



German-Brazilian Workshop on Breaking Boundaries of In Situ Synchrotron X-ray Methods

6-10 March 2023

Institute of Chemistry – University of São Paulo

São Paulo, Brazil

PROGRAMME

Day 1 -Monday (06.03.2023) – State of art methods for in situ materials characterization

am	08.00 – 08.40	Registration Welcome Coffee	
	08.40 – 09.00	Opening	
	09.00 – 09.45	Franziska Emmerling	Combination of complementary methods for in situ studies
	09.45 – 09.55	Discussion	
	09.55 – 10.40	Amélie Rochet	X-ray synchrotron techniques for studies of catalysts.
	10.40 – 10.50	Discussion	
	10.50 – 11.10	Break	
	11.10 – 11.55	Tristan Petit	In situ X-ray spectromicroscopy of energy materials
	11.55 – 12.05	Discussion	
	12.05 – 12.50	Liane Rossi	In-situ X-ray in the studies of catalysts for CO ₂ valorization
	12.50 – 13.00	Discussion	
	13.00 – 14.00	Lunch	
	pm	14.00 – 14.45	Ana Flávia Nogueira
14.45 – 14.55		Discussion	
14.55 – 15.40		Uwe Mueller	Trends in macromolecular crystallography.
15.40 – 15.50		Discussion	
15.50 – 16.10		Break	
16.10 – 16.55		Tulio Rocha	Perspectives of Resonant Inelastic X-ray Scattering at Sirius
16.55 – 17.05		Discussion	
17.05 – 17.50		Gerald Falkenberg	In situ and multimodal scanning X-ray microscopy at the Hard X-ray Micro/Nano-Probe beamline P06 at DESY
17.50 – 18.00	Discussion		

Day 2 - Tuesday (07.03.2023) – Towards the future of synchrotron experiments

am	09.00 – 09.45	Christian Bressler	FELs and their use in structural dynamics research
	09.45 – 09.55	Discussion	
	09.55 – 10.40	Anders Madsen	Ultrafast X-ray Scattering and Imaging
	10.40 – 10.50	Discussion	
	10.50 – 11.10	Break	
	11.10 – 11.55	Matthew Tucker	PDF and Total Scattering: The local view of materials discovery
	11.55 – 12.05	Discussion	
pm	12.05 – 12.50	Allan Pinto	High Throughput Visualization, Processing, and Analysis of Large Volumes in X-ray Microscopy Imaging.
	12.50 – 13.00	Discussion	
	13.00 – 14.00	Lunch	
	14.00 – 14.45	Narcizo M. Souza-Neto	X-ray techniques for studies under extreme conditions.
	14.45 – 14.55	Discussion	
	14.55 – 15.40	Andrea Lausi	SESAME – Light for the Middle East
	15.40 – 15.50	Discussion	
15.50 – 16.10	Break		
16.10 – 16.30	π tec	Detectors for X-rays	
16.30 – 16.40	Discussion		
16.40 – 17.10	Funding Agencies	<p>Marcio Weichert – The German Centre for Research and Innovation (DWIH) São Paulo – Head of Programme / Alexander von Humboldt Foundation.</p> <p>Francine Camelim – German Academic Exchange Service/ DAAD.</p> <p>Christina Peters – German Research Foundation (DFG) Director, DFG Office Latin America.</p> <p>Cristóvão de Albuquerque – Sao Paulo Research Foundation – FAPESP – Collaborations for Research.</p>	
17.10 – 17.20	Discussion		
17.20 -	Poster session		

Day 3 - Wednesday (08.03.2023) – Excursion to LNLS/CNPEM

am	08.00	Departure from São Paulo - Institute of Chemistry - USP	
	10.00 – 13.00	LNLS/Sirius visit	
	13.00 – 14.00	Lunch	
pm	14.00 – 16.00	LNLS/Sirius visit	
	16.00 – 18.00	Trip back to São Paulo	

Day 4 – Thursday (09.03.2023) – Workshop/Mini-courses “Beamtime proposal + beamline design”

am	09.00 – 11.00	Franziska Emmerling	Beamtime proposal writing, and remote access – how to prepare
		Uwe Mueller	
	11.00 – 11.20	Break	
	11.20 – 13.00	Christian Bressler	VLab: how to do your own ultrafast x-ray experiment – Part I
pm	13.00 – 14.00	Lunch	
	14.00 – 15.30	Christian Bressler	VLab: how to do your own ultrafast x-ray experiment – Part II
	15.30 – 15.50	Break	
	15.50 – 17.30	Amélie Rochet	Concepts and elements of beamline design
		Itamar Neckel	
19.00 – 22.00	Conference Dinner	Restaurant - Consulado Mineiro - Pinheiros	

Day 5 – Friday (10.03.2023) – Workshop/Mini-course “Cell designing” + Closing

am	09.00 – 10.30	Tristan Petit	Designing cells for in situ studies
		Itamar Neckel	
	10.30 – 10.50	Break	
	10.50 – 11.50	Tristan Petit	Designing cells for in situ studies
		Itamar Neckel	
	11.50 – 12.10	Adam Michalchuk	Why in situ and real time? Do I need it?
	12.10 – 12.30	Poster Prize	
		Closing remarks	

COMBINATION OF COMPLEMENTARY METHODS FOR IN SITU STUDIES

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In situ studies are essential for understanding the behaviour of materials and systems under realistic conditions. Synchrotrons play a crucial role in facilitating these studies by allowing real-time monitoring of different materials, time and length scales.

An overview of different techniques used in in-situ studies is given, together with their advantages and disadvantages. The limitations of each method are highlighted, leading to a discussion of the concept of complementary methods. It explains how different techniques can be combined to overcome these limitations and provide a more comprehensive insight into complex systems.

Case studies of successful combinations of complementary methods in in situ studies will be presented to demonstrate the benefits of a multi-technique approach. The results and conclusions of these studies will be presented and their implications for future research will be discussed.

X-RAY SYNCHROTRON TECHNIQUES FOR STUDIES OF CATALYSTS

Amélie Rochet

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Synchrotrons have been used to study heterogeneous catalysis for as long as synchrotrons have existed. Due to high penetration of X-rays and non-destructive nature of analysis, X-rays are perfectly suited for studies of catalytic phenomena under in situ/operando conditions. The development of 4th generation synchrotron radiation facilities, such as SIRIUS [1], with improvement of brilliance and coherence properties, opens new ways towards catalysts characterisation, in particular with emerging imaging methodologies [2]. Moreover, the possibility of working with faster acquisition, better spatial resolution, higher sensitivity to various chemical and physical properties opens new avenues for the exploration of catalytic reactions.

In this talk, I will present an overview of hard X-ray techniques that are/will be available at Sirius for getting a deep understanding of catalytic materials. In particular, I will focus on recent studies of chemical, morphological and structural properties of both model and real catalysts under in situ or operando conditions.

[1] Lin, L., Milas, N., Mukai, A. H. C., Resende, X. R., De Sá, F. H. (2014) *J. Sync. Rad.* **21** 904. [2] Passos, A. R., Rochet, A., Manente, L. M., Suzana, A. F., Harder, R., Cha, W., Meneau, F. (2020) *Nat. Comm.* **11** 4733.

IN SITU X-RAY SPECTROMICROSCOPY OF ENERGY MATERIALS

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The characterization of the solid-water interface with nanomaterials is essential for applications involving chemical and electronic processes such as in energy storage and conversion. To this aim, soft X-ray spectroscopies are particularly relevant as they enable the selective characterization of either the electrolyte or the material of interest thanks to their element specificity.¹ Furthermore, the high spatial resolution (<50 nm) offered by soft X-ray spectromicroscopy enables the chemical imaging of nanomaterials, which can provide precious information about local inhomogeneities at the nanoscale. In this talk, I will introduce synchrotron-based in situ soft X-ray spectromicroscopy techniques and explain how they can be applied to investigated solid-liquid interfaces. A special emphasis will be provided on in situ cells allowing characterization under controlled atmosphere or in liquid in the soft X-ray range. These techniques will be illustrated by our recent work on the characterization of carbon materials and 2D titanium carbides, so-called MXenes, for applications in energy storage and conversion.

