

Supplementary Information

Automated monitoring of electrocatalyst corrosion as a function of electrochemical history and electrolyte formulation

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1 Methods

1.1 Chemicals

HNO₃ (69%, Omnitrace), Chelex® 100 in sodium form with a 50-100 mesh, and phosphoric acid (≥99.999%) were purchased from Sigma Aldrich. HClO₄ (70%) was purchased from Thermo Fischer. All chemicals were used as received without any further purification.

1.2 Sample preparation

The thin Pt electrode was prepared using radio-frequency (RF) magnetron sputtering of a Pt target (ACI Alloys) onto a 100 mm-diameter Si wafer substrate with an oxide layer. A custom-designed combinatorial sputtering system (Kurt J. Lesker, CMS24), described in detail previously,¹ was used. The deposition proceeded in Ar (5.1 mTorr) gas with 10⁻⁸ Torr base pressure. A 10 nm Ti adhesion layer was deposited first with 50 W power. A 100 nm Pt layer was then deposited subsequently at 50 W. The entire process was conducted at room temperature.

1.3 Physical characterization

Electrochemical testing

The core method development of the ADSS is discussed elsewhere.² In short, a leak-free miniature Ag/AgCl reference electrode (LF2, Innovative Instruments) was connected to the measurement cell to be in contact with the main working electrode recirculation system. Measured potentials, $E_{\text{Ag/AgCl}}$, were all corrected to the reversible hydrogen electrode (RHE) scale. A Pt wire served as a counter electrode and was separated from the main recirculation via a bipolar membrane (FumaSEP). 0.1 M HClO₄ was used as the electrolyte, which was purified with Chelex® before usage. The purification was conducted by stirring 500 mL of 0.1 M HClO₄ with 20 g of Chelex® overnight. All electrochemical measurements were controlled with a Gamry 1010 potentiostat. The recirculation velocity was controlled by a peristaltic pump (Masterflex) and was adjusted to ca. 0.2 mL s⁻¹.

Inductively coupled plasma mass spectrometry

Each 100 µL aliquot taken during the ADSS experiment was further diluted 10x by adding 900 µL of 2% HNO₃ using a pipetting robot (Hamilton Microlab STARlet). The resulting 1 mL vial for each aliquot was loaded into the autosampler connected to an ICP-MS (Thermo Fisher

Scientific iCAP™ RQ), where three measurements were performed per vial to determine the concentration of dissolved metals. The instrument was calibrated using calibration solutions wherein 0.1 M HClO₄ was diluted 10x with 2% nitric acid and injected with elemental standards comprising 0.5, 1, 5, and 10 ppb for each of the following elements: Ag, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Tl, V, Zn, Sb, Pt.

1.4 ADSS operating procedure

The starting condition for a campaign conducted by the ADSS starts with the recirculation system being empty and the measurement cell residing in the cleaning position. From here, the following processes are sequentially executed:

1. The translational stage moves the measurement cell to a certain sample and establishes contact by pressing the cell against the sample.
2. The electrolyte syringe pump infuses 7 mL of 0.1 M HClO₄ into the recirculation cell. The same syringe is immediately refilled by aspirating 7 mL of 0.1M HClO₄ from an electrolyte reservoir.
3. The electrolyte is recirculated in the main recirculation system, which fills the measurement cell with the electrolyte.
4. An initial 10-second OCP measurement is performed to check for potential bubbles that were introduced during the filling of the ADSS cell (see below for a detailed description of the detection algorithm). If a bubble is detected, the peristaltic pump direction is reversed to fill the ADSS cell with air. The direction is then reversed to refill the ADSS cell with electrolyte again. Another OCP is measured for 10s to check whether the bubble was successfully removed. This operation is repeated until no bubble is detected anymore.
5. The protocol shown in Fig S 1 is started.
6. The peristaltic pump drains the 0.1 M HClO₄ from the main recirculation system into a waste reservoir.
7. The translational stage decontacts the measurement cell from the sample and moves it to the cleaning position.
8. The measurement cell is cleaned by first infusing 12 mL of water into the main recirculation system via the water syringe pump. The water is recirculated and drained into a waste reservoir. The same procedure is repeated with 6 mL. The water syringe is refilled by aspirating 18 mL of water from a water reservoir.
9. Repeat cycle from 1.

