Mapping pH Variations in the Local Reaction Environment Using *Operando* Fluorescence Confocal Microscopy

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The development of the next generation of fuel cells and electrolysers relies on a better understanding of the phenomena occurring in the local reaction environment (LRE) *i.e.*, in the immediate vicinity of the electrodes.[1] During electrochemical reactions such as the ones involved in the hydrogen electrochemical cycle, the pH in the LRE can vary as a function of the applied potential, diverging from the bulk pH of the electrolyte by up to several pH units. This is due to the involvement of H^+/OH^- in these reactions. Hence, understanding these variations is crucial to optimize the design of new electrocatalysts adapted to their real, rather than hypothesized, operating conditions.

We developed a method allowing for the *operando* mapping of the pH in the LRE (**Fig. 1**). Confocal Laser Scanning Microscopy (CLSM) is a technique that allows for the 3D mapping of a volume with a sub-micrometric resolution. Combined with a library of pH-sensitive ratiometric fluorescent probes and the use of transparent electrodes inside a bespoke electrochemical cell, it allows us to obtain three-dimensional maps of the pH within the LRE. This new tool was validated by evaluating the pH changes in the LRE of electrodeposited Pt electrodes for the hydrogen evolution and hydrogen oxidation reactions (HER and HOR respectively) in 0.1 M $NaClO_4$, before being tested in systems of practical interet for proton exchange membrane fuel cells and electrolysers, *e.g.*, the HER/HOR and the oxygen reduction reaction in acidic media.

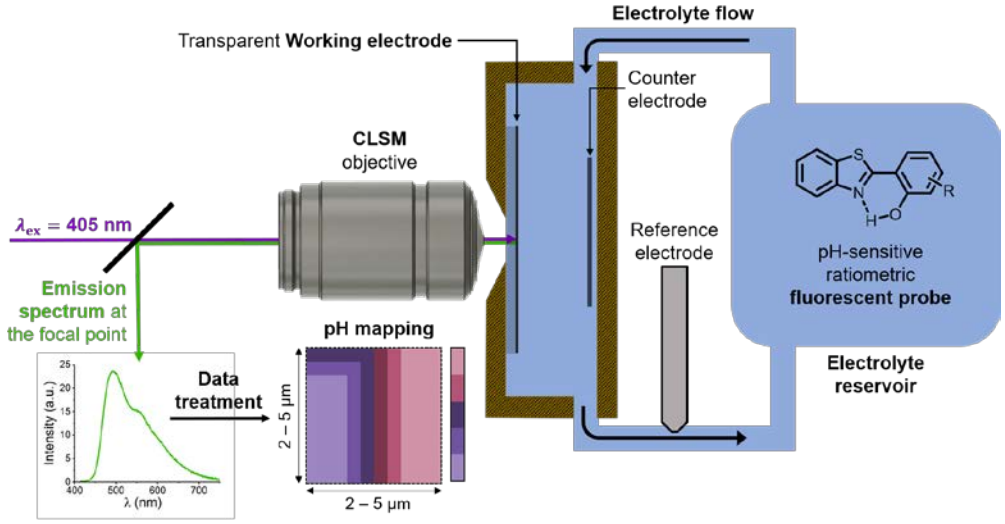

Figure 1 – Scheme of the developed *operando* method. The transparent working electrode is imaged by the objective of the confocal laser scanning microscope (CLSM). An electrolyte containing a pH-sensitive fluorescent probe is circulated in the electrochemical cell and an electrical potential is then applied. The microscope can scan the local reaction environment (LRE) in the three spatial dimensions in order to map the light emitted by the probe as a function of the applied potential, allowing to determine the local pH in the LRE.

[1] Chen *et al.*, Local Reaction Environment in Electrocatalysis, *Chem. Soc. Rev.*, 2024, **53**, 2022

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