[1] Petit, T., Lounasvuori, M., Chemin, A. & Bärmann, P. Nanointerfaces: Concepts and Strategies for Optical and X-ray Spectroscopic Characterization. ACS Phys. Chem. Au (2023).
<https://doi.org/10.1021/acspchemau.2c00058>

IN SITU X-RAY IN THE STUDIES OF CATALYSTS FOR CO₂ VALORIZATION

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Carbon capture storage and utilization (CCSU) technologies are key for an immediate and sustained reduction in greenhouse gas emissions. Once captured, CO₂ could be stored or even converted into liquids via catalytic hydrogenation. The hydrogenation of CO₂ can lead to various C1 products, such as CO via the reverse water–gas shift (RWGS) reaction, CH₄ via Sabatier or methanation reaction, CH₃OH via selective hydrogenation and, ultimately, C₂+ hydrocarbons, olefins, or even oxygenates. This is a complex set of concomitant reactions and selectivity remains an issue. The first step, which is the hydrogenation of CO₂ through RWGS to form CO and water, is an equilibrium-limited endothermic reaction favoured at high temperatures and methane is concomitantly formed over most catalysts as an undesired side product at low temperatures (< 600 °C). Here, we describe a multi-technique in situ and operando approach to characterize and understand how carbon accumulation on Nickel catalysts under CO₂ hydrogenation conditions affected the reaction selectivity. The Ni catalyst was tested under CO₂ hydrogenation conditions (10 °C min⁻¹ from 100 to 800 °C) under 1/4 CO₂/H₂. The freshly reduced catalyst produced CO (RWGS) and CH₄ (methanation reaction) concomitantly at temperatures between 300 and 600 °C. However, the production of CH₄ was suppressed on recycling tests of the spent catalyst, and CO was the only product at all temperatures. Spectroscopic studies by CO-DRIFTS, XPS, and EXAFS under operando conditions suggest that a Ni₃C-like phase accumulates on the catalyst surface, which may be responsible for preventing the formation of CH₄. Overall, the adsorption strength of CO is greatly diminished with the deposition of C on the surface of metallic Ni particles, which ultimately results in the almost complete elimination of the CO methanation pathway.

We gratefully acknowledge support of the RCGI – Research Centre for Greenhouse Gas Innovation, hosted by the University of São Paulo (USP) and sponsored by FAPESP (2014/50279-4 and 2020/15230-5) and Shell Brasil, and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation. Acknowledgments are given to LNNano (proposal #TEM-24456) and LNLS for access to DXAS and XAFS2 beamlines (proposals #20170290 and #20170171). Acknowledgements are given to the Environmental Molecular Sciences Laboratory (EMSL), a DOE Office of Science User Facility located at the Pacific Northwest National Laboratory, for access to Transient Kinetics Analysis (proposal #50697).

IN SITU EXPERIMENTS USING SYNCHROTRON RADIATION: AN EXPERIENCE WITH HALIDE PEROVSKITES

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In this presentation, I will summarize important results using in situ time-resolved grazing incidence wide angle X-ray scattering (GIWAXS), in situ small angle X-ray scattering (SAXS), synchrotron infrared nanospectroscopy (nano-FTIR) and high-resolution XRD applied to perovskite materials, for both solar cells and light emitting diodes. All measurements were taken at the Brazilian Synchrotron National Laboratory, SSRL-Stanford and ALS-Berkeley. In situ PL was also important to complement the investigation. The materials investigated had the triple cation composition (organic and inorganic cations, and mixed halide anions) and dimensions from 2D to 3D.

TRENDS IN MACROMOLECULAR CRYSTALLOGRAPHY

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Macromolecular crystallography (MX) is an X-ray diffraction method investigating macromolecules in single crystal specimens to elucidate the underlying three-dimensional shape of these molecules at a high-resolution level. The knowledge of macromolecular structures is one of the foundations for the understating of its biological function within any organism.

The presentation will provide an overview about the method, its strengths and limitation and its state-of-the-art implementations at modern X-ray sources like electron storage ring facilities.

Current developments and directions of Structural Biology using MX and complementary methods are presented as well.

PERSPECTIVES OF RESONANT INELASTIC X-RAY SCATTERING AT SIRIUS

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Resonant inelastic X-ray scattering (RIXS) has emerged as a powerful technique for studying the elementary excitations of materials (like magnons, excitons and phonons), offering several advantages over other methods such as inelastic neutron scattering and optical spectroscopy. With its ability to provide element-specific information, high energy resolution, sensitivity to both spin and charge excitations, and momentum dispersion, RIXS has become a valuable tool for probing elementary excitations in quantum materials. The Brazilian scientific community will soon have access to RIXS at the IPE beamline of Sirius, making it an exciting time to explore the capabilities of this technique. This talk will cover the principles of RIXS and showcase recent results from investigations of unusual 1D electronic ordering and collective excitations in CuSb₂O₆, as well as preliminary experiments with cuprate thin films and 2D materials. These studies demonstrate the power of RIXS for probing the magnetic and electronic excitations of materials and highlight the exciting new possibilities that this technique will enable, particularly for low-dimensional materials. Additionally, the status of the RIXS instrument under commissioning at the IPE beamline will be presented, with emphasis on the perspectives for in situ and operando experiments. Overall, the talk will provide valuable insights into the capabilities of RIXS that might be of interest to researchers who are eager to explore this cutting-edge tool for future.

IN SITU AND MULTIMODAL SCANNING X-RAY MICROSCOPY AT THE HARD X-RAY MICRO/NANO-PROBE BEAMLINE P06 AT DESY

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After 10 years of user operation the experimental conditions at the Hard X-ray Micro/Nano-Probe beamline P06 at the synchrotron radiation facility PETRA III are reviewed. Special emphasis is given to In-Situ and Multimodal experiments. Two permanent setups are provided at the P06 beamline in separate hutches: the Nanoprobe and the Microprobe:

The Nanoprobe experiment utilizes nano-focusing lenses (NFL) for focusing the coherent part of the X-ray beam to typical beam sizes of 50-100 nm. The optics can be exchanged for Fresnel zone plates or Multilayer Laue Lenses for low energies or extreme focusing. The experiment is designed for scanning coherent X-ray diffraction microscopy (ptychography) [1], but is used also for nano-XRF and nano-XRD imaging. Recently, the Nanoprobe experiment was upgraded for highest stability including interferometric sample and optics position control to improve ptychographic imaging towards 10 nm resolution [2], ptycho-tomography [3] and resonant ptychography [4]. The setup operates in air environment for easy sample and optics exchange. Though the free distance between last optical element and sample is only a few millimeters, dedicated sample environments for heating, gas and fluidic environments have been developed for in-situ and in-operando experiments. Grote et al [5,6] developed a heated fluidic cell for imaging Cu_2O nanocube growth and hollowing in solution by quantitative in situ X-ray ptychography. The group of Th. Sheppard (KIT) constructed a reactor cell based on a micro-electro-mechanical systems (MEMS) Wildfire Nano-Chip. Weber et al. [7] used an upgraded version for in situ 2D hard X-ray ptychography (XRP) for monitoring the development of hierarchical porosity in Ni/ Al_2O_3 and Al_2O_3 catalysts with connected meso- and macropore networks. In situ XRP allows to follow textural changes of a dried gel Ni/ Al_2O_3 sample as a function of temperature during calcination, activation and CO_2 methanation reaction.

Fast X-ray fluorescence (XRF) element mapping coupled with a sub-micrometer sized X-ray beam (utilizing JTEC KB-mirrors at a flux of some 10^{10} ph/s) characterizes the basic experiment in the microprobe hutch [8]. Modes of operation are two-dimensional lateral scanning [9], (XRF-) tomography of virtual slices [10], and, on smaller particles, real three-dimensional scanning XRF tomography [11]. Spectro-microscopic XANES imaging by creating energy stacks of 2D element maps [12] has recently been adapted to XANES tomography of virtual slices [13]. Scanning XRF can be complemented by (powder) X-ray diffraction [14] for simultaneous imaging of structure and element composition since the advent of fast hybrid pixel detectors with millisecond dwell time like the Pilatus 300k, Lambda and Eiger X 4M at P06. The small pixel size of the Eiger detector together with a large propagation distance made fast Ptychographic measurements possible at the Microprobe. The large focal distance of the KB system allows the implementation of various sample environments like cryostreams, cryogenic sample chambers, chemical reactors,

diamond anvil cells and other user supplied equipment. The recent innovation of phase plates for aberration correction of X-ray optics [15] made the application of compound refractive lenses (CRL) attractive as complementation of the KB system for focusing down to 100 nm beamsizes at intermediate energies (8-20 keV) [10] and submicrometer focusing at 35 keV. The 100 nm beam with large focal distance has enabled multimodal measurements on solar cells including X-ray beam induced current (XBIC) and X-ray excited optical luminescence (XEOL) in addition to X-ray fluorescence and ptychography [16].

