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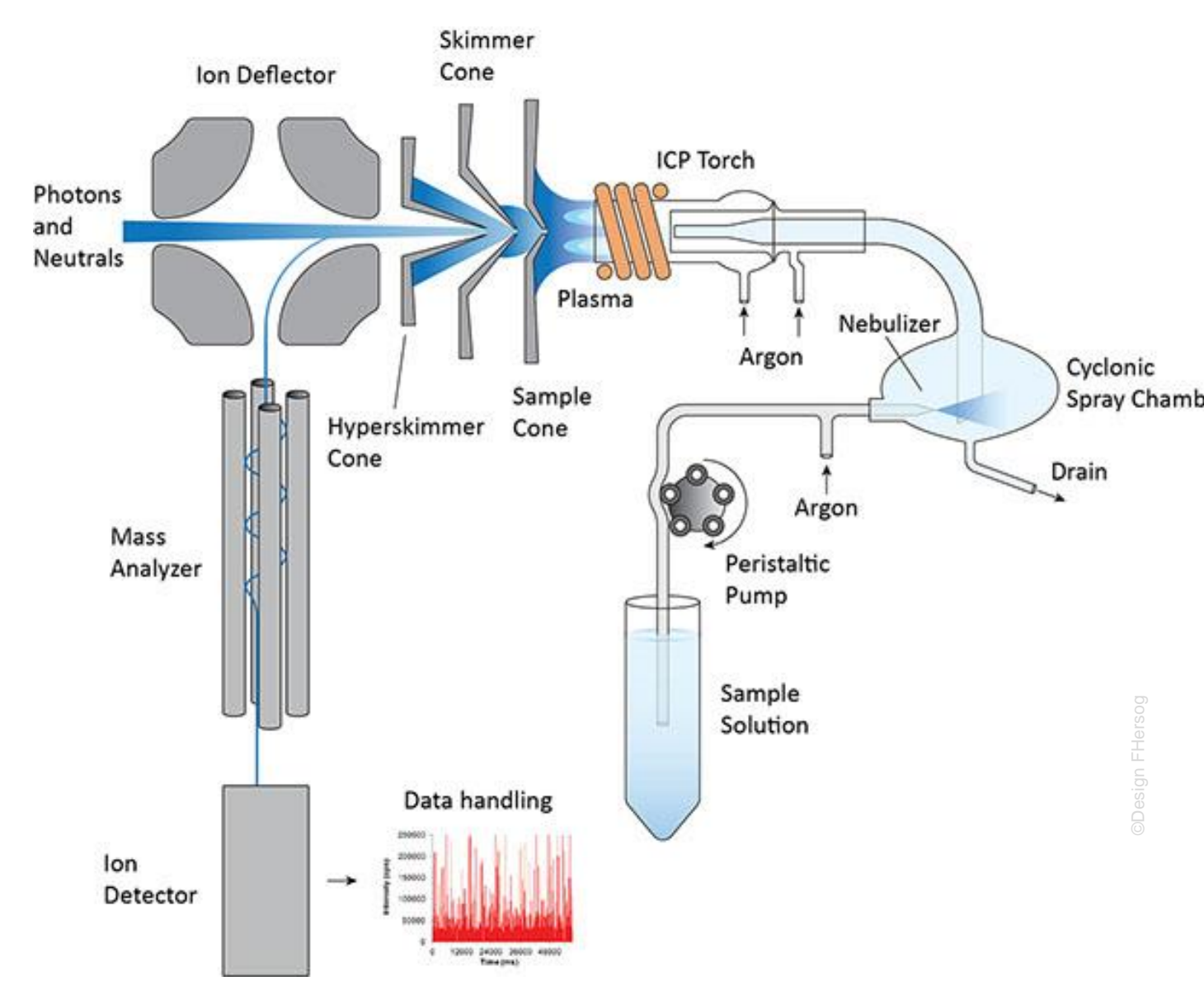
Inductively Coupled Plasma Mass Spectrometry Serving Electrochemistry

