Platinum electrochemistry through a magnifying glass

Jacobse, L.

Citation

Jacobse, L. (2018, November 29). *Platinum electrochemistry through a magnifying glass*. Retrieved from https://hdl.handle.net/1887/67104

Version:	Not Applicable (or Unknown)
License:	[Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)
Downloaded from:	https://hdl.handle.net/1887/67104

Note: To cite this publication please use the final published version (if applicable).

Cover Page

Universiteit Leiden

The handle http://hdl.handle.net/1887/67104 holds various files of this Leiden University dissertation.

Author: Jacobse, L.
Title: Platinum electrochemistry through a magnifying glass
Issue Date: 2018-11-29

E | Details on SECCM experiments

E.1 Methods

Fresh electrolyte solutions are prepared before each experiment from ultrapure water (SELECT-HP, Purite, 18.2 MΩ·cm resistivity at 25 °C), HClO$_4$ (ca. 70% solution in water, Acros Organics), and hydrazine monohydrate (Acros Organics). Pd–H$_2$ is used as a quasi-reference counter electrode (QRCE) for SECCM and as a reference electrode (RE) for macroscale and microscale experiments. This electrode is prepared by evolving hydrogen on a Pd wire (99.9% purity, 0.25 mm thickness; Alfa Aesar) in a supporting electrolyte (0.1 M HClO$_4$) solution. All potentials are reported against the reversible hydrogen electrode ($E_{Pd–H_2}^{\ominus} = 50$ mV vs RHE).[1]

Macroscopic CV measurements are carried out in a traditional three-electrode setup. A polycrystalline Pt wire is used as the working electrode, with the Pd–H$_2$ RE and another Pt wire as the counter electrode. Prior to each experiment these Pt electrodes are cleaned by flame-annealing. The exposed surface area of the working electrode is on the order of a few tens of mm^2 and varies somewhat between different experiments. No attempt is made to determine the exact electroactive surface area, as the hydrogen underpotential deposition region of the CV contains oxygen reduction reaction features for the experiments performed in the presence of oxygen.

A 25 μm diameter Pt-disk ultramicroelectrode (UME) is prepared by sealing a Pt microwire into glass.[2] It is then polished on a 0.1 μm diamond-lapping disc (PSA, Buehler) until a flat surface was obtained. Before use, the Pt UME is prepared by further mechanical polishing (MasterPrep 0.05 μm alumina polishing suspension, Buehler) and finally through the use of a clean polishing pad without alumina, followed by thorough rinsing with ultrapure water. For experiments under deaerated conditions, the electrolyte solution (10 mL) is flushed with N$_2$ for 30 min before the measurements.

A polycrystalline Pt foil (>99.95% purity, 0.010 mm thickness; Advent Research Materials) is used as the sample (working electrode) for the SECCM imaging experiments. Prior to each experiment, the foil is cleaned by rinsing with ultrapure water and flame-annealing. An area of interest on the foil is marked by focused ion beam milling (JEOL 4500, JEOL). Scanning electron microscopy (SEM) images

of the Pt sample were recorded after each imaging experiment on a Zeiss SUPRA 55 variable-pressure field emission-scanning electron microscope. Electrolyte residues from the SECCM meniscus in the hopping mode employed are observed with SEM and provide valuable information about the exact droplet size and measurement location (vide infra). Before each new experiment, all residues from any previous imaging are cleaned by immersing the foil in a diluted H_2SO_4 solution overnight. SECCM data analysis is performed in Matlab (R2014B, Mathworks) and visualized using WaveMetrics Igor Pro software.

Electron backscatter diffraction (EBSD) images of the polycrystalline Pt sample, in the same area of the SECCM measurements, are recorded on a Zeiss SUPRA 55 FE-SEM equipped with an EDAX TSL EBSD system. Before performing EBSD measurements, the Pt foil is cleaned carefully. The measurements are carried out at 20 kV at a working distance of 25 mm on a substrate tilted at 70°, with a data collection step of 2.5 μm. The EBSD data is analyzed using Orientation Imaging Microscopy software.

