

## Supplementary information for:

# Electrochemical recovery of Pt/C electrocatalyst: optimization of the potential range on the leaching process and application to an aged MEA

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## S1. Electrochemical cell

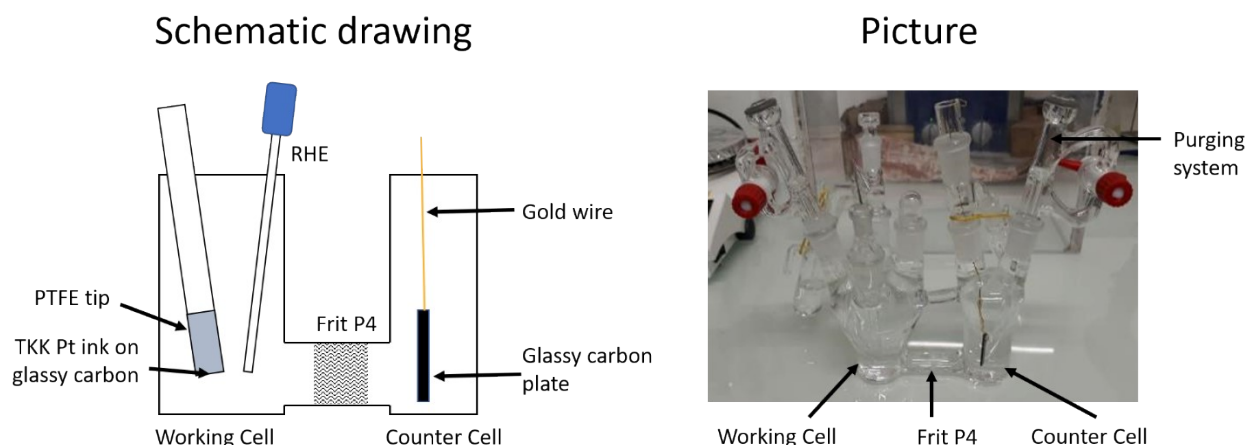


Figure S1 : Schematic representation and picture of the H-cell used for electrochemical dissolution

Figure S1 gives a schematic representation and a picture of the electrochemical H-cell used in this work. The different elements are described in the experimental section for electrochemical measurements on Pt/C catalysts (PTFE RDE tips with deposition of commercial Pt/C-based ink, daily prepared home-made reversible hydrogen electrode (RHE), glassy carbon plate counter electrode and argon purging system).

## S2. TKK Pt/C activity, $H_{UPD}$ and ECSA

Figure S2 presents a voltamperogram of this catalyst TKK Pt/C 20% between 0 and 1.5 V vs RHE. The platinum oxidation begins near to 1.1 V vs RHE and the peak of the reduction of platinum oxide occurs under 0.9 with a peak at 0.75 V. The hatched area represents the charge for calculation of  $H_{UPD}$ .

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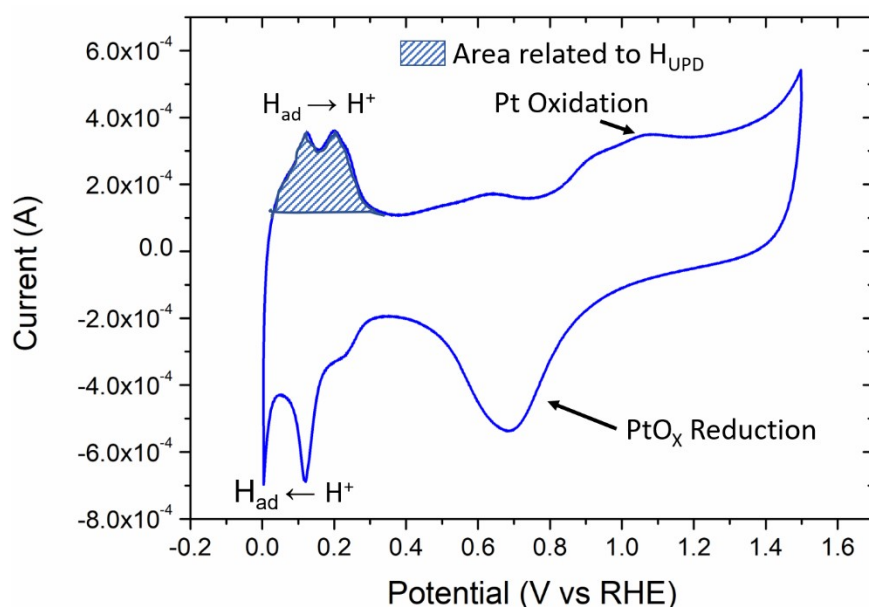


Figure S2 : Voltamperogram of Pt TKK 20 % in 1M  $H_2SO_4$ , scan rate at  $50 \text{ mV s}^{-1}$ . The  $H_{UPD}$  is calculated from the value of hatched area.

