

Insertion Material for (Photo)Catalytic Hydrogen Production (IMatH2)

1. Scientific context of project

In the domain of Aqueous Batteries, the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER) constitute a drastic limitation for their development, limiting the operating voltage of the battery, its coulombic efficiency, its longevity, or even becoming a safety issue depending of the amount of gas formed. Tremendous works have been devoted to find solutions to promote a noncatalytic behavior for the electrode material towards these two reactions.¹ **In this work, we would like to look at inserting electrode material (i.e. ion host in Li-ion batteries) in a disruptive way, from the complete opposite point of view from aqueous batteries, as a noble metal-free (photo)electrocatalytic candidate for HER/OER.** This approach has been so far widely overlooked², yet, in 2020, Yang et al.³ investigated α -Li₂IrO₃ as electrocatalyst for OER, and Hu et al.⁴ used internal built-in electric field formed by ex-situ electrochemically lithiated LiTiO₂/TiO₂ to develop more efficient photocatalyst for OER. Here, we propose to investigate, ***in situ* electrochemically inserted mesoporous (thereby high surface area) anatase TiO₂ as a potential (photo)electrocatalyst for HER in alkaline or neutral media**, where HER kinetics has shown to be sluggish and challenging. In J. Sum's thesis (2022), we have shown that *in situ* formed Li-rich TiO₂ could both enhance HER and also induce solar HER in the VIS range in extremely concentrated aqueous electrolyte (water-in-salt), we are therefore confident that this study will bring very fruitful data for bettering photo(electrocatalysis) materials for HER reaction. In this proposal, we intend to investigate the interplay between cation insertion and HER, playing on both thermodynamic and kinetic factors, like the applied potential, the cations *in situ* electrochemically inserted (H⁺, Li⁺, Na⁺, Mg²⁺, Al³⁺)^{5, 6, 7} changing the nature of the mix of salt present in the electrolyte, their concentrations in the electrolyte, the pH, and eventually the presence of other solutes (redox shuttles, simulated seawater or biological medium) to consider media used in different applications. On the electrode point of view, the crystallite size or degree of crystallinity of the nanoparticles can be tuned. Classical (photo)electrochemistry using non inserted system as reference will allow to highlight favorable (photo)electrocatalytic configurations.

In order to understand how the electrode characteristics and the interface chemistry dictate the catalytic behavior, we will rely on two different operando techniques.

Operando Electrochemical Quartz Microbalance (EQCM)^{8,9} will give access to the nature and the quantity of the species transferred at the interface electrode/electrolyte together with their kinetics. This information is especially precious, since based on electrochemical experiments alone, it is impossible to know the nature of the inserted species (H⁺ or Li⁺ for instance). Film formation can also be characterized through this tool. However, setting up operando techniques is never trivial, and ideally requires a complementary view of the system, in order to adjust the models taking into account, for instance, the electrode porosity, or potential adsorbates at the interface (Solid Electrolyte Interface¹⁰ in the case of TiO₂) for example.

We propose to enrich our approach using **Operando Electrochemical Spectroscopic Ellipsometry (OESE)**.^{11,12} The evolution of the optical absorption intensity in the visible (bare material is white) will give access to the number of Ti³⁺ centers (providing blue color) resulting from cation insertion. This information is especially interesting here since electrochemistry alone will not differentiate in between a reductive current coming from cation insertion or hydrogen production. Besides, data collected in the IR part of the spectrum will give access to the nature of adsorbents present at the interface. Also, an accurate description of the film porosity will be accessible using *ex situ* porosimetric ellipsometry. The here-studied mesoporous films are of especially well-suited for this analysis given their very nice optical quality.