1.5 Bubble detection

It was derived from preliminary tests that bubble inclusion in the measurement cell was characterized by heavy oscillation, discontinuity, sudden changes, and a large offset of the potential during OCP measurements. Thus, for the bubble detection procedure, a 10s OCP measurement was conducted, and the entirety of this data (raw data, i.e., working electrode potential vs. Ag/AgCl) was subjected to an on-the-fly analysis, which was divided into four tests. Each test would check for a certain threshold value set by the experimentalist. If any of the tests fail (i.e., if a bubble is detected according to one test), the algorithm would indicate the detection of a bubble, and according hardware actions are executed as outlined in the ADSS procedure above. The four tests are conducted as follows:

- *“relative standard deviation test”*:
 - A bubble is detected if the relative standard deviation of the data (RSD_{data}) is higher compared to a threshold value ($RSD_{threshold}$).
- *“potential value test”*:
 - A bubble is detected if the last potential value (E_{data}) is lower than a threshold value ($E_{threshold}$).
- *“potential change test”*:
 - The difference between potential values recorded every second is calculated (ΔE_{data}). A bubble is detected if any of the ΔE_{data} is above a threshold value ($\Delta E_{threshold}$).
- *“oscillation amplitude test”*:
 - The average amplitude of the oscillating potential signal is calculated ($E_{amplitude_{data}}$). A bubble is detected if $E_{amplitude_{data}}$ is above a threshold value ($E_{amplitude_{threshold}}$).

Before implementing the bubble detection algorithm into the ADSS workflow, a feasibility study was conducted on a curated dataset. The dataset is an extended OCP measurement where bubbles were deliberately introduced and removed from the ADSS cell (see Fig S 2). The algorithm was iteratively applied to 10s snippets of this dataset. The green shaded areas in Fig S 2 correspond to 10s regions where no bubble was detected, matching the expectations from the manual inspection of the data. The threshold values used for this demonstration were:

- $RSD_{threshold}$: 1
- $E_{threshold}$: 0.3
- $\Delta E_{threshold}$: 0.01
- $amplitude_{threshold}$: 0.05

These thresholds were also applied during the automated ADSS campaigns.

2 Supplementary figures

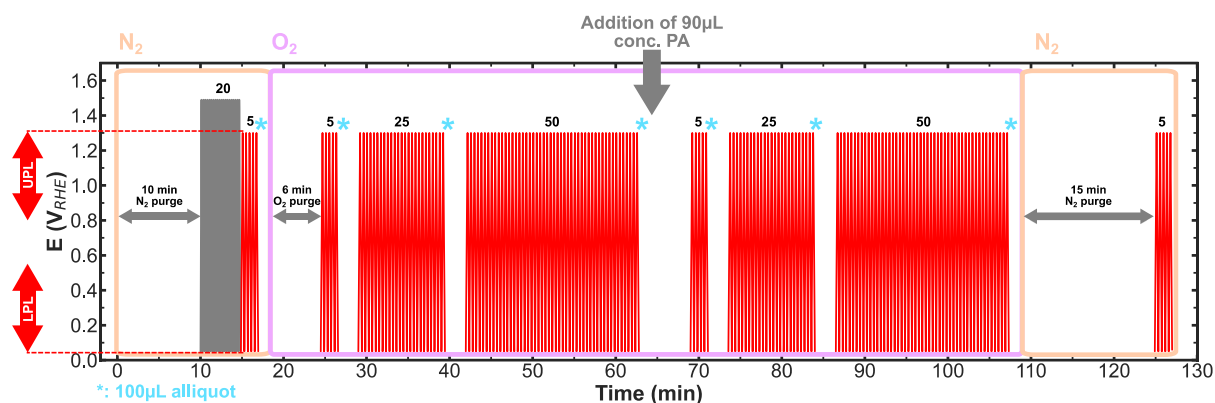


Figure S1: Measurement protocol used for the ADSS campaign. The numbers on top of the CVs indicate the number of cycles. The grey CVs are the cleaning cycles and were recorded at 200 mV s⁻¹. The following red CVs were all recorded at 100 mV s⁻¹ and were subject to changing LPL-UPL combinations per sample. The supporting electrolyte was 0.1 M HClO₄.