The first parameter to quantify how platinum evolves is to determine the electrochemical surface area (ECSA) using the catalyst's CV and more precisely the region of  $H_{ad}$  desorption called the  $H_{UPD}$  region. The ECSA is related to  $H_{UPD}$  charge, which corresponds to the charge determined by the integration of the oxidation current between 0 and 0.4 vs RHE with respect to a baseline defined by the value of oxidation current at 0.4 V vs RHE, the so-called double-layer current (figure S2). Even if Sharma *et al.* demonstrated that this way of ECSA determination is biased due to carbon support baseline, it remains an acceptable approximation [1]. The value of ECSA is not calculated for cycles but rather as a ratio of the  $H_{UPD}$  of the current cycle and the  $H_{UPD}$  of the pristine catalyst. This parameter is called %  $H_{UPD}$  loss and it is defined by:

$$\%H_{UPD}loss = \frac{C}{C_0} \times 100 \#(S1)$$

Where  $C$  is the charge of  $H_{UPD}$  of the current cycle and  $C_0$  the charge of  $H_{UPD}$  of the pristine catalyst. Since ECSA and  $H_{UPD}$  charge are related, the loss of  $H_{UPD}$  is equal to the loss of ECSA.

### S3. Preliminary experiments - Effect of chloride on Pt leaching

Preliminary experiments were carried out with commercial Pt/C catalyst to confirm the role of chloride in platinum electrodisolution by cycling between 1.1 V vs RHE, the potential of  $PtO_x$  formation, and 0.65 V vs RHE to reduce  $PtO_x$ . The electrochemical surface area was determined via hydrogen underpotential deposition ( $H_{UPD}$ ) and  $H_{UPD}$  loss was used to monitor the changes in platinum electrochemical surface area. It results that the addition of chloride from NaCl, at a concentration 100 times higher than platinum, significantly accelerates the dissolution of platinum. 25% of  $H_{UPD}$  loss was reported for 100 cycles in the presence of chloride against 5% without chloride and 87% of  $H_{UPD}$  loss after 3000 cycles against 48% without chloride (figure S3). It confirms that cycling between oxidation and reduction alternating between Pt oxidation and reduction in the presence of chlorides leads to

efficient Pt leaching. It is however not relevant to use  $H_{UPD}$  loss as a descriptor of Pt dissolution since Pt particle size/morphology evolves continuously during the electrochemical protocol complicating the interpretation. Furthermore, chloride poisoning occurs in parallel and biased the ECSA values [2].

