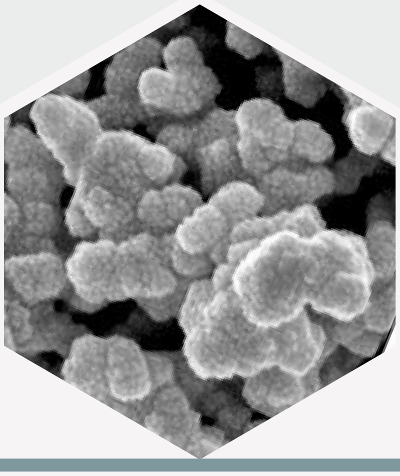
ECATALYTIX

X-RAYS AND ELECTRONIC OPERANDO TECHNIQUES FOR ELECTROCATALYSIS



ECPM - CRONENBOURG CAMPUS - STRASBOURG
03-05 April 2024

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Marie-Ingrid Richard, CEA, France
Andrea Zitolo, Synchrotron SOLEIL, France

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X-rays and electronic *operando* techniques for electrocatalysis (EcatalytiX)

ECPM, Strasbourg, France, April 03-05, 2024

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ABSTRACTS BOOKLET

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Summary

- Welcome
- General Program
- Abstracts
  - ✓ Wednesday, April 3rd
  - ✓ Thursday, April 4th
  - ✓ Friday, April 5th
- Posters Session
- Company Advertisement

Welcome!

Electrocatalysis is the cornerstone of the next generation of technologies aiming to convert electrical power collected from intermittent, renewable sources into basic chemicals and fuels or the conversion of the latter in electricity. In this regard, electrocatalytic reactions, such as the electrochemical oxidation and reduction of water, the hydrogen oxidation or the carbon dioxide and oxygen reduction are all of critical importance.

The EcatalytiX symposium aims at taking a look at the current and future techniques, based on X-rays or electron beams, to observe these reactions under conditions as close as possible to operation. Gathering scientists from all Europe, the meeting wishes to shape directions to answer some of the following questions:

- **How is the coupling of X-rays and electron-based techniques to electrocatalysis going to evolve in the near future and what are the main limits,** challenges and solutions that it is currently facing (e.g., time resolution, beam effect, multi-scale analysis)?
- **What can we learn, by operando approaches, from model systems that can be applied to large-scale electrocatalytic systems.** Conversely, how can we mimic applied electrolysers or fuel cells for large instruments analytical techniques?

Bienvenue !

L'électrocatalyse est la pierre angulaire du développement des technologies capables de convertir l'énergie électrique provenant de sources renouvelables intermittentes en produits chimiques de base et en carburants et, réciproquement, de transformer des carburants verts en énergies renouvelables. Dans cette optique, les réactions électrocatalytiques, telles que l'oxydation et la réduction électrochimique de l'eau, l'oxydation de l'hydrogène ou la réduction du dioxyde de carbone et de l'oxygène, sont toutes d'une importance cruciale.

Le symposium EcatalytiX vise à faire un état des lieux des techniques actuelles et à venir, basées sur les faisceaux de rayons-X ou d'électrons, permettant d'observer ces réactions dans des conditions aussi proches que possible de leur fonctionnement. Réunissant des scientifiques de toute l'Europe, ce symposium ambitionne de définir les lignes directrices qui permettront de répondre aux questions suivantes :

- **Comment les approches couplant spectroscopie et/ou microscopie électronique et électrochimie vont-elles évoluer**, et quelles sont les principales limites et verrous auxquelles elles sont aujourd'hui confrontées (*e.g.,* résolution temporelle, effet du faisceau, analyse multiéchelle)
- **Que peut-on apprendre des systèmes modèles étudiés par des méthodes *operando* qui puissent être appliqués aux systèmes électrocatalytiques à grande échelle ?** Par ailleurs, comment combiner des systèmes électrochimiques industriels, tels que des électrolyseurs ou des piles à combustibles aux techniques d'analyse des grands instruments ?

