

Role of surface oxygenated-species and adsorbed hydrogen in the oxygen reduction reaction (ORR) mechanism and product selectivity on Pd-based catalysts in acid media

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1. Experimental

1.1 Reagents: Palladium nitrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) from Alfa Aesar[®]; perchloric acid (70 % HClO_4 , EMSURE[®] ACS with maximum chloride content below 3 ppm), sodium borohydride (NaBH_4), sodium hydroxide (NaOH), cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and isopropanol from Merck were used for the synthesis and characterization of the catalyst nanoparticles.

1.2 Catalyst Synthesis: Pd and Pd_3Co oxide catalysts were synthesized by the simple borohydride reduction method. The as-prepared Pd was synthesized as follows: the required amount of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 mL of water and diluted to 400 mL in a 1L beaker. The solution was heated to 80°C and the pH of the solution was adjusted to ~10 by the drop-wise addition of 1 wt% NaOH solution. Thereafter, a carbon-slurry, prepared by sonicating 160 mg of Vulcan XC-72 carbon in water for 10 minutes, was added to the above solution. After proper mixing, the solution was reduced with 1 wt% NaBH_4 solution. After the reduction, the catalyst containing solution was cooled to room temperature. The carbon-supported catalyst was filtered, washed, and was dried overnight in an air oven at 80°C. The dried catalyst was transferred to a mortar and it was ground with a pestle to fine powder. The precious metal loading on the carbon-support was 20 wt%. For the synthesis of as-prepared Pd_3Co , required amount of $\text{Co}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution was added to the pH-adjusted $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ solution, and

the pH of the solution was again adjusted to ~10 by adding 1 wt% NaOH solution. Thereafter, the solution was mixed with carbon slurry and reduced with NaBH₄ solution as that mentioned for the synthesis of as-prepared Pd catalysts. The as-prepared catalysts were subjected to oxidative heat-treatment as follows. A quartz tube containing the catalyst sample was placed in an indigenous tubular furnace. Argon gas containing 5% oxygen was purged through the furnace at a flow rate of 20 sccm for 1 h. Thereafter, the sample was heated from room temperature to 400 °C at a heating rate of 1.5 °C min⁻¹. The sample was kept at 400 °C for 1 h and then it was cooled to room temperature in 8 h in the same atmosphere.²⁹

1.3 Physical characterization: X-ray diffraction (XRD) patterns of the catalysts were recorded using a PANalytical X'Pert Pro machine (30 mA, 40 kV) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), in the scan range of 30° to 90° with a step size of 0.017°. X-ray photoelectron spectra (XPS) were recorded using a MultiLab Thermo VG Scientific spectrometer with Al K α radiation. The fitting of the XPS spectra was performed using XPS peak fit 4.1 software with Shirley background correction.

1.4 Electrochemical Characterization: Catalyst ink was prepared by the method reported in the literature.^{8, 45} Catalyst suspension (0.33 mg catalyst/mL) was made by mixing appropriate quantity of the catalyst with water-isopropanol solution (1:2) and 10 μ L of 5 wt% Nafion (Aldrich) as binder. The mixture was sonicated for 15 min. to get a homogeneous catalyst ink. It was drop-cast on a glassy-carbon disk electrode using a micropipette and was dried in air-atmosphere to form a uniform layer of the catalyst. The precious metal loading on the disk electrode was maintained at 15 μ g cm⁻².