Vincent Martin, Kavita Kumar, Arnaud Viola, Camille Roiron, Laetitia Dubau, Frédéric Maillard
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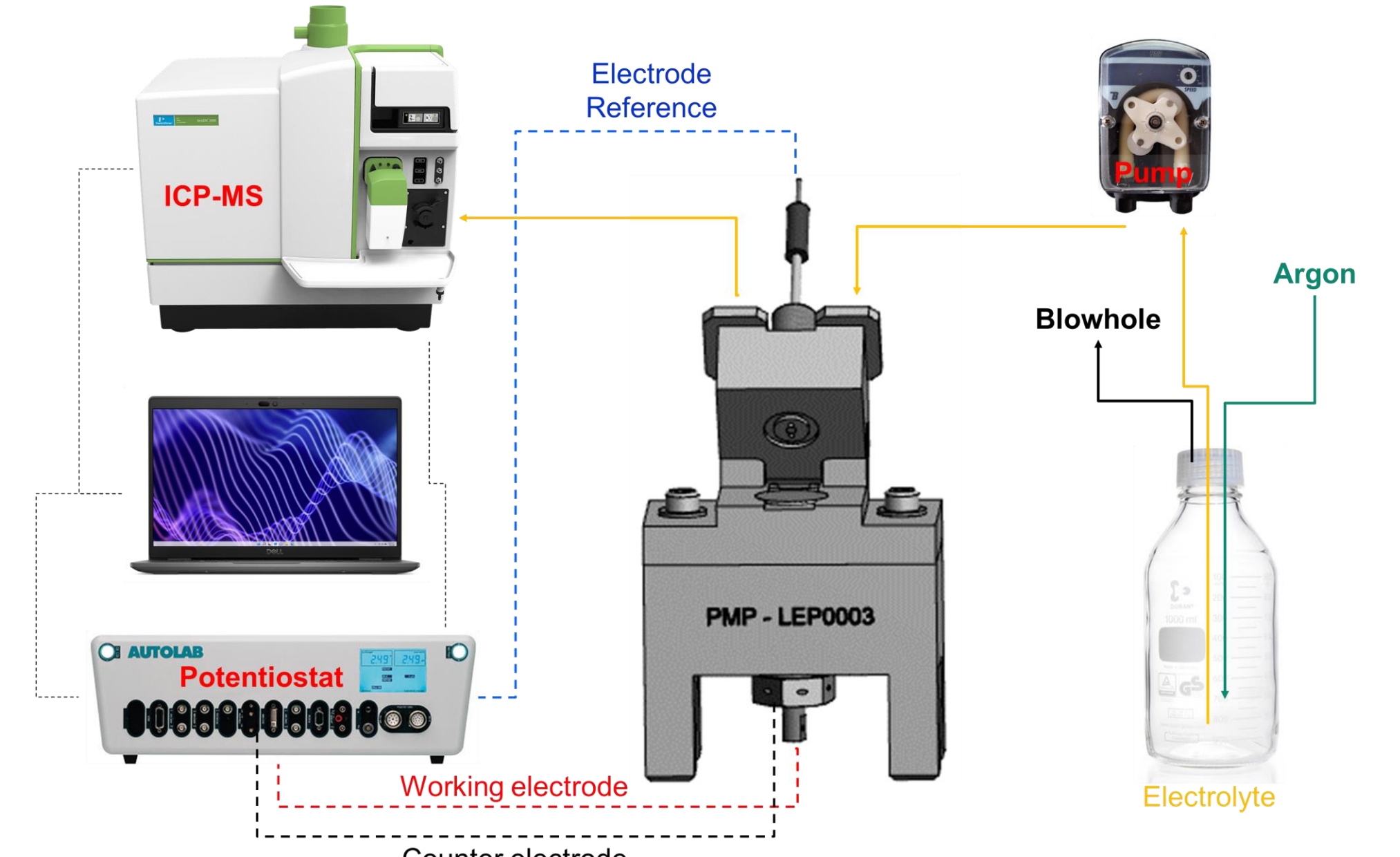
Since their commercialization in the 1980s, inductively coupled plasma mass spectrometers (ICP-MS) have demonstrated exceptional performance in elemental analysis, boasting detection limits in the range of ng/L. This is of particular interest in the realm of electrochemistry.