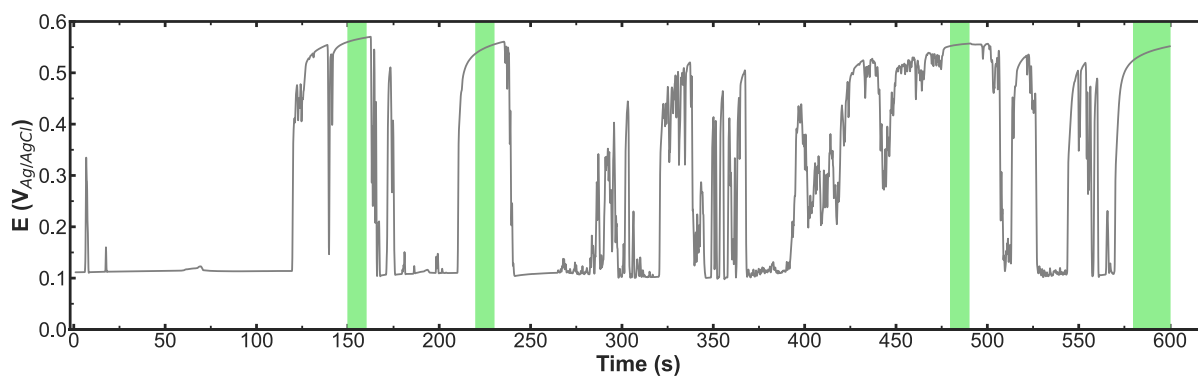


Figure S2: A demonstrative open circuit potential measurement on Pt in 0.1 M HClO₄ where bubbles were intentionally introduced and removed. The green shade indicates 10s regions where no bubble was detected using the bubble detection algorithm outlined above.

