PhD proposition at Laboratoire d'Electrochimie Moléculaire - Paris - France

Title : Electrochemical O_2 Reductive Activation using bioinspired Fe and Mn complexes.	
Key words : Molecular electrochemistry – spectroelectrochemistry – Fe and Mn complexes synthesis – Electrocatalysis	
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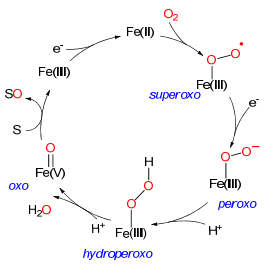
Contract : 3 years; monthly gross salary: 1685 € ; starting; Oct 2018	

Project summary : 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 to study the mechanistic aspects of the activation of O_2 with Fe and Mn complexes. Our project will contribute to identify metal-activated oxygen intermediates (M-superoxo, M-(hydro)peroxo, and M-oxo) and to decipher reaction mechanisms under catalytically relevant aerobic conditions. Concomitantly, the complexes that show the most promising catalytic activity will be tested for electrocatalytic oxidation of organic substrates with O_2. The performances (efficiency and selectivity) of the catalytic system will be quantified and ultimately optimized.

General Scientific context : The 21th century's challenges require development of economically sound and ecologically viable chemical processes. The ideal oxidant for "green" oxidations is O_2 for it is abundantly available, inexpensive and environmentally benign (H_2O as by-product). Due to O_2 triplet state (S=1), oxidation reactions with O_2 suffer from huge activation energies which discard its use under mild conditions. Thus, O_2 needs to be activated, and this can be achieved through reduction following the so-called *reductive activation of O_2* paradigm. Metalloenzymes, such as Fe oxygenases achieve highly efficient and selective oxidations under mild (physiological) conditions unravelling the O_2 potent oxidizing power through its reductive activation. This corresponds to a *partial and controlled reduction of O_2 bound at the metal active site via* sequential e^- and H^+ transfers to achieve O-O bond cleavage and generate the reactive high valent Fe-oxo (FeO) species. 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. In particular various intermediates such as Fe-superoxo (FeOO•), Fe-peroxo ($FeOO^-$), and Fe-hydroperoxo (FeOOH) have been evidenced in the enzymatic cycle (scheme) and synthetic analogues have been chemically prepared. Although a plethora of catalysts have been reported in the literature, 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, electrochemical reductive activation of O_2 is a highly promising approach that will contribute to a better understanding of the parameters that govern the reactivity of the oxygenated intermediates. Being able to control this reactivity is a key step for the development of electrosynthetic processes for the controlled oxidation of organic substrates using highly efficient bioinspired metal complexes as catalysts. In this context our objective is to mimic the catalytic cycle using bioinspired synthetic Fe (and Mn) complexes and electrochemical O_2 activation. As such we will ultimately develop highly-efficient catalysts using O_2 as the oxidant.



Laboratory place in the context : Understanding how small molecule (CO_2, O_2, N_2) can be activated is at the heart of scientific progress of REACTE team at LEM. In the case of O_2 activation, we recently evidenced the parameters that govern the breaking of the O–O Bond *vs.* Mn–O bond in a Mn–OO peroxo complex,[1] but also identified for the first time the electrochemical reduction of the Fe–O_2 adduct resulting from O_2 complexation to an Fe(II) porphyrin[2] or non-porphirin complex[3] (coll. Pr. F. Banse, ICMMO, Univ Paris-Saclay). Such cases illustrate the strenght and relevance of our approach combining bioinspired complexes, spectroscopy and electrochemistry, in this internationally

competitive field.[4] Building on our expertises and collaboration, we want to make further headways in understanding O_2 reductive activation mechanism, but also in developing electrocatalytic systems for organic substrat oxidation.

Objectives. Our objectives are to generate oxidizing species from O_2 using earth-abundant metal catalysts (Fe, Mn) under mild conditions. Electrodes will be used to inject electrons in a controlled manner, reminiscent of the role of reductases in metalloenzymes. Starting with Fe complexes, our guidelines are : *(i)* to identify and optimize the electronic and electrostatic parameters that govern the coordination of O_2 to Fe yielding the Fe-superoxo and its subsequent controlled reduction to Fe-(hydro)peroxo species; *(ii)* to understand how these intermediates evolve into the high valent FeO upon O-O bond cleavage; *(iii)* to carefully examine the reactivity of FeOO•, FeOO(H) and FeO in the absence and in the presence of an organic substrate, and to dissect the mechanisms involved in the oxidation reaction; *(iv)* to develop rationally optimized Fe-based efficient systems for electrochemical reductive activation of O_2 and test them in catalytic oxidation of organic molecules. Taking advantage of our previous expertise, we will run the same approach on Mn complexes.

Strategy and methodology:

The ultimate goal is to perform the electro-assisted catalytic oxidation of organic molecules by O_2. Achieving such a goal requires to better understand the electrochemical activation of O_2 at a metal center. We previously reported on the electrochemical formation and reactivity studies of metal-peroxo intermediates resulting from the interactions between metal complexes, O_2 and electrons.[1-3] Molecular electrochemical approaches are extremely powerful to elucidate complex reaction mechanisms. These strategies consist in adjusting the spatial or temporal electrochemical observation window to the characteristic kinetics of the system allowing deciphering reaction mechanisms (reaction orders, number of electrons involved, etc.). Our approach combine the following parts:

1- Synthesis and characterization of LFe complexes (performed in collaboration with ELIAS group at LEM). Modulation of the Fe coordination sphere, resulting both in modification of E^0 and O_2 activation, will be obtained by modifying the ligand. Note that such a case has proven to be effective in the case of modified Fe porphyrins used as catalysts for CO_2 activation in REACTE group at LEM.[5]

2- Using Fe^{II} complexes as starting precursors, electrochemical access to $Fe^{III}OO^{-}$ species will be studied according to the reaction $Fe^{II} + O_2 + e^- (+ H^+) \rightarrow Fe^{III}OO(H)$. Reactivity of the $FeOO^-$ and FeOOH will be explored using cyclic voltammetry (CV). Preliminary results have been obtained in the case of Fe porphyrin $F_{20}TPPFe^{III}Cl$. Simulations show that the catalytic current depends on the proton content and the CV scan rate. In a fashion similar to redox catalysis,[6] valuable kinetic studies requires to access high scan rates (>10^4 V/s are expected) comparable to the rate of the protonation or the O-OH bond breaking steps. In presence of organic substrate (S), similar studies will give access to the kinetics of the oxidation reaction Back and forth interactions between Fe complexes synthesis and electrochemical studies will lead to the identification of the parameters governing the key steps involved in the O_2 activation.

3- The final objective is to set the optimal electrochemical conditions (solvent, source of proton…) to perform the catalytic oxidation of organic molecules by O_2. We will run preparative scale electrolysis on $\{Fe^{II} + O_2 + e^- + H^+ + S\}$ systems displaying catalytic response and quantitatively analyze the products using chromatography.

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