Electronic Supporting Information (ESI)

Revisit of the Oxidation Peak in the Cathodic Scan of Cyclic Voltammogram of Alcohol Oxidation on Noble Metal Electrodes

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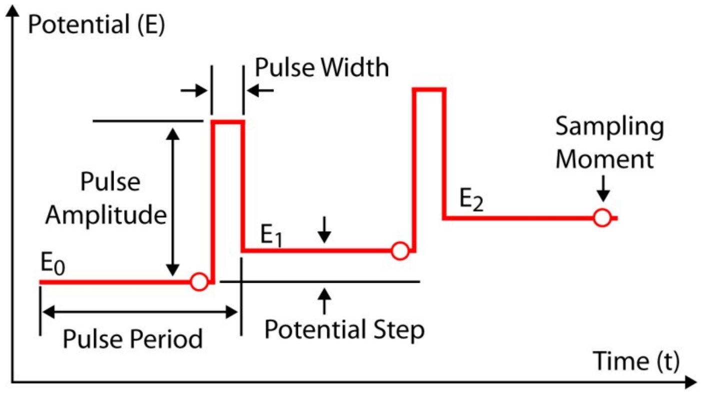
1. Experimental Details

Differential pulse voltammetry (DPV): DPV can be considered as a derivative of linear sweep voltammetry or staircase voltammetry (**SI-Scheme 1**).[1] It utilizes a series of periodic voltage pulses superimposed on the potential linear sweep or staircase wave. The current is sampled twice in each pulse period (one right before the pulse and the other at the end of the pulse), and the difference between these two current values is recorded and displayed. As a result, the interference from the capacitive current can be minimized. In our measurement, the pulse period was 1.0 second, the pulse width was 0.1 second, the pulse amplitude was 25 mV, and the potential step was 2 mV.



ESI-Scheme 1. Illustration of the DPV measurement.

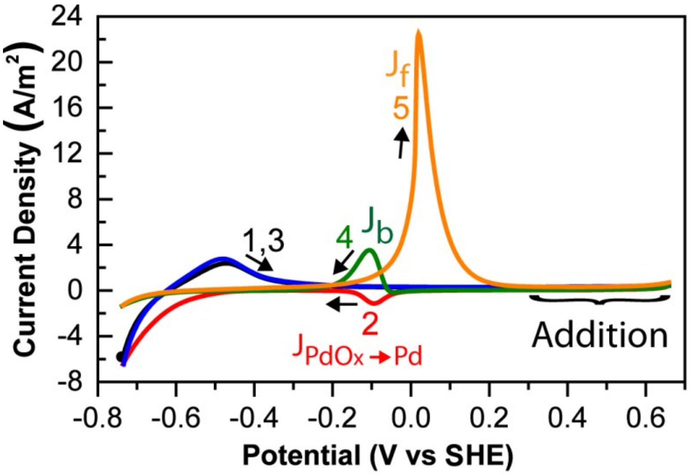
Scanning electron microscope (SEM) images were taken on a Field Emission SEM (FESEM, JEOL JSM-7000F), where the acceleration voltage was 5 kV.

Data Processing:

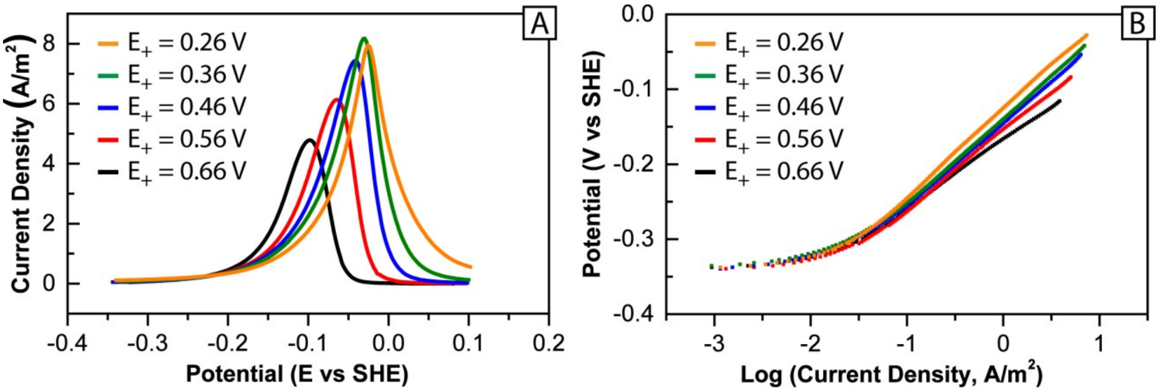
The electrochemical surface area (ECSA) of Pd was calculated from the PdO_x reduction peak in the CV of Figure 1B, as in the literature.[2] The total charge associated with that peak (Q_{Pd}) divided by the charge density (q_{Pd}) of 420 μC/cm² equals to the ECSA. All data with error bars were based on three individual measurements.