As of 2024, a dozen laboratories have successfully developed a method to couple an electrochemical flow cell with ICP-MS analysis, offering numerous advantages. The coupling of electrochemistry with ICP-MS facilitates direct, real-time correlation of metal dissolution with potential variations. It also provides fundamental insights into the degradation mechanisms of electrocatalysts and the associated changes in the kinetics and selectivity of electrocatalytic reactions.

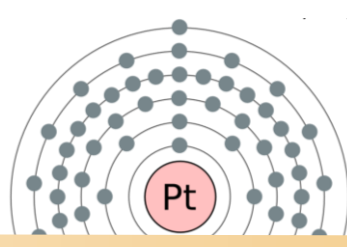
[1] O. Kasian, S. Geiger, K.J.J. Mayrhofer, S. Cherevkov, Chem. Rec., 19, 2019, 19, 2130-2142.



Schematic of on-line ICP-MS

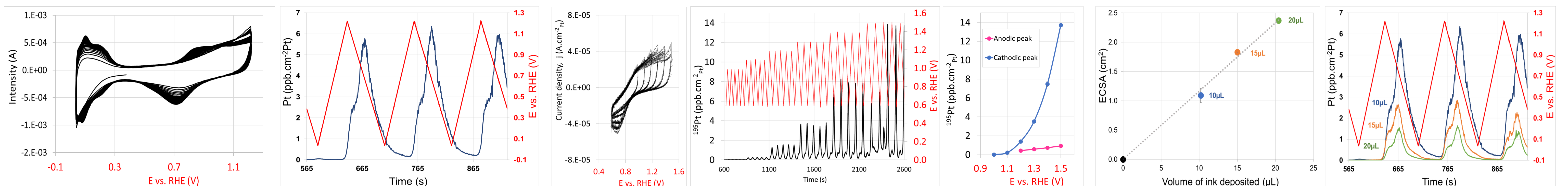


Schematic of EC/ICP-MS coupling



Platinum catalyst

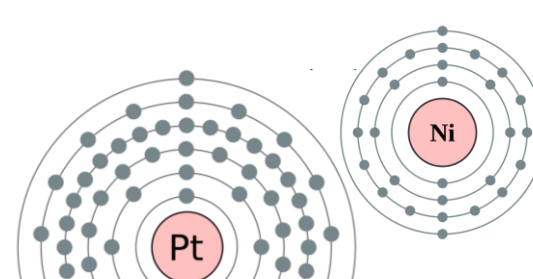
The combination of EC and ICP-MS has unveiled the intrinsic correlation between Pt dissolution and electrochemical potential, revealing that Pt dissolves in two distinct phases : anodic dissolution occurs during the formation of surface oxides, and cathodic dissolution occurs during their reduction (via the so-called "place-exchange" process, where Pt and oxygen atoms swap places at high electrode potential). As Pt²⁺ ions are released into the solution, the residence time in the thin-film electrode used for the online EC/ICP-MS becomes a crucial parameter. When high potential sweep rates are used, the released Pt²⁺ species may be redeposited, leading to apparently low Pt dissolution. The same is true for the thin-film electrode : thick catalyst layers result in high residence time and, when combined with a high potential sweep rate, low apparent Pt dissolution.



➤ Dissolution of Pt occurs in two phases : direct dissolution of Pt (anodic region) and reduction of Pt oxides (cathodic region).

