PhD contract offer in Electrochemistry

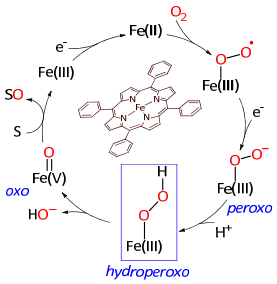
O_2 Reductive Activation in bioinspired Fe complexes. An Electrochemical Approach.

Working contrat: Labex MiChem – Paris Diderot – 3 years; monthly gross salary: 1685 €
Beginning: September 2016
Place: Laboratoire d'Electrochimie Moléculaire (LEM) UMR 7591 UPD-P7 and Laboratoire Interfaces et Systèmes Electrochimiques (LISE) UMR 8235 UPMC-P6 in collaboration with ITODYS UMR 7086 UPD-P7.
Contact : Dr. Elodie ANXOLABEHERE elodie.anxolabehere@univ-paris-diderot.fr, Pr. Emmanuel MAISONHAUTE emmanuel.maisonhaute@upmc.fr, Dr. Frederic KANOUFI frederic.kanoufi@univ-paris-diderot.fr

Summary of the project: Inspired by metalloenzymes activity where O_2 activation is mediated by earth-abundant metals, we propose an original strategy using complementary synthetic, spectroscopic and electrochemical tools (ultrafast cyclic voltammetry and SECM) to study the mechanistic aspects of the activation of O_2 with Fe complexes. Our project will contribute to identify metal-activated oxygen intermediates and to decipher reaction mechanisms under catalytically relevant aerobic conditions. This complementary approach involve expertise from Laboratoire d'Electrochimie Moléculaire and ITODYS (Univ. Paris Diderot) and Laboratoire Interfaces et Systèmes Electrochimiques (Univ. Pierre et Marie Curie).

Context and objectives: The 21th century's challenges require development of economically sound and ecologically viable chemical processes such as the use of molecular O_2 to conduct oxidation reactions in mild conditions.[1] The cleavage of the O–O bond is involved in essential natural processes such as the reductive activation of O_2 taking place in oxygenase enzymes leading to oxygen atom insertion into weakly reactive substrates.[2] The observed reactivity in these processes at the Fe containing active site of the enzymes is a great source of inspiration for developing new earth abundant metal containing molecular catalysts for oxidation reactions. Although a plethora of catalysts have been reported in the literature,[3] the factors that control the O–O bond cleavage as well as the detailed mechanism involved in the O_2 activation reaction need to be better understood. In this context, the major objective of this project is to significantly contribute to a better understanding of the parameters that govern the O–O bond cleavage. The ultimate goal of these fundamental studies is the development of highly efficient catalysts for O_2 electrochemical activation using bioinspired metal complexes.

Strategy and methodology: Fe-peroxo, Fe-hydroperoxo and oxo species have been proposed as key reactive intermediates in the catalytic cycle of Fe containing enzyme (*eg.* CytP450) capable of cleaving the O-O bond and of inserting oxygen atom in organic substrates S (scheme 1). We aim at **reproducing such a catalytic cycle using bioinspired synthetic Fe complexes** (and ultimately other metals such as Mn) **and O_2 electrochemical activation**. In this project we will develop new experimental and mechanistic approaches to examine the formation of the key intermediate FeOOH, and its reactivity (cleavage of the O-O bond) in absence and in presence of substrates. Building on previous results[4], we will use an original strategy based on complementary synthetic, spectroscopic (EPR, UV-Vis) and electrochemical tools (at LEM) including also ultrafast cyclic voltammetry (at LISE) and SECM (at ITODYS) to study the mechanistic aspects of the O_2 activation by bioinspired Fe complexes.



Scheme 1: Fe intermediates species in catalytic cycle of Fe oxygenase enzymes.

Our multiscale (temporal and spatial) approach for tackling intricate reaction mechanisms and evidencing the reaction intermediates involved in catalytic O_2 activation systems is innovative and strongly promising.

Expected skills of the PhD candidate: electrochemistry, physical chemistry, coordination chemistry, spectroscopy. The candidate should show a strong interest in experimental work.

---

[1] Preface on Forum on "Dioxygen Activation and Reduction" W.B. Tolman, E.I. Solomon Inorg.Chem. **2010**, 49, 3555-3556.
[2] (a) B. Meunier, S. P. de Visser, S. Shaik, *Chem. Rev*. **2004**, *104*, 3947–3980; (b) D. Rinaldo, D. M. Philipp, S. J. Lippard, R. A. Friesner *J. Am. Chem. Soc.* **2007**, *129*, 3135–3147
[3] (a) K. Ray, F.F. Pfaff, B. Wang, W. Nam *J. Am. Chem. Soc.*, **2014**, *136*, 13942-13958; (b) D. Mansuy, *Comptes Rendus Chimie*, **2007**, 10, 392-413
[4] (a) 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*, 2304-2310; (b) N. Ségaud, E. Anxolabéhère-Mallart, K. Sénéchal-David, L. Acosta-Rueda, M. Robert, F. Banse *Chem. Sci.* **2015**, *6*, 639-647;