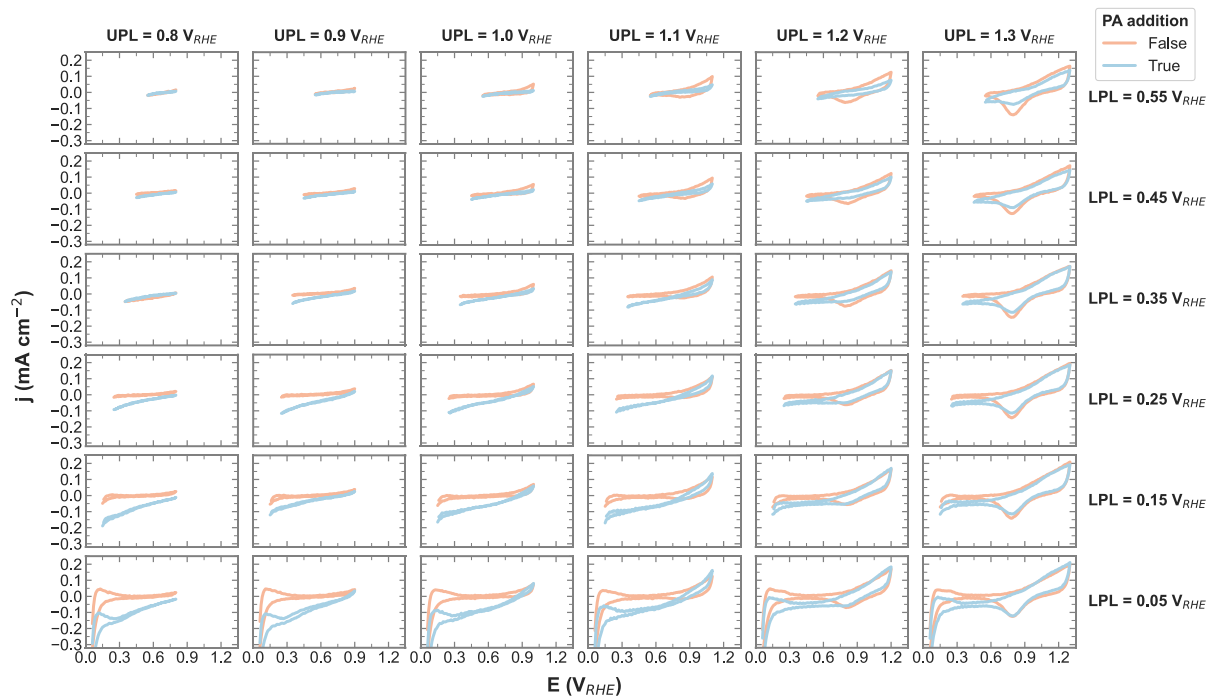


Figure S3: Last cycle of the 5 CVs conducted in N_2 . Color coding indicates whether it is the first (without PA addition) or last (with PA addition) set.

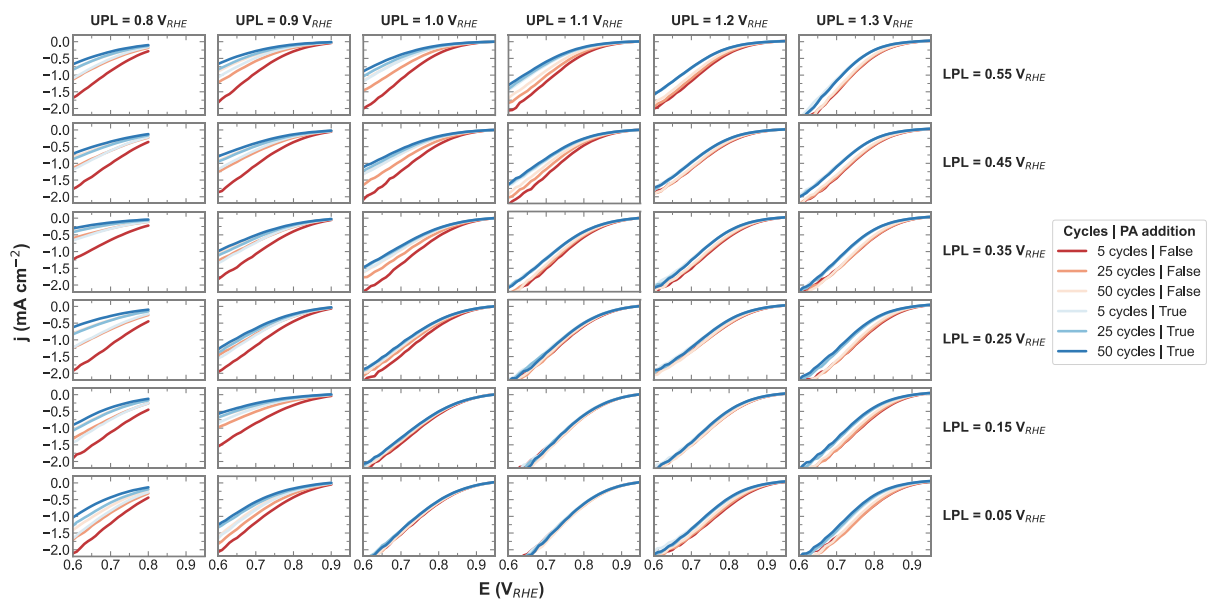


Figure S4: Anodic sweep of last cycle for all CVs recorded in O_2 . Each J-V curve is shown in the kinetic regions. Red traces indicating CVs before PA addition. Blue traces indicating CVs after PA addition.