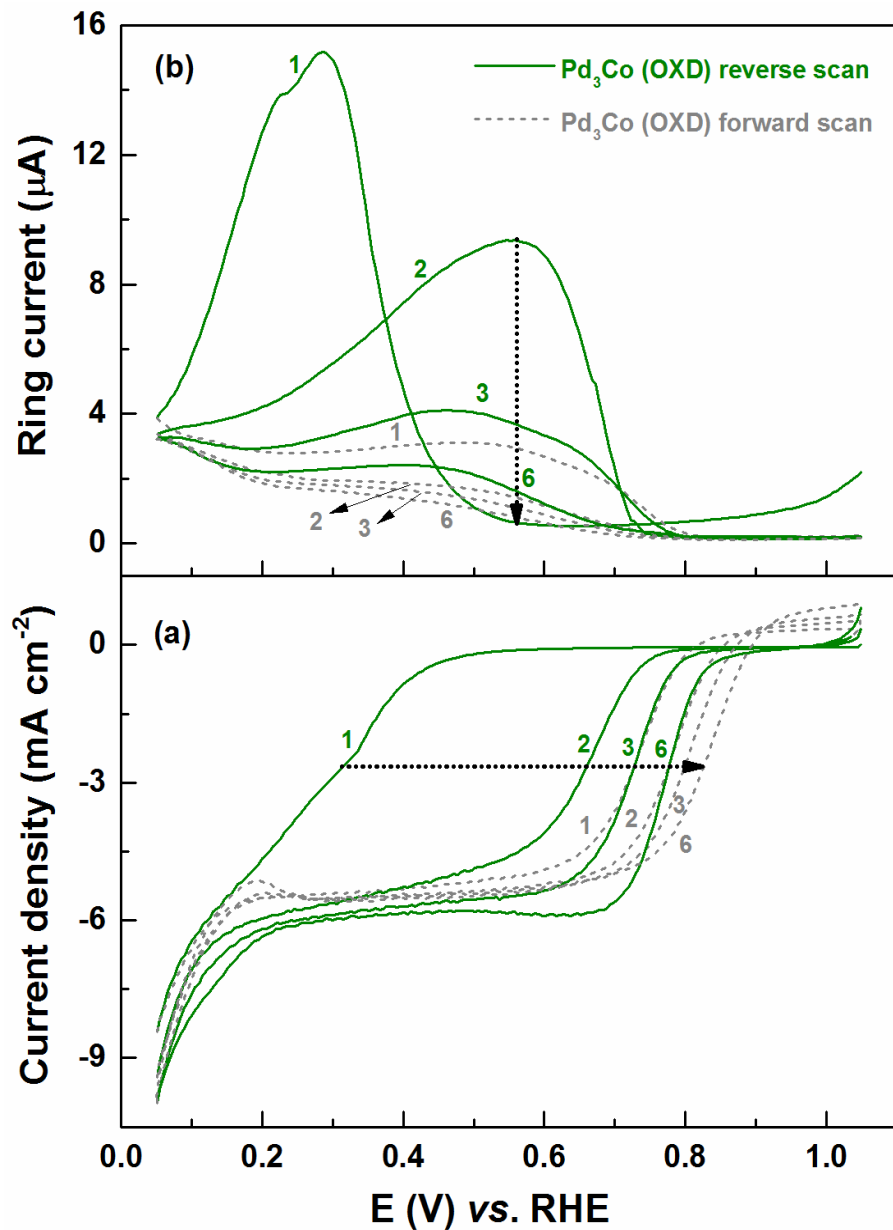


Fig. S1 ORR voltammograms (a) and the corresponding ring current (H_2O_2 oxidation current) (b) of the carbon-supported Pd_3Co (OXD) catalyst recorded in oxygen-saturated 0.1 M HClO_4 at a scan rate of 20 mV s^{-1} with 1600 rpm; the electrode potential was held at 0.85 V vs. RHE for 5 min. prior to recording the voltammograms. The solid and dashed lines refer to reverse (1.05 to 0.05 V) and forward scans (0.05 to 1.05 V), respectively. The numbers 1–6 refer to different scans.