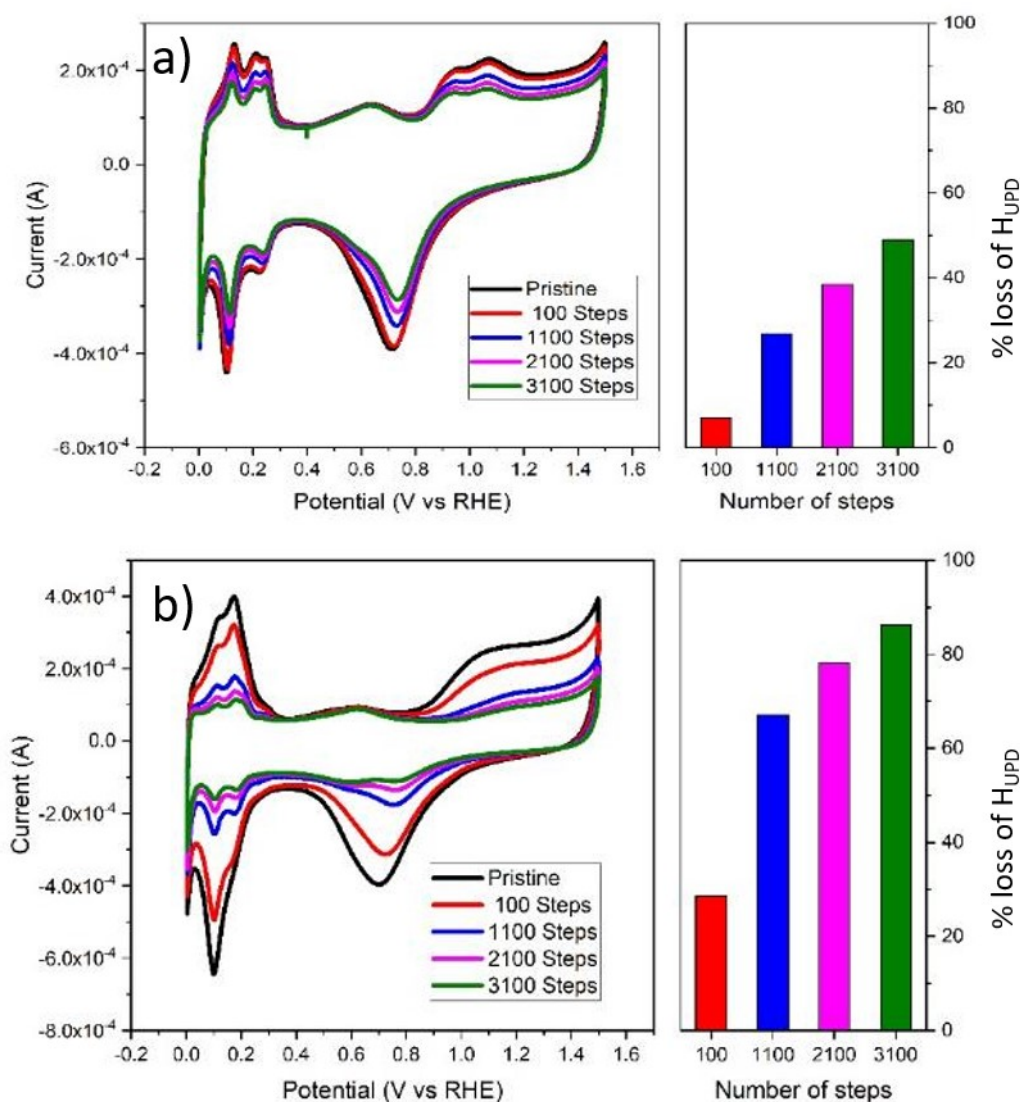


Figure S3: Evolution of voltamperograms from pristine to 3100 cycles and the associated loss of  $H_{UPD}$  for of a) 1 M  $H_2SO_4$  and b) 1 M  $H_2SO_4 + 0.01$  M NaCl

#### S4. Preliminary experiments – Identical Location TEM characterization

Figure S4 presents the Identical Location TEM (IL-TEM) images at different stages of the 1.2-0.4 V vs RHE electrochemical protocol with and without chloride. Without chloride, no or little dissolution of particles happens, but rather aggregation/coalescence of Pt particles. These observations are in agreement with the Ostwald ripening and crystallite migration mechanisms reported in the literature [3]. The major contributor of  $H_{UPD}$  loss is directly linked to the decrease of platinum surface area induced by aggregation/coalescence of particles (figure S3 a). With chloride, substantial growth of particles can be observed but EDX analysis confirms that they exhibit a high content of gold, coming from the instability of the TEM grid used for IL-TEM experiments. This result prohibits the use of IL-TEM to monitor Pt leaching in the presence of chloride.