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Programme

Wednesday, April 3rd

12:00 – 13:00 Welcome registration, coffee

13:00 – 13:30 Introduction

Session #1: State-of-the-art techniques: Where are we standing?

Chair: Jean-Jacques Gallet

13:30 – 14:00 Steps towards understanding the oxygen evolution reaction enigma by operando quick X-ray absorption spectroscopy

***Emiliana Fabbri** - PSI, Villingen, Switzerland*

14:00 – 14:20 Insights from operando QXAFS and PCA for the pulsed eCO$_2$RR using Cu-based bimetallic catalysts

***Martina Ruscher** - Fritz-Haber Institute, Germany*

14:20 – 14:40 Operando X-ray scattering for electrocatalysis and beyond

***Meryem Ennaji** - ICGM, Montpellier, France*

14:40 – 15:00 Spectroscopic and electrochemical considerations for in situ and operando soft X-ray photon-in–photon-out spectroelectrochemistry

***Marc F. Tesch** - Max Planck Institute, Mülheim an der Ruhr, Germany*

15:00 – 15:30 Coffee break

15:30 – 16:00 Structure of carbon-supported nanoparticle electrocatalysts probed with operando X-ray scattering

***Rebecca Pittkowski** - Copenhagen University, Denmark*

16:00 – 16:20 Mechanistic studies of electrocatalysts for hydrogen economy exploiting X-ray absorption spectroscopy under operating conditions

***Raul Garcia-Diez** - Helmholtz-Zentrum Berlin, Germany*

16:20 – 16:40 Structural transformations in NiFe layer double hydroxide and Ni (Oxy)hydroxides under operating conditions for oxygen evolution

***Fabio Dionigi** - Technische Universität Berlin, Germany*

16:40 – 17:00 Liquid TEM study of Cu and CuPd thin films for nitrate electroreduction

***Maria Letizia De Marco** - Institut de physique et de chimie des matériaux de Strasbourg, France*

17:00 – 17:45 Round table: Current Challenges in Operando Studies

*Chairs: **Tristan Asset and Benedikt Lassalle-Kaiser***

17:45 – 20:00 Poster Session and Alsatian Cocktail

Thursday, April 4th

Session #2: Model system

Chair : Nathaly Ortiz

08:30 – 09:00	Electrochemistry in the light of in situ Bragg coherent diffraction imaging ***Marie-Ingrid Richard*** *- CEA, Grenoble, France*
09:00 – 09:20	Amine-mediated electroreduction of CO_2 to formic acid and CO by COFbpyMn single-site catalyst in aqueous media ***Changwei Liu*** *- Institut Català d'Investigació Química, Tarragona, Spain*
09:20 – 09:40	Spectro-electrochemical examination of Pt electrocatalysis using in-situ NAP-XPS ***Hassan Javed*** *- Leiden Institute of Chemistry, The Netherlands*
09:40 – 10:00	Towards operando transmission electron microscopy in aqueous electrolytes: optimized liquid flow configuration ***Marco Fontana*** *- Politecnico di Torino, Italy*
10:00 – 10:30	*Coffee break*
10:30 – 11:00	Resolving the gold-electrolyte interface using in situ X-ray photoelectron spectroscopy ***Sheena Louisia*** *- Leiden Institute of Chemistry, The Netherlands*
11:00 – 11:20	The charge distribution at electrochemical interfaces probed with in situ surface resonant X-ray diffraction ***Yvonne Soldo-Olivier*** *- Leiden Institute of Chemistry, The Netherlands*
11:20 – 11:40	Operando XAS study of Fe incorporation effects on Ni-Fe Prussian blue analogue for electrocatalytic water oxidation ***Guixiang Huang*** *- Max Planck Institute, Mülheim an der Ruhr, Germany*
11:20 – 11:40	Seeing inside palladium hydrides with X-rays ***Frédéric Maillard*** *- LEPMI, Gières, France*
12:00 – 14:30	*Lunch*

Session #3: Emerging techniques and challenges: Where are we going?