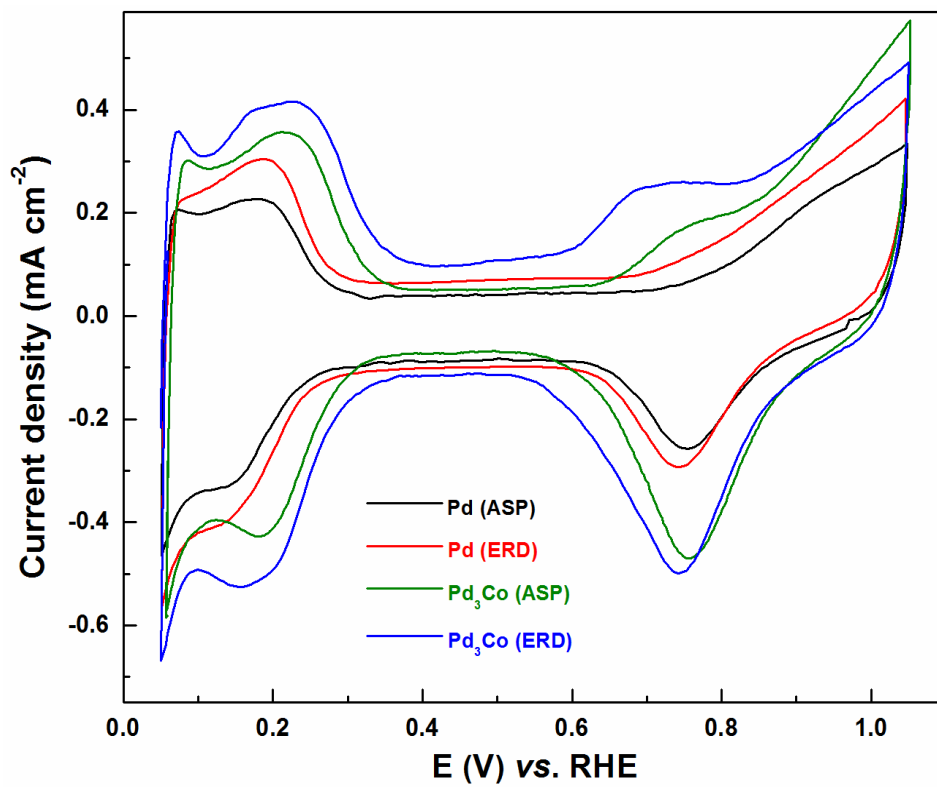


Fig. S2 CVs of carbon-supported Pd (ASP), Pd (ERD), Pd₃Co (ASP), and Pd₃Co (ERD) catalysts recorded in argon-saturated 0.1 M HClO₄ at a scan rate of 20 mV s⁻¹.

