2 + 11 \frac{v}{3} + 1$$

$$N_{\text{Surface Pd}}(v) = 10v^2 + 2$$

$$N_{\text{F}}(v) = 6(v-1)^2$$

$$N_{\text{T}}(v) = 4(v-1)(v-2)$$

$$N_{\text{E}}(v) = 24(v-1)$$

$$N_V(\nu) = 12$$

We note that i) the $N_{\text{Surface Pd}(\nu)}$ is equal to the difference of $N_{\text{Total Pd}(\nu)}$ and $N_{\text{Total Pd}(\nu-1)}$; ii) the sum number of all sites ($N_{\text{All sites}}$), i.e., $N_F(\nu) + N_T(\nu) + N_E(\nu) + N_V(\nu)$, is equal to the $N_{\text{Surface Pd}(\nu)}$. Further, the $N_{\text{Surface Pd}}/N_{\text{Total Pd}}$ and $N_{(F+T) \text{ sites}}/N_{\text{All sites}}$ as a function of ν can be calculated easily.

The Pd particle size (D , nm) as a function of the number of layers of atoms around the central atom (ν) can be expressed as:

$$D(\nu) = \frac{d_i(\nu) + d_o(\nu)}{2}$$

Where, $d_i(\nu)$ is the diameter of the circumscribed sphere of the cuboctahedral Pd with ν layers, and $d_o(\nu)$ is the diameter of the sphere that can be encapsulated by the cuboctahedral Pd with ν layers, respectively. The $d_i(\nu)$ and $d_o(\nu)$ can be given by:

$$d_i(\nu) = 2 \cdot (V(\nu) \cdot \frac{3}{5} \cdot 2^{-1/2})^{1/3} \quad d_o = 2^{1/2} \cdot (V(\nu) \cdot \frac{3}{5} \cdot 2^{-1/2})^{1/3}$$

Where, $V(\nu) = N_{\text{Total Pd}(\nu)} \frac{V_{\text{Unit cell}}}{4}$, $V_{\text{Unit cell}}$ is the unit-cell volume of face-centered cubic Pd (4 atoms per unit cell). The unit-cell volume of Pd is calculated to be 0.058183 nm^3 according to the Pd atomic radius of 0.137 nm .

The $N_{\text{Total Pd}}$ and D as a function of ν from 0 to 21 are tabulated in Table S1.

For the $\text{Pt}_{\text{ML}}/\text{Pd}$ nanoparticle prepared by UPD and galvanic replacement technique with the Cu UPD occurring on all surface sites, and on the F- and T-sites only, respectively, the Pt coverage (θ) on the cuboctahedral Pd equals the numeric ratio of the number of Pt atoms (N_{Pt}), i.e., the number of specific sites, $N_{\text{All sites}}$ or $N_{\text{F+T sites}}$, to the number of surface Pd atoms with the layer of $(\nu+1)$ for a full covering on the Pd cuboctahedron with ν layers.

$$\theta_{\text{All sites}(\nu)} = \frac{N_{\text{All sites}(\nu)}}{N_{\text{Surface Pd}(\nu+1)}} = \frac{10\nu^2+2}{10(\nu+1)^2+2}$$

$$\theta_{\text{F+T sites}(\nu)} = \frac{N_{\text{F+T sites}(\nu)}}{N_{\text{Surface Pd}(\nu+1)}} = \frac{6(\nu-1)^2+4(\nu-1)(\nu-2)}{10(\nu+1)^2+2}$$

And the Pt/Pd atomic ratio equaled the numeric ratio of N_{Pt} to $N_{\text{Total Pd}}$

$$\left(\frac{\text{Pt}}{\text{Pd}}\right)_{\text{All sites}}(\nu) = \frac{N_{\text{All sites}}(\nu)}{N_{\text{Total Pd}}(\nu)} = \frac{10\nu^2+2}{10\frac{\nu^3}{3}+5\nu^2+11\frac{\nu}{3}+1}$$

$$\left(\frac{\text{Pt}}{\text{Pd}}\right)_{\text{F+T sites}}(\nu) = \frac{N_{\text{F+T sites}}(\nu)}{N_{\text{Total Pd}}(\nu)} = \frac{6(\nu-1)^2+4(\nu-1)(\nu-2)}{10\frac{\nu^3}{3}+5\nu^2+11\frac{\nu}{3}+1}$$

