PhD proposal

Electrochemistry and Spectroscopies operando for reaction monitoring in molecular catalysis. Application to CO_2 reduction and O_2 activation

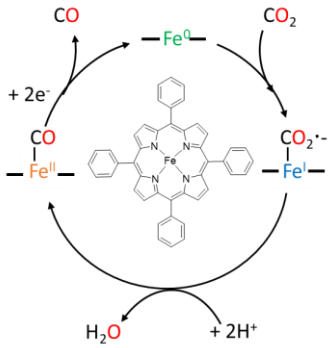
Laboratoire : Laboratoire d'Electrochimie Moléculaire UMR 7591 : http://www.lemp7.cnrs.fr/
Equipe REACTE: https://reacte.lem.univ-paris-diderot.fr/

Key Words: spectroscopies operando; spectroelectrochemistry, XAS, IR; mass spectrometry; molecular electrocatalysis; activation of small molecules

Context: Electrochemical activation of CO_2 is an extremely active and competitive research area as the field of carbon capture and utilization (CCU) is highly attractive and a de-carbonized pathway towards high value chemicals using renewable electricity sources.[1] Thus fundamental knowledge is a pre-requisite to better understand the reaction mechanisms that are at play in the CO_2RR, to improve catalysis and ultimately increase operational cost of electrolytic process. In this context, in collaboration with beam scientists at SOLEIL, REACTE group at LEM has made recent pioneering advances in developing new spectro-electrochemical set-up for coupling X-ray absorption spectroscopy (XAS) to cyclic voltammetry (CV) in order to identify and spectroscopically label intermediate species that are critical for the CO_2RR.

One specificity of our studies relies on the development of cells and studies aiming at using molecular catalysts, either in homogeneous solutions or deposited at conductive carbon electrodes. We have focused our study on Fe porphyrins, based on our great expertise in electro- and photo-driven CO_2 reduction[2] and O_2 activation[3] using these complexes as molecular catalysis.

The present PhD project proposes to intensify the use of this very innovative approach for XAS experiments, IR spectroscopy and Mass spectrometry. This approach, which until now has been little developed by other groups[4] will ultimately provide design guidelines for new CO_2 reduction catalysts and suggest catalytic pathways in order to reach higher selectivity and ultimately orient reactions towards the formation of C-C bonds. This approach will also be applied to O_2 activation using the same Fe porphyrin (scheme 1). These operando approaches will allow to determine the geometric and electronic structures of transient reaction intermediates and provide unprecedented mechanistic insights. This knowledge will help designing catalysts with improved efficiency and selectivity. The candidate will acquire knowledge in molecular electrochemistry, spectroscopies, mechanistic analyses and electronic structure determination to produce unprecedented results that will lead to high quality scientific production.



Scheme 1 : Possible mechanism for the electrocatalytic reduction of CO_2 into CO with FeTPP complex.

Working environment: Our group, REACTE ("Reactivity and Catalysis using Electron Tranfers",) is recognized at an international level in the field of molecular electrochemistry and electron transfer reactivity. The group have established a strong collaboration with Dr. Benedikt Lassalle at SOLEIL. [5]

Candidate profile: we are seeking for a candidate with MSc degree in chemical or physical sciences (inorganic chemistry, physical chemistry, analytical chemistry). 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,
- an academic transcript (Bachelor + Master 1 and first semester Master 2)
- contact information of at least two references (name+e-mail+phone number)
Contacts : Dr. Elodie Anxolabéhère elodie.anxolabehere@u-paris.fr ; Marc Robert marc.robert@u-paris.fr (LEM); Benedikt Lassalle benedikt.lassalle@synchrotron-soleil.fr (Synchrotron).
Funding: ED388 – starting Fall 2021
Location: LEM : Bât. Lavoisier, 15, rue Jean de Baïf, 75205 Paris Cedex 13, France & Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, 91192 Gif-sur-Yvette, France.

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