Chair: Ovidiu Ersen

14:30 – 15:00	Bridging the nanoscale and the ensemble through correlated operando electron and X-ray microscopy experiments ***See Wee Chee*** *- Fritz-Haber Institute of the Max Planck Society, Berlin, Germany*
15:00 – 15:20	In situ studies of copper catalysts for electrochemical CO_2 reduction by soft X-ray spectro-microscopic characterization ***Chunyang Zhang*** *- McMaster University, Hamilton, Canada*

15:20 – 15:40	In situ hydration study of proton conductor electrolytes using a high-throughput approach ***Giulio Cordaro*** *- Université Paris-Saclay, Gif-sur-Yvette, France*
15:40 – 16:00	Unraveling the oxidation behavior of phosphorus impurities in HT-PEMFCs via in situ tender X-ray spectroscopy at the Pt|aqueous H_3PO_3 interface ***Romualdus E. Wibowo*** *- Helmholtz-Zentrum Berlin, Germany*
16:00 – 16:30	*Coffee break*
16:30 – 17:00	Tracking the evolution of Ni-based single atom catalysts for the CO_2 electroreduction reaction: An operando XAS/XES study assisted by machine learning techniques ***Andrea Martini*** *- Fritz-Haber Institute, Berlin, Germany*
17:00 – 17:45	Round table: Future Challenges of Operando Studies *Chairs:* ***Elena Savinova and Jakub Drnec***
19:00 - 22:00	*Conference dinner in downtown Strasbourg*

Friday, April 5th

Session #4: *Applied and industrial systems*

Chair: Clément Sanchez

08:30 – 09:00	Bridging discovery to application: Utilizing Synchrotron techniques in electrocatalysis ***Andrea Zitolo*** *- Synchrotron Soleil, Saint-Aubin, France*
09:00 – 09:20	Paradigm shift of platinum oxidation below fuel cell open-circuit voltage ***Raphaël Chattot*** *- Institut Charles Gerhardt, Montpellier, France*
09:20 – 09:40	An operando zero-gap MEA cell for combined spectroscopy, diffraction, and imaging, applied to the study of ion effects in CO_2 electrolysis ***Matthew Mayer*** *- Helmholtz-Zentrum Berlin, Germany*
09:40 – 10:00	Operando X-ray studies of gas evolving and consuming electrocatalysts ***Andrea Russell*** *- University of Southampton, United Kingdom*
10:00 – 10:30	*Coffee break*
10:30 – 11:00	Electrolyte distribution in silver gas diffusion electrodes for electrochemical CO_2 reduction measured by operando Synchrotron tomography ***Jens Osiewacz*** *- Clausthal University of Technology, Clausthal-Zellerfeld, Germany*
11:00 – 11:20	Electrochemical and structural study of NiRux heterofunctional catalysts for the alkaline HER ***Marie-Sophie Fernandes-Diaz*** *- Synchrotron Soleil, Saint-Aubin, France*
11:20 – 11:40	Set-ups for in-operando X-ray absorption spectroscopy/electrochemistry in half-cell and fuel-cell configurations: The case study of palladium deactivation in direct alcohol fuel cells ***Enrico Berretti*** *- CNR-ICCOM, Firenze, Italy*
11:40 – 12:00	Characterizing microstructure and gas transport properties of electrospun gas diffusion layers in proton exchange membrane fuel cells through high-resolution imagery ***Bertrand Roussillo--David de Beaufort*** *- CEA, Grenoble, France*
12:00 – 14:30	*Concluding Remarks, Followed by Lunch*

ABSTRACTS

Wednesday, April 3rd, 2024

Wednesday, April 3rd

Session 1: State-of-the-art techniques: where are we standing?