The initial Pt_{ML}/Pd particle size can be calculated by the same method for Pd case. But the $V_{\text{Pt}_{\text{ML}}/\text{Pd}}(\nu) = (N_{\text{Total Pd}}(\nu) + N_{\text{Pt}}(\nu)) \frac{V_{\text{Unit cell}}}{4}$, where, only the unit-cell volume of Pd is used because the epitaxial Pt lattice is same with the lattice of Pd substrate. Further, the initial Pt_{ML}/Pd surface area (S) as a function of ν can be expressed as:

$$S_{\text{Pt}_{\text{ML}}/\text{Pd}}(\nu) = \frac{S_{i(\text{Pt-ML/Pd})}(\nu) + S_{o(\text{Pt-ML/Pd})}(\nu)}{2}$$

Where, $S_{i(\text{Pt-ML/Pd})}(\nu)$ is the surface area of the circumscribed sphere of initial Pt_{ML}/Pd particle derived from the cuboctahedral Pd with ν layers, and $S_{o(\text{Pt-ML/Pd})}(\nu)$ is the surface area of the sphere that can be encapsulated by the initial Pt_{ML}/Pd particle derived from the cuboctahedral Pd with ν layers, respectively. The $S_{i(\text{Pt-ML/Pd})}(\nu)$ and $S_{o(\text{Pt-ML/Pd})}(\nu)$ can be expressed as:

$$S_{i(\text{Pt-ML/Pd})}(\nu) = \pi(d_{i(\text{Pt-ML/Pd})}(\nu))^2 \quad S_{o(\text{Pt-ML/Pd})}(\nu) = \pi(d_{o(\text{Pt-ML/Pd})}(\nu))^2$$

Where, $d_{i(\text{Pt-ML/Pd})}(\nu)$ and $d_{o(\text{Pt-ML/Pd})}(\nu)$ are the diameters of the circumscribed- and encapsulated- sphere of initial Pt_{ML}/Pd particle derived from the cuboctahedral Pd with ν layers, respectively.

For the full-covered Pt_{ML}/Pd nanoparticle, assuming that the number of Pt atoms, N_{Pt} , is constant during self-healing, the N_{Pt} for two cases of Cu UPD is known as follows:

$$N_{\text{Pt(All sites)}}(\nu) = N_{\text{All sites}}(\nu) = 10\nu^2 + 2$$

$$N_{\text{Pt(F+T sites)}}(\nu) = N_{\text{F+T sites}}(\nu) = 6(\nu-1)^2 + 4(\nu-1)(\nu-2)$$

According to the N_{Pt} we have known, assuming that all Pt atoms locate on the top surface (outmost layer) of the full-covered Pt_{ML}/Pd particle, the total number of atomic layers, ν' , can be expressed by:

$$N_{\text{Pt}} = 10(\nu')^2 + 2 \quad \text{or} \quad \nu' = \sqrt{\frac{N_{\text{Pt}}-2}{10}}$$

Furthermore, the number of the total Pt and Pd atoms, $N_{(\text{Pt+Pd})}$, can be calculated based on

the model of the close-packed cuboctahedron for full-covered Pt_{ML}/Pd

$$N_{(\text{Pt+Pd})}(v') = 10 \frac{(v')^3}{3} + 5(v')^2 + 11 \frac{(v')}{3} + 1$$

Therefore, the number of undissolved Pd atoms, $N_{\text{undissolved Pd}}$, and Pt/Pd atomic ratio for full-covered Pt_{ML}/Pd particle can be calculated by the following expressions:

$$N_{\text{undissolved Pd}}(v') = N_{(\text{Pt+Pd})} - N_{\text{Pt}} = \left(10 \frac{(v')^3}{3} + 5(v')^2 + 11 \frac{(v')}{3} + 1 \right) - (10(v')^2 + 2)$$

$$\left(\frac{\text{Pt}}{\text{Pd}} \right)_{\text{All sites}} = \frac{N_{\text{Pt(All sites)}}(v)}{N_{\text{undissolved Pd}}(v')} = \frac{10v^2 + 2}{\left[\left(10 \frac{(v')^3}{3} + 5(v')^2 + 11 \frac{(v')}{3} + 1 \right) - (10(v')^2 + 2) \right]}$$

$$\left(\frac{\text{Pt}}{\text{Pd}} \right)_{\text{F+T sites}} = \frac{N_{\text{Pt(F+T sites)}}(v)}{N_{\text{undissolved Pd}}(v')} = \frac{6(v-1)^2 + 4(v-1)(v-2)}{\left[\left(10 \frac{(v')^3}{3} + 5(v')^2 + 11 \frac{(v')}{3} + 1 \right) - (10(v')^2 + 2) \right]}$$

Here, we need to mention that the v' , $N_{(\text{Pt+Pd})}$ and $N_{\text{undissolved Pd}}$ are not restricted to be integer. The full-covered Pt_{ML}/Pd particle size and surface area can be calculated by the same expressions for initial Pt_{ML}/Pd case according to the value of the $N_{(\text{Pt+Pd})}(v')$.