E.2 Cyclic voltammetry

Figure E.1 shows CVs of hydrazine oxidation at a Pt UME and a Pt foil in a SECCM setup. Three subsequent cycles are recorded in both experiments. Different from CVs in Fig. 4.2 (page 55), these CVs are obtained by sweeping the potential up to a higher value (1.45 V vs RHE) to oxidize the Pt surface more extensively. CVs from the Pt UME and in the SECCM setup show very similar characteristics. Independent of the cycle number, under both conditions, hydrazine oxidation shows a pre-wave peak at around 0.70 V and a diffusion-controlled plateau at high potential range. The CVs shown here are similar to the 'stabilized' CVs reported in a fairly recent study[3] which required significant pre-activation. However, unlike the results of that study, we did not observe any shifts in potentials upon repeated cycling despite some variations in electrochemical current. Thus, to limit the scan time for SECCM imaging, only a single CV (first cycle) was recorded at each pixel.

E.3 Droplet residues

Figure E.2 shows a SEM image of a scanned area on a Pt foil after performing a voltammetric SECCM imaging in an aerated environment. The black dots are the droplet residues left on the surface due to the quick break of droplets during pipet retracting. It can be seen that the footprints of most droplets are consistent in size,
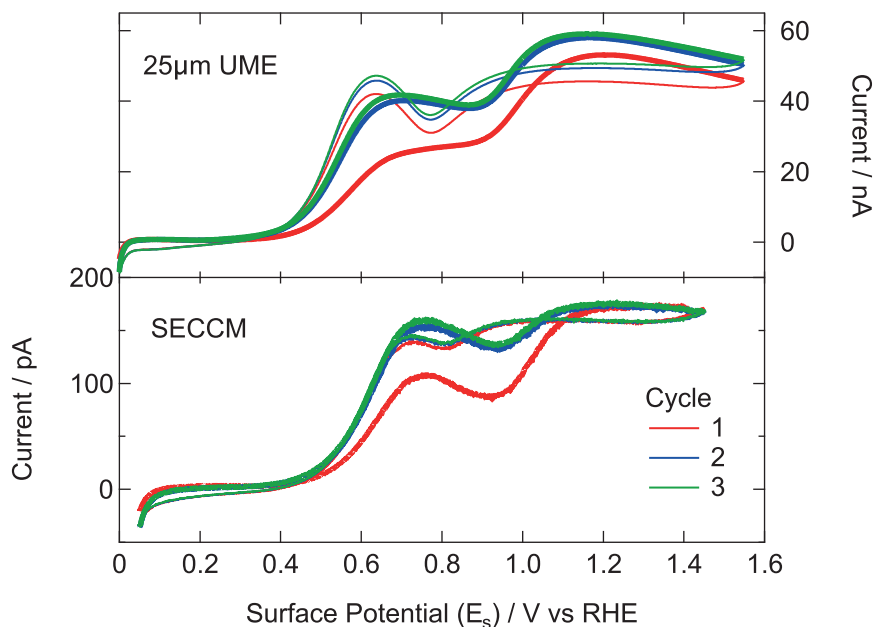
Fig. E.1 | Hydrazine oxidation at large overpotentials: First three CV cycles of hydrazine oxidation at a Pt UME (top) and at a Pt foil (bottom) in an SECCM setup. The thick lines indicate the anodic scan, the thin lines the cathodic scan. For both experiments, nitrogen was flowed to deaerate the electrolyte solution. The electrolyte is 2 mM N_2H_4 in 0.1 M $HClO_4$ and the potential scan rate is 100 mV·s^{-1}.
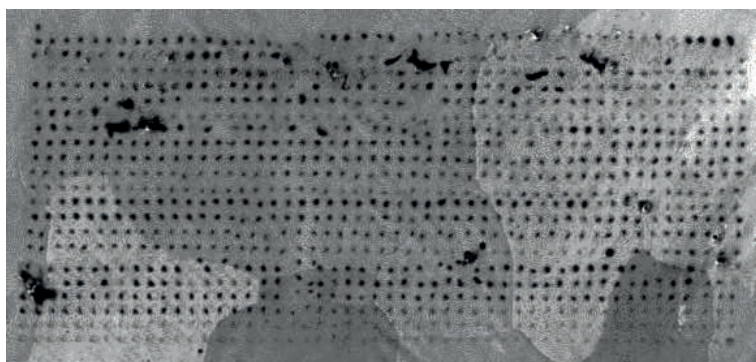

Fig. E.2 | SECCM droplet residues: SEM image showing the droplet residues after a SECCM imaging experiment.

indicating the stability of droplets in voltammetric SECCM imaging and, most importantly, grain structure-independent droplet wetting.

