MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Internship Proposal 2022-2023

Specialty(ies) :

☑ Chimie Analytique, Physique et Théorique / *Analytical, Physical and Theoretical Chemistry*
☐ Chimie Moléculaire / *Molecular Chemistry*
☐ Chimie et Sciences Du Vivant / *Chemistry and Life Sciences*
☑ Chimie des Matériaux / *Materials Chemistry*
☐ Ingénierie Chimique / *Chemical Engineering*

Host Institution

Name : Laboratoire de Réactivité de Surface (LRS)
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Hosting Team : LRS

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*Internship period:** Ideally from January 2022 for 5 months

Title: Improving the electrochemical performance of noble-free metal catalysts in water splitting through a novel approach to prepare the active sites

Scientific Project

1. Description of the project

Today, hydrogen (H_2) is at the heart of many research activities as a clean and renewable energy carrier or fuel. One of the most promising hydrogen production technologies is the water splitting[1], which is also an eco-friendly approach that could provide answers to environmental pollution problems (stable output and zero greenhouse gas emission) and the energy crisis. Water splitting corresponds to the simultaneous execution of two electrochemical reactions: the reduction of water at the cathode to form hydrogen (HER) and the oxidation of water at the anode to form oxygen (OER). Both reactions are pH dependent and best performances are achieved for noble metal catalysts (Pt, Ir, Rh). However, the HER suffers from sluggish catalytic activity in basic electrolyte when compared to acidic electrolyte, and the overall mechanism requires an overpotential to occur at an appreciable rate. To influence the kinetics of the HER, a promising way could be to play on the configuration of the electro-catalytically active sites (single-atoms *vs.* small aggregates *vs.* small or medium-size nanoparticles). Recently, mainly in the literature on perovskite materials, a phenomenon called "exsolution" was reported. The latter consists in the

* *min. 5 months not earlier than January, 30st 2023.*
End of internship at the latest July 13, 2023 or Sept. 29, 2023 (dates of graduation).

migration of metals incorporated on bulk sites of the material towards the surface under a reducing thermal treatment. It leads to metal nanoparticles having a controlled size and distribution (depending on the temperature, the composition of the reducing atmosphere, etc.), and being socketed at the surface, thus unable to agglomerate under reaction conditions. On the other hand, in preliminary works carried out at LRS, it was shown that exsolution of metals can also occur within another type of materials, namely hydroxyapatite. In that case, the exsolution leads to highly dispersed metal sites at the surface rather than to nanoparticles. Thus, depending on the materials, the exsolution of metals seems to lead to different configurations of the metal sites, each of these configurations being more or less appropriate depending on the catalytic process of interest. In the present project, the idea is to exploit this new tool, exsolution, to control the configuration of electro-catalytically active sites on noble-free Ni-Co and Co-Fe mixed oxides and thereby improve their performance in the HER. Materials prepared by metal exsolution have already been used in heterogeneous catalysis[2] for reactions such as dry reforming of methane to produce syngas (CO_2, H_2) for energy storage and for further chemical synthesis,[3, 4] and carbon dioxide conversion using high temperature electrolysis.[5] Only few works, however, are reported on water splitting.[6-10] Exsolution can be controlled by different methods,[2] thus allowing for infinite combinations of catalytically active sites. It has also been shown on different systems that exsolution materials seem to be more stable, which is a crucial advantage over other materials.[2]

The main objective is thus to use metal exsolution to develop highly reactive nanocatalysts being able to catalyze both HER and OER.

2. Specific techniques or methods

Materials will be prepared by co-precipitation, and their physicochemical properties will be characterized by techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), infrared, UV-Visible and Raman spectroscopies, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy, etc.

Electrochemical characterization will be performed by cyclic voltammetry at rotating disk electrode (RDE), rotating ring-disk electrode (RRDE), and impedance spectroscopy. The electrocatalytic properties will be benchmarked against those of the base nanomaterials (before exsolution) and Pt

3. Applicant profile

- Student in 2nd year of Master or 3rd year of engineering school with a good background in material science and/or electrochemistry
- Autonomous, meticulous, rigorous
- A good level of English is required

4. References

[1] I. Roger, M. A. Shipman, M. D. Symes *Nature Reviews Chemistry*. **2017**, *1*.

[2] X. Sun, H. Chen, Y. Yin, M. T. Curnan, J. W. Han, Y. Chen, Z. Ma *Small*. **2021**, *17*, e2005383.

[3] S. Joo, O. Kwon, K. Kim, S. Kim, H. Kim, J. Shin, H. Y. Jeong, S. Sengodan, J. W. Han, G. Kim *Nat Commun*. **2019**, *10*, 697.

[4] A. C. Chien, B. Y. Liao, W. Y. Chen *Catalysis Science & Technology*. **2021**, *11*, 4570-4580.

[5] S. Park, Y. Kim, Y. Noh, T. Kim, H. Han, W. Yoon, J. Choi, S.-H. Yi, W.-J. Lee, W. B. Kim *Journal of Materials Chemistry A*. **2020**, *8*, 138-148.

[6] Y. Wei, Y. Zheng, Y. Hu, B. Huang, M. Sun, P. Da, P. Xi, C. H. Yan *ACS Appl Mater Interfaces*. **2022**, *14*, 25638-25647.

[7] K. S. Roy, C. Subramaniam, L. S. Panchakarla *ACS Applied Materials & Interfaces*. **2021**, *13*, 9897-9907.

[8] Y. Jiang, Z. Geng, Y. Sun, X. Wang, K. Huang, Y. Cong, F. Shi, Y. Wang, W. Zhang, S. Feng *ACS Sustainable Chemistry & Engineering*. **2019**, *8*, 302-310.

[9] M. Kim, J. Park, H. Ju, J. Y. Kim, H.-S. Cho, C.-H. Kim, B.-H. Kim, S. W. Lee *Energy & Environmental Science*. **2021**, *14*, 3053-3063.

[10] O. Kwon, S. Joo, S. Choi, S. Sengodan, G. Kim *Journal of Physics: Energy*. **2020**, *2*.