Supplementary figures

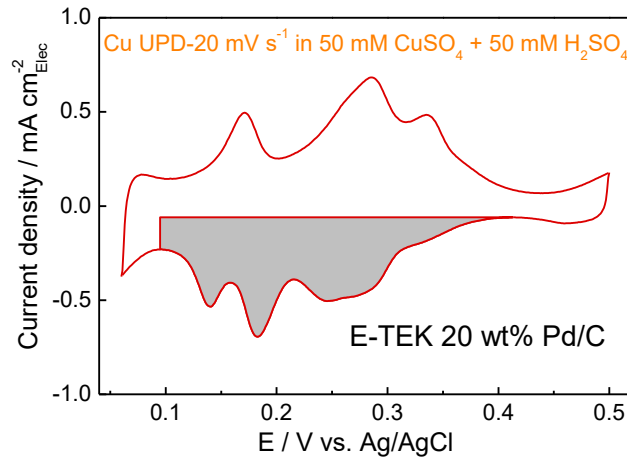


Figure S1. Cu UPD and stripping curves of E-TEK Pd/C with a scan rate of 20 mV s⁻¹ in Ar-saturated 50 mM CuSO₄ + 50 mM H₂SO₄ solution. The coulombic charge of a UPD Cu monolayer was calculated by the shaded area.

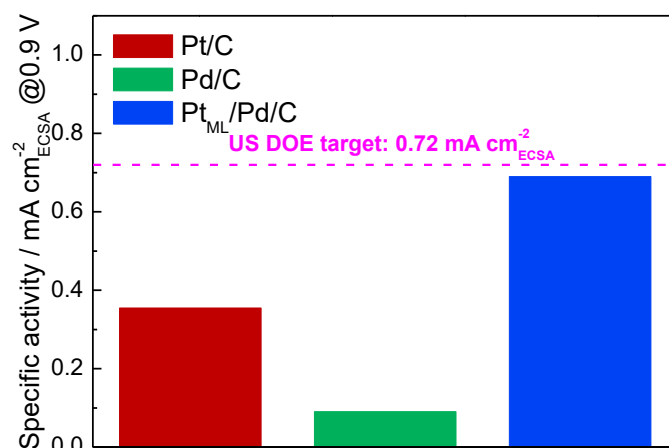


Figure S2. Specific activities of E-TEK Pt/C, E-TEK Pd/C, and Pt_{ML}/Pd/C calculated by their kinetic currents at 0.9 V, respectively.

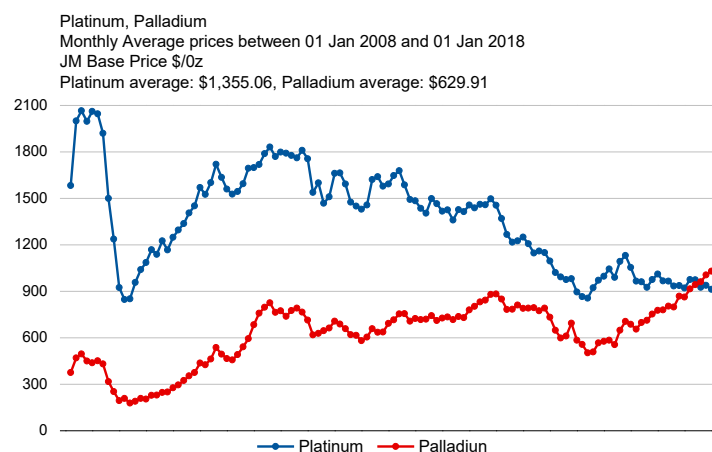


Figure S3. Changes in price of Pt and Pd in the last ten years from the website: <http://www.platinum.matthey.com/prices/price-charts>. The average prices of Pt and Pd were obtained by averaging those in the last ten years.

Considering the daily fluctuations of noble metal prices, the calculation of dollar activity of Pt_{ML}/Pd/C catalyst is made based on the average prices of Pt and Pd over the past ten years in order to more objectively evaluate its cost-effectiveness. As shown in Figure S3, the 10-year average prices of Pt and Pd are \$1,355.06 oz⁻¹ and \$629.91 oz⁻¹, respectively. Furthermore, since 1 troy ounce equals 31.10 grams, the Pt price of \$1,355.06 oz⁻¹ can be converted to \$43.57 g⁻¹ and the Pd price of \$629.91 oz⁻¹ is equivalent to \$20.25 g⁻¹. Finally, according to the Pt and Pd loadings given in the caption of Figure 1, the dollar activity of the Pt_{ML}/Pd/C catalyst can be derived. The target of US DOE 2020 PGM mass activity (0.44 A mg_{PGM}⁻¹@0.9 V_{iR-free}) would be the equivalent of 10.1 A per US dollar (A \$⁻¹), if the PGM is considered to be Pt only.