Chair: ***Jean-Jacques Gallet***

IT-01	Steps towards understanding the oxygen evolution reaction enigma by operando quick X-ray absorption spectroscopy ***Emiliana Fabbri***
OC-01	Insights from Operando QXAFS and PCA for the Pulsed eCO_2RR using Cu-based Bimetallic Catalysts ***Martina Ruscher***
OC-02	Operando X-ray scattering for electrocatalysis and beyond ***Meryem Ennaji***
OC-03	Spectroscopic and electrochemical considerations for in situ and operando soft X-ray photon-in–photon-out spectroelectrochemistry ***Marc F. Tesch***
ET-01	Structure of carbon-supported nanoparticle electrocatalysts probed with operando X-ray scattering ***Rebecca Pittkowski***
OC-04	Mechanistic studies of electrocatalysts for hydrogen economy exploiting X-ray absorption spectroscopy under operating conditions ***Raul Garcia-Diez***
OC-05	Structural transformations in NiFe layer double hydroxide and N (Oxy)hydroxides under operating conditions for oxygen evolution ***Fabio Dionigi***
OC-06	Liquid TEM study of Cu and CuPd thin films for nitrate electroreduction ***Maria Letizia De Marco***

Steps towards Understanding the Oxygen Evolution Reaction Enigma by Operando Quick X-ray Absorption Spectroscopy

E. Fabbri

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ABSTRACT

The development of a sustainable and environmentally friendly energy economy encompasses efficient hydrogen production from renewable energies via electrolysis. In this context, great efforts have been recently dedicated to the development of more efficient of cost-effective electrocatalysts. Understanding the mechanism of the oxygen evolution reaction (OER) on non-noble metal catalysts is of great interest, but the reaction and system complexity render the characterization of active sites and the understanding of reaction mechanism challenging.[1] Indeed, since half of a decade, it is generally recognized that the OER might also involve the oxidation of lattice oxygen and significant catalyst surface reconstruction. This has been early proved by our group performing Quick X-ray Absorption Spectroscopy by under real operating conditions[2] and by other relevant experiments.[3]

Time resolved Quick-XAS can provide dynamic snapshots of the electronic and local structure of nanocatalysts, revealing the “real active phase” of the catalyst, which can substantially differ from the as prepared catalyst powder or the catalyst in form of an electrode under non-operating conditions.

In this contribution, several examples will be presented showing how operando XAS can reveal catalyst-support interactions, changes in the reaction mechanism, and dynamic reversible/irreversible changes in the electronic and local structure of OER catalysts.[4-6] In particular, time-resolved operando XAS studies of spinel/rock salt CoOx-based catalysts, perovskite oxides, and MOF-based catalysts will be presented.

Overall, the information gained from these studies represents a further step in the understanding of the key physicochemical properties of OER catalysts and their reaction mechanism.

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Insights from Operando QXAFS and PCA for the Pulsed eCO$_2$RR using Cu-based Bimetallic Catalysts

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ABSTRACT

In order to reduce the increased levels of the greenhouse gas CO$_2$ in the atmosphere caused by anthropogenic emissions, advanced technologies to reutilize excessive CO$_2$ need to be employed. The CO$_2$ electroreduction is a promising strategy to close the carbon cycle by producing valuable resources, such as "green" fuels and feedstock chemicals. Major efforts have been put into this area of research to find the right catalyst, that can achieve high selectivity and activity, while providing excellent stability under operating conditions. While the first commercially available solutions are already emerging, our understanding of the fundamental aspects of catalyst working mechanisms needs to be advanced to be able to efficiently steer the reaction pathway toward the desired products, e.g., by actively controlling the reaction environment. The most efficient catalyst for C-C coupling towards more energy dense products is Cu. Previous studies have shown, that by changing the operating conditions such as (i) static vs. pulsed conditions,[1, 2] (ii) the catalyst particle shape,[3] or (iii) the oxidation state of the precatalyst,[4] we can steer the selectivity towards different products.