The ECSA of Pt was calculated from the hydrogen adsorption peak (SI-Figure 6), following the literature method.[3] The total charge associated with that peak (Q_{H_2}, not including the background current from electrical double layer) divided by the charge density (q_{H2}) of 210 μC/cm² equals to the ECSA.

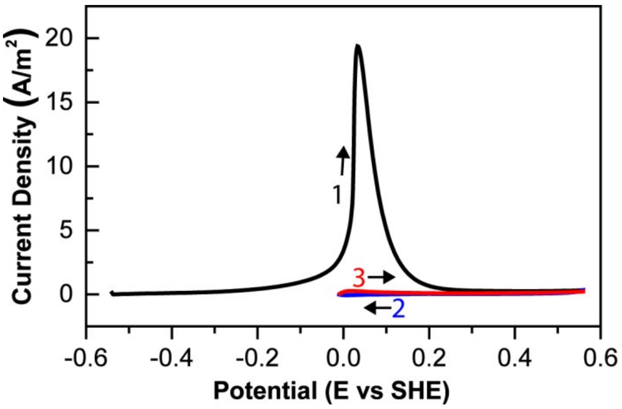
2. Figures:



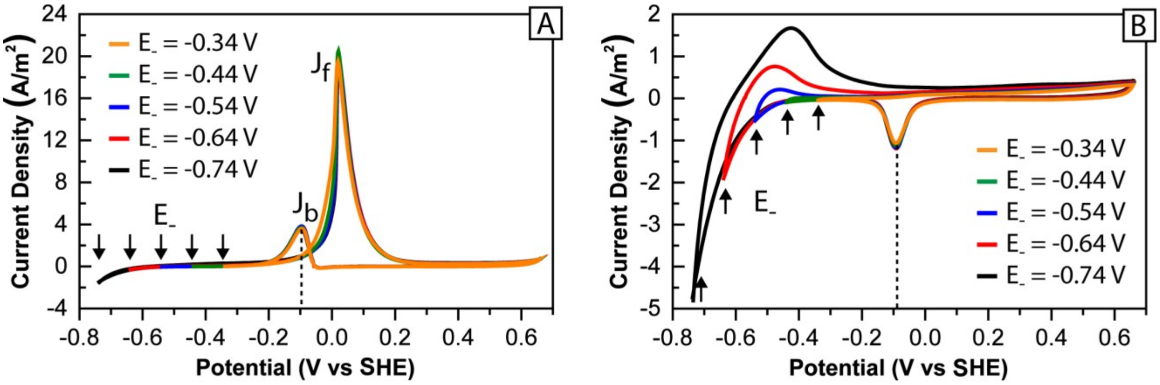
SI-Figure 1. The complete CV scenario of determining the trigger-consequence relationship between $J_{PdOx\rightarrow Pd}$ (the reduction peak in line 2) and J_b (the oxidation peak in line 4), by adding MeOH into the NaOH solution at the beginning of cathodic scan (line 4).