➤ By studying the dissolution of Pt with an increasing potential, we show 2 different phenomena ; a cathodic reaction taking place in volume upper 1,2V (place-exchange) and a reaction limited to the surface (reduction of oxides).
➤ Cathodic dissolution predominates as the upper potential limit increases.

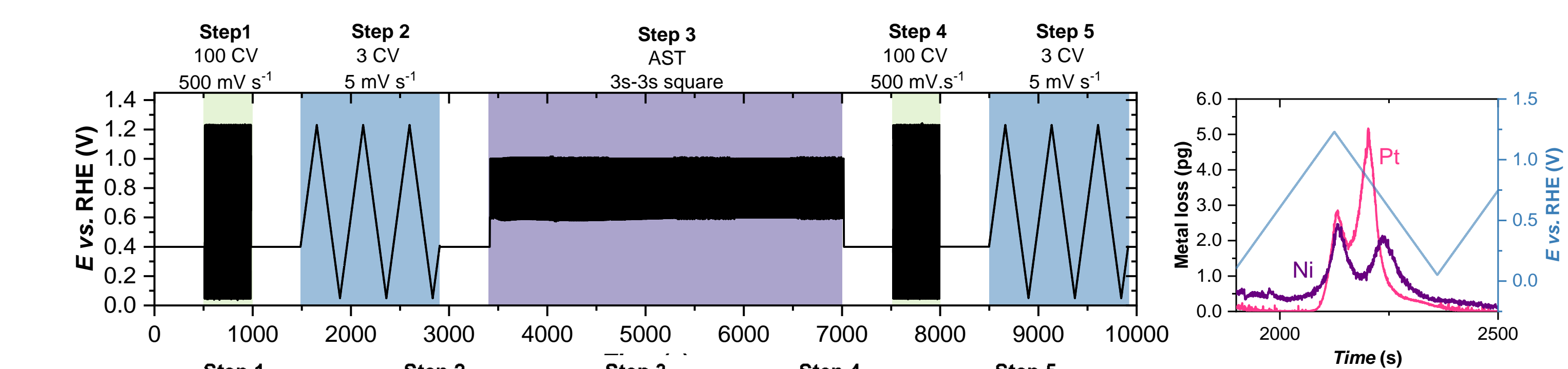
➤ Upon increasing the Pt loading in the thin-film electrode, ECSA increases but apparent Pt being dissolved decreases due to redeposition of Pt²⁺ ions in the thin-film electrode.