Among other strategies, the addition of a secondary metal has been suggested as a promising pathway to tune the atomistic and electronic structure of the Cu-based catalysts[5], leading to improved CO$_2$RR functionalities. In our work, we systematically investigate the effect of the secondary metal on the redox behavior of Cu, its stability and alloy formation by introducing small amounts of Ag, Au, Pd and Zn onto Cu nanocubes. Further, pulsed reaction conditions have been shown to be beneficial for pure Cu to further enhance C$_{2+}$ products. The selectivity of the CO$_2$RR, however, is highly dependent on the potential of the redox conditions as well as the pulse durations. Blind exploration of such huge parameter space is a laborious task. Therefore, we have applied quick X-ray absorption spectroscopy (QXAFS) to first understand the dynamics of our catalyst at work, which can then be related to the processes at our catalyst interface. Thus, the regions in the parameter space where distinct functionalities can be expected can be identified, guiding the catalytic performance studies. QXAFS is a powerful tool for *operando* studies of working multi-metallic catalysts, on the one hand, because of its sub-second time resolution, but also because it can provide element specific information from the perspective of Cu and the secondary metal.

The results obtained provide valuable insights into the subtle differences in the redox, dissolution and alloying processes seen in the different bimetallic catalysts, which can have a significant impact on the required operating parameters. Principal component analysis (PCA) was used to disentangle complex alloying processes as well as the presence of different oxidized species. By using *operando* QXAFS and employing PCA, we aim to provide valuable insights into the intricate interplay between different processes during the CO$_2$RR to advance the design of bimetallic catalysts for improved CO$_2$ conversion efficiency.

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Operando X-ray Scattering for Electrocatalysis and Beyond

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ABSTRACT

The energy transition stands as one of the greatest challenges of today's society. In this context, electrocatalyst materials at the heart of electrochemical energy conversion devices such as fuel cells and water electrolysers are expected to play an increasing crucial role in the near future. The urgent bottleneck to be overcome in electrocatalyst materials development to allow the widespread deployment of electrochemical systems is thus reaching combined high activity and long-term stability at low cost. Despite the diversity in electrocatalyst materials, the latter being largely imposed by the various types of electrochemical systems (noble vs. non-noble metals in acidic vs. alkaline media for example) and the prerequisites of the different electrochemical processes (oxidation or reduction reactions of various species at different electrode potential ranges), most activity and stability properties of electrocatalysts directly derive from their (surface) chemistry and structure [1]. Such properties (and their temporal evolution) can thus be directly investigated by means of in situ or operando high energy X-ray scattering (XRD) technique [2].

In this presentation, the versatility of in situ and operando XRD technique in addressing key bottlenecks in electrocatalyst materials development, notably by probing adsorption and oxidation trends [3], will be showcased. After an overview of previous contributions from the literature, the talk will focus on our ongoing works which encompass the study of Pt-based nanocatalysts for the oxygen reduction reaction (ORR) at proton-exchange membrane fuel cells (PEMFCs) anode, carbon-capped Ni@C catalyst for the hydrogen oxidation reaction (HOR) at anion-exchange membrane fuel cells (AEMFCs) anode and IrCu unsupported aerogel catalyst for the oxygen evolution reaction (OER) at proton-exchange membrane water electrolysers (PEMWEs) anode.

Finally, the ability of operando XRD to provide device-relevant insights at the macroscale (such as ionomer hydration in PEMFCs or water distribution in AEMFCs) beyond electrocatalysts microstructural properties will be presented.