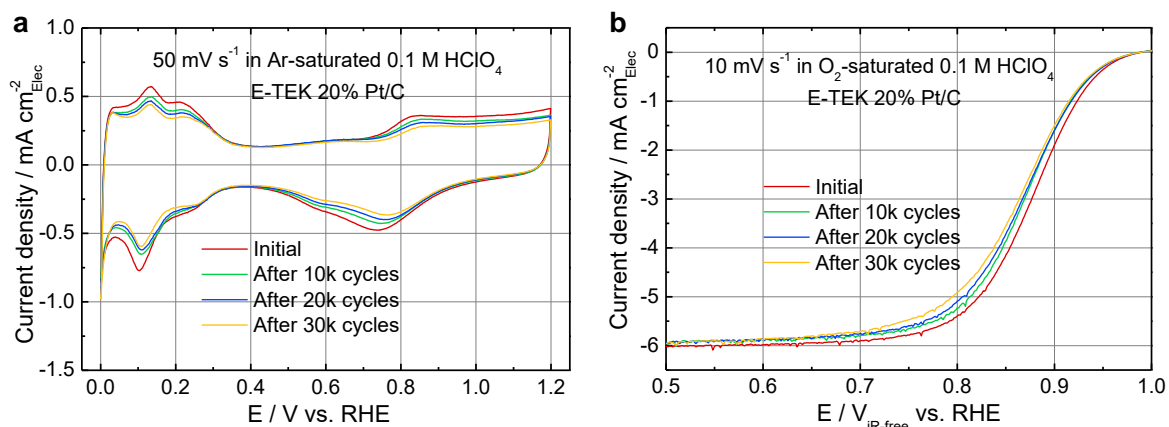


Figure S4. (a) Cyclic voltammetry curves (50 mV s^{-1}) and (b) ORR polarization curves (10 mV s^{-1} , 1600 rpm) of E-TEK Pt/C with the Pt loadings of $10.2 \mu\text{g cm}^{-2}$ measured at initial state and after a certain number of potential cycles ($0.65 \leftrightarrow 1.05 \text{ V}$) during the ADT in a 0.1 M HClO_4 solution.

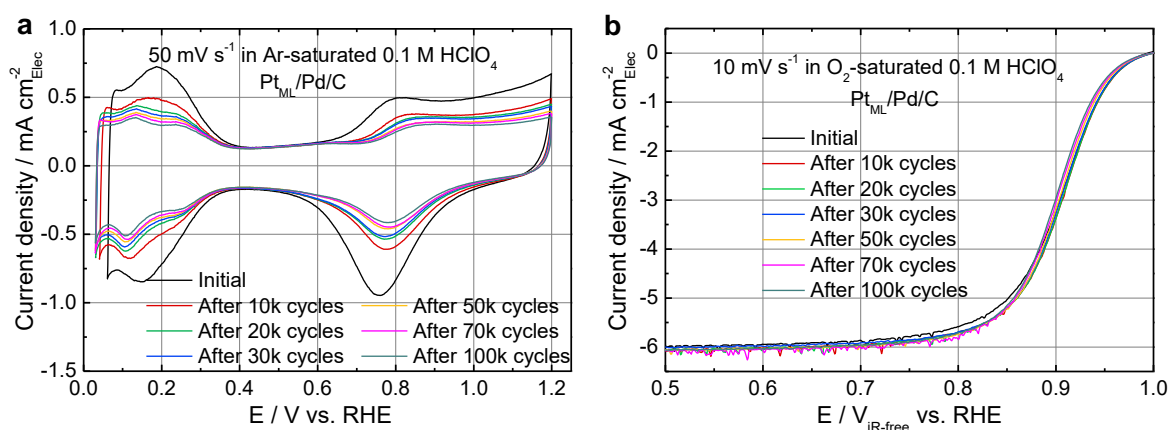


Figure S5. (a) Cyclic voltammetry curves (50 mV s^{-1}) and (b) ORR polarization curves (10 mV s^{-1} , 1600 rpm) of $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ with the (Pt+Pd) loading of $19.7 \mu\text{g cm}^{-2}$ measured at initial state and after a certain number of potential cycles ($0.65 \leftrightarrow 1.05 \text{ V}$) during the ADT in a 0.1 M HClO_4 solution.