E.4 Quantitative multimicroscopy

The SEM data showing the SECCM droplet residues contain, as stated before, extremely useful information about the imaging experiment. Because the analysis of the data in chapter 4 is rather qualitative, no effort is made to extract all the detailed information. In the simplest case, the SEM images give the exact location of the pixels in the SECCM maps, and also give a rough indication of the stability of the droplet cell. The ion conductance current from the SECCM experiment confirms in this case the absence of any major issues with the imaging experiment.

A more detailed analysis could enable a more quantitative correlation of the observed structure-activity relationships. In such an approach, high-resolution SEM images deliver not only information on thermal drift, which distorts the SECCM maps, but also deatils about scanning artefacts and 'defect' pixels. Importantly, it would be possible to normalize the SECCM sample current to the cell footprint determined by SEM, leading to the determination of current densities. Although the 2D-interpolated and 'raw' maps as shown in Fig. 4.4 (page 59) are a useful, visually attractive, and (for our analysis) accurate way to represent the data, it might obscure what is really measured in the experiments. To illustrate this, Fig. E.3 shows three different representations of the data shown in Fig. 4.4. Figure E.3A shows the typical way of displaying SECCM data, a 2D interpolated version, which was also shown in Fig. 4.4. Figure E.3B is a surface-filling representation of the raw data. This visualization is particularly useful during the data analysis, because it gives a clear and quick overview of the data set. Figure E.3C shows the data in a way that is closest to the way it was truly measured. This last representation would serve best as input to apply distortion corrections and unit conversions. After processing, the 2D interpolated version could be expected to be the clearest way to represent the data. However, one should always be aware of the possible presence of highly localized effects, which could disappear upon interpolation. An example of such effects, is the increased activity of CO_2 electroreduction at grain boundaries of a polycrystalline gold electrode.[4]
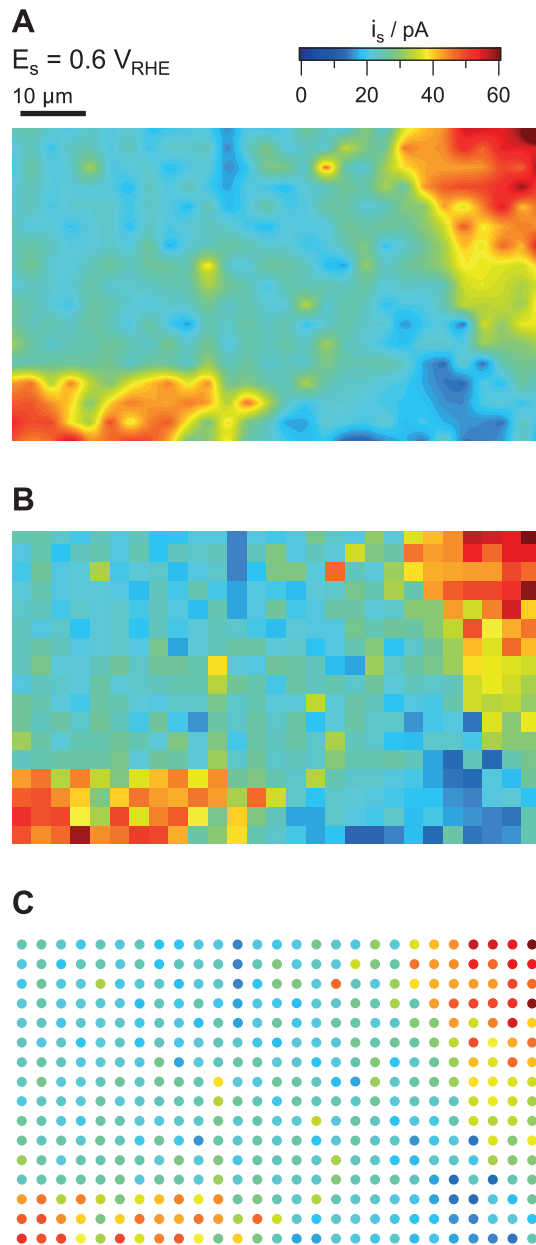
A

$E_s = 0.6\ V_{RHE}$

10 μm

i_s / pA

0   20   40   60

B

C

Fig. E.3 | SECCM data visualization: Various representations of the same SECCM data: **(A)** 2D linear interpolation; **(B)** surface filling 'raw' data; and **(C)** Raw data with appropriate (set) pixel position and size, which should serve as input for distortion corrections and unit conversions.

