

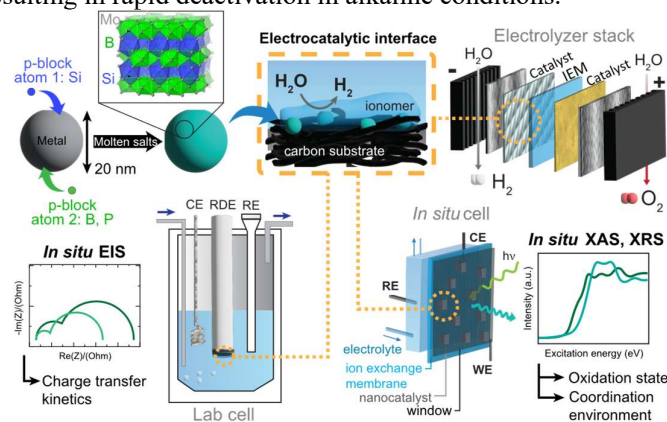
The role of interfaces on silicon-based electrocatalysts during the alkaline hydrogen evolution reaction

A. Scientific context of the project

Context. The production of green hydrogen (H_2) through water splitting has gathered significant interest over the last few years, as it could replace fossil fuels with carbon-free and energy-dense H_2 . Today, proton exchange membrane water electrolyzers (PEMWEs) have reached a relatively high level of technological maturity, producing 0.3 Mt of H_2 or 40% of the global green H_2 production in 2023.¹ This performance stems from their compact membrane electrode assembly architecture, high current densities, and fast reaction kinetics. Despite these advantages, **the scalability of PEMWEs is constrained by materials considerations**: the reliance on perfluorosulfonic acid membranes (e.g., Nafion) and Pt group metals (PGMs), such as Pt for the hydrogen evolution reaction (HER) and Ir for the oxygen evolution reaction, puts a strain on their commercial viability.² Therefore, a transition from acidic to alkaline conditions has been undertaken to retain the architectural benefits of PEMWEs while enabling the use of Earth-abundant materials, leading to anion exchange membrane water electrolyzers (AEMWEs). Unfortunately, AEMWEs lag behind PEMWEs in both efficiency and durability, particularly at technologically relevant current densities.³ A central challenge is the **development of alkaline-stable HER catalysts** that can match the activity and robustness of Pt. While transition metal phosphides and sulfides have shown encouraging performance in acidic media, they undergo surface reconstruction, oxidation, or dissolution, resulting in rapid deactivation in alkaline conditions.⁴

Recent advances suggest that this limitation may be overcome by **expanding the compositional space of HER catalysts beyond conventional binary compounds. In particular, the incorporation of p-block elements into transition metals** emerges as a powerful strategy to tune electronic structure, surface chemistry, and stability. Notably, Portehault et al. recently reported the synthesis of nickel silicophosphide nanocrystals via an inorganic molten salt reaction medium,⁵ enabling the controlled introduction of both Si and P into Ni nanoparticles. This ternary phase exhibits high and sustained catalytic activity for the alkaline HER, highlighting the untapped potential of multicomponent, p-block-modified transition metal catalysts. Other borosilicides, designed in a similar way,⁶ show even higher performances for alkaline HER (not published). These findings point to a largely unexplored family of silicon-based materials as a promising direction for the rational design of next-generation alkaline HER catalysts from Earth-abundant elements. Nonetheless, the origin of these performances remains unclear: stability versus corrosion is probably related to the covalence of the crystal structures provided by the p-block elements, but the atomic and electronic structures of the catalyst surface remain unknown. Additionally, **the role of the interfaces formed between the catalyst, electrolyte, and the ionomer in the catalyst film is poorly understood.** In this project, we propose to study these interfaces for original silicophosphide and borosilicide nanomaterials during the alkaline HER, to **identify design rules for optimized non-PGM electrocatalysts**.

Scientific approach. This project aims to **optimize the activity and stability of silicophosphides and borosilicides** beyond that of non-PGM catalysts reported so far, by combining **systematic**



electrochemical examination with advanced structural characterization. The two central hypotheses are that (1) the incorporation of p-block elements (e.g., Si, B, P) into transition metals modulates water dissociation, intermediate stabilization, and hydrogen/hydroxide adsorption kinetics in alkaline media; and that (2) the nature of the ionomer and of the electrolyte (counter cations) in the vicinity of the catalyst surface will impact adsorption processes, as known for more conventional catalysts.⁷

The nanocatalysts (NCs) will be synthesized in molten salts to activate reactions that otherwise would require too high temperatures.⁸ Our idea is to incorporate the p-block elements by diffusion into pre-made metal nanoparticles dispersed in molten salts, as recently described.⁵ This protocol will deliver nanocrystals of Ni₂Si_{0.7}P_{0.3} and of Mo₅SiB₂, with a diameter of ca. 20 nm, ensuring a high surface area and enhanced mass-normalized catalytic activity. At present, our team is the only one able to design such nano-objects, as shown for Ni₂Si_{0.7}P_{0.3} nanocrystals.⁵ We will apply the approach to original Mo borosilicides.