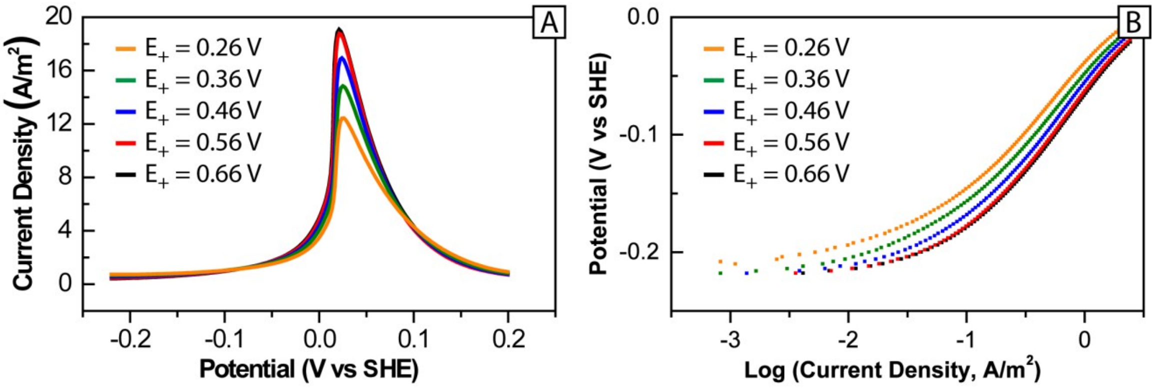
SI-Figure 2. Further analysis of the E_+-dependent properties associated with J'_b. (A) the CVs in the range of J'_b; and (B) the corresponding Tafel plots.



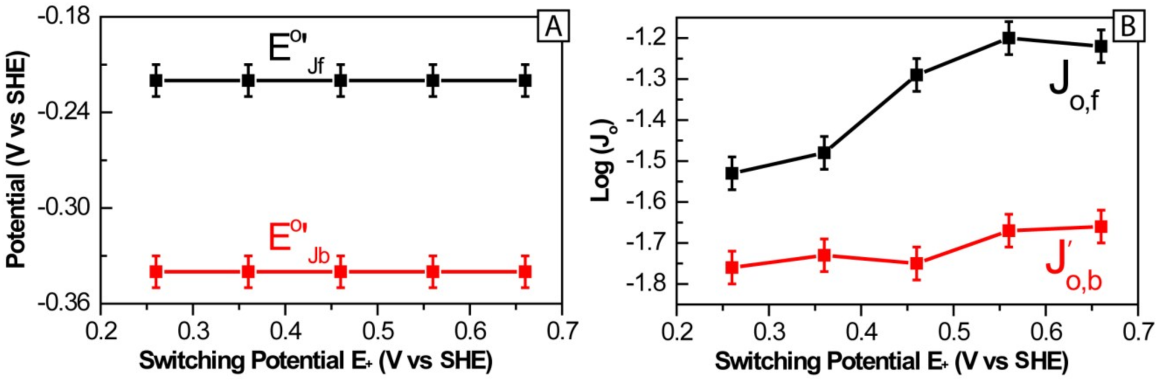
SI-Figure 3. The CV to study the capability of the oxidized Pd surface for oxidizing methanol in 0.5 M NaOH + 1.0 M CH_3OH, by switching the cathodic potential at 0.0 V before the onset of $J_{PdOx\rightarrow Pd}$.



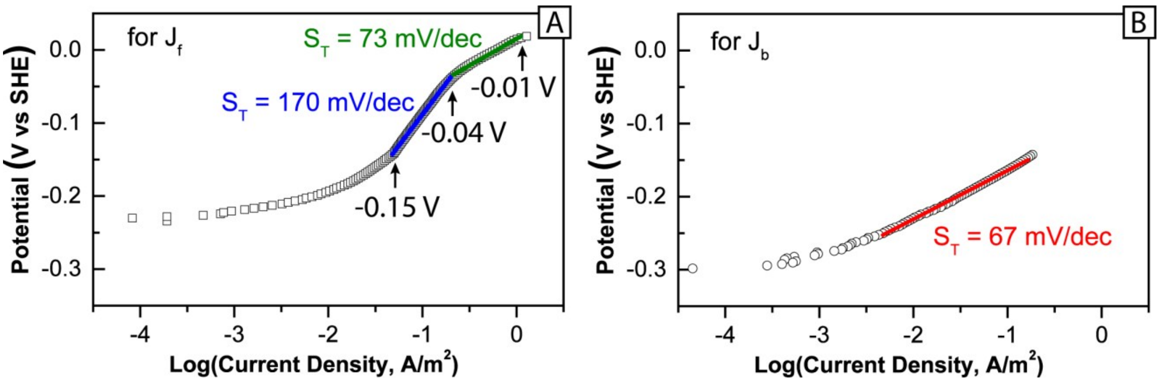
SI-Fig. 4. Study of the switching potential in cathodic scans (E_-) on J_b and J_f. (A) CVs in 0.5 M NaOH + 1.0 M CH_3OH; and (B) CVs in 0.5 M NaOH.



