Ecole Doctorale ED 388 Chimie Physique et Chimie Analytique de Paris Centre

PhD proposal

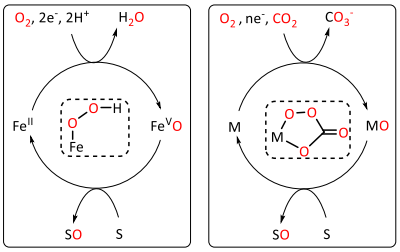
From O_2 electrochemical activation to the development of sustainable oxidation processes of organic substrates

Laboratoire : Institut Parisien de Chimie Moléculaire (IPCM) - UMR 8232- Sorbonne Université
https://ipcm.fr/en/en-home/
eMOCA group : https://ipcm.fr/en/category/research/emoca-group/

Key Words: electrochemistry – molecular catalysis – operando spectroscopy – reductive activation of O_2

Context: Oxidation chemistry in industrial processes constitutes a multimegaton commodity production valuing tens of billions dollars. The current economic and environmental contexts require to urgently replace the energy-demanding and harmful technologies often used with economically viable and environmentally sound alternatives.[1] Through the reductive activation of O_2, metalloenzymes, such as heme and nonheme Fe oxygenases achieve efficient and selective oxygenations by unravelling O_2 oxidizing power. This is achieved through partial and controlled reduction of O_2 bound at the Fe active site, involving sequential e^- and H^+ transfers to the Fe-oxygen adduct and formation of various oxidizing intermediates during the catalytic cycle.[2] We have developed *an electrochemical reductive O_2 activation strategy and succeeded in mimicking the oxygenase activity* by using Fe and Mn porphyrins to generate and to characterize various M-oxygen oxidizing species[3] and to tune their reactivity.[4] This original approach is part of the development of green electrosynthesis in an effort to electrify homogeneous catalysis.[5]

Based on our expertise, **the present PhD project** proposes to generalize this concept to a wider range of substrates both in organic and aqueous media and to focus on the impact of CO_2's Lewis acidity (scheme 1). **Our objective is** to get new and unprecedented knowledge of the electrochemical O_2 reductive activation using Fe and Mn catalysts under mild conditions, focusing on the acidic properties of CO_2 as co-substrate. **Our roadmap includes** *(1)* optimizing and maturing efficient electrocatalytic systems for oxidation of a wide range of organic substrates under homogeneous conditions, *(2)* deciphering the mechanisms of oxidation reactions and providing spectroscopic signatures (UV-Vis, EPR, IR) for intermediates species (M(OO°), M(OO), M(OOH), M(O), peroxocarbonato M(OOC(O)O) involved in the catalytic process (M = Fe, Mn) and finally *(3)* transferring the reactivity to heterogeneous conditions at liquid/solid interfaces.



Scheme 1: left: proton assisted Fe-O_2 activation with Fe(OOH)intermediate; right: M-O_2 activation using CO_2 as acid with putative peroxocarbonato intermediate.

Working environment: Understanding how small molecule (CO_2, O_2, N_2) can be activated using metal complexes is at the heart of the scientific efforts developed in the eMOCA group, which internationally recognized in the competitive field of molecular electrochemistry and catalysis. All necessary equipment and expertise are available in the eMOCA team (synthesis, electrochemistry set-up, GC, GC-MS, LC-MS, UV-Vis, IR spectroscopies, high performance NMR spectroscopy, etc.).

Candidate profile: Excellent MSc degree in chemistry or physical chemistry. Focus on electrochemistry and/or coordination chemistry and interest in mechanistic understanding is appreciated. Self-motivation and the ability to achieve goals independently as well as to contribute effectively to the group. The candidate should be highly motivated, hardworking, able to work as part of a team. No French level required if good proficiency in English (B1).

To apply, submit the following files:

- a covering letter
- a detailed CV
- academic transcripts (Bachelor + Master 1 and first semester Master 2)
- contact information of at least two references (name + e-mail + phone number)

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Gross salary: ~2200 €/month.
Location: Institut Parisien de Chimie Moléculaire (IPCM), Equipe eMOCA - Couloir 32-42 4ieme étage – Sorbonne Université, Campus Jussieu, 4 place Jussieu, 75252 Paris Cedex 05.

References

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