[1] Schropp A., et al., *Journal of Applied Crystallography* **53** (2020), 957-971; [2] Schroer CG, et al. *Proceedings of SPIE* 10389, 1038901 (2017); [3] Dam, H., et al. *Adv. Energy Mater.* **5** (1) (2014) 1400736; [4] Hoppe R., et al. *Appl. Phys. Lett.* **102** (2013), 203104; [5] Grote L., et al. *Nature Communications* (2022)13:497; [6] Grote L., et al. *Scientific reports* **13**, 318 (2023); [7] Weber S., et al., *Adv. Sci.* **2022**, 2 105432; [8] Boesenberg et al. *J. Synchrotron Rad* **23**: 1550–1560 (2016); [9] Stauffer T., et al., *Antioxidants*, **2022**, **11**, 1532; [10] Mishra S, et al. *J Exp Botany*. **67**:4639-4646 (2016); [11] Kalirai S et al. *ChemCatChem* **7**: 3674–3682 (2015); [12] Monico L et al. *JAAS* **30**: 613-626 (2014); [13] Mijovilovich A et al. *Spectrochimica Acta Part B* **157**, (2019) 53-62; [14] Vanmeert F et al. *Angewandte Chemie* **54**: 3607-3610 (2015); [15] Seiboth F et al. *Nature communications* **8**: 14627 (2017); [16] Ossig, C., et al. *Materials* **14** (2021)

FELS AND THEIR USE IN STRUCTURAL DYNAMICS RESEARCH

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Structural dynamics research concerns the movement of atoms, e.g., during ongoing chemical reactions. Their movements are governed by the changing electronic forces, e.g., after a light-triggered excitation. Femtosecond x-ray spectroscopies and scattering offer a unique capability to monitor both the movement of these atoms as well as the changing electronic structures which drive these structural modifications. We will demonstrate the power of synchrotron and FEL-related studies to dive into atomic-scale structural and femtosecond time-resolved modifications of molecules in action and of new-born radicals in solution, as observed with x-ray absorption and emission spectroscopies next to x-ray scattering.

TIME-RESOLVED X-RAY SCATTERING AND IMAGING AT EUROPEAN XFEL

Anders Madsen

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In the talk I will give examples of time-resolved scattering and imaging experiments from the Materials Imaging and Dynamics (MID) instrument at the European XFEL. The time scales will range from femtoseconds to microseconds, depending on the phenomenon and sample studied as well as the experimental technique used. In the talk I will discuss X-Ray Photon Correlation Spectroscopy (XPCS) experiment on protein dynamics in solution, X-ray holography and scattering from cavitation bubbles and the surrounding water, as well as ultrafast X-ray diffraction from SrTiO₃ probing a strain wave travelling through the crystal excited by an infrared laser pulse. The examples illustrate the unique experimental possibilities offered by hard X-ray FEL sources in general and by European XFEL and the MID station in particular.

PDF AND TOTAL SCATTERING: THE LOCAL VIEW OF MATERIALS DISCOVERY

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The importance of local structure and disorder is being recognized more and more as a key property of many functional materials. From negative thermal expansion to solid state amorphization, improved fuel cell and battery technology to carbon capture, a clear picture of the local atomic structure is essential to understanding these phenomena and solve the associated problems.

Total scattering an extension of the powder diffraction method, this also includes the Pair Distribution Function (PDF) method, is increasingly being used to study materials. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. To maximise the structural information from such data, three-dimensional atomistic models consistent with all aspects of the data are often required.

In this presentation I will introduce the technique and methodology, describe the various analysis approaches, illustrate their application with a few science examples and finally give a brief perspective on future developments.

HIGH THROUGHPUT VISUALIZATION, PROCESSING, AND ANALYSIS OF LARGE VOLUMES IN X-RAY MICROSCOPY IMAGING

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X-ray computed microtomography (μ CT) is a non-destructive technique useful to investigate bio-based systems in multiple application areas. The importance of this technique has recently increased due to several advances obtained with studies using μ CT characterization, capable of revealing three-dimensional (3D) material structures and quantifying features such as defects and microporosity. Recently, X-ray tomography (CT) beamlines coupled to synchrotron light sources have also enabled nanotomography (nCT) and four-dimension (4D) characterization, allowing in situ, in vivo, and in operando characterization from the micro- to nanostructure. This kind of experiment can produce massive datasets which require real-time analysis and visualization to provide fast feedback. On this matter, deep learning techniques have risen as a powerful tool that permits the analysis of large datasets, as well as recent advances in scientific visualization to deal with real-time visualization. This talk brings an overview of recent deep learning-based mechanisms that enable the design of deep learning architectures for real-time applications.

X-RAY TECHNIQUES FOR STUDIES UNDER EXTREME CONDITIONS

Narcizo M. Souza-Neto

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With the advent of fourth-generation synchrotron sources, such as Sirius in Brazil, many opportunities are open to study energy-related materials with conditions yet nonexistent. This is the case, as an example, for superconducting and magnetic materials, for which we still face several challenges in providing a complete and general understanding of their microscopic physical mechanisms. To tackle this problem, we have in place a complex set of interconnected synchrotron techniques to probe several materials under extreme conditions of high pressure/strain, low/high temperature, and high magnetic field. With x-ray spectroscopy and diffraction techniques we can then access such materials' atomic and magnetic structure under those conditions and help draw a clearer picture of their microscopic phenomena. In this talk, I will show how this is possible with a combination of state-of-the-art new instrumentation in our facility to perform several x-ray techniques under non-ambient thermodynamical conditions. In addition, I will show a few examples of studies on superconducting and magnetic materials performed in the first experiments at the extreme condition beamline (EMA) of the new Brazilian Synchrotron source, Sirius. We hope this is just the beginning of an exciting journey into understanding complex and exotic new materials under combined thermodynamical conditions on the atomic and electronic scale.

SESAME - LIGHT FOR THE MIDDLE EAST

Andrea Lausi

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Officially opened in Jordan on 16 May 2017, SESAME (Synchrotron-light for Experimental Science and Applications in the Middle East) is a cooperative venture by scientists and governments of the region, the first synchrotron light source in the Middle East and neighbouring countries, and the region's first major international centre of excellence for research. The need for an international light source in the Middle East was first recognised more than 30 years ago by the Pakistani Nobel Laureate Abdus Salam. The idea of building a light source was very attractive thanks to the rich diversity of fields of science that can make use of such a facility and was later shared by the Middle East Scientific Co-operation (MESCO) group, led by Sergio Fubini and located in CERN and the Middle East. Nowadays, SESAME is a third-generation synchrotron light source with three beamlines already open to users, which will be soon joined by two which are in the commissioning phase.

WORKSHOP 1: BEAMTIME PROPOSAL WRITING, AND REMOTE ACCESS – HOW TO PREPARE

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This mini-course provides researchers with hands-on experience in bringing a specific experiment to beamtime. The course covers the essential elements of a successful beamtime proposal, remote access requirements and procedures, effective communication with beamline staff, and sample preparation and safety requirements. We will distinguish between applications for highly standardised synchrotron experiments and proposals that require detailed planning by the applicant and beamline scientist.

The practical component of the course will allow participants to put their knowledge into practice by solving a representative problem during a beamtime application. This component will also provide an opportunity to apply the skills and knowledge acquired during the course and to identify areas for further development.

WORKSHOP 2: VLAB: HOW TO DO YOUR OWN ULTRAFAST X-RAY EXPERIMENT

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Synchrotron and XFEL-related experiments are quite similar in terms of their setup. Both rely on relativistic electrons to generate the x-radiation, and need to guide the beam onto the sample with a well-defined focal spot size. We will explore together the X-ray generation process and measure its spectrum at the beamline with a new virtual software package, VLab. We will then perform two femtosecond time-resolved experiments, one investigating a reacting transition metal complex in solution, and the other exploring ultrafast melting of a laser-shocked thin metallic film. Participants can accompany this voyage on their own pace with their own laptops using a web-based version of VLab: <http://webgl.univrlab.com/XFEL2/>

WORKSHOP 3: CONCEPTS AND ELEMENTS OF BEAMLINE DESIGN

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The basic concepts for hard X-ray beamline design will be presented followed by two practical examples developed for the first phase Sirius beamlines. The first example is the QUATI beamline dedicated to Quick X-ray absorption spectroscopy for in situ and operando experiments. The second is the CARNAÚBA beamline, the X-ray nanoprobe dedicated to multi-technique analysis under environmental conditions.

WORKSHOP 4: DESIGNING CELLS FOR IN SITU STUDIES

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The course will approach and answer questions about electrochemistry cell design for experiments in multiple beamlines. It will be presented some recent results of in situ and operando experiments as well as the instrumentation employed. Based on the liquid environment constraints, challenges will be introduced, raising questions about enhancements in current developments of cells for multi-technique employed in analysis using a wide energy range.