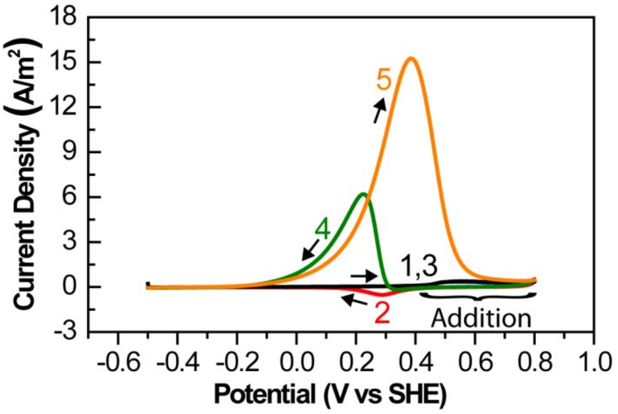
SI-Figure 5. Further analysis of the E_+-dependent properties associated with J_f. (A) The plots of J_f; and (B) the corresponding Tafel plots.



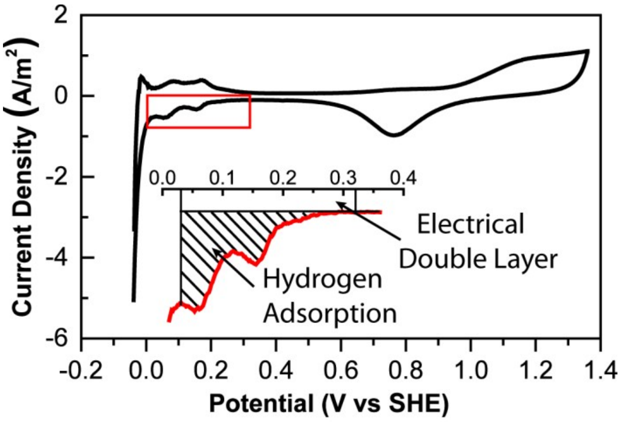
SI-Figure 6. Further analysis of the E_+-dependent properties. (A) $E^{o'}_{Jf}$ and $E^{o'}_{Jb}$; and (B) $J_{o,f}$ and $J'_{o,b}$.



SI-Figure 7. Tafel plots for J_f (A) and J_b (B) of the differential pulse voltammograms in Figure 4B.



SI-Figure 8. The CV scenario to observe the trigger-consequence relationship between $J_{AuOx \rightarrow Au}$ (the reduction peak in line 2) and J_b (the oxidation peak in line 4), by adding EtOH into the NaOH solution at the beginning of cathodic scan (line 4).



SI-Figure 9. The CV portion used for calculating the electrochemical surface area of Pt for methanol electrooxidation based on the hydrogen adsorption phenomenon.

3. References:

(1) Bard, A. J.; Faulkner, L. R., *Electrochemical methods: fundamentals and applications*. 2nd ed.; John Wiley and Sons Inc.: 2001.

(2) Álvarez, G. F.; Mamlouk, M.; Scott, K. *Int. J. Electrochem.* **2011**, *2011*, 12.

(3) Biegler, T.; Rand, D. A. J.; Woods, R. *J. Electroanal. Chem. Interf. Electrochem.* **1971**, *29*, 269-277.