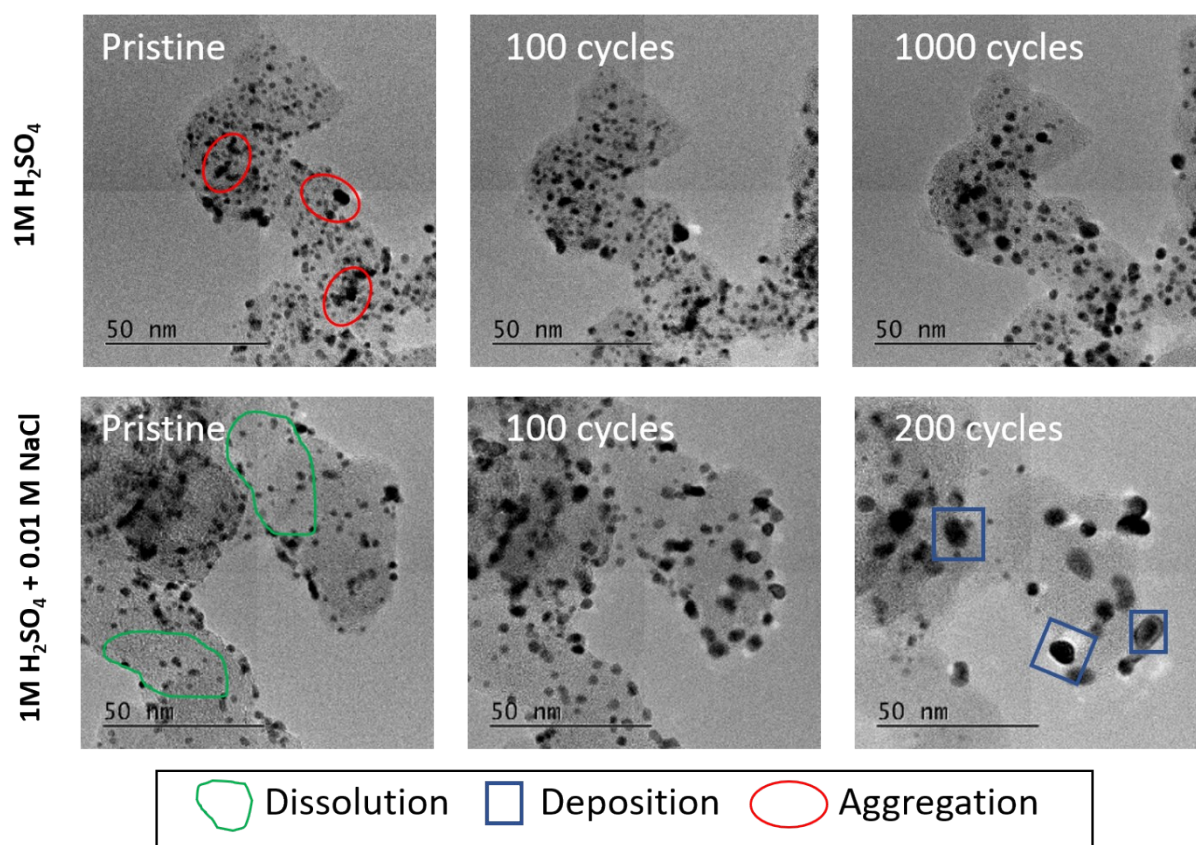


Figure S4: Evolution of Pt particles via IL-TEM observations in 1M  $H_2SO_4$  for pristine, 100 cycles and 1000 cycles and 1 M  $H_2SO_4$  + 0.01 M NaCl for Pristine, 100 cycles and 200 cycles. The red ellipses highlight some examples of aggregation of particles, the green areas highlight some examples of particles dissolution and the blue squares correspond to Pt particles with gold deposition.

## S5. Tables of parameters

The different parameters for analysis TEM-based model are given in table S1 for the 1.2 – 0.4 V vs RHE protocol and in table S2 for the 1.2 – 0.85 V vs RHE protocol.

Table S1 : number of isolated particles, aggregated particles, ratio between isolated and aggregated particles and average projected area of isolated and aggregated particles for pristine, 100, 500, 800 and 1000 cycles between 1.2 and 0.4V vs RHE.

| Number of cycles             | Pristine | 100  | 500  | 800  | 1000 |
|------------------------------|----------|------|------|------|------|
| $n_{iso}$                    | 277      | 240  | 146  | 97   | 97   |
| $n_{agg}$                    | 79       | 142  | 179  | 115  | 176  |
| $r_{iso}$ (%)                | 77.8     | 62.8 | 44.8 | 45.5 | 35.5 |
| $r_{agg}$ (%)                | 22.2     | 37.2 | 55.2 | 54.5 | 64.5 |
| $A_{iso}$ (nm <sup>2</sup> ) | 4.24     | 2.32 | 1.97 | 1.57 | 1.49 |
| $A_{agg}$ (nm <sup>2</sup> ) | 9.48     | 9.23 | 9.45 | 7.43 | 4.93 |
| $r_{A,agg}$ (%)              | 38.9     | 70.2 | 85.6 | 85.0 | 85.7 |
| $r_{A,iso}$ (%)              | 61.1     | 29.8 | 14.4 | 15.0 | 14.3 |
| $A_{tot}$ (nm <sup>2</sup> ) | 5.40     | 4.89 | 6.10 | 4.76 | 3.71 |