POSTERS

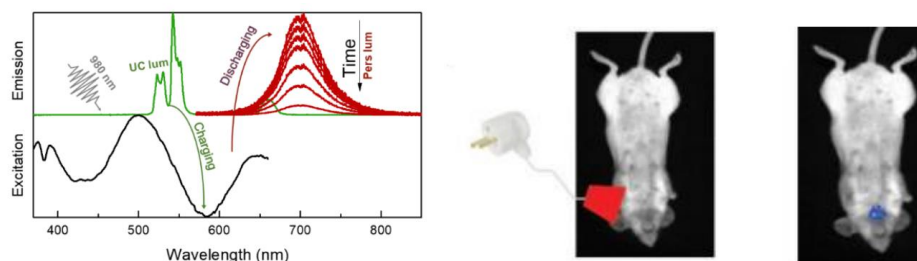
CHARGING ZGSO:CR³⁺ PERSISTENT LUMINESCENCE USING NAGDF₄:YB³⁺,ER³⁺ UPCONVERSION FOR BIOIMAGING APPLICATIONS

Luidgi Giordano,^{1,2} Lucas C.V. Rodrigues,¹ and Bruno Viana²

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Recently, a promising trend in the field of persistent luminescence involves the use of an infrared laser and an up-conversion process for charging.^{1,2} This innovative method increases the potential applications for persistent luminescent materials. In particular, if the emission wavelength is also within the biological window, this method provides rechargeability capacity for bioimaging in the infrared. This study proposes a novel approach to charging persistent luminescent materials using energy transfer on associated materials. β -NaGd_{0.8}Yb_{0.17}Er_{0.03}F₄ and Zn_{1.33}Ga_{1.335}Sn_{0.33}Cr_{0.005}O₄ nanoparticles were combined, forming a hybrid material that exhibits persistent luminescence at 700 nm when charged with a 980 nm laser, both inside the biological window. A mechanism is proposed to explain the energy transfer process between the two types of nanoparticles, and the hybrid material's capabilities as a rechargeable persistent nanoprobe for in vivo applications are demonstrated.³



[1] J. Mater. Chem. C, 6, 2018, 8002-8010. [2] Nano Res., 10, 2017, 1840-1846. [3] Adv. Optical Mater. 2023, 2201468.

AN INVESTIGATION OF THE MORPHOLOGY EFFECT IN Nb₂O₅ ANODES FOR LITHIUM-ION BATTERY.

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Electrochemical energy storage (EES) has played a pivotal role in our society and is an indispensable part of our daily lives. All evidence shows that the growth of EES will continue almost relentlessly in the future of the expanse of portable consumer electronics, electric vehicles, high-end wearables, and many more applications¹. However, materials are needed to enable fast charging and deliver high power for long periods. Niobium oxide has become a very promising candidate for application in EES due to the intercalation pseudocapacitance mechanism, which exhibits fast ion lithium intercalation². Nonetheless, the poor electronic conductivity and limited/superficial electrochemical active sites of Nb₂O₅ should be overcome before the practical application³.

Different morphologies are prepared through a simple hydrothermal method to solve these problems. In particular, different forms of rods, shells, spheres, and flowers of different sizes are prepared. The nanomaterials were characterized by XRD, BET, SEM, and TEM. The electrochemical characterization was performed in different morphologies, rods, spheres, and flowers, presenting the best rate capability and the electrochemical cycling (75%, 77%, and 80% capacity retention after 150 cycles at 50 mA g⁻¹ for rods, flowers, and spheres, respectively). Additionally, shells presented poor capacity retention, and spheres showed the best material at higher current density.

[1] Nature Reviews Materials, 2020, 5, 5. [2] Nature Materials, 2013, 12, 518. [3] Nano Letters, 2014, 14, 158.

ELECTROCHEMICAL REDUCTION OF N₂ AND CO₂ TO C-N COUPLING

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Urea is an important chemical input in different fields, for example, a source of nitrogen in fertilizers. Its production is proceeded through Haber-Bosch process, in which N₂ and H₂ reacts to form NH₃ and after it, NH₃ reacts with CO₂ to produce urea¹. Several problems are associated to it, once this process is responsible for 2% of global energy consumption and emits gases associated to the greenhouse effect. Then, the co-electrolysis of N₂ and CO₂ is one of the approaches that have been investigated to promote the C-N coupling to produce urea in a green way². The catalyst BiVO₄/BiFeO₃ was synthesized and characterized by different techniques. The catalyst was immobilized in the carbon cloth electrode by drop-casting.

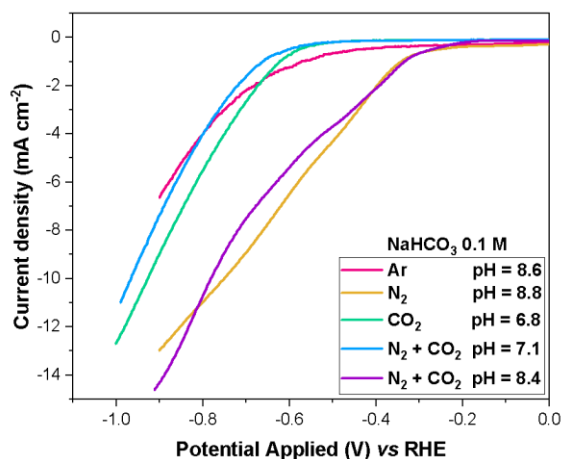


Figure 1. Linear sweep voltammetry in 0.1 M NaHCO₃ at 10 mV s⁻¹.

Electrochemical experiments were performed in NaHCO₃ 0.1 M in the presence of N₂, CO₂ and argon and in the mixture of N₂ + CO₂ at different pHs. The data revealed that in the presence of N₂ + CO₂ (pH = 8.4) there is an increase of current density after -0.4 V vs RHE, which is consistent with a catalytic process. The next perspective is to incorporate metallic nanoparticles, like Ag, and investigate how it can contribute to the C-N coupling. Furthermore, controlled potential electrolysis experiments will be carried out in order to quantify urea.

[1] EES Catalysis, 2023, 1, 45 [2] J. Mater. Chem. A, 2023, 11, 232

IN-SITU AND OPERANDO INVESTIGATION OF LITHIUM/SULFUR BATTERIES WITH POROUS ELECTRODE SYSTEMS

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Positive conversion electrodes for the next generation of lithium-sulfur (Li-S) batteries have attracted considerable interest. However, the Li-S system has some drawbacks that need to be circumvented¹. A detailed understanding of the underlying electrochemical reaction mechanism and kinetics, as well as the degradation process are crucial for the process. X-ray imaging such as phase and transition contrast computed tomography (CT) can give information on the morphological changes. The coupling techniques, especially Electrochemical and Images, in situ and operando experiments, can provide a great insight about the Li-S issues. Here, during the cell operation, was utilized μ CT or Synchrotron Radiography and EIS simultaneously to analyze the structural evolution of sulfur and the internal resistance in two different cells: 1- Carbon Black/Sulfur as a standard and 2- A covalent organic framework incorporated with sulfur MTP-1/Sulfur, as showed at Figure 1.

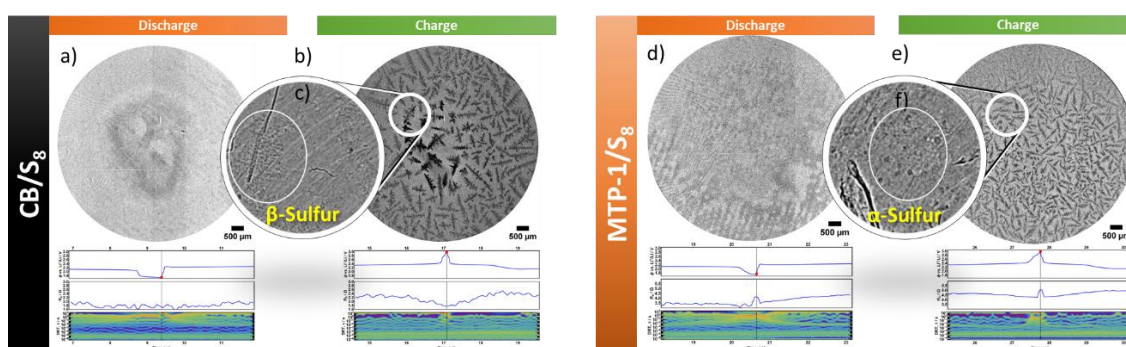


Figure 1. In Operando experiments of μ Ct Radiography in lab, fully charged and discharged state, and EIS (resistance) for CB/S₈ (a, b) and MTP-1/S₈ (c, d) and using synchrotron source (c and f).