References

1. Vasile, M. J. & Enke, C. G. The Preparation and Thermodynamic Properties of a Palladium-Hydrogen Electrode. *J. Electrochem. Soc.* **112,** 865 (1965).

2. Macpherson, J. V. & Unwin, P. R. Determination of the Diffusion Coefficient of Hydrogen in Aqueous Solution Using Single and Double Potential Step Chronoamperometry at a Disk Ultramicroelectrode. *Anal. Chem.* **69,** 2063–2069 (1997).

3. Aldous, L. & Compton, R. G. The mechanism of hydrazine electro-oxidation revealed by platinum micro-electrodes: role of residual oxides. *Phys. Chem. Chem. Phys.* **13,** 5279–5287 (2011).

4. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO2 electroreduction activity at grain-boundary surface terminations. *Science* **358,** 1187–1192 (2017).

F | UME methods

UMEs were prepared from platinum wire (50 μm diameter, Goodfellow, 99.99 %) which was electrochemically etched to the desired thickness.[1,2] Next, the wire was dipped in freshly prepared piranha (3:1 v/v H_2SO_4 (Sigma-Aldrich, Puriss. p.a.) and H_2O_2 (Merck)) for a few seconds and rinsed with ultrapure (>18.2 MΩ·cm, Millipore Milli-Q) water. The electrode was made by sealing the wire into a soda lime glass capillary using a butane torch. The absence of bubbles surrounding the seal was confirmed using optical microscopy. A microdisk was exposed by polishing with increasingly fine-grained sandpaper, after which alumina (Kemet α-alumina powder solution) or diamond paste (Kemet diamond emulsion) was used for a final polish on a microcloth (Buehler). To finish, the electrode was rinsed thoroughly with ultrapure water, acetone (Sigma-Aldrich, 99 % Puriss.) and ethanol (Sigma-Aldrich, 99.8 % Puriss. p.a.) after which it was sonicated (Bransonic 2510, Branson) in ultrapure water to remove any residues of the polishing process. When the UME was used for experiments, mechanical polishing and sonicating were applied only when blank voltammetry indicated this to be necessary, to increase reproducibility and 'lifetime' of the electrode (e.g. Pt/glass seal, surface conditions).

Different previously reported (see e.g. Ref. [2–5]) UME cleaning methods were used to prepare the UME for daily use of which the following routine gave the best and most reproducible results. At the start of each day, the UME was subsequently rinsed with ultrapure water; sonicated in ultrapure water (5 min.); cycled 500 times between 0.06 and 1.60 V vs. RHE (0.5 M H_2SO_4 at 1 V·s^{-1}) to yield a blank voltammogram that was reproducible over multiple days when the same pretreatment was applied. In between experiments on the same day, the electrode was rinsed with ultrapure water and cycled (same conditions as before) 100 times. At the end of the day, the UME was cycled 500 times once again, rinsed with ultrapure water and stored in a desiccator until the next use. Adsorption of CO by bubbling through the electrolyte or from methanol decomposition followed by CO stripping, commonly used to clean Pt nanoparticles[6,7], was also tested to clean the UMEs. However, this did not improve the blank voltammetries while increasing the risk of introducing contamination. The platinum electrodes used for comparison (referred to as macroelectrode) have a much larger geometric

surface area (tens of mm^2) than the UMEs and were cleaned by annealing in a butane flame.