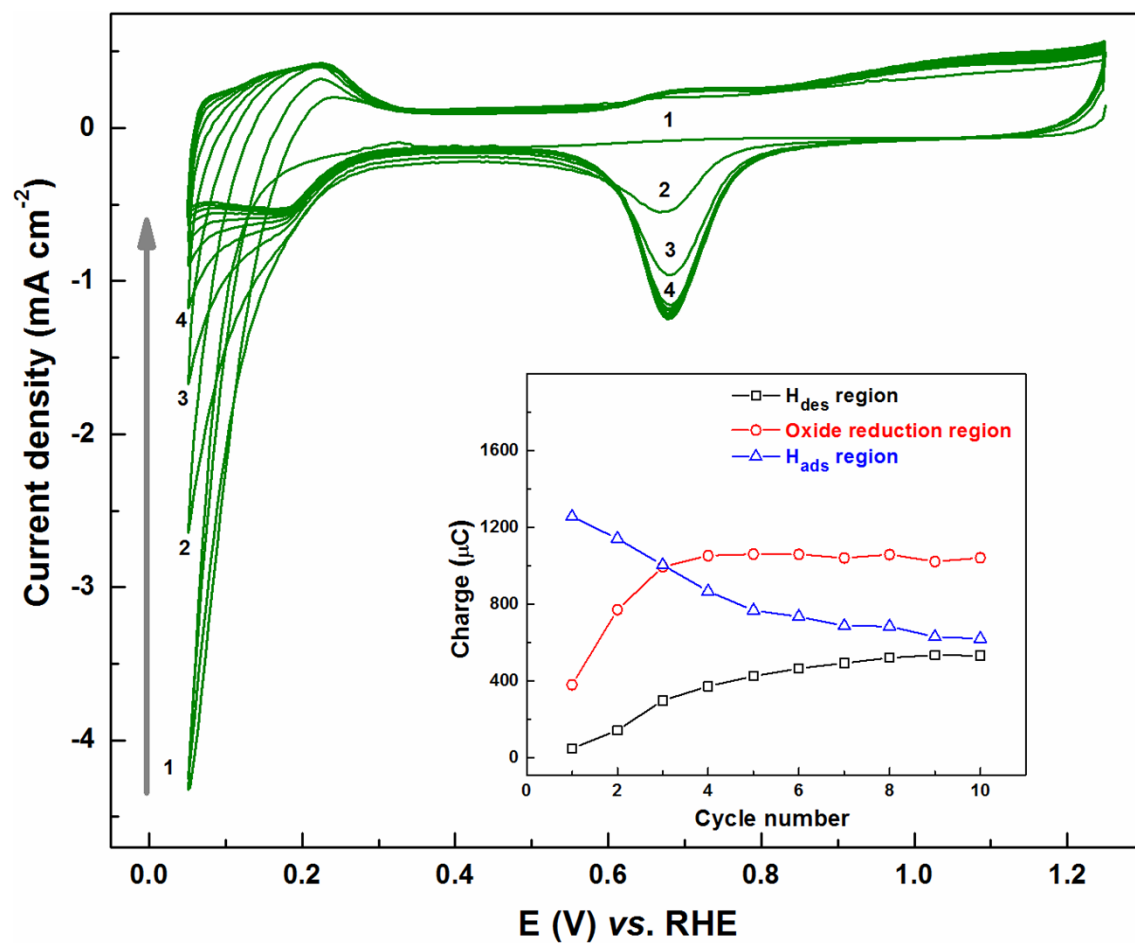


Fig. S3 Initial CVs of Pd₃Co (OXD) recorded in argon-saturated 0.1 M HClO₄ at a scan rate of 20 mV s⁻¹. Inset shows the charge estimated from the H_{des}, oxide reduction, and H_{ads} regions of the voltammograms with potential cycling.

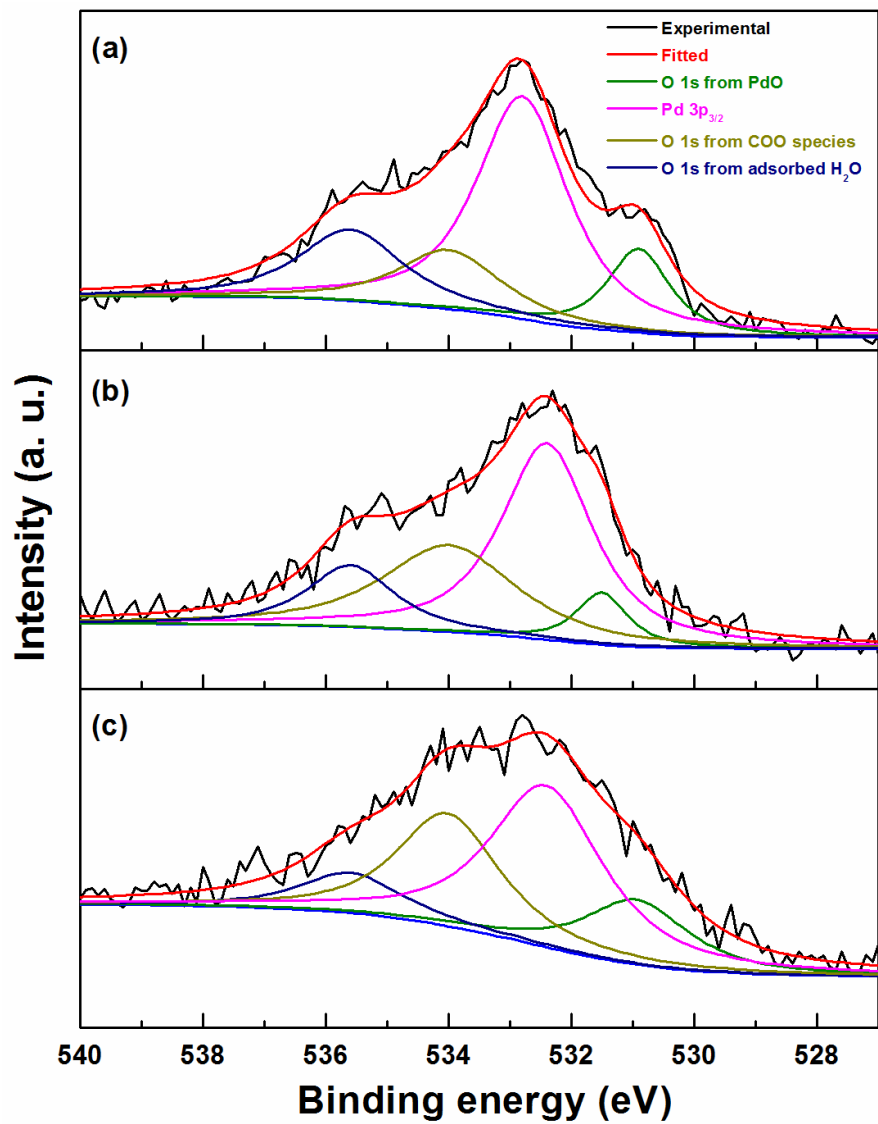


Fig. S4 O 1s core-level XPS spectra of carbon-supported Pd (OXD) (a), Pd (ERD) (b), and Pd (ASP) (c).