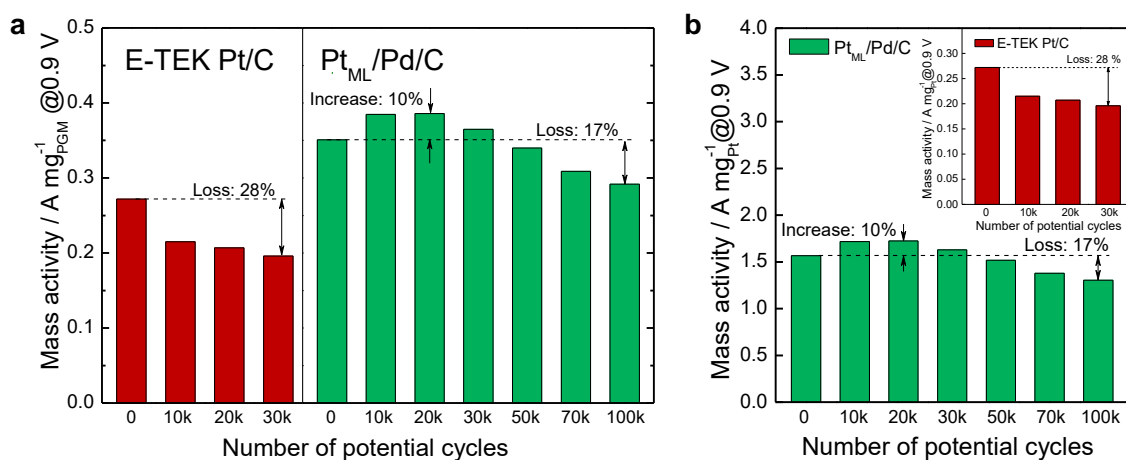


Figure S6. (a) PGM mass activities and (b) Pt mass activities of E-TEK Pt/C and $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ at 0.9 V as a function of the number of potential cycles ($0.65 \leftrightarrow 1.05 \text{ V}$) during the ADT.

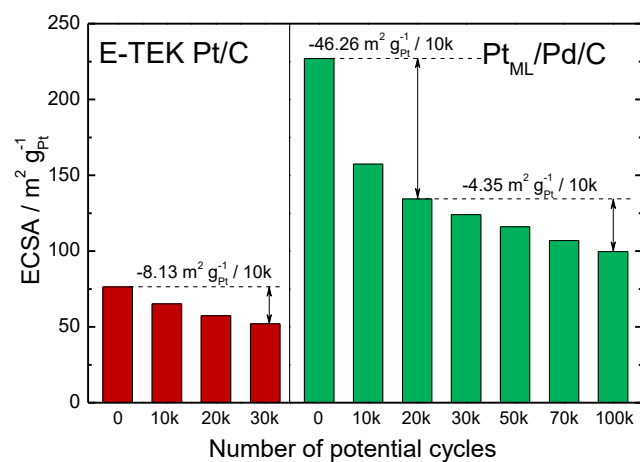
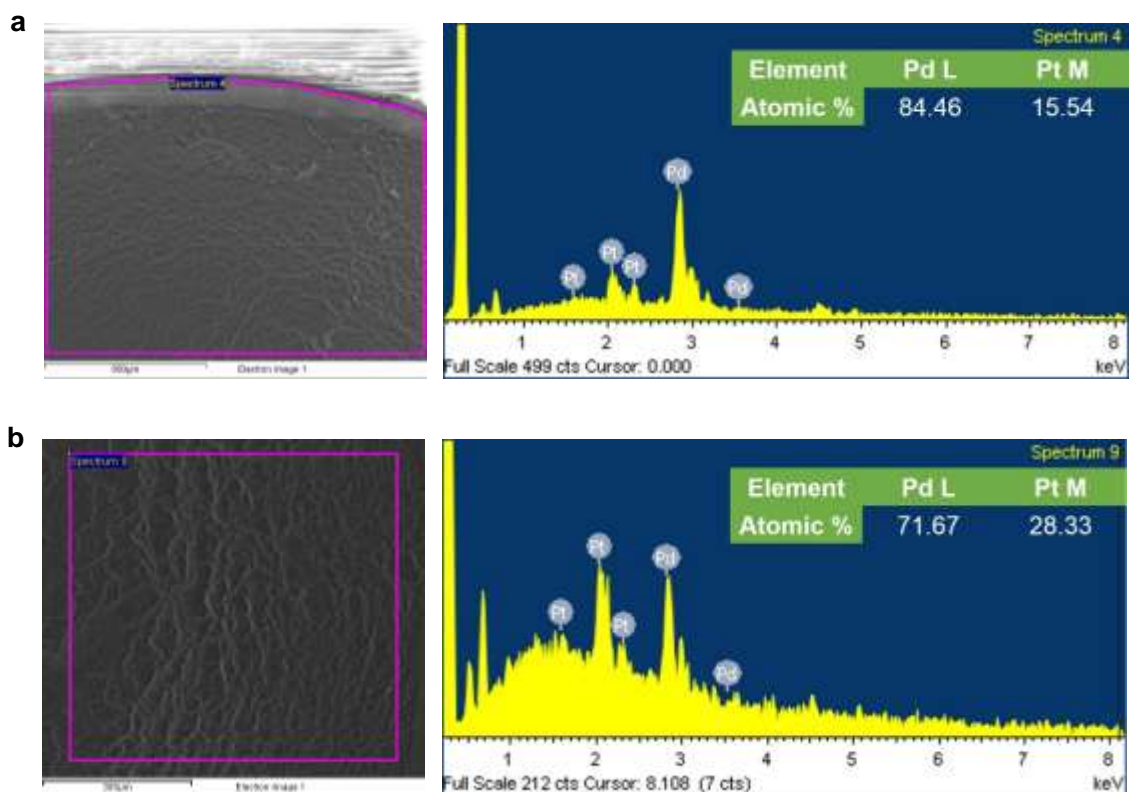