We combined electrochemical information, such as the voltage curve, with radiographic information about the cell's interior. At charged state, is evident that significant macroscopic sulfur crystals are present and are smaller in MTP-1/S₈ than in CB /S₈. Additionally, using the synchrotron source at the MTP-1 surface, α -sulfur crystals growing are favored in relation to the β -sulfur². These observations suggest that the sulfur is more trapped in the MTP-1 pores than in CB. Likewise, internal resistance is generally more discrete across cycles for MTP-1/S₈ than for CB. All these observations in MTP-1, indicate that the shuttle effect has been minimized, which is the reason for the higher specific capacities and better charge storage.

[1] J. Electroanal. Chem. 2021, 896, 115459, [2] Physical Chem. Chemical Physics, 2016, 18, 10630.

AMORPHOUS LEWIS-ACIDIC ZIRCONIUM CHLORO FLUORIDE AS A HETEROGENEOUS HF SHUTTLE

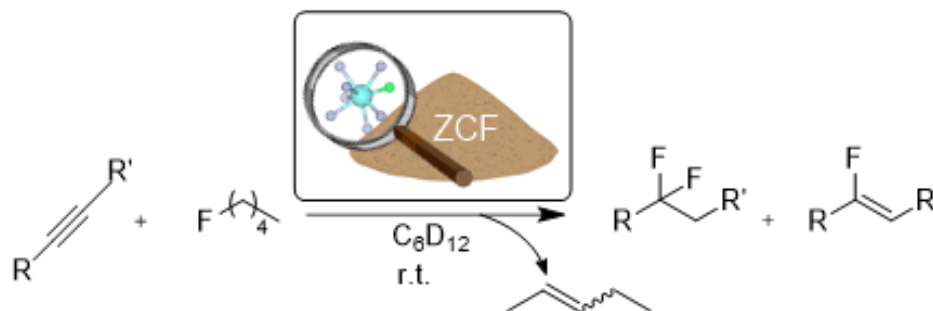
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In recent years, fluorine chemistry has gained increasing political attention. Owing to a growing shortage of fluorspar, a raw material used for producing fluorinated base chemicals, fluorspar has been named among the 30 critical raw materials in the EU.^[1] As such, it becomes increasingly important to recycle existing fluorinated compounds and make them available as sources of fluorine for reactions. Significant progress has been made in the field of C-F bond activation using heterogeneous catalysts such as aluminium chloro fluoride (ACF).^[2] However, the transfer of fluorine atoms from one molecule to another using heterogeneous catalysts has not yet been reported.

In this study,^[3] we successfully synthesized amorphous zirconium chloro fluoride (ZCF), which exhibits medium Lewis acidity. In addition to investigating the local coordination sphere around the Zr atoms and the material properties, we were able to establish a catalytic behaviour of ZCF in C-F bond activation reactions. We present a heterogeneous catalyst that performs dehydrofluorination of a fluoroalkane and consecutive hydrofluorination of an alkyne at room temperature.



Scheme 1: Reaction scheme for catalytic HF transfer from fluoropentane to alkynes (R:alkyl,aryl, R': H, alkyl).

[1] S. Bobba, S. Carrara, J. Huisman, F. Mathieux, C. Pavel, European Commission **2020**, 100. [2] a) M. Ahrens, G. Scholz, T. Braun, E. Kemnitz, *Angew Chem Int Ed Engl* **2013**, 52, 5328-5332; b) G. Meißner, D. Dirican, C. Jäger, T. Braun, E. Kemnitz, *Catalysis Science & Technology* **2017**, 7, 3348-3354; c) M. C. Kervarec, E. Kemnitz, G. Scholz, S. Rudic, T. Braun, C. Jager, A. A. L. Michalchuk, F. Emmerling, *Chemistry* **2020**, 26, 7314-7322. [3] C. Heinekamp, A. Guilherme Buzanich, M. Ahrens, T. Braun, F. Emmerling, manuscript in work **2023**.

SINGLE-ATOMS ON CRYSTALLINE CARBON NITRIDES: THE ROLE OF XAS TO IDENTIFY UNIQUE REACTION MECHANISMS

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As an innovative material for catalytic and photocatalytic applications, crystalline carbon nitrides, especially in their poly(heptazine imide) structure (PHI), are ideal supports for single atom stabilization. In a recent work of our group¹, iron single atoms were coordinated on PHI framework, generating isolated iron sites along the carbon nitride, which were applied for selective photocatalytic oxidation of hydrocarbons, such as benzene or ethylbenzene. The atomically dispersion of these metal sites can be proved by EXAFS analysis, which indicates that Fe-Fe bonds are not present in the material. Single atom (SA) materials are extremely important to modern catalysis since exhibits unique electronic and catalytic properties. Also, these compounds can emulate the high selectivity and metal utilization of metal complexes, which means that some SAs can possess mechanism similar to natural catalysis, or enzymes. For instance, cytochrome P450 enzymes are involved in the oxidation of aromatic hydrocarbons to water-soluble metabolites. These enzymes contain iron atoms coordinated to porphyrin rings as active sites, which reacts with molecular oxygen (O₂) to produce highly reactive iron-oxo intermediates (Fe=O). The synthesis of metal SAs in recent years enables the generation of such species in heterogenous supports, such as graphene or N-doped carbons. However, the production of these materials shows poor reproducibility due the uncontrolled metal loading and variability of coordination environments for the SAs. On the other hand, crystalline carbons nitrides are easily reproducible materials, possessing high control of metal loading and homogenous coordination sites. Recently, our group have found some evidences that iron oxo groups could be the reactive species for the selective oxidation of hydrocarbons using Fe-PHI photocatalysts. The production of iron oxo species occurs via oxidation of the metal center, i.e. Fe(III) into Fe(IV) or Fe(V), probably helped by the photogeneration of holes in the valence band of carbon nitride. X-ray absorption spectroscopy analysis could help us to investigate the electronic changes in the iron site under reaction conditions. In situ analysis with O₂ and light demonstrate slightly shifts to higher energies, which suggests the presence of oxidized species promoted by the activation of oxygen along with charge separation induced by visible-light irradiation. These results are clearly highly important as they pavement the way to elucidate the mechanism behind single atom catalysts and the closely relationship to metal complexes or enzymes.

[1] Applied Catalysis B: Environmental **2022**, 304, 120965.

STUDY OF CO₂ PLASMON-ASSISTED ELECTROREDUCTION OVER CU₂O-AU NANOSTRUCTURES TOWARDS C₂ COMPOUNDS SYNTHESIS

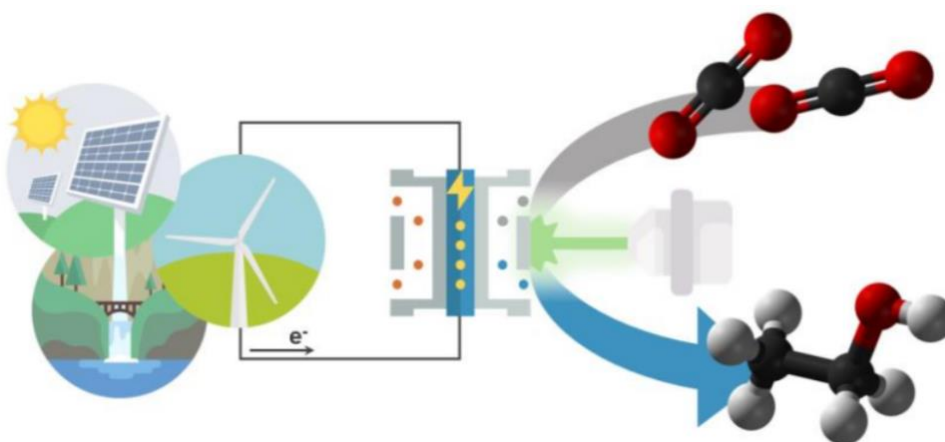
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Allied to the growing global energy demand, the increase in the global average temperature due to continuous fossil fuels use brought impacting consequences to the planet. One strategy to mitigate CO₂ emissions and promote sustainable means of obtaining energy and chemical precursors is the electrochemical CO₂ reduction reaction (CO₂RR) to higher value-added chemicals. Despite being a well-researched reaction, there are still limitations that prevent its application on a large scale, mainly the low selectivity towards C₂ compounds (ethanol, ethylene, among others) and low operational current density. Furthermore, plasmon-assisted electrochemical reactions have been studied in the last decades as a strategy to avoid macroscopic limitations, since the light stimulus in nanometric structures allows reaction pathways that are not possible in purely electrochemical conditions or in non-nanostructured electrocatalysts. However, there is a lack of detailed studies for the plasmon-assisted CO₂RR and their possible enhancements regarding the selectivity towards C₂ compounds, as the use of plasmon-assisted reactions demands an extensive characterization of nanostructured electrocatalysts.

