Supporting Information to

Effect of Trace Impurities in Perchloric Acid on Blank Voltammetry of Pt(111)

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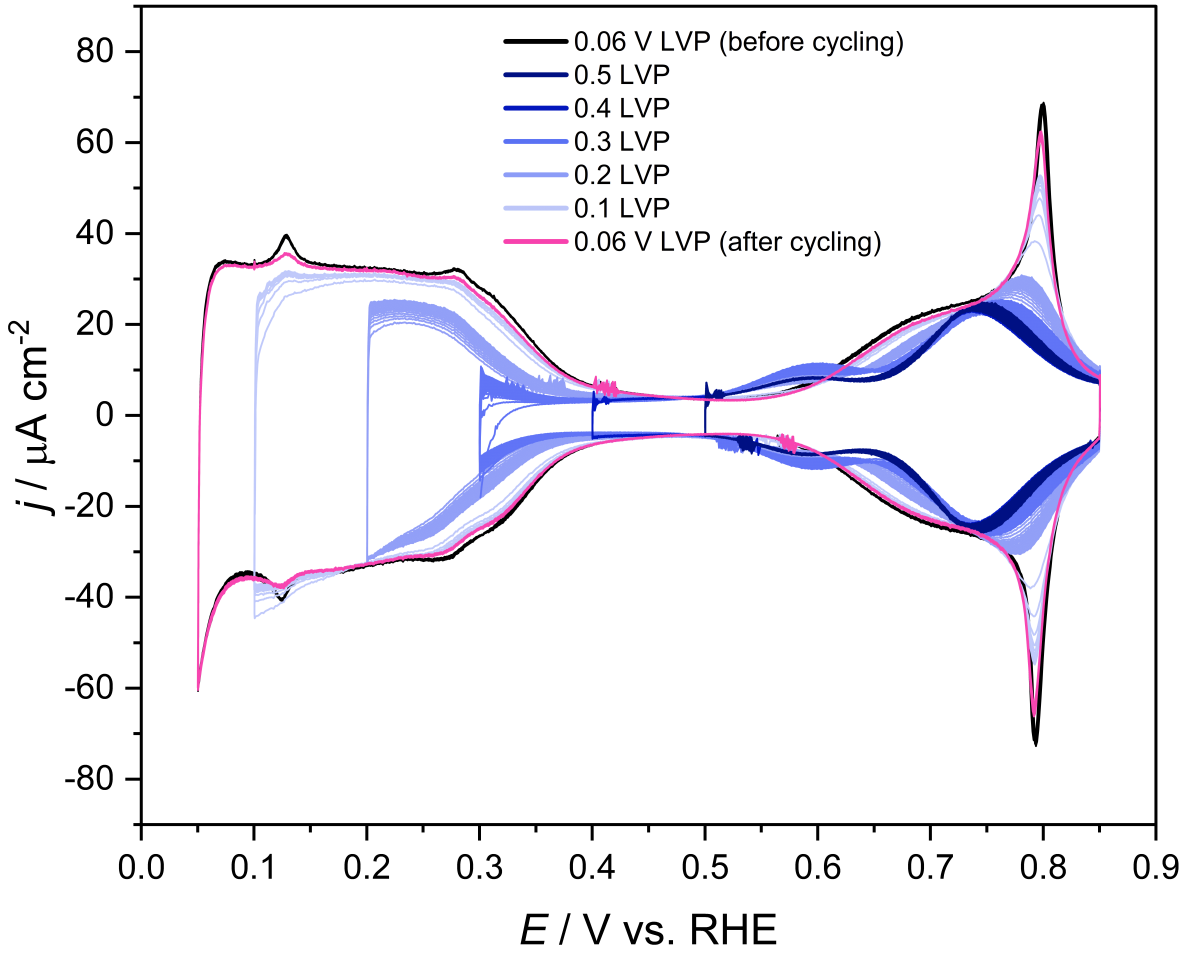
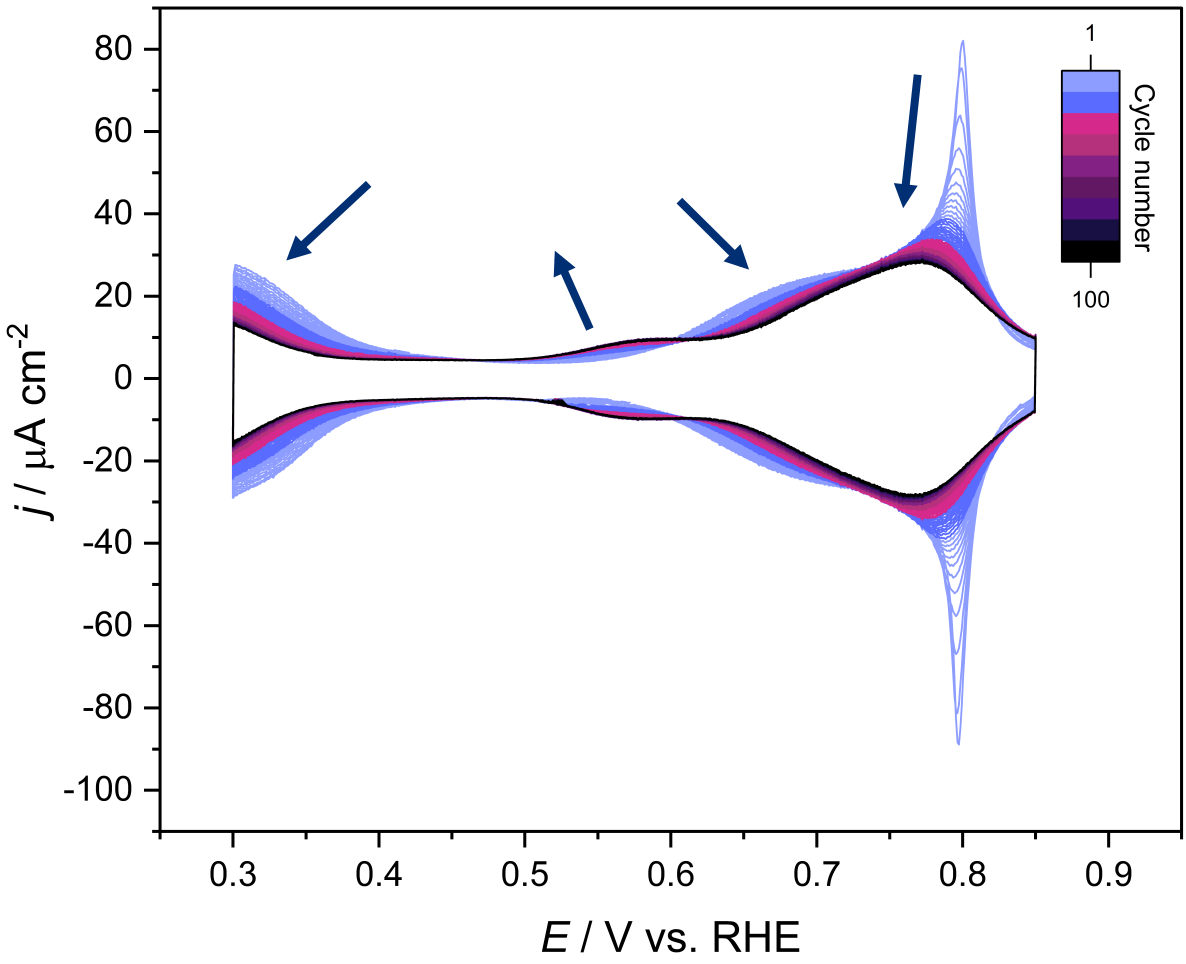
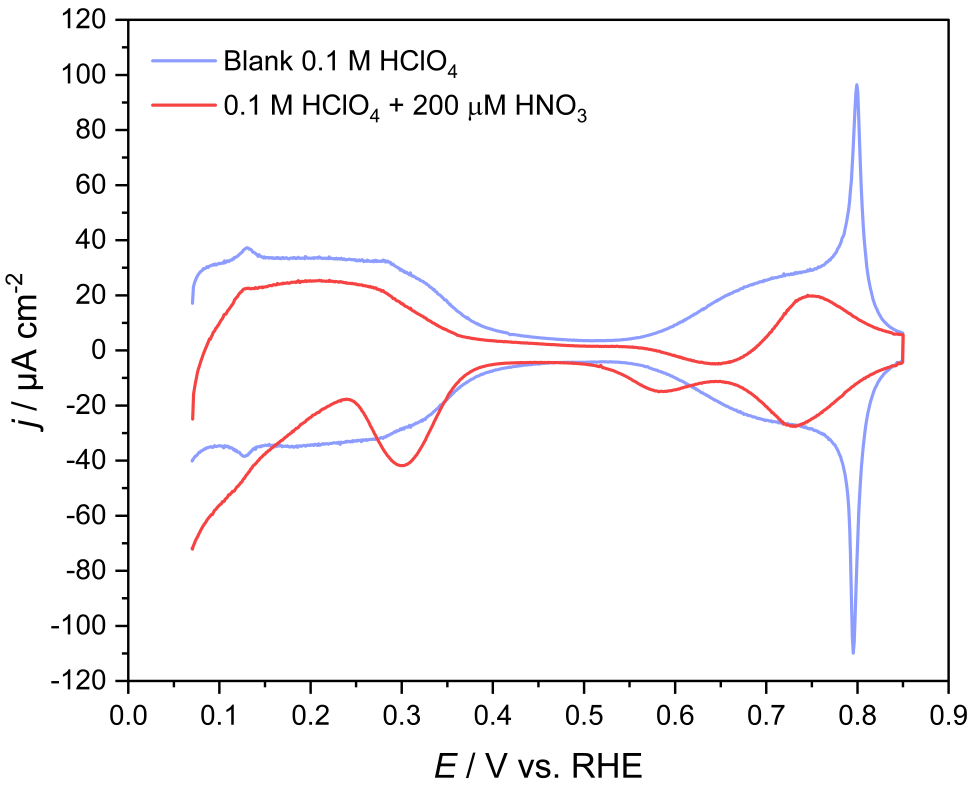