All glassware was cleaned by initially boiling in a 3:1 v/v mixture of sulfuric acid (Sigma-Aldrich, Puriss. p.a.) and nitric acid (Sigma-Aldrich, ACS reagent grade) and stored in permanganate solution (1 g·L^{-1} KMnO$_4$ dissolved in 0.5 M H$_2$SO$_4$) in-between experiments. Prior to each experiment, trace amounts of residual permanganate and manganese oxide were removed with dilute piranha, after which the glassware was cleaned by repeated boiling in ultrapure water. Electrolyte solutions were prepared by dissolving the appropriate amount of chemicals in 25 or 100 mL ultrapure water. The electrolyte was purged of oxygen by bubbling argon for 20 minutes.

Two different set-ups were used. The macroelectrode experiments were carried out in a two-compartment electrochemical cell with the reference separated by a Luggin capillary. Microelectrode measurements were carried out in a one-compartment cell in a Faraday cage situated on a weighted table. A Pt wire was used as a counter electrode (CE). A reversible hydrogen electrode (RHE) (blank CVs and catalytic reactions) and a Ag|AgCl|KCl$_{sat}$ electrode (outer sphere redox reactions) were employed as reference electrodes. All potentials are reported versus the reversible hydrogen electrode scale. Potentials were controlled using a potentiostat/galvanostat from either Autolab (PGSTAT12) or Bio-Logic (SP-300). [Ru(NH$_3$)$_6$]·3 Cl (Acros organics, 98%), FcCH$_2$OH (Aldrich, 97%), methanol (Fluka, 99.9% LC-MS CHROMASOLV), N$_2$H$_4$·H$_2$O (Sigma-Aldrich, 98%), NaNO$_3$ (Sigma-Aldrich), KCl (Sigma-Aldrich, ACS reagent grade), H$_2$SO$_4$ solution (Fluka, for trace analysis), and hydrogen and argon (Linde 6.0) were used as received.

All data shown here (except the green curves in Fig. 5.1B and 5.2 on page 72 and 75, respectively) result from a single UME. Other Pt UMEs always showed similar behavior. The geometrical surface area of the electrode was determined via the limiting current of the outer sphere redox couples, assuming a microdisk geometry. Both redox couples were measured in triplo and yielded very similar values for the disk radius (4.2 ± 0.01 and 4.5 ± 0.05 μm for [Ru(NH$_3$)$_6$]$^{3+}$ and FcCH$_2$OH respectively). The average radius of 4.4 μm is in line with observations from optical microscopy.

The electrochemically active surface area was calculated from the hydrogen desorption integral in the region 0.06 < E < 0.6 V after subtraction of the double layer, using the recently revisited value of 230 μC·cm^{-2} for a polycrystalline Pt

surface in sulfuric acid.[6] The ratio between the electrochemically active and geo-metrical surface area yielded roughness factors that were typically in the 10-12 range, which is reasonable comparing the size of the the UME with the polishing material.

References

1. Forster, R. J. Microelectrodes - Retrospect and prospect. *Encycl. Electrochem.* **3,** 160–195 (2002).
2. Zoski, C. G. Ultramicroelectrodes: Design, Fabrication, and Characterization. *Electroanalysis* **14,** 1041–1051 (2002).
3. Sun, T., Blanchard, P.-Y. & Mirkin, M. V. Cleaning nanoelectrodes with air plasma. *Anal. Chem.* **87,** 4092–5 (2015).
4. Evans, S. A. G. *et al.* Detection of Hydrogen Peroxide at Mesoporous Platinum Microelectrodes. *Anal. Chem.* **74,** 1322–1326 (2002).
5. Fromondi, I., Shi, P., Mineshige, A. & Scherson, D. A. In situ, time-resolved normal incidence reflectance spectroscopy of polycrystalline platinum microelectrodes in aqueous electrolytes. *J. Phys. Chem. B* **109,** 36–9 (2005).
6. Chen, Q.-S., Solla-Gullón, J., Sun, S.-G. & Feliu, J. M. The potential of zero total charge of Pt nanoparticles and polycrystalline electrodes with different surface structure: The role of anion adsorption in fundamental electrocatalysis. *Electrochim. Acta* **55,** 7982–7994 (2010).
7. Solla-Gullon, J., Montiel, V., Aldaz, a. & Clavilier, J. Synthesis and electrochemical decontamination of platinum- palladium nanoparticles prepared by water-in-oil microemulsion. *J. Electrochem. Soc.* **150,** E104–E109 (2003).