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Spectroscopic and Electrochemical Considerations for *in situ* and *operando* Soft X-ray Photon-in–Photon-out Spectroelectrochemistry

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ABSTRACT

Soft X-ray spectroscopy is a powerful method to analyze materials on an element selective level with respect to phases, oxidation states, and local electronic structure. This renders it a valuable tool to investigate material changes in electrochemical applications. The implementation of *in situ* and *operando* soft X-ray spectroscopy, however, is technically challenging. To this end, spectroscopic considerations specific to photon-in–photon-out techniques in the soft X-ray regime as well as electrochemical considerations with respect to the usually rather confined conditions in such experiments will be discussed. Further, a spectroelectrochemical flow-cell[1] will be presented (Figure 1), providing optimized and mutually balanced spectroscopic and electrochemical conditions. The application of this highly sensitive mode of analysis will be demonstrated on a NiOx thin film for the alkaline oxygen evolution half reaction. Beside potentiostatic X-ray absorption spectroscopy, also potentiodynamic spectroelectrochemical experiments will be discussed[2] combing cyclic voltammetry with X-ray absorption measurements at a fixed photon energy, which enables tracking phase changes in an element selective and time resolved fashion (Figure 2).

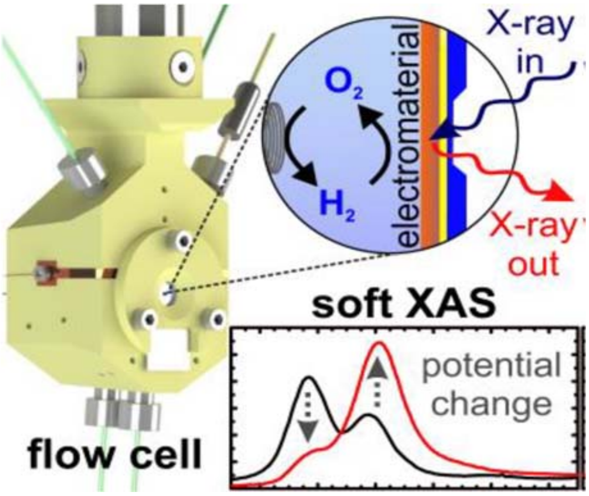

Figure 1 Schemes of the spectroelectrochemical flow cell and potential induced changes in a soft X-ray spectrum (bottom right).

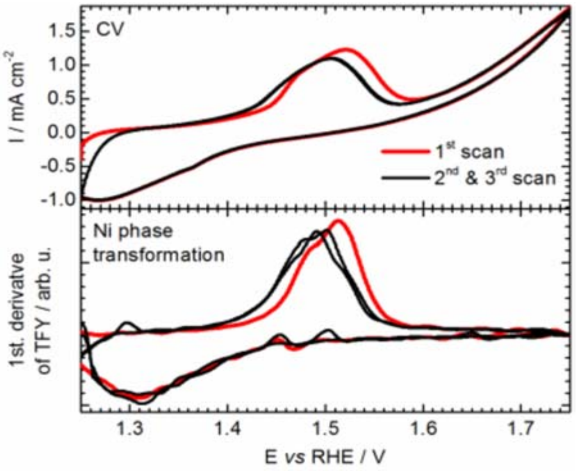

Figure 2 Top: Cyclic voltammogram of a NiOx thin film. Bottom: Fixed energy soft X-ray absorption measurement, tracking the phase transition of Ni during the CV.

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Structure of Carbon-supported Nanoparticle Electrocatalysts Probed with *Operando* X-ray Scattering

