

# Best practices using EC-MS system for HER

## EC-MS Technical Note #17

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### Introduction

The *EC-MS Application Note #3* gives a thorough introduction on the benefits of using the EC-MS for HER studies. In this document, we list some best practices recommended to obtain the best possible results with your Spectro Inlets EC-MS.

### Best practices when utilizing the EC-MS for HER

The following points are important to consider when designing your HER EC-MS experiment(s):

- Utilize non-aqueous chips in alkaline and standard aqueous chips in acid (never use HF).
- Dependent on the catalyst/support, these materials may reduce during cycling, *i.e.* charge transfers observed by the potentiostat may go towards other reduction process which the EC-MS may or may not be able to measure. Hence, dependent on the materials and the experiment, **full calibration using a calibration gas** for exact quantification of faradaic efficiencies, TOFs and even stability insights is strongly recommended. A procedure for calibration is described in *EC-MS quantification EC-MS Application Note #2*).
- For any materials investigated we urge the users to look up relevant material properties, limitations and consider these in the context of the electrochemical environment, especially the catalyst's/support's dissolution potential(s). We recommend EC-MS users to always confer with *Pourbaix* diagrams [1] for the elemental constituents of the investigated materials.
- Prior to any experiment we recommend users to clean EC-MS components in touch with the electrode/electrolyte following the guidelines described in *Cleaning Procedures EC-MS Technical Note #12*. Always store electrolytes in clean glassware/PFA

bottles and refrain from using alkaline electrolytes more than a day old, as CO<sub>2</sub> uptake may change electrochemical responses. Note, even trace amounts of Pt (or Pd, Ir *etc.*) will dominate as the active site for HER. Pt is dissolved by fresh Piranha, but *aqua regia* is superior at removing these traces.

- Match scan rate and bandwidth filter to ensure minimum feedback waves in the CV is observed, for more info on this important issue see ***Potentiostat instability EC-MS Technical Note #3***.
- Using potentiodynamic methods like LSV and CV is recommended to identify on-set/offset potentials of redox processes. This can be used, for example, to evaluate whether these match with what would be expected from *Pourbaix* diagrams [1]. Note that repeated oxidation/reduction of the catalyst may roughen the catalyst or completely detach/dissolve catalyst material. Also, be aware that significant parasitic current due to reduction processes can be imposed on HER current, when cycling to potentials where the electrode is oxidized.
- For quantitative EC-MS evaluation of HER performance we recommend conducting potentiostatic measurements to minimize the influence of (transient) parasitic processes in combination with a H<sub>2</sub> gas calibration procedure (see ***EC-MS quantification EC-MS Application Note #2***). Note, that if it's sought to measure the actual HER activity of a catalyst, the system should be free of mass transport limitations within the range investigated and the electrolyte should be saturated with H<sub>2</sub> throughout the experiment (i.e. via H<sub>2</sub> make-up gas) to avoid a Nernst shift of the potential scale. Prevent H<sub>2</sub> bubble formation by using currents > -0.3 mA and reduce the ohmic resistance of the system by using sufficiently conductive electrolyte. If necessary, we recommend post-correction for the *IR*-drop.
- Characterization of the catalyst is recommended both prior and post any prolonged electrochemical experiment, also when using the EC-MS. This can be done ex-situ, or electrochemically *e.g.* using *pseudo* stable CVs (at varying scan rates), CO-stripping [2] (see ***CO-stripping Technique EC-MS Application Note #1***) or by integrating known redox features in the CVs.

## References

- [1] K. A. Persson, B. Walwick, P. Lazic, and G. Ceder, "Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states," *Phys. Rev. B*, vol. 85, p. 235 438, 23 Jun. 2012. DOI: [10.1103/PhysRevB.85.235438](https://doi.org/10.1103/PhysRevB.85.235438).
- [2] A. López-Cudero, A. Cuesta, and C. Gutiérrez, "Potential dependence of the saturation CO coverage of Pt electrodes: The origin of the pre-peak in CO-stripping voltammograms. Part 1: Pt (111)," *Journal of Electroanalytical Chemistry*, vol. 579, no. 1, pp. 1–12, 2005.