This project combines the plasmonic properties of Au nanospheres with the selectivity towards C₂ compounds of Cu₂O-derived electrocatalysts, synthesizing Cu₂O-Au nanoparticles with different exposed (100-cubes) and (111-octahedra) facets. The detailed characterization of these materials is mandatory to a proper evaluation of the plasmonic and semiconductor contributions to the CO₂RR, allowing mechanistic insight in the electrocatalyst-electrolyte interface. Furthermore, the CO₂ adsorption and C-C coupling are surface-dependent, and as Cu₂O electrocatalysts can be modified during the reaction, the efficiency and selectivity of the material are susceptible to change over time. The possibility of analyzing the electrocatalysts' properties along with electrochemical procedures utilizing In Situ Synchrotron X-Ray characterization techniques, such as XRD, SAXS, among others, are strategies to fine-tune the Cu₂O-Au surface and enhance C₂ synthesis.



[1] Nat. Photonics, 2014, 8, 95 [2] Chem. Eng. J., 2021, 414, 128825 [3] ACS Energy Lett., 2019, 4 (5), 1098 [4] Nano Lett., 2018, 18 (4), 2189

DEVELOPING ELECTRON CRYSTALLOGRAPHY FOR NANOMATERIALS: EXPLORING QUASI-KINEMATICAL PRECESSION ELECTRON DIFFRACTION (PED) INTENSITIES FOR PAIR DISTRIBUTION FUNCTION (PDF) AND AUTOMATED CRYSTAL ORIENTATION MAPPING (ACOM)

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The widespread use of nanomaterials has brought a strong need to characterize materials at a level beyond of common crystallography techniques. Electron crystallography is an alternative to common x-ray/neutron ones, especially when high spatial resolution is required or small sample mass is available. Quantitative use of electron diffraction (ED) is limited by the dynamical nature of electron scattering (multiple scattering). The kinematical nature of x-ray diffraction can be partially recovered by using PED, where intensity displays ‘quasi-kinematical’ nature.¹ The main application of PED has been the study of texture in materials with high spatial resolution (ACOM)¹, where a focused electron nanobeam is scanned and a PED pattern is measured for each pixel.² This approach is based on diffracted beam positions and intensities are not exploited. PED diffraction can be calculated by kinematical approximation and crystal model quality may be quantitatively compared to experiment using a residue metric. Here, we describe a novel approach to map crystal orientation from quantitative analysis of PED intensities, where we have applied this method to characterize distortions in an Eshelby twisted nanowire (InP, diameter ~ 45 nm).³ This has allowed the measurement of orientation changes with an angular resolution of ~ 0.03°, much lower than previously reported (~1°).³ A second PED application has been developed to perform PDF analysis using a parallel electron beam.⁴ This PED + PDF technique has been applied to study of few-nm-wide metal nanoparticles (NPs), indicating that the sample is mostly composed of decahedral NP ~ 3 nm. Adding a size distribution to the model, the structural determination quality (residue ~ 15 %) is comparable with the ones achieved with synchrotron sources (20% – 10%). A low sample mass has been used (~ 4fg) and a conventional transmission electron microscope (200 keV, LaB6 gun) has been utilized, what shows that PED + PDF is a viable and accessible alternative to synchrotron PDF analysis.

[1] *IUCrJ*, **2015**, 2, 126. [2] *Micro. Microanal.* **2019**, 25, 563. [3] *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.*, **2015**, 71, 740–751; pre-print (submitted): <https://doi.org/10.48550/arXiv.2301.10286>. [4] T. Egami et al., *Underneath the Bragg Peaks Structural Analysis of Complex Materials*, Elsevier, Oxford, 2003; *ACS Appl. Nano Mater.*, **2021**, 4, 12541. [5] This research was supported by CNPq, CAPES and FAPESP (Brazil) and the Department of Defense (USA).

MN OXIDATION AS A RELEVANT PROCESS FOR ASTROBIOLOGICAL EXPLORATION ON MARS

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Fundamental questions exist about the nature and history of redox processes operating on the martian surface environment. On Earth, the rise of O₂ greatly increased the diversity of mineralogy and the distribution of redox-sensitive elements like Fe, Mn, and S. Regarding Mn, its behavior provides a powerful context for understanding planetary evolution and unraveling the past history of both surface redox conditions and liquid water.

Surprisingly, Mn-enriched minerals have been observed in rock targets on Mars by NASA's Curiosity rover [1]. These results show that the Martian surface has at some point in time hosted much more highly oxidizing conditions than has previously been recognized. Some studies interpreted these minerals as indicators of atmospheric oxygen on early Mars. In this work, it is proposed that the oxidation of Mn on the planet was caused by the reaction between dissolved Mn(II) and oxyhalogen species: chlorate and bromate ions. If true, that would suggest that the mineral phases detected may record an active halogen cycle rather than substantial atmospheric oxygenation.

A set of X-ray absorption spectroscopy techniques would be greatly valuable to determine the speciation of Mn and the electronic environment of Mn oxides produced in the laboratory under early Martian conditions. Also, time-resolved in-situ measurements could contribute to understanding the mechanism of various Mn oxide formation pathways [2].

[1] Lanza, Nina L., et al. "Oxidation of manganese in an ancient aquifer, Kimberley formation, Gale crater, Mars." *Geophysical Research Letters* 43.14 (2016): 7398-7407. [2] Johnson, Jena E., et al. "Real-time manganese phase dynamics during biological and abiotic manganese oxide reduction." *Environmental science & technology* 50.8 (2016): 4248-4258.

METAL NANOPARTICLES/ZIF-8 AS HYBRID MATERIALS IN ELECTROCATALYSIS

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The engineering of new materials in electrocatalysis is a key point for the solution of various challenges, including performance, stability, and selectivity. In the study of the electroreduction of N₂ to NH₃, the detailed study of the catalytic material used in the electrode is a determining factor to achieve favourable results in this system¹. The use of materials based on metal-organic frameworks (MOFs), have stood out in science². Specifically, the Zeolitic Imidazole framework, (ZIF), characterized by its stability and high porosity³, has a variety of applications in gas storage, ion exchange and catalysis⁴. In this work, we use ZIF-8 is (Zn-imidazolate) as matrix for active Au and/or Ag nanoparticles deposition, generating a hybrid electrocatalytic material for the N₂ reduction to NH₃, with a double water-blocking function⁵. We aim to study both the fine structure of this hybrid material as well as the electrode-electrolyte interface during the electrocatalytic applications. X-ray based techniques can certainly offer unprecedented insights to understand the mechanisms of N₂ reduction, including possible intermediates of reaction and of different phases of the active material.

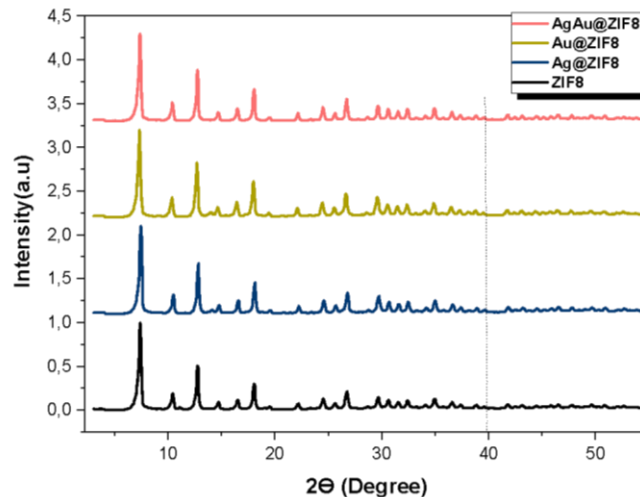


Figure 1 X-ray diffraction of M@ZIF8 materials.