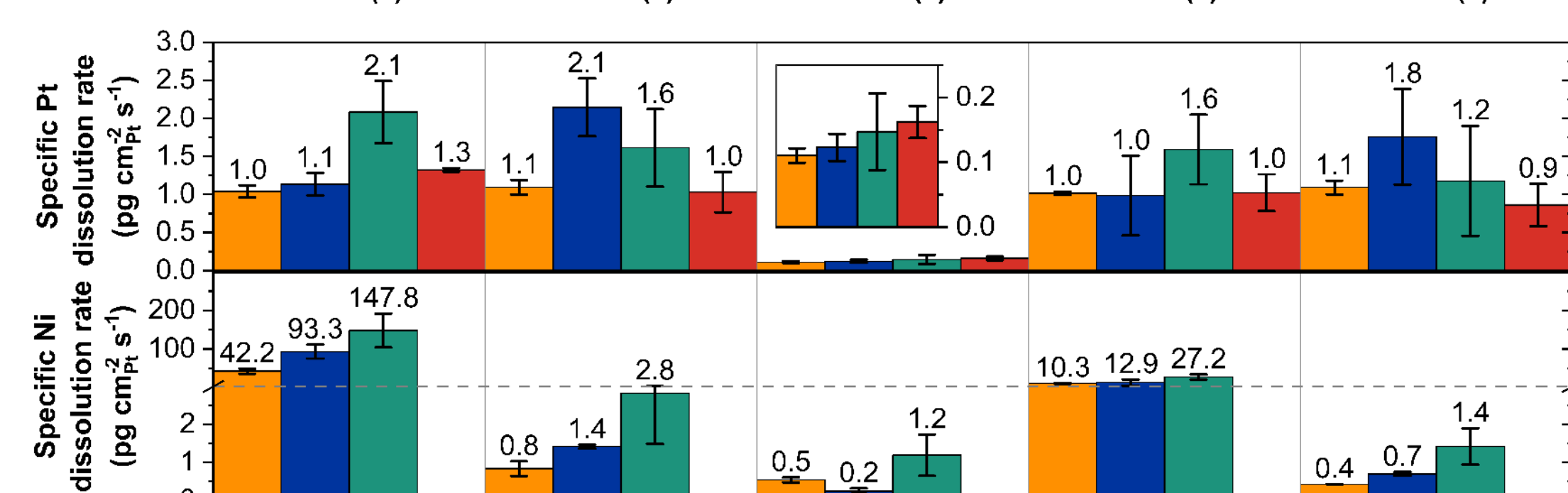
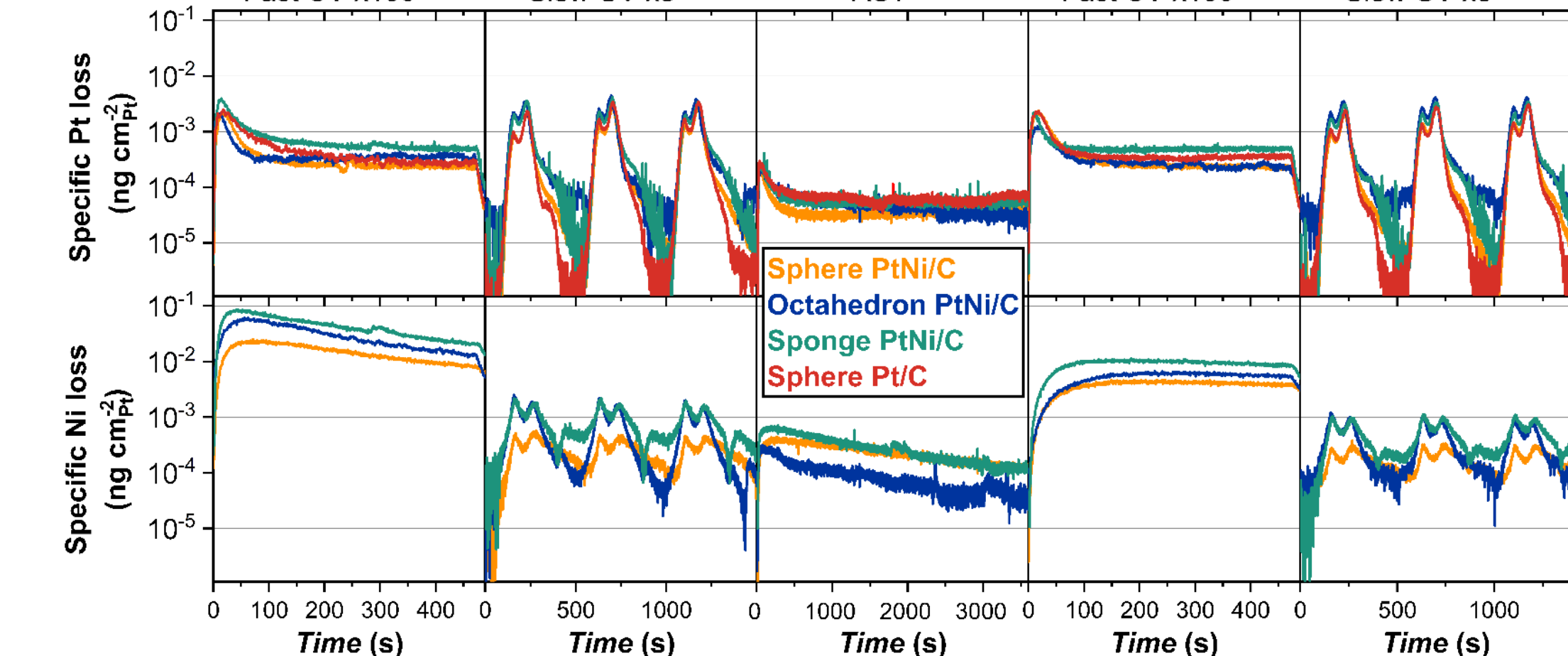
Platinum/nickel catalyst