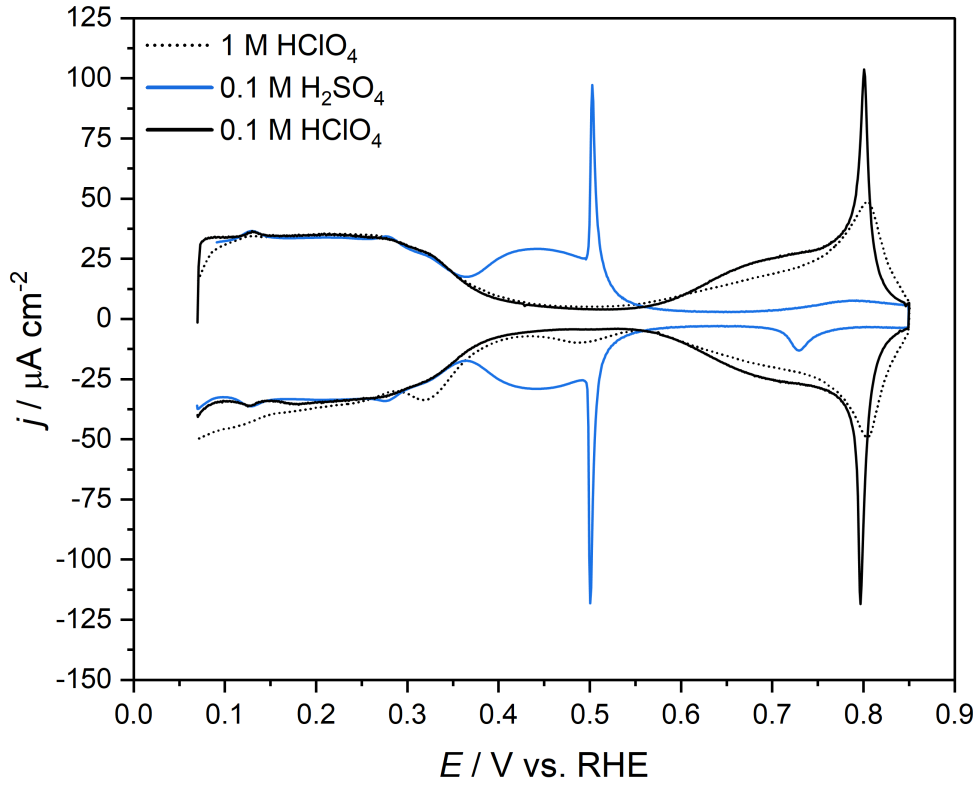
SI Fig. 1 CV data for Pt(111) in 0.1 M $HClO_4$ changing the lower vertex potential (LVP) from 0.06 V (10 cycles), to 0.5 V (30 cycles), to 0.4 V (30 cycles), to 0.3 V (60 cycles), to 0.2 V (30 cycles), to 0.1 V (40 cycles), to 0.06 V (30 cycles). The CVs with LVPs of 0.06 V before cycling (black) and after cycling (pink) show similar current densities across the CV, showing the "recovery" of the charge density, whereas other LVPs show marked quenching as a function of cycling. Scan rate = 50 mV s^{-1}.