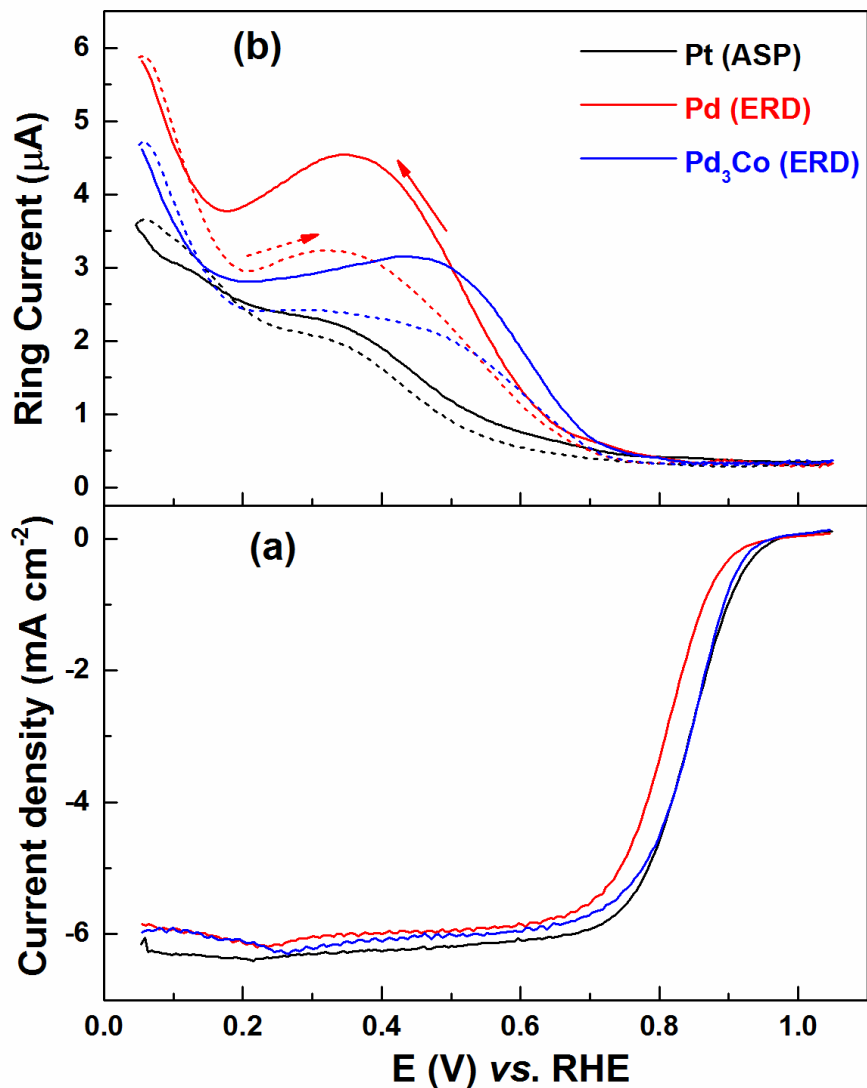


Fig. S5 ORR voltammograms (a) and the corresponding ring current (b) of carbon-supported Pt (ASP), Pd (ERD) and Pd₃Co (ERD) recorded in oxygen-saturated 0.1 M HClO₄ at a scan rate of 20 mV s⁻¹ with 1600 rpm. The solid and dashed lines refer to reverse (1.05 to 0.05 V) and forward scans (0.05 to 1.05 V), respectively.

