

Postdoctoral fellowship

Greener Oxygenations and Halogenations *via* Electrochemical O₂ Activation

Financial Support : Agence National de la Recherche (ANR - France)

Working contract: 12 months (possible extension)

Starting: January 2023

Gross Salary: 2800€/m

Location: Laboratoire d'Electrochimie Moléculaire UMR CNRS 7591 Université Paris Cité
Bâtiment Lavoisier, 15, rue Jean-Antoine de Baïf, 75013 Paris. (<https://lem-uparis.cnrs.fr/>)

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Key words: Molecular electrochemistry, Redox reactions, Organic synthesis, Flow chemistry

Working environment:

The activity of the Laboratoire d'Electrochimie Moléculaire UMR 7591 (LEM) is centred on the study of chemical reactivity with electrochemistry as the main investigation tool. LEM is composed of 15 researchers and teacher-researchers, 6 technical staff and an average of 20 PhD and post-doctoral students.

The research activities cover all aspects of chemical reactivity. Our research is particularly focused on the study of activation processes of small molecules (O₂, CO₂, N₂) by metal complexes catalysts (Fe, Co, Ni, Mn) in an effort to address contemporary synthetic challenge (electrolytic catalysis) or energy challenges (storing energy into chemical bonds).

Project description:

Oxygenation or halogenation of hydrocarbons are fundamental **oxidation** reactions to incorporate functional groups on an organic backbone for a variety of applications. The economic and environmental contexts require to urgently replace the current energy demanding or harmful technologies with economically viable and environmentally sound alternatives.

Taking inspiration from metalloenzyme such as Cyt P450 where O₂ activation is mediated by earth-abundant metals through the so-called **reductive activation of O₂** paradigm, we develop an original strategy for performing mild oxidation reactions (no harmful chemical oxidants, room temperature...) using complementary synthetic, spectroscopic and electrochemical tools aiming at reproducing their catalytic activities. Our group has contributed to identify metal-activated oxygen intermediates (M-superoxo, M-(hydro)peroxo, and M-oxo) and to decipher reaction mechanisms under catalytically relevant aerobic conditions.^{1,2,3,4,5} Recently, our group has shown that reactive species can be generated following this strategy,^{4,6} which led to the electrocatalytic oxygenation or chlorination of cyclooctene, depending on the presence of Cl⁻.⁷

We now aim at intensifying our research studies on electrocatalytic oxidation of various organic substrates, of major importance in chemical industry, using O₂ and metal complexes that show the most promising catalytic activity.

The project is part of the **ANR GOAL** project which gathers 3 groups: LCI- ICMMO Université Paris Saclay (Pr F. Banse) ; LEM (Université Paris Cité) and ITODYS, Université Paris Cité (Dr. J.-M. Noël).

Activity:

The candidate will study the catalytic activities of selected Fe and Mn complexes. The performances (efficiency and selectivity) of the catalytic system will be quantified and optimized. To achieve this task, the candidate will:

- Analysis of the electrocatalytic activity of the various systems by running cyclic voltammetry or other classical electrochemical methods,
- Run electrolysis on the most promising systems with various substrates and analyses the various product using classical analytical tool (NMR, GS-MS, HPLC),
- When necessary, characterize reaction intermediates (M-oxygenated species) using low T UV-Vis spectroelectrochemistry

Skills:

- PhD-thesis in molecular electrochemistry, physical-chemistry, coordination chemistry
- Practical experience with modern synthetic methods in preparative organic chemistry, such as electrosynthesis, flow chemistry, microwaves etc., homogeneous catalysis and typical treatments (extraction, separation and purification *via* column chromatography, crystallization, lyophilisation)
- Experience in using HPLC, UV, IR, NMR, MS/LC-MS and molecular electrochemistry
- Autonomy in setting up research plans, literature search/survey and continuous follow-up of key research topics
- Mechanistic understanding

Soft skills:

- Fluent in French and/or English
- Comfortable with interdisciplinary and inter-team settings
- Good organisation and communication skills
- Conscious of confidentiality rules
- Clear reporting ability

We are looking for a candidate with a solid experience in coordination chemistry and organic synthesis with knowledge in molecular electrochemistry. Additional skills in bioinorganic chemistry would be appreciated. All applications should include a cover letter and a CV.

¹ R. Oliveira, W. Zouari, C. Herrero, F. Banse, B. Schollhorn, C. Fave, E. Anxolabéhère-Mallart, *Inorg. Chem.* **2016**, *55*, 12204.

² H. Y. V. Ching, E. Anxolabéhère-Mallart, H. E. Colmer, C. Costentin, P. Dorlet, T. A. Jackson, C. Policar, M. Robert, *Chem. Sci.* **2014**, *5*, 2304.

³ A.A. Massie, N. Kostopoulos, E.N. Grottemeyer, J.-M. Noël, T.A. Jackson, E. Anxolabéhère-Mallart *ChemElectroChem* **2022**, *9* (11).

⁴ N. Kostopoulos, C. Achaïbou, J.-M. Noël, F. Kanoufi, M. Robert, C. Fave, E. Anxolabéhère-Mallart, *Inorg. Chem.* **2020**, *59*, 11577.

⁵ N. Ségaud, E. Anxolabéhère-Mallart, K. Sénéchal-David, L. Acosta-Rueda, M. Robert, F. Banse *Chem. Sci.*, **6**, **2015**, 639-647.

⁶ J.-M. Noël, N. Kostopoulos, C. Achaïbou, C. Fave, E. Anxolabéhère-Mallart, F. Kanoufi, *Angew. Chem. Int. Ed.* **2020**, *59*, 16376.

⁷ N. Kostopoulos, F. Banse, C. Fave, E. Anxolabéhère-Mallart, *Chem. Commun.* **2021**, *57*, 1198.