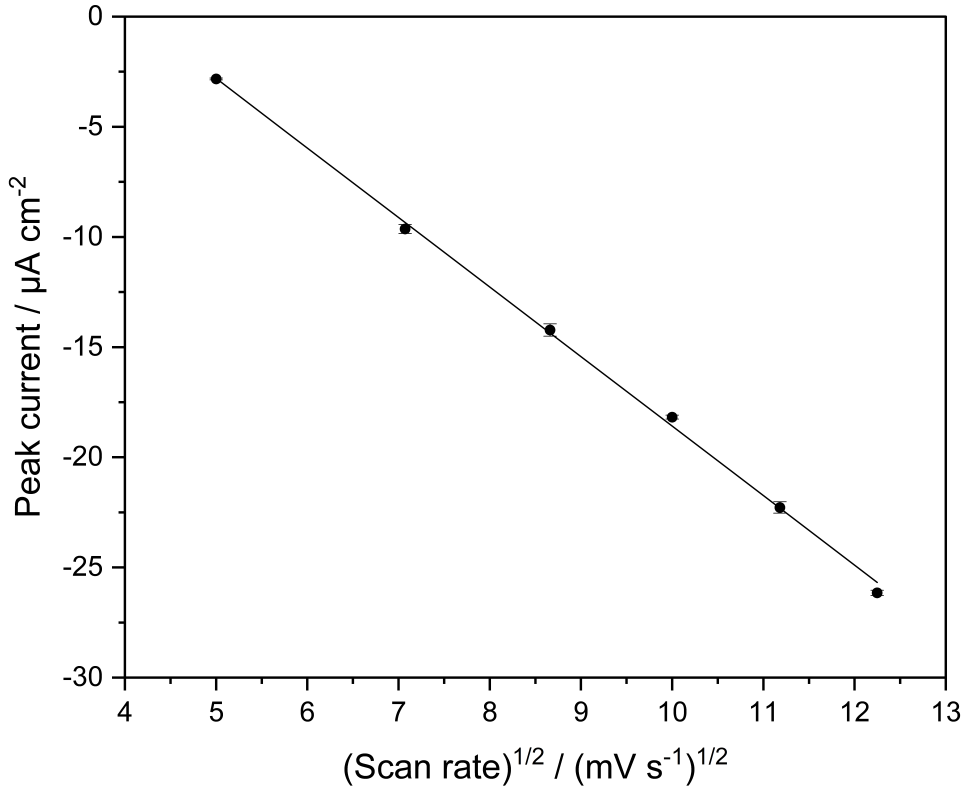
SI Fig. 2 CV data for Pt(111) in 0.1 M $HClO_4$ when carrying out 100 potential cycles. Arrows indicate the changes over cycling. Scan rate = 50 mV s^{-1}.