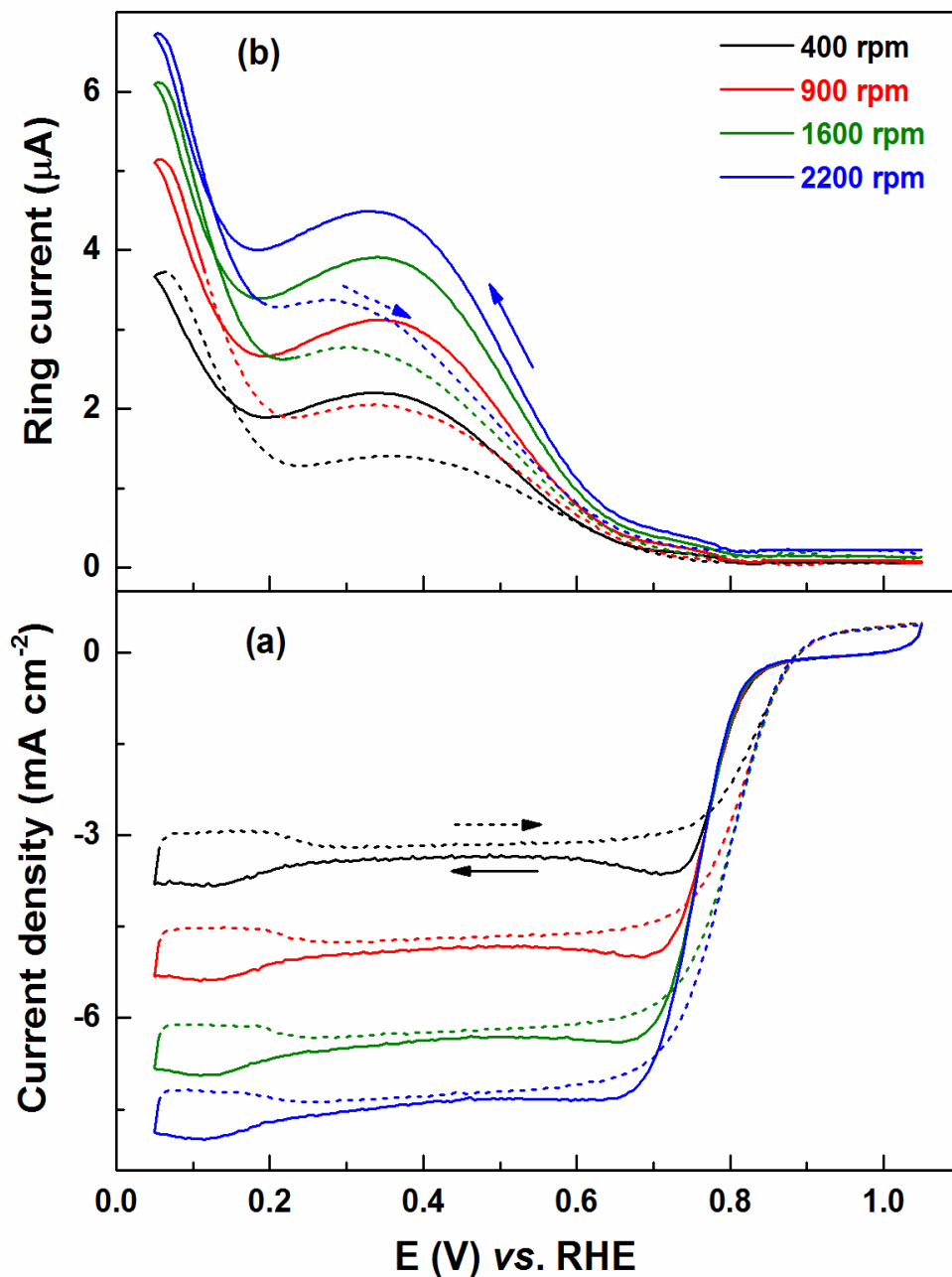


Fig. S6 ORR voltammograms (a) and the corresponding ring current (b) of carbon-supported Pd (ERD) catalyst recorded in oxygen-saturated 0.1 M HClO_4 at a scan rate of 20 mV s^{-1} with different rpms. The solid and dashed lines refer to reverse (1.05 to 0.05 V) and forward scans (0.05 to 1.05 V), respectively.