This **fundamental study (Figure 1) examines systematically how electrochemically driven cation insertion/extraction within TiO₂ nanoparticles impacts their interaction with water** (and inversely), in the dark or in the presence of light. In this study, we will induce and observe using (photo)electrochemistry the interplay between the two reactions (i.e. cation insertion and HER). We will also aim at actually understanding the complex drives of this interplay using advanced operando techniques. The originality of the work **is that it is conceptually very simple; yet very rich** given the combination of adjustable parameters available; **and yet very complex** in terms of understandings since it requires following operando dynamical interfaces. This study could certainly feed the **discussions of different scientific communities who are interested in TiO₂ nanoparticles interfacing**

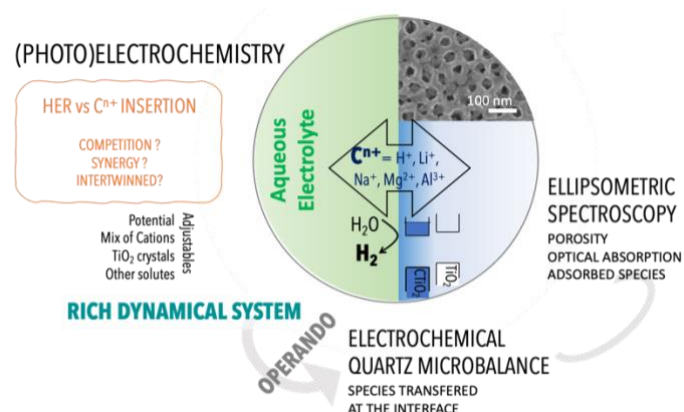


Figure 1. Can Inserting Material play (photo)electrocatalyst for Hydrogen Evolution Reaction in Aqueous Electrolyte ?

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aqueous-based solution (i.e. these nanoparticles are then potential candidate for interfacial cation transport and (solar) HER): like the debate around thermochemically activated proton-coupled electron transfer mechanism¹³, but also technologies coupling energy storage and conversion¹⁴, pollution remediation and water desalination¹⁵, but also health and environmental impact of TiO₂ nanoparticles¹⁶.

This project will be co-led by three teams: **LCMCP (SU) (RMES team, represented by N. Krins, MHP team, represented by C. Boissière)** and **LISE (SU) (represented by H. Perrot)**. LCMCP has mastered anatase TiO₂ mesoporous films synthesis and characterization for years. LCMCP-RMES will bring knowledge in energy-related applications (solar watersplitting, aqueous batteries, supercapacitors, combined conversion and storage technologies), plus all the required equipments (potentiostat, Xenon lamp, IPCE, IMPS/IMVS) to perform basic (photo)electrochemistry. The two specific and highly demanding operando techniques will benefit from the long-term established expertise of LISE for EQCM, and LCMCP-MHP for OESE.

2. Research plan with provisional calendar

This research is built on three main experimental axis (Table 1): I.1. The (photo)electrochemistry (RMES-LCMCP). I.2. Operando EQCM (LISE), and I.3. Operando Ellispometry (RMES-MHP). The first part will consist in exploring the combinations of adjustable parameters that will lead to interesting synergies between cation insertion and HER using (photo)electrochemistry. The best spotted system will be the focus on both operando techniques (I.2 and I.3). The training on both operando is quite advanced and will require to be performed successively. Publication of this fundamental work will be considered in journals of transversal interests: advanced materials (because of its dynamic), advanced interface characterizations, energy storage and conversion, and for more advanced electrolytes (other solutes aiming towards seawater for example), we will be considering environmental journals dealing with water treatment or pollution, since HER could be a side reaction to consider when dealing with nanoparticles in cation-rich media. A simplified provisional calendar is presented in Table 1. Part I.1 has been stopped early for clarity's sake but could be pursued individually with more advanced electrolytes. The PIs will highly encourage the PhD candidate to engage in science diffusion, given the importance of connecting Science and Society.

Table 1. Provisional Calendar of the PhD candidate

Thesis Provisional Calendar	2022				2023				2024				2025			
	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sept	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sept	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sept	Oct-Dec	Jan-Mar	Apr-Jun	Jul-Sept
I. Experimental Part																
I.0. Film Synthesis & Characterization																
I.1. (Photo)Electrochemistry																
I.2. Operando EQCM (OEQCM)																
I.3. Operando Ellispometry																
II. Communication																
II.1. Scientific Publication																
II.2. Thesis Writing																
II.3. Seminar Presentation																
III. Training																
III.1 Lab																
III.2 Doctoral School																

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