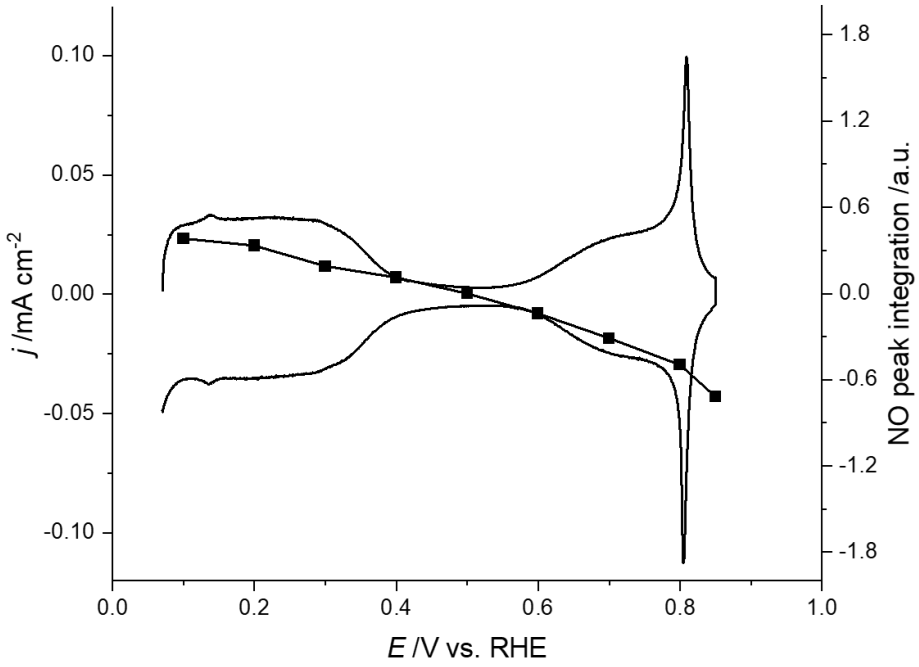
SI Fig. 31 CV of Pt(111) in 0.1 M $HClO_4$ with a 200 μM addition of HNO_3, showing the marked appearance of the reduction peak at 0.32 V not observable in blank 0.1 M $HClO_4$. Scan rate = 50 mV s^{-1}.



SI Fig. 42 Blank Pt(111) CVs in 0.1 and 1 M $HClO_4$ and 0.1 M H_2SO_4, showing that the double-layer electroreduction peak at 0.48 V in 1 M $HClO_4$ is consistent with the potential of the sharp sulphate adsorption feature in 0.1 M H_2SO_4. Scan rate = 50 mV s^{-1}.



SI Fig. 53 Scan-rate dependence of the peak current of the cathodic double-layer reduction peak in 1 M $HClO_4$ with linear fit in accordance with Randles-Ševčík equation (Equation 1 in manuscript). R^2 = 0.999.



SI Fig. 64 Integrated *in situ* FTIR peak at 1650 cm^{-1} corresponding to NO as a function of potential of Pt(111) in 0.1 M $HClO_4$.