To relate the NCs to their electrochemical properties, they will be studied on a rotating-disk-electrode (RDE) to decouple intrinsic activity from mass-transport effects. Beyond conventional activity metrics, the electrochemical properties will be evaluated using electrochemical impedance spectroscopy (EIS). In fact, EIS applied in alkaline conditions can distinguish changes in interfacial capacitance, hydrogen adsorption, and overall HER charge transfer kinetics as a function of catalyst composition and structure.⁷ Quantifying those electrochemical observables and correlating them with *ex situ* structural information (X-ray photoelectron spectroscopy, transmission electron microscopy, X-ray absorption spectroscopy (XAS) for Ni, Mo, Si, and P, X-ray Raman spectroscopy (XRS) for B) will highlight structure-activity relationships. Moreover, the impact of the electrolyte and ionomer on the electrochemical interface close to the NCs will be probed through voltammetry and EIS by modulating the pH, cation identity, and ionomer quantity. The cation and polymer chain of the anion exchange ionomer, e.g. Piperion, can play a strong role in tuning the interface in favor of the HER.⁹ To decouple the effects of both components, the electrochemical properties will also be studied using *N*-alkylpiperidinium cations in the absence of ionomer.

To ensure causality between catalyst structure and electrochemical behavior, the synthesized NCs will be investigated using *in situ/operando* XAS within an electrochemical H-cell in the hard X-ray regime, where measurements at the metal (Ni K-edge XANES and EXAFS, Mo K-edge HERFD-XANES) will provide direct insight into the evolution of local coordination environments before, during, and after HER, allowing dynamic structural motifs associated with high activity or degradation to be identified. The Si and P K-edges, and the Mo L_{2,3}-edge, which is very sensitive to oxidation state and coordination,¹⁰ will be monitored in the soft X-ray regime. XRS will enable us to probe the B K-edge as well. Coupled to *operando* EIS, **these studies will relate the catalyst structure and composition, the electrolyte composition, and the catalyst/ionomer ratio to optimize catalytic performances.**

Finally, the most promising catalytic ensemble will be integrated into an AEMWE with porous electrodes to maximize mass transfer to (1) validate the transferability of RDE-derived activity trends to device-relevant conditions and (2) evaluate the catalyst durability under sustained high-current operation. From fundamental kinetics to applied testing, this approach will provide a **rigorous framework for assessing the viability of silicon-based catalysts for next-generation AEMWEs.**

Risks and mitigation

- The synthesis bears no risk for Ni₂Si_{0.7}P_{0.3}, already set,⁵ and a medium risk for borosilicides, for which synthesis conditions will have to be screened to identify the conditions for structure and size control. This two-sided approach mitigates the risks for the overall project.
- *Operando* XAS, HERFD-XANES, and XRS will require access to synchrotron beamlines (SOLEIL-SAMBA/GALAXIE/LUCIA, ESRF-ID26/ID20, ALBA-CLAESS¹¹, MAX IV-HIPPIE, EMIL-BESSY¹²), for which the applicants have extensive experience and a good success rate to call for proposals. Regular XAS measurements can be performed on the lab-scale XA spectrometer recently installed at Uni. Paris Cité, of which the LCMCP is a partner. This will ensure the *ex situ* measurements.
- Material deterioration might take place during XAS measurements. This can be overcome by controlling the beam dose (i.e., beam intensity, focus, beam spot size, systematic scanning) and flushing the cell to prevent accumulation of water radiolysis by-products (i.e., radicals).

Adequacy to the call. The development of new non-PGM NCs for the alkaline HER aligns with the

“*Matériaux innovants pour une société soutenable*” research axis of the iMAT call. By combining a **unique nanomaterials synthesis strategy with a fundamental, mechanism-driven electrochemical investigation**, the project adopts an interdisciplinary approach essential for expanding the performing reach of PGM-free electrocatalysts as part of a complex catalyst-ionomer-electrolyte ensemble. The project bridges the expertise in developing advanced inorganic nanomaterials and electrocatalysts from the Lab. LCMCP with the mechanistic and methodological expertise of the Lab. LISE, toward energy production and storage applications. With this project, iMAT will also establish a **new collaboration**.

Skills and coherence of the team. Dr. Louisia (S.L., CNRS CR, LISE) will lead the project with Dr. Portehault (D.P., CNRS DR, LCMCP) as co-director. The LISE is a world leader in the fundamental investigation of electrochemical systems through EIS. S.L. combines expertise in the study of NCs for electrocatalysis^{11–13} and the application of EIS to alkaline HER.⁷ The LCMCP is a world-leader in the development of innovative nanomaterials. D.P. applies unique synthetic methods, including the use of inorganic molten salt solvents, to design original electrocatalysts.^{5,6,8} Together, this team gathers expertise in the design, synthesis, characterization, and utilization of nanomaterials for electrocatalytic applications. S.L. and D.P. are experienced in using synchrotron radiation and have worked across 10 (7 European) different facilities, including *in situ/operando* characterization of nanocatalysts.^{5,11–14}

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Research plan with provisional calendar

Research steps and deliverables	Year 1		Year 2		Year 3	
	1	2	1	2	1	2
Synthesis and characterization of borosilicides (LCMCP)	■	■				
Synthesis and characterization of silicophosphides (LCMCP)		■	■			
Electrochemical testing of borosilicide (LISE)	■	■				
Electrochemical testing of silicophosphide (LISE)		■	■			
<i>In situ/operando</i> XAS characterization (LISE+LCMCP)			■	■	■	
Electrolyzer + durability testing (LISE)			■	■	■	
Articles writing + publication + dissemination (LISE+LCMCP)				■	■	■
Thesis composition + defense						■