Figure S7. Pt-mass specific ECSAs of E-TEK Pt/C and Pt_{ML}/Pd/C as a function of the number of potential cycles (0.65 ↔ 1.05 V) during the ADT.



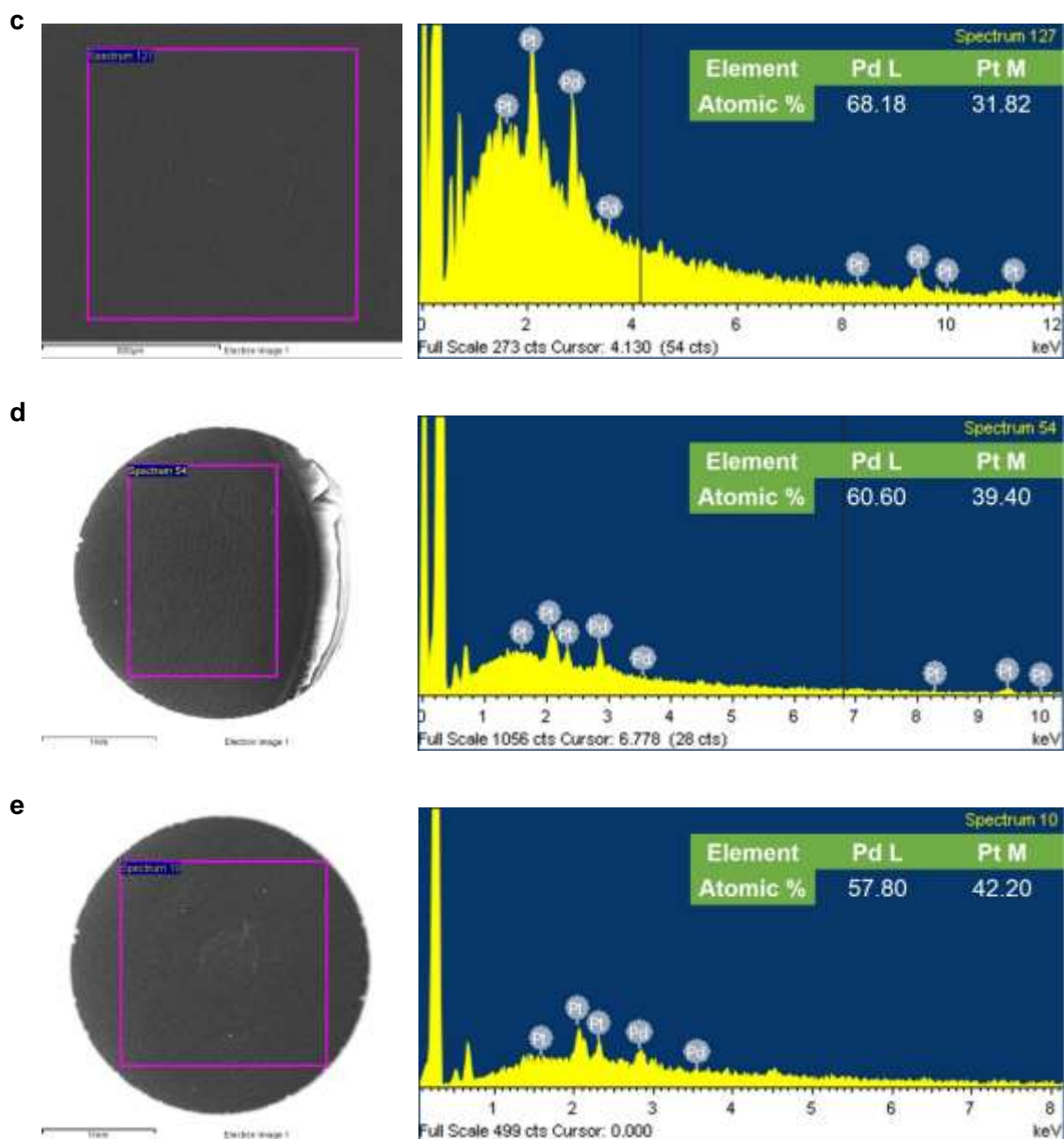


Figure S8. Low-magnification SEM images along with EDX spectra acquired from the marked area in SEM image. The SEM and EDS spectra were measured with the Pt_{ML}/Pd/C electrocatalyst loaded on glassy carbon electrode at (a) initial state and after (b) 20k, (c) 30k, (d) 70k, and (e) 100k potential cycles (0.65 ↔ 1.05 V) during the ADT. The inset table of EDX spectrum is the atomic percentage of Pd and Pt.

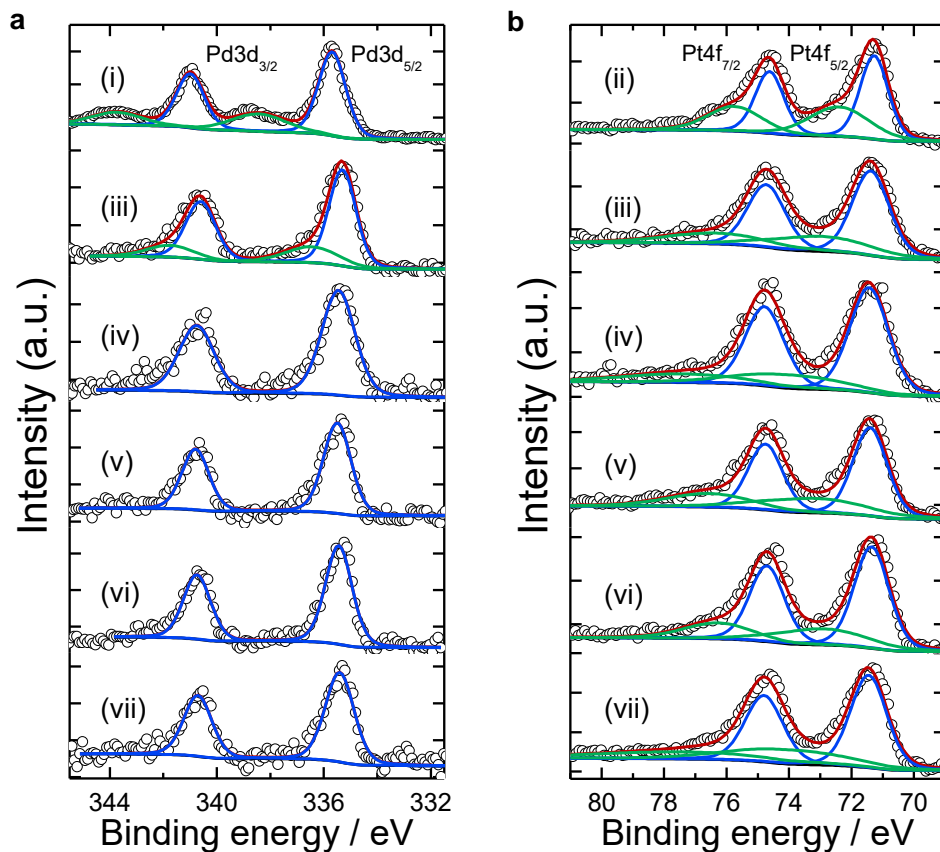


Figure S9. (a) Pd3d electron and (b) Pt4f electron XPS spectra of the Pt_{ML}/Pd/C sample at initial state and after a certain number of potential cycles (0.65 ↔ 1.05 V) during the ADT. The XPS measurement to Pd/C and Pt/C also was conducted for comparison. (i) E-TEK Pd/C; (ii) E-TEK Pt/C; (iii) Initial Pt_{ML}/Pd/C; (iv) Pt_{ML}/Pd/C after 20k cycles; (v) Pt_{ML}/Pd/C after 30k cycles; (vi) Pt_{ML}/Pd/C after 70k cycles; (vii) Pt_{ML}/Pd/C after 100k cycles. The blue curves and green curves belong to the metallic state and the oxidation state, respectively. The red curve was the superposition of blue curve and green curve. The Pd/(Pd+Pt) atomic ratio calculated by the corresponding peak areas and sensitivity factors were shown in Table S1.