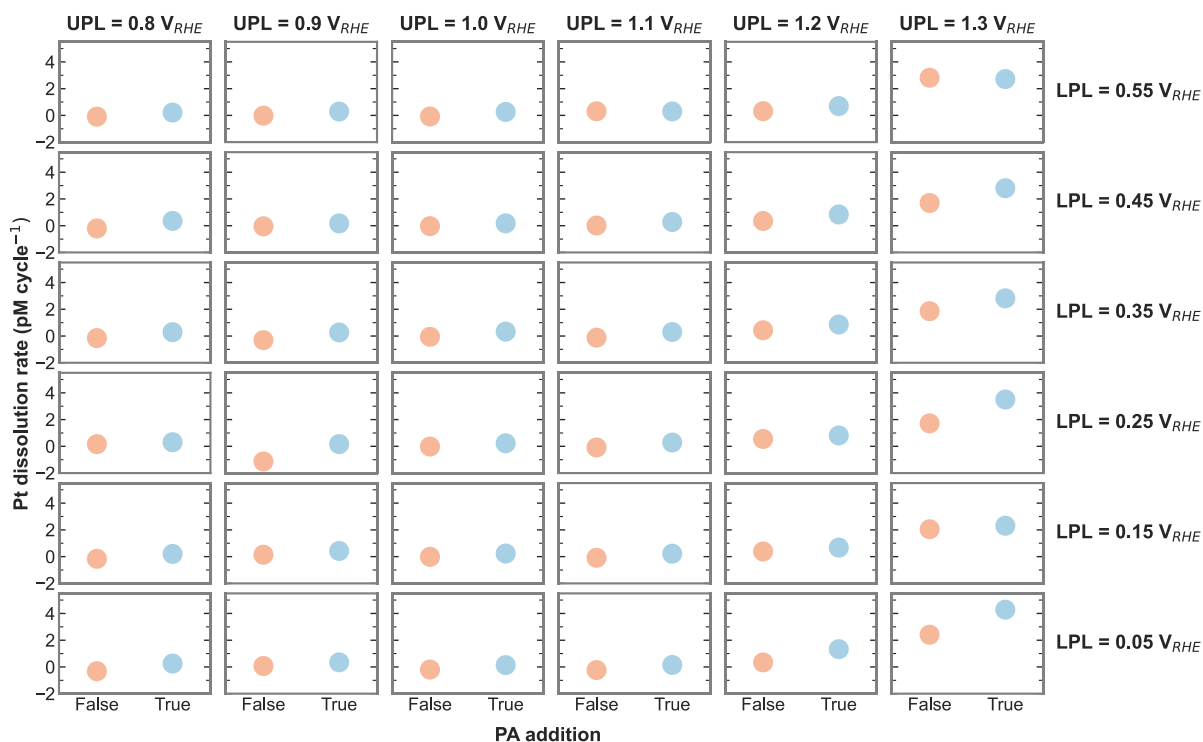


Figure S5: Pt dissolution rate before and after PA addition. The rates are calculated as a linear fit from the three Pt concentrations in O_2 recorded before and after PA addition, which are shown in Fig 2.