Table S2 : number of isolated particles, aggregated particles, ratio between isolated and aggregated particles and average projected area of isolated and aggregated particles for pristine, 20, 100, 300, 500, 700, 900 and 1500 cycles between 1.2 and 0.85 V vs RHE

| Number of cycles                         | Pristine | 20    | 100  | 300  | 500  | 700  | 900  | 1500 |
|--|----------|-------|------|------|------|------|------|------|
| $n_{iso}$                                | 277      | 414   | 252  | 274  | 277  | 299  | 223  | 190  |
| $n_{agg}$                                | 79       | 116   | 58   | 13   | 0    | 0    | 0    | 0    |
| $r_{iso}$ (%)                            | 77.8     | 78.2  | 81.3 | 95.5 | 100  | 100  | 100  | 100  |
| $r_{agg}$ (%)                            | 22.2     | 21.8  | 18.7 | 4.5  | 0    | 0    | 0    | 0    |
| $A_{iso}$ (nm <sup>2</sup> )             | 4.24     | 2.72  | 1.93 | 1.29 | 0.85 | 0.85 | 0.68 | 0.39 |
| $A_{agg}$ (nm <sup>2</sup> )             | 9.48     | 8.24  | 7.24 | 2.14 | 0    | 0    | 0    | 0    |
| $A_{tot}$ (nm <sup>2</sup> )             | 13.72    | 10.95 | 9.17 | 3.43 | 0.85 | 0.85 | 0.68 | 0.39 |
| $\langle d^3 \rangle$ (nm <sup>3</sup> ) | 13.6     | 6.8   | 4.1  | 2.2  | 1.2  | 1.3  | 1.0  | 0.4  |

## S6. Effect of platinum salt in solution

All the experiments of electrodisolution of platinum have been carried out in an initial electrolyte without platinum salt inside the electrolyte. For an industrial application of this process, there will be a significant increase of the concentration of the platinum ionic species in the electrolyte upon cycling. Moreover, in a flow cell, the local concentration could reach a higher level. The study demonstrates that leaching of Pt is more efficient with a reduction potential of 0.85 V vs RHE compared to 0.4 V vs RHE. However, there is still a dissolution of platinum with a reduction potential at 0.4 V. The idea is to test these two reduction potentials with a 1 mM H<sub>2</sub>PtCl<sub>6</sub> added in the electrolyte to check the influence of the presence of Pt salt in the electrolyte. All others experimental conditions remain the same.

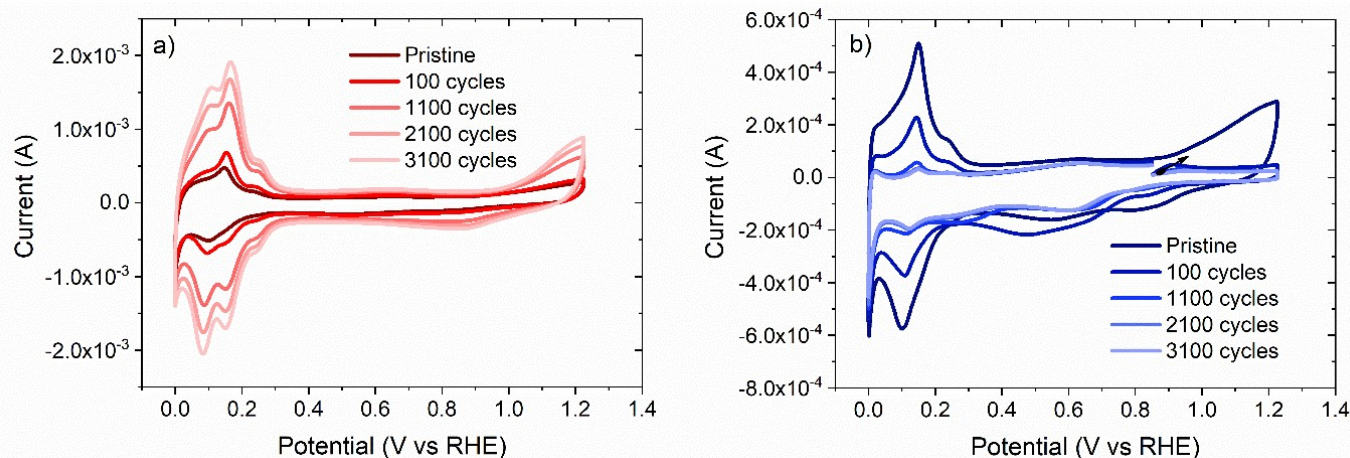


Figure S5 : Voltamperograms of commercial Pt/C in 1 M H<sub>2</sub>SO<sub>4</sub> +, 0,01 M NaCl and 1 mM H<sub>2</sub>PtCl<sub>6</sub> at different stages of the electrochemical protocol between a) 1.2 – 0.4 V vs RHE and b) 1.2 – 0.85 V vs RHE, scan rate at 50 mV s<sup>-1</sup>.