SI Table 1: Purity and impurities listed by manufacturer for liquids for electrolyte

Chemical **Vendor and Item ID**	**Impurities listed by manufacturer**
Ultra High Purity Water Millipore	< 5 ppb total organic content (TOC) 18.2 MΩ·cm at 25 °C
Perchloric Acid ($HClO_4$) 60% Merck 100518 Supelco EMSURE® ACS Grade	Color ≤ 10 Hazen Chlorate (ClO_3): ≤ 10 (ppm) Chloride (Cl^-): ≤ 10 (ppm) Phosphate and Silicate (as SiO_2): ≤ 5 (ppm) Free chlorine (Cl): ≤ 0.5 (ppm) Sulfate (SO_4): ≤ 10 (ppm) Total nitrogen (N): ≤ 10 (ppm) Heavy metals (as Pb): ≤ 1 (ppm) Ag: ≤ 0.1 (ppm) Al: ≤ 0.05 (ppm) As: ≤ 0.05 (ppm) Ba: ≤ 0.02 (ppm) Be: ≤ 0.02 (ppm) Bi: ≤ 0.1 (ppm) Ca: ≤ 0.5 (ppm) Cd: ≤ 0.05 (ppm) Co: ≤ 0.05 (ppm) Cu: ≤ 0.1 (ppm) Fe: ≤ 1.0 (ppm) Ge: ≤ 0.05 (ppm) K: ≤ 0.1 (ppm) Li: ≤ 0.02 (ppm) Mg: ≤ 0.5 (ppm) Mn: ≤ 0.02 (ppm) Mo: ≤ 0.05 (ppm) Na: ≤ 0.5 (ppm) Ni: ≤ 0.1 (ppm) Pb: ≤ 0.05 (ppm) Sr: ≤ 0.02 (ppm) Ti: ≤ 0.1 (ppm) Tl: ≤ 0.05 (ppm) V: ≤ 0.05 (ppm) Zn: ≤ 0.1 (ppm) Zr: ≤ 0.1 (ppm) Residue on ignition (as sulfate): ≤ 30 (ppm)
Sulfuric Acid (H_2SO_4) ≥ 95 % Merck Suprapur®	Chloride (Cl^-): ≤ 100 ppb Nitrate (NO_3^-): ≤ 200 ppb Phosphate (PO_4^{3-}): ≤ 100 ppb
Sodium perchlorate monohydrate ($NaClO_4.H_2O$) ≥ 99% Merck EMSURE®	Chloride (Cl^-): ≤ 0.002% Chloride, Chlorate (as Cl): ≤ 0.002% Sulfate (SO_4): ≤ 0.002% Total nitrogen (N): ≤ 0.0005%

	Ca: ≤ 0.002% Fe: ≤ 0.0003% K: ≤ 0.005% Heavy metals (as Pb): ≤ 0.0005%
Nitric acid (HNO_3) ≥ 65% Merck Suprapur®	Chloride (Cl) ≤ 50 ppb Phosphate (PO_4) ≤ 10 ppb Sulfate (SO_4) ≤ 200 ppb
Perchloric Acid ($HClO_4$) 70% Merck Suprapur®	Chloride (Cl^-): ≤ 1000 ppb Phosphate: ≤ 100 ppb Sulfate (SO_4): ≤ 1000 ppb Total nitrogen (N): ≤ 5000 ppb

SI Table 2: Purity listed on cylinder and impurities for gases used to purge electrolyte, supply H_2 to the reversible hydrogen electrode (RHE), and to quench Pt(111) after annealing with a butane torch.

Chemical **Vendor and Item ID**	**Impurities listed by manufacturer**
Argon Linde 5.0 grade ≥ 99.999%	N_2 ≤ 5 ppm O_2 ≤ 2 ppm Total hydrocarbon content (THC) ≤ 0.2 ppm H_2O ≤ 3 ppm
Hydrogen Linde 5.0 Detector Grade ≥ 99.999%	N_2 ≤ 3 ppm Total hydrocarbon content (THC) ≤ 0.5 ppm O_2 ≤ 2 ppm H_2O ≤ 5 ppm