
Working contract: 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 O₂ 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 O₂ 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 21st century’s challenges require development of economically sound and ecologically viable chemical processes such as the use of molecular O₂ 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 O₂ 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 O₂ 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 O₂ 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 O₂ 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 results⁴, 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 O₂ activation by bioinspired Fe complexes.

Our multiscale (temporal and spatial) approach for tackling intricate reaction mechanisms and evidencing the reaction intermediates involved in catalytic O₂ 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.