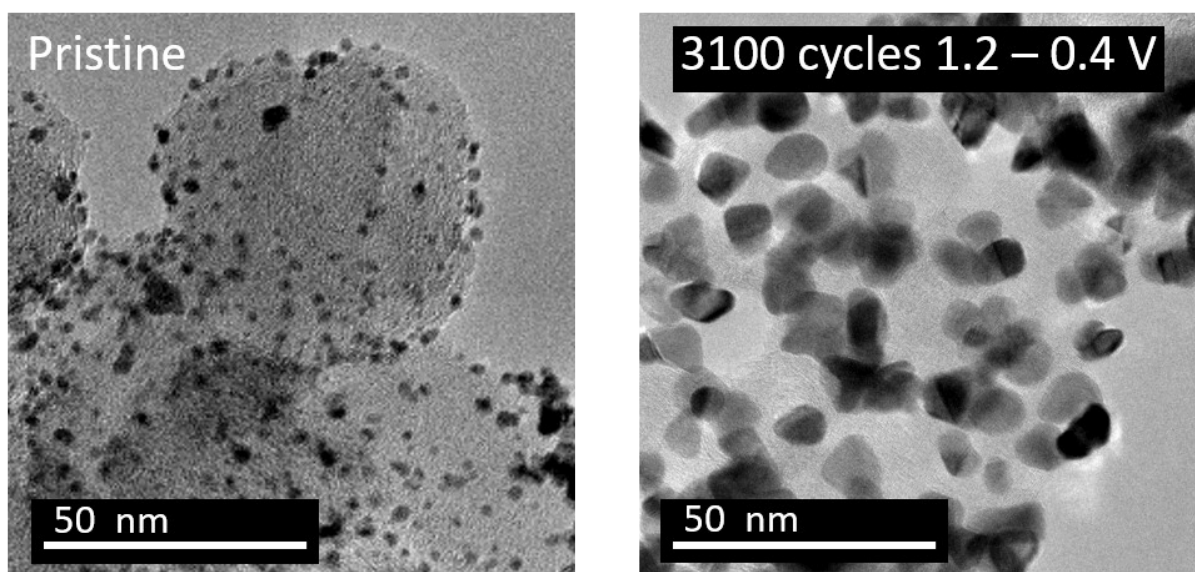


Figure S6: Comparison of Pt particles of the pristine catalyst and after 3100 cycles between 1.2 – 0.4 V vs. RHE protocol in 1 M  $H_2SO_4$ , 0,01 M NaCl and 1 mM  $H_2PtCl_6$ .

For the 1.2 V - 0.4 V vs RHE protocol, the  $H_{UPD}$  increases significantly, signifying huge electrodeposition of Pt in agreement with the TEM images showing Pt particles growth (figure S6). The electrochemical dissolution with such a low reduction potential appears to be largely prevented in the presence of Pt ionic species. Conversely, the  $H_{UPD}$  decreases for the 1.2 V - 0.85 V vs. RHE protocol, proving the efficient dissolution of platinum particles (figure S5). In conclusion, the presence of platinum ionic species in the electrolyte confirms that 0.85 V vs RHE is an optimal reduction potential.

## Reference

- [1] R. Sharma, S. Gyergyek, and S. M. Andersen, "Critical thinking on baseline corrections for electrochemical surface area (ECSA) determination of Pt/C through H-adsorption/H-desorption regions of a cyclic voltammogram," *Appl. Catal. B Environ.*, vol. 311, p. 121351, Aug. 2022, doi: 10.1016/j.apcatb.2022.121351.
- [2] N. Job, M. Chatenet, S. Berthon-Fabry, S. Hermans, and F. Maillard, "Efficient Pt/carbon electrocatalysts for proton exchange membrane fuel cells: Avoid chloride-based Pt salts!," *J. Power Sources*, vol. 240, pp. 294–305, Oct. 2013, doi: 10.1016/j.jpowsour.2013.03.188.
- [3] Y. Shao-Horn, W. C. Sheng, S. Chen, P. J. Ferreira, E. F. Holby, and D. Morgan, "Instability of Supported Platinum Nanoparticles in Low-Temperature Fuel Cells," *Top. Catal.*, vol. 46, no. 3, pp. 285–305, Dec. 2007, doi: 10.1007/s11244-007-9000-0.