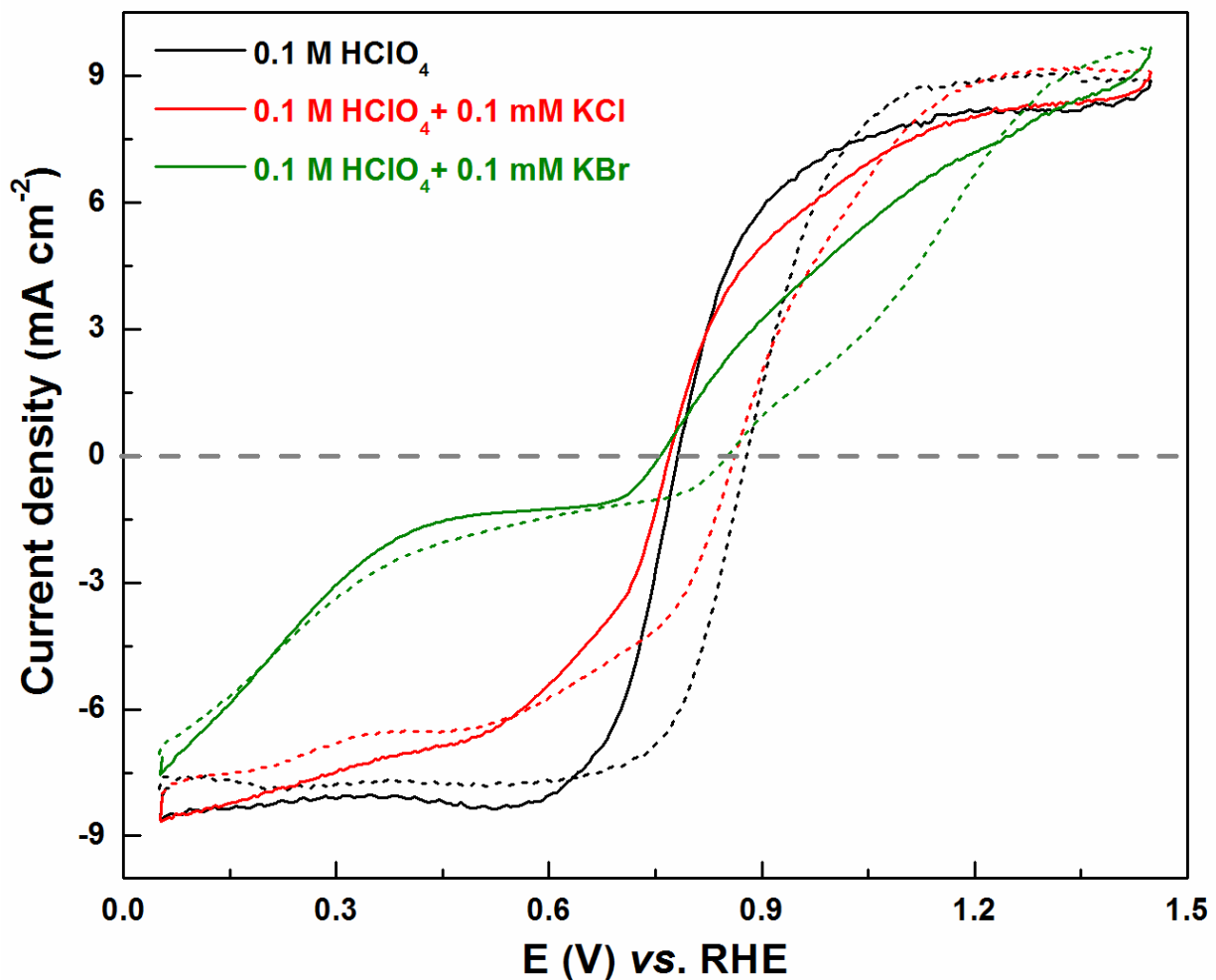


Fig. S7 CVs of Pt (ASP) recorded in argon-saturated 0.1 M HClO₄ electrolyte in the presence of 4 mM H₂O₂ with and without halide ions (0.1 mM KCl and 0.1 mM KBr) at a scan rate of 20 mV s⁻¹ with 1600 rpm. The solid and dashed lines refer to reverse (1.05 to 0.05 V) and forward scans (0.05 to 1.05 V), respectively.

Table S1 Crystallite size of the catalysts calculated from the peak broadening of the XRD patterns.

Catalyst	Crystallite size from XRD (nm)*
Pt (ASP)	5
Pd (ASP)	5.1
Pd ₃ Co (ASP)	2.8

*Calculated from the {220} peak of (ASP) catalysts.