[3] C. Roiron, V. Martin, K. Kumar, L. Dubau, F. Maillard, Electrochimica Acta, 2024, 477, pp.143760.

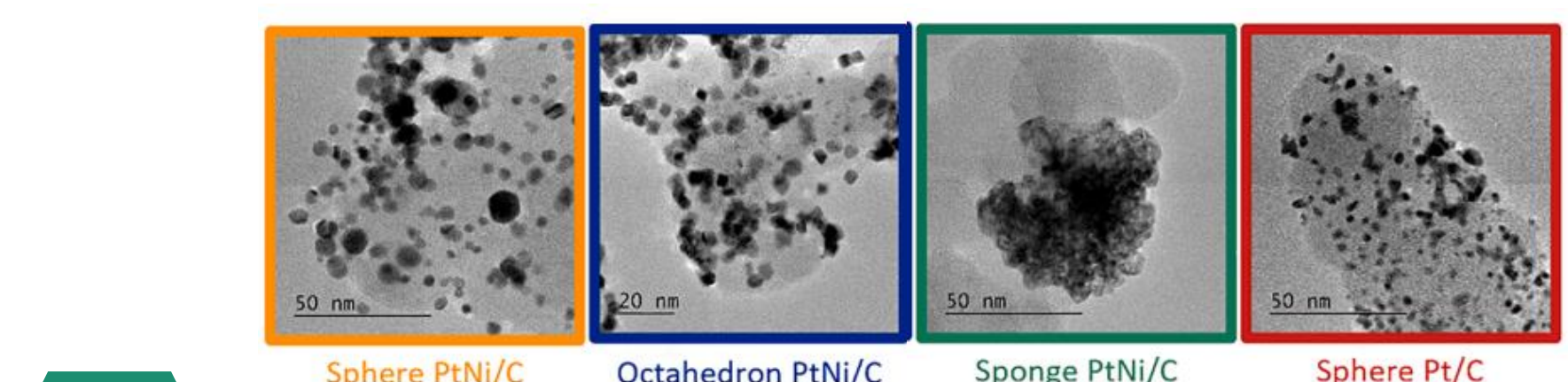
Platinum-nickel nanoparticles supported onto high surface area carbon are used to electrocatalyze the sluggish oxygen reduction reaction (ORR) in proton-exchange membrane fuel cells (PEMFC) cathode. PtNi/C octahedra or truncated octahedra with specifically oriented facets and well-controlled atomic composition are currently perceived as the most promising next-generation ORR electrocatalysts. However, on-line EC/ICP-MS results show that Pt and Ni dissolution rates are morphology-dependent. This study has also showed that long AST are needed for steady state dissolution and catalyst's lifetime prediction.



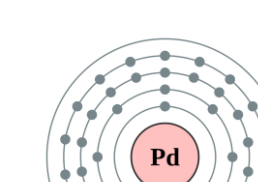
➤ Anodic sweep - Pt and Ni dissolution are simultaneous.
➤ Cathodic sweep - Pt dissolution precedes Ni dissolution.
➤ Pt and Ni dissolution profiles are similar for all PtNi/C catalysts (Sphere, Octahedron, Sponge) - Pt and Ni dissolution mechanisms are independent of morphology.



➤ Very low dissolution during AST compared to CV (effect of upper potential limit).
➤ Almost 2 orders of magnitude between Pt and Ni dissolution during step 1 and 4.
➤ Effect of the sweep rate linked to Pt redeposition (High Ni dissolution at high sweep rate).
➤ Ni dissolution less pronounced after AST (steady state).