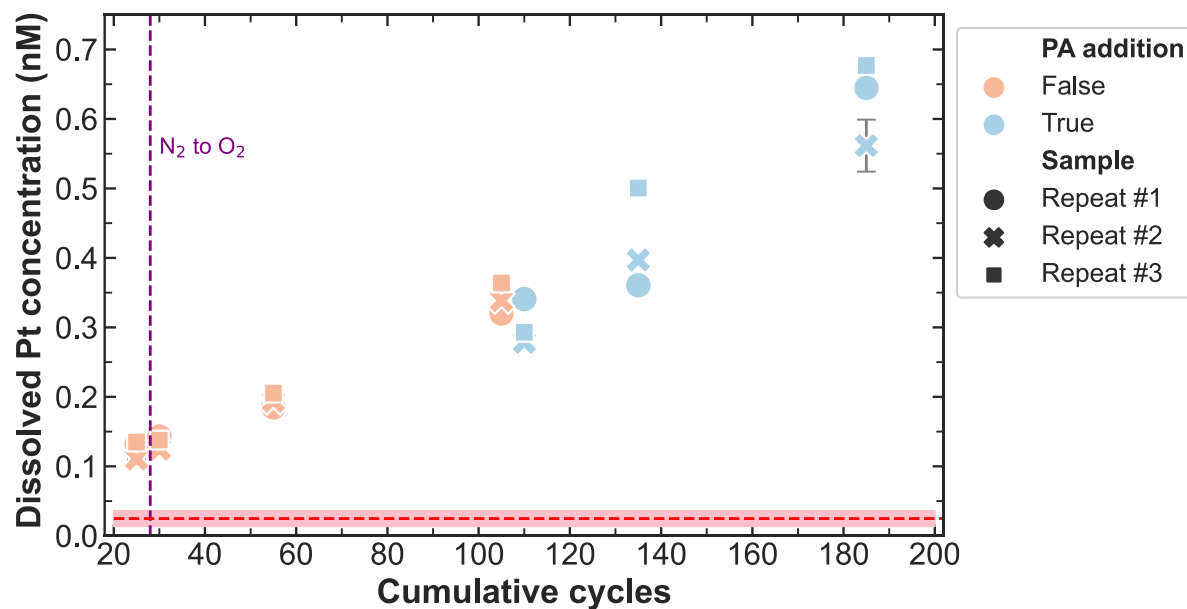


Figure S6: Dissolved Pt concentration for three repeat measurements using the widest potential window (LPL: $0.05 V_{RHE}$ and UPL: $1.3 V_{RHE}$).

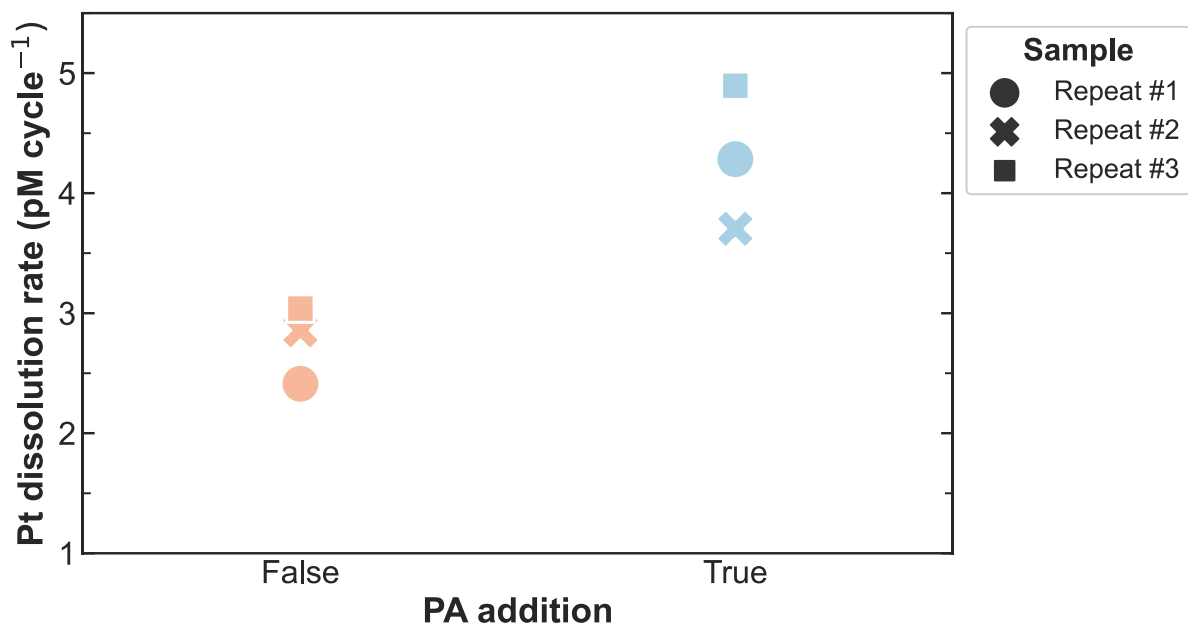


Figure S7: Pt dissolution rate for three repeat measurements using the widest potential window (LPL: 0.05 V_{RHE} and UPL: 1.3 V_{RHE}). The rates are calculated as a linear fit from the three Pt concentrations in O_2 recorded before and after PA addition, which are shown in Fig S 6.

3 Supplementary references

- 1 Suram, S. K. *et al.* Combinatorial thin film composition mapping using three dimensional deposition profiles. *Rev Sci Instrum* **86**, 033904 (2015). <https://doi.org/10.1063/1.4914466>
- 2 Kan, K. *et al.* Accelerated Characterization of Electrode - Electrolyte Equilibration. *ChemCatChem* **16** (2023). <https://doi.org/10.1002/cctc.202301300>