¹ Suryanto, B. H. R. et al. *Nat. Catal.* **2**, 290–296 (2019). ² Hoseinpour, V. & Shariatinia, Z. *issue Cell* **72**, 101588 (2021). ³ Wang, H. et al. *Energy Storage Mater.* (2021). ⁴ Wong-Ng, W. et al. (2011) ⁵ Lee, H. K. et al, *Sci. Adv.* **4**, (2018)

ELUCIDATING THE MECHANISMS OF CONTROLLED GROWTH OF NI EXSOLUTIONS FROM LACRO3 AND LASRTIO3 PEROVSKITES FOR OPTIMIZED CATALYTIC REACTION OF ETHANOL STEAM REFORM

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Catalysts based in exsolved nanoparticles are promising materials that have been demonstrating better performance compared to regular catalysts of deposited nanoparticles. They are structurally stable and resistant against coke deposition and sintering. By controlling the thermochemical treatment, size and dispersion of exsolved nanoparticles can be tailored with the purpose to optimize catalytic activity. Exsolution formation, growth from the bulk matrix and stability requires a careful investigation. In this project we are working with LaCrO₃ with exsolutions of Ni and Ru, and LaSrTiO₃ with Ni exsolutions. To approach these scientific questions we want to carry out X-ray diffraction (XRD) experiments with in situ conditions of reducing H₂ atmosphere and temperature range between 650 °C and 1000 °C, and Bragg coherent diffraction imaging (BCDI) with the same in situ conditions. With XRD in situ experiment we expect to address the question of how the nanoparticle size distribution nucleates and grows as a function of temperature, time and atmosphere. With BCDI we expect to measure a strain map inside the exsolved nanoparticle and correlate with catalytic activity, as they take part of the active sites in the catalytic reaction. Previous characterization with Scanning and Transmission Electron Microscopy (SEM/TEM) have displayed nanoparticles with mean size between 10 nm and 50 nm and with oriented growth from the bulk perovskite matrix in samples of La_{0.4}Sr_{0.4}Ti_{0.8}Ni_{0.2}O₃. XRD characterization demonstrated that the bulk perovskite is crystalline with defined XRD peaks.

XRF-NANOMAPPING OF TRANSLUCENT FILMS WITH PLASMON ENHANCED UPCONVERSION

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The upconversion phenomenon converts two or more lower-energy photons into one higher-energy photon¹ and one of its main limitations is the phenomenon's inherent low yield.² One of the path taken in order to mitigate this problem is enhancing effect of metallic nanoparticles on composites with upconverting properties.³ In this work, yttrium fluoride nanoparticles doped with ytterbium and erbium were prepared by a solvothermal method and metallic nanoparticles with surface plasmon resonance were incorporated into hydroxypropylmethylcellulose (HPMC) films using a drop-casting process.

X-ray fluorescence nanomapping registered at the Carnaúba beamline from Sirius Synchrotron facility was done, primarily, to understand the disposition of Nps in the HPMC film. The measurements showed, serendipitously, that the gold nanoparticles interact preferentially with the fluoride nanoparticles over the carbonyl ends of the HPMC, phenomena already observed in other plasmon enhanced upconversion cases^{4,5}, but not yet explained. Finally, the photoluminescence study showed an intensification of the upconversion phenomenon only in the presence of gold nanoparticles.

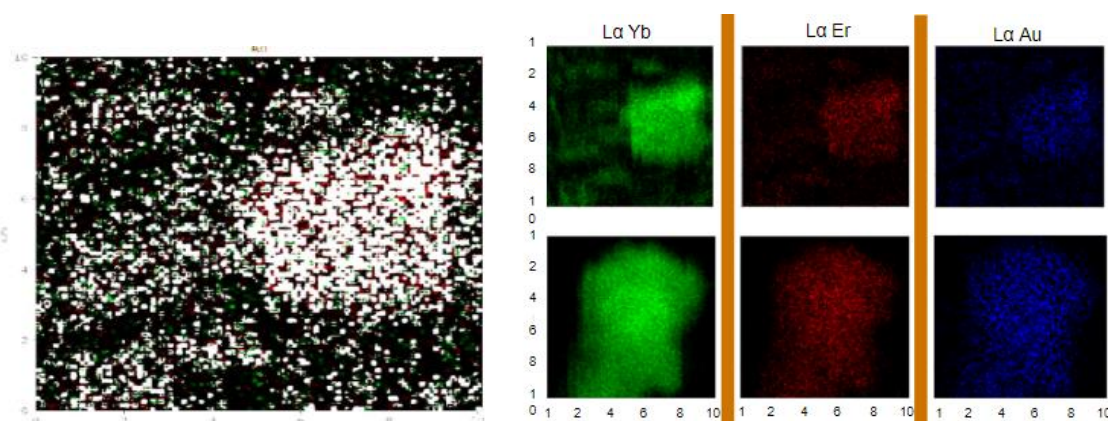


Figure 1: X-ray fluorescence nanomapping in a 10x10 μm square, using the $L\alpha$ of both Yb, Er and Au; and the image obtained from position correlation of the the three $L\alpha$.

[1] Chem Rev, **2004**, 104, 139–173, [2] Chem Rev, **2015**, 115, 395–465, [3] Optics Express, **2014**, Vol. 22, Issue 10, pp. 11516–11527, [4] Metal Nanostructures for Photonics, **2019**, 19–36, [5] J Lumin, **2016**, 170, 271–274.

ELECTRO-CATALYTIC CONVERSION OF CO₂ TO C₂+ PRODUCTS UTILIZING IONIC LIQUIDS

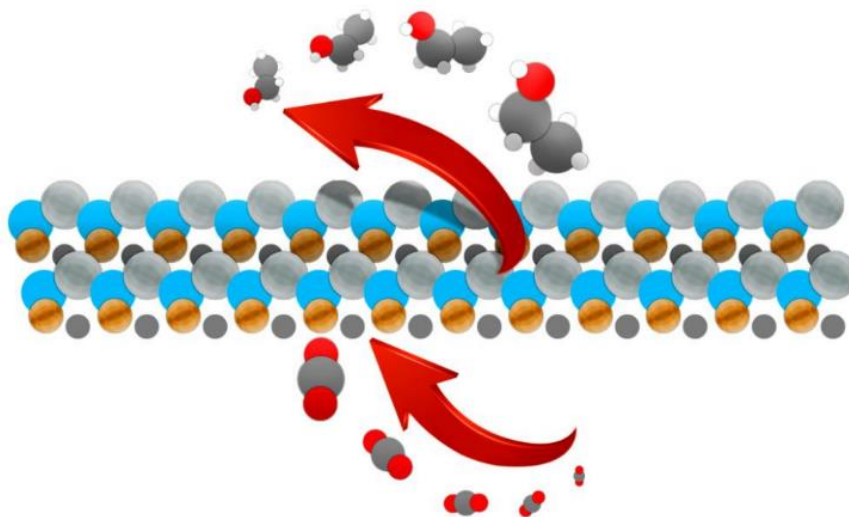
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In the last decade, 2D MXenes have been studied due its high conductivity and surface area in addition to the activity and selectivity for CO₂ Reduction Reaction (CO₂RR) [1,2]. Ag-based catalysts show high yield of CO from CO₂, an important intermediate at the mechanism for making molecules with two or more carbons, also known as more valuable or C₂+ products. However, Ag alone is incapable of making C-C coupling. However, since the earliest publications about metals for CO₂RR, Cu has demonstrated to be one of the few that can produce considerable amounts of C₂+ molecules, for example ethanol [3]. Materials containing Ag & Cu are showing promising results to enhance the C₂+ production, achieving faradaic efficiency (FE) of nearly 40% and 30% with 300 mA cm⁻² for ethanol and ethylene, respectively [4].

Meanwhile, there is a need to increase the selectivity for CO₂RR compared to the Hydrogen Evolution Reaction (HER), the main competitor reaction. Based on this, there is a need to use an electrolyte that can avoid or at least diminish the HER. To face this challenge, there are many researchers utilizing Room Temperature Ionic Liquids (RTIL) to increase the electrochemical stability window of the cell and, with nearly to 10 ppm of water, produce less hydrogen and more of two carbon products [5]. The study of this project is then to combine the properties of Ag, Cu and 2D MXenes with RTIL to further enhance the FE for C₂+ products with good stability and selectivity for CO₂RR.



[1] Han, M. et al, ACS Nano 14, 5008–5016 (2020); [2] Handoko, A. D. et al, J. Mater. Chem. A 6, 21885–21890 (2018); [3] Nitopi, S. et al, Chem. Rev. 119, 7610–7672 (2019); [4] Li, Y. C. et al, J. Am. Chem. Soc. 141, 8584–8591 (2019); [5] Zarandi, B. et al, J. Environ. Chem. Eng. 3, 103141 (2019).