➤ PtNi ratio evolves from 3 to 3,6 (30 % of Ni atoms removed by acid leaching)
➤ Amount of Pt dissolved not impacted and less Ni dissolution (*ex situ* acid leaching mitigates but does not prevent the electrochemical dissolution of Ni)

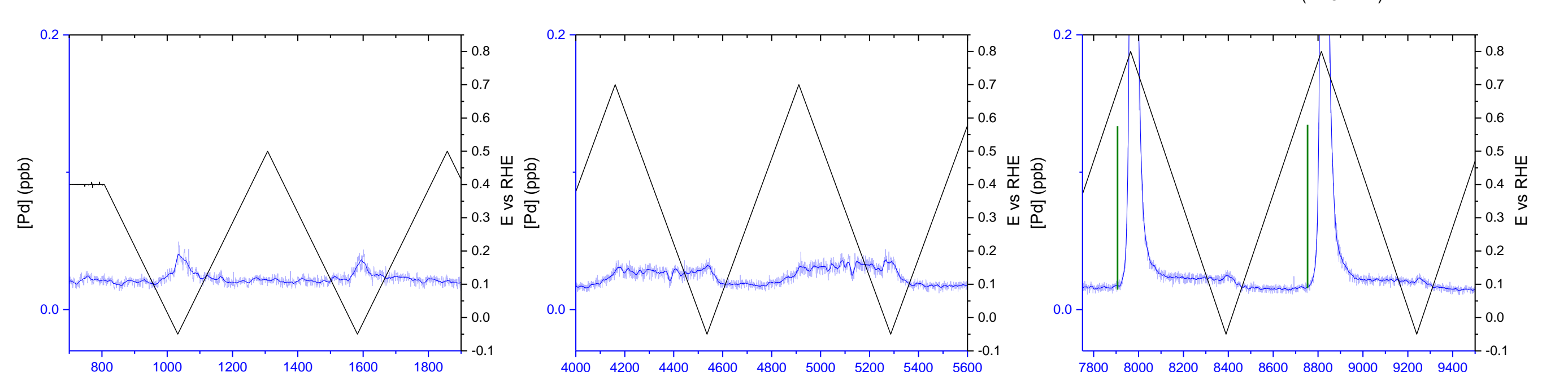
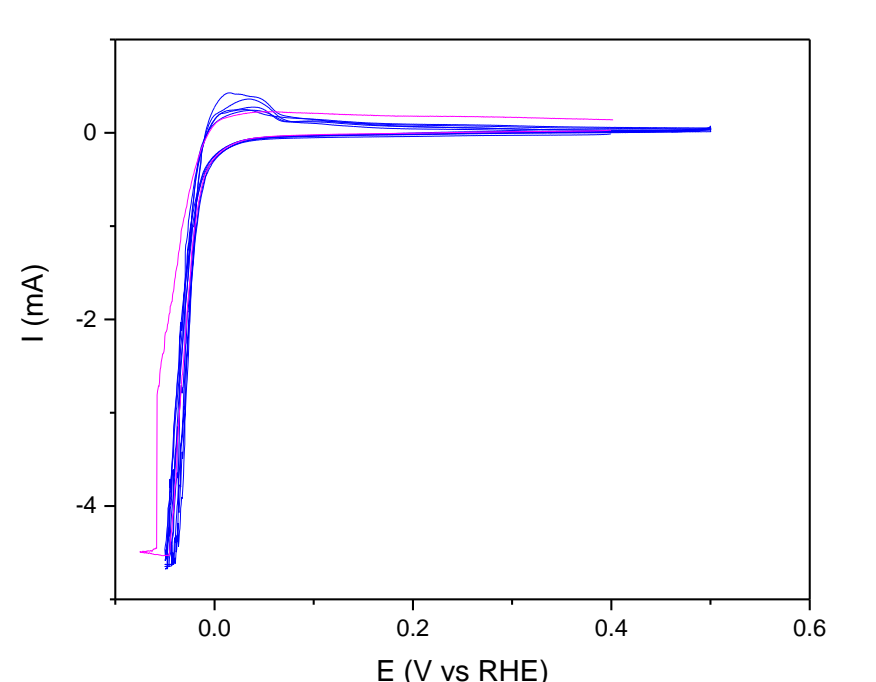


