Master 2 Physical chemistry and Materials internship

Spatially resolved pH determination in photoelectrochemical reactions

Context

The increase in energy consumption has raised environmental challenges due to the reliance on fossil fuels. To reduce this reliance, hydrogen production could be a solution, as it serves as an energy vector in many sectors. However, this requires to shift from the current means of hydrogen production, *i.e.*, fossil fuel reforming, toward green hydrogen production. Photoelectrochemical (PEC) water splitting emerged as an attractive approach to produce H_2 directly from water and sunlight. For an efficient conversion, it is essential to employ photoelectrodes that combine several key properties, such as strong light-harvesting ability, effective catalytic activity to promote redox reactions and long-term stability. To combine these properties while maximizing the efficiency, the development of composite electrodes that integrate multiple materials is necessary.[1] However, this approach still faces challenges, particularly when discussing the degradation of these high-performing materials due to photo-corrosion. Indeed, local pH changes during photoelectrochemical reaction can be a significant source of degradation of the semiconducting (light absorber) and/or cocatalyst material. They can also significantly alter the reaction efficiency by changing the reaction pathways.[2] Despite their impact, these local pH effects are currently largely unexplored, the development of analytical tools to investigate their extent and their role in the PEC reactions is critical.

The Photocatalysis team of ICPEES developed, in the past years, local PEC techniques to allow for rapid optimization of photoelectrode materials, which incidentally would allow to induce, and study, local pH variations through localized illumination. In parallel, the COMBO & ECE teams of ICPEES developed fluorescent, ratiometric, probes sensitive to pH variations in aqueous media and the microscopy tools associated to allow for an operando assessment of the local pH at electrode interfaces.

Objective

In this project, we will combine pH imaging methods with local photoelectrochemistry to determine the experimental (*e.g.*, light intensity, applied potential) and structural (*e.g.*, photoelectrode design) parameters controlling the local pH variations during a PEC reaction and their range. To reach this objective, the intern will synthesize oxide materials-based photoelectrodes, such as TiO_2 and $BiVO_4$ that could be activiated under UV (365 nm) and visible (450 nm) light respectively. These electrodes will be modified by local photodeposition of cocatalyst particles such as Au, Pt, CoO_x, and NiO_x, with varying sizes and densities.[3] After material (XRD, SEM, XPS) and photoelectrochemical characterizations, the photoelectrodes will be integrated in a cell adapted to both PEC and local pH assessement, with the goal of assessing the feasibility of performing local PEC while simultaneously tracking the local pH

and, then, of measuring both the local photocurrent and local pH and identifying correlations between efficiency, local pH and the properties (*e.g.*, stability) of the composite electrode.

Expected Outcomes

The internship is expected to yield a deeper understanding of the factors influencing local pH changes in PEC reactions and its resulting influence on the material stability. By correlating these changes with properties of the composite catalysts, the project will help optimizing photoelectrodes and, thus, develop more efficient PEC systems. Additionally, enabling local pH detection to domains beyond pure electrochemistry would be of interest in broadening the applicability and impact of the fluorescent and microscopy tools herein used.

Skills and Qualifications

This internship is intended for a Master 2 student in physico-chemistry, or materials science. The student will be trained to carry out photoelectrochemical and spectroscopic measurements. The work will involve materials characterization (UV-Vis spectroscopy, X-ray diffraction, Scanning Electron Microscopy, X-ray photoelectron spectroscopy) and complex *operando* experiments, bibliographic research, data analysis, and active participation in team day-to-day life. The ideal candidate for this internship has a strong background in materials science, chemistry, or a related field, with experience in laboratory techniques and data analysis. Familiarity with photoelectrochemical systems and semiconductor materials will be an advantage. The candidate should be motivated, detail-oriented, and capable of working independently as well as part of a team.

The financial cost to conduct the experiments for the internship is supported by ongoing research projects in the different teams. The internship will take place at ICPEES on the Cronenbourg campus (ZRR). Depending on progress and interest, this internship may also open the door to a PhD on similar topics.

For more information and to apply, please send a **CV and a motivation letter** and your M1 academic transcript **to Thomas Cottineau (cottineau@unistra.fr) and Tristan Asset (t.asset@unistra.fr).**

References

1 J. H. Kim, D. Hansora, P. Sharma, J.-W. Jang and J. S. Lee, *Chem. Soc. Rev.*, 2019, **48**, 1908–1971.

2 F. Liang, F. F. Abdi and R. Van De Krol, *EES Sol.*, 2026, 10.1039.D6EL00057F.

3 T. Favet, S. Sharna, V. Keller, M. A. El Khakani and T. Cottineau, *Materials Today Energy*, 2023, **37**, 101376.