SYNTHESIS OF PD NANOPARTICLES SUPPORTED ON ZNO BY MECHANOCHEMICAL ROUTE

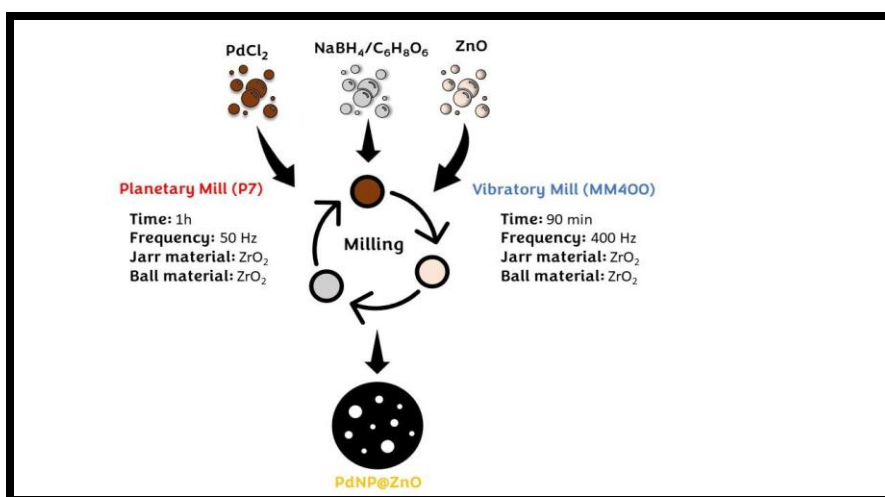
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Mechanochemistry uses mechanical energy to promote chemical reactions in the solid state, dismissing, in the most of reactions, heating up and the use of solvents, being a potential green approach, alternative to conventional methods of synthesis.¹ Because of its advantages, different scientific areas have been using mechanochemistry to obtain a number of chemicals and materials,² including metallic nanoparticles.³ In the synthesis of nanoparticles specifically, mechanochemistry can be used in several methods named as bottom-up or top-down.³ Metallic nanoparticles synthesized in the process can be used for many applications, for example catalysis, biosensing, imaging and energy.⁴ The bottom-up mechanochemical reactions of metal nanoparticles are performed by milling the metal precursor salt with the supporting material in the presence of a reducing agent. In this synthesis, we can easily modify the parameters of the equipment such as frequency and milling time, the milling material and the milling procedure that is being used in the reaction, which can drastically change the outcoming results.

The focus of this work is the mechanochemical synthesis of Pd nanoparticles supported on ZnO, including studies of the partial defective support⁵ in the catalytic activity in model reactions. Pd nanoparticles are synthesized by the mechanochemical route using two different milling procedures (vibratory and planetary) and then characterized by different techniques to obtain information about the size, shape structure electronic and final composition. This defective system containing Pd nanoparticles are employed as a catalyst in the hydrogenation of phenylacetylene, aiming to probe the potential selectivity and efficiency of this system. Finally, it is important to relate the structure of the nanomaterial and the performance.



¹A. L. Michalchuk, E. v. Boldyreva, A. M. Belenguer, F. Emmerling and V. v. Boldyrev, *Front Chem*, 2021, 9, 1–29. ²W. Jones and M. D. Eddleston, *Faraday Discuss.*, 2014, 170, 9–34. ³P. F. M. de Oliveira, R. M. Torresi, F. Emmerling and P. H. C. Camargo, *J Mater Chem A Mater*, 2020, 8, 16114–16141. ⁴C. Xu, S. De, A. M. Balu, M. Ojeda and R. Luque, *Chemical Communications*, 2015, 51, 6698–6713. ⁵V. Šepelák, S. Bégin-Colin and G. le Caër, *Dalton Transactions*, 2012, 41, 11927.

TESTING ELECTROCATALYSTS FOR FUEL CELLS AND WATER ELECTROLYZERS: $\Delta\mu$ XANES APPROACH TO FOLLOW ADSORBED SPECIES

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The increasing demand for new catalysts for the generation and storage of clean energy requires sophisticated techniques to better understand the reaction mechanisms to ultimately improve the performance of these systems. In-situ techniques are desirable because they allow to follow in real time and conditions the modifications in the catalyst structure, which can be linked with the reaction mechanism. The in-situ $\Delta\mu$ XANES technique [1] consists of a differential method that allows tracking the “signatures” of the species adsorbed on the element under observation (e.g. Pt, Ir, Sn, etc.). To correctly employ this method, it is necessary to obtain a reference spectrum where the catalyst’s surface composition is constant and has the lowest number of adsorbed species. Then, without changing the position of the sample, different spectra are obtained with the different parameters (e.g. temperature, electrolyte composition and potentials). When the reference spectrum is subtracted from these spectra, “signatures” of the adsorbed species are obtained. However, to interpret these data, it is necessary to obtain a simulated XANES spectrum using FEFF. Like in the experimental method, a catalyst’s model cluster without any adsorbed species (denoted as “clean surface”) is used to generate the reference spectrum. The possible adsorbed species (e.g. O, OH, H, etc.) are then “positioned” at different active sites (e.g. atop, bridged, etc.) of the cluster structure, and the respective theoretical spectra are simulated. A subsequent subtraction of the reference spectrum gives the theoretical “signatures” for the different possible species involved in the reaction, which will be finally used as a basis for the interpretation of the experimental results.

It is important to mention that the method is not quantitative, and since it is a differential method, it is important to make sure that the spectrum signal before subtraction has a good intensity and a high signal-to-noise ratio. In fuel cell systems, the adsorption of e.g. O, OH, and H is expected and can be followed with the $\Delta\mu$ XANES approach at different potentials, temperatures and pH. In this poster, we will present some of our recent results in high temperature polymer membrane fuel cells (HT-PEMFC). Here, phosphoric acid is utilized as proton conductor at 180 °C. However, it can be leached out during operation as well as block the catalytically active sites. PO₄ and PO₃ adsorption on Pt has been monitored in-situ [2, 3].

[1] Physical Chemistry Chemical Physics, 2010,12(21), 5514. [2] Journal of Electroanalytical Chemistry, 2022,116450. [3] ACS Catalysis, 2022,11472.

CHARACTERIZATION OF SOLID-STATE COMPLEXES BY XAS

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Atomically dispersed metal-nitrogen doped carbons (M-N-C) are promising catalysts for activation of small molecules such as O₂ and CO₂. These single atom catalysts (SAC) operate at the interface between homogeneous and heterogeneous catalysts. They combine advantages of both worlds, such as high atomic efficiency in homogeneous catalysis and more readily application in industrial processes, for example as electrocatalysts in proton exchange membrane fuel cells (PEMFC). The oxygen reduction reaction (ORR) is the rate-limiting step in PEMFC, thus highly efficient electrocatalysts are needed based on sustainable and environmentally friendly resources. Currently, many examples of M-N-C are known today with good ORR activity but lacking a controlled synthesis of the active site of the precatalyst. Recently, our group has facilitated the synthesis of pure pyrrolic TM-N₄ sites using Zn ions as imprinters.^[1] Synthetic control over the selective formation of specific active sites would allow a better understanding of the structure-property relationships on activity, selectivity, catalyst stability and better insights into the reaction mechanism. These amorphous materials including Zn-N-C and Fe-N-C obtained by active site imprinting method are characterized at the BAMline (Bessy II) by X-ray absorption spectroscopy (XAS) measurements and their XANES and EXAFS spectra are fitted with different models to evaluate the structural configuration of M-N₄ sites. For a better understanding of dynamic changes in the active site structure under operating conditions, in-situ/operando measurements will be crucial in future work.

[1] J. Am. Chem. Soc. **2021**, 143, 18010.

HIGH-ENTROPY METAL-GLYCEROLATE AS A PRECURSOR TEMPLATE OF SPHERICAL POROUS HIGH-ENTROPY OXIDE MICROPARTICLES

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High-entropy materials have received notable attention concern on account of their unique structure, tunable properties, and unprecedented potential applications in many fields. In this work, for the first time a NiCoMnZnMg-containing high-entropy glycerolate (HE-Gly) particles has been synthesized using a scalable solvothermal method. The HE-Gly particles were used as a precursor in design of porous high-entropy oxide (HEO) microparticles. The morphological and structural characterizations demonstrate that the temperature of the annealing process, and the composition of the metal ions in the HE-Gly precursors play important roles in determining porosity, crystallinity, and phase separation in HEOs. In fact, HE-Gly exhibited a porous structure of spinel HEOs with secreted MgO phase after annealing process at 800 °C, while the annealing process at 400 °C led to a low-crystallinity spinel phase without phase segregation. Overall, this work describes HE-Gly as a new precursor for altering the composition, crystallinity, and porosity of HEOs. This strategy is scalable for potential high mass productions, paving a new path toward industrial application of high-entropy materials.

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