Palladium Catalyst

[2] A. Viola, R. Chattot, V. Martin, G. Tarilina, J. Nelayah, et al., Journal of Physical Chemistry C, 2023, 127 (36), pp.17761-17769.

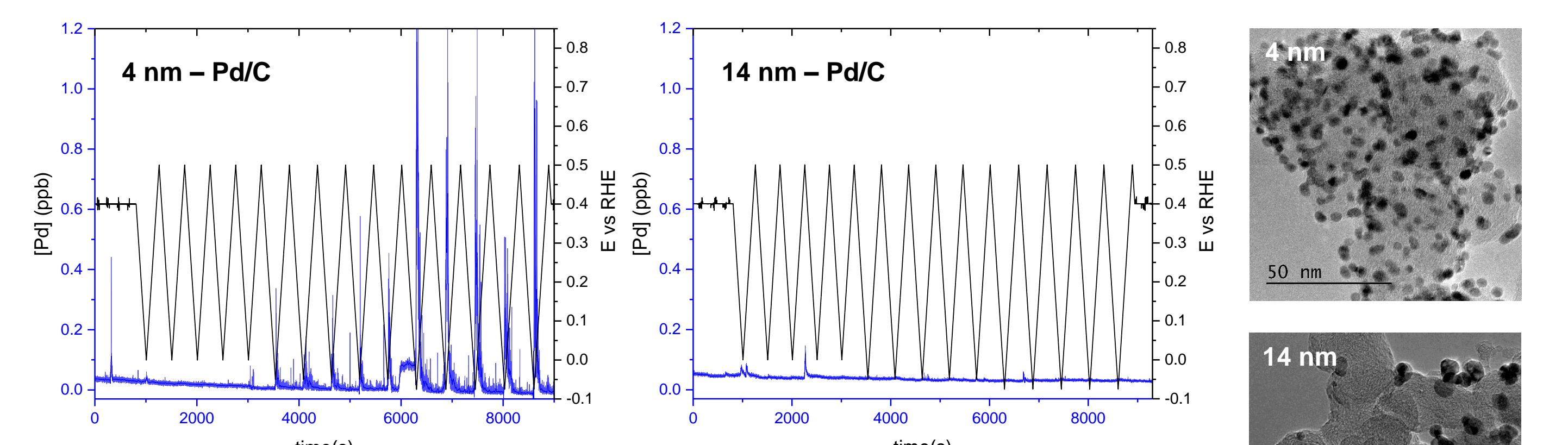
On-line EC/ICP-MS coupling used for understanding of Pd/C catalysts stability during electrochemical cycling. Two phenomena have been identified :

- Direct Pd dissolution at E > 0.7 V vs. RHE (similar to what was observed with Pt/C)
- subtle Pd losses at E < -0.05 V vs. RHE, only corresponding to the HER reaction.



➤ Pd losses in HER conditions. Different from cathodic Pd dissolution
➤ Anodic dissolution of Pd at high potential
➤ The higher the upper potential limit, the higher the Pd concentration in solution.

Our hypothesis are being confirmed with Pd nanoparticles of different sizes. The high noise level of the ICP signal at these potentials suggests the detachment of Pd from the high surface area carbon support or detachment of the thin-film electrode



➤ Larger Pd nanoparticles are more stable at both high (less undercoordinated sites) and low (more sluggish HER kinetics) potentials.
➤ The high noise level of the ICP signal at these potentials suggests the detachment of Pd rather than dissolution.