As shown in Figure S9a, there was obviously a pair of peaks of oxidation state in Pd3d XPS spectra of both E-TEK Pd/C and initial Pt_{ML}/Pd/C. However, no peak of oxidation state can be observed in the Pd3d XPS spectra of Pt_{ML}/Pd/C after 20k to 100k cycles. This indicates that the exposed Pd atoms were totally dissolved out during initial 20k-cycle; Hereafter, the rest of Pd atoms were effectively protected by Pt. The higher ratio of metallic state and oxidation state (M/O) of Pt for Pt_{ML}/Pd/C than that for E-TEK Pt/C indicated that the bond of oxygenated species to Pt_{ML} surface is weaker (Table S2). The results about the peak positions of binding energies of Pd3d electron and Pt4f electron would not be further discussed at moment due to that it is beyond the aim of this study.

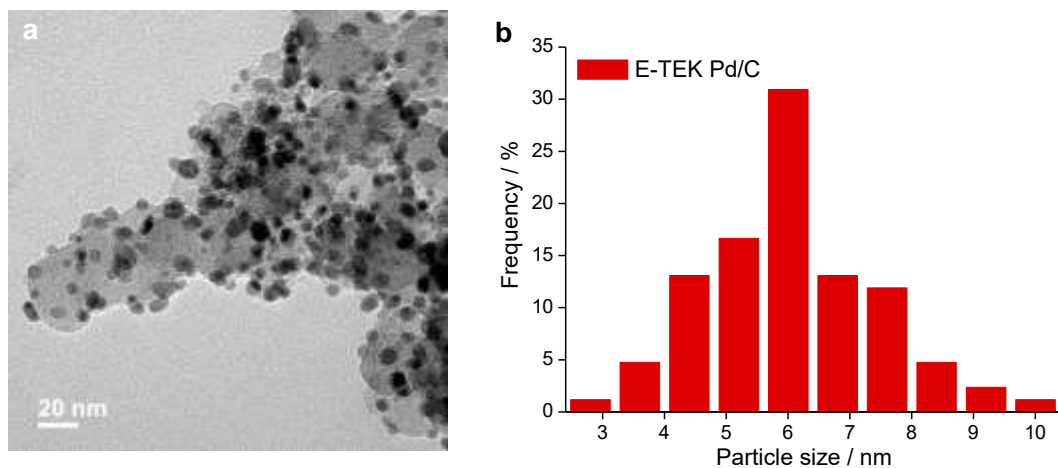


Figure S10. (a) Low-magnification TEM image of E-TEK Pd/C and (b) the Pd particle size distribution.

Supplementary tables

Table S1. The number of total Pd atoms, $N_{\text{Total Pd}}$, and the Pd particle size, D , as a function of the number of layers of atoms around the central atom, ν (from 0 to 21).

ν	$N_{\text{Total Pd}}$	D (nm)	ν	$N_{\text{Total Pd}}$	D (nm)
0	1	0.274	11	5083	5.384
1	13	0.736	12	6525	5.851
2	55	1.191	13	8217	6.319
3	147	1.653	14	10179	6.787
4	309	2.117	15	12431	7.254
5	561	2.582	16	14993	7.721
6	923	3.049	17	17885	8.189
7	1415	3.515	18	21127	8.656
8	2057	3.982	19	24739	9.124
9	2869	4.449	20	28741	9.591
10	3871	4.917	21	33153	10.059

Table S2. The Pd/(Pd+Pt) atomic ratio and the ratio of metallic state and oxidation state of Pt. The Pd/(Pd+Pt) atomic ratio calculated by peak areas of the corresponding spectra of Pd3d and Pt4f in Figures S9a&b and sensitivity factors. The Pt-M/O obtained according to peak areas of metallic state and oxidation state of Pt4f XPS spectra in Figure S9b.

Sample	Pd/(Pd+Pt) atomic ratio	Pt-M/O
T-TEK Pt/C	-	1.328
Initial Pt _{ML} /Pd/C	56.8%	2.127
Pt _{ML} /Pd/C after 20k cycles	39.1%	2.859
Pt _{ML} /Pd/C after 30k cycles	33.9%	1.969
Pt _{ML} /Pd/C after 70k cycles	31.7%	2.418
Pt _{ML} /Pd/C after 100k cycles	25.8%	1.96

References

- [1] M. Nesselberger, S. Ashton, J. C. Meier, I. Katsounaros, K. J. J. Mayrhofer and M. Arenz, *J. Am. Chem. Soc.*, 2011, **133**, 17428-17433.