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ABSTRACT

Electrocatalysis plays a major role in energy conversion technologies such as electrolyzers and fuel cells. Small nanoparticles, typically less than 5 nm in size, provide a high surface-to-bulk-atom ratio which is crucial for efficient utilization of the catalyst material, often based on scarce precious metals like Pt for fuel cells[1] and Ir for electrolyzers.[2] By distributing the nanoparticles on carbon supports a high catalyst dispersion is achieved. However, these small nanoparticles suffer often from instability in electrochemical environments, and the structural transformations that occur are, so far, not fully understood. In this context, synchrotron techniques using hard X-rays are valuable tools for unraveling the catalyst's structural changes during operation. *In-situ* and *operando* experiments enable us to monitor the evolution of atomic structures. With small-angle X-ray scattering (SAXS), changes in size and morphology can be tracked,[3] while X-ray diffraction provides insights into the crystalline atomic structure.[1] This can provide valuable information on the mechanisms that dominate catalyst degradation and can help to devise new strategies for stability optimization.[4] I will focus on the strengths and limitations of the different *operando* scattering techniques, SAXS, XRD, and X-ray total scattering with PDF analysis, and how they can be combined, also with X-ray absorption spectroscopy (XAS).[5] This offers a complete picture of the catalyst structure at applied potentials, which is fundamental for establishing structure-property relations.

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Mechanistic Studies of Electrocatalysts for Hydrogen Economy Exploiting X-ray Absorption Spectroscopy under Operating Conditions

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ABSTRACT

The transition to a hydrogen economy is pivotal for the rapid decarbonization of contemporary Western societies, where water electrolyzers and hydrogen fuel cells are envisioned to play a central role. While precious metal-based catalysts such as iridium and platinum are currently the dominating electrocatalysts for the Oxygen Evolution Reaction (OER) in acidic electrolyzers and for Proton Exchange Membrane Fuel Cells (PEM-FC) [1], respectively, the necessity to reduce costs has motivated extensive research aiming toward more economically viable alternatives, e.g. copper as a promising candidate for alkaline OER [2]. In this pursuit of efficiency and cost-effectiveness, understanding the performance-limiting mechanisms at electrochemical interfaces under real operating conditions is paramount. One of these research avenues employs *operando* synchrotron-based X-ray Absorption Spectroscopy (XAS) as a powerful tool to probe the chemical and electronic structure of electrocatalysts during operation, since photon-in/photon-out XAS provides insights into the local density of states, oxidation state, and local geometry around probed atoms. Benefiting of the high chemical sensitivity of XAS, we present *operando* studies in both, the soft and hard X-ray regime to demonstrate the applicability of this approach for relevant electrocatalysts.

Firstly, at the Cu L_3-edge, *operando* XAS reveals the formation of a novel chemical species in an electrodeposited Cu-based catalyst during alkaline OER, which is potentially associated with the elusive high-valent Cu intermediate. In the hard x-ray regime, *operando* studies at the Ir L_3-edge shed light on the mechanistic complexity of OER activity and Ir dissolution in highly active amorphous hydrous iridium oxides under relevant acidic OER conditions [3]. Furthermore, this work introduces experimental results obtained at the Operando Absorption and Emission Spectroscopy at EMIL (OÆSE) endstation at the Bessy-II storage ring in Berlin, Germany [4]. Focusing on the Pt | H_3PO_3 interface, crucial for high-temperature PEM-FC [5], we showcase the *operando* XAS capabilities of this newly developed infrastructure. These findings contribute to unravel intricate electrochemical processes, paving the way for the design of more efficient and cost-effective electrocatalysts for the hydrogen economy.

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Structural Transformations in NiFe Layer Double Hydroxide and Ni (Oxy)hydroxides under Operating Conditions for Oxygen Evolution

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ABSTRACT

The catalytic activity for the oxygen evolution reaction (OER) of $Ni(OH)_2$ in alkaline electrolytes is significantly enhanced by presence of Fe species in the electrolyte.[1] These species can incorporate into the brucite-like $Ni(OH)_2$ crystal structure and cause structural transformations. The resulting hydrotalcite-like crystalline structure is known as NiFe layered double hydroxide (LDH). NiFe LDH catalysts are among the most active OER electrocatalysts in alkaline electrolytes, but still show a considerable overpotential.[2] Understanding the nature of the catalytic active sites and the catalytic mechanism in NiFe LDHs, as well as the fundamental understanding of the role of the Ni-based host structure, are key challenges to develop more active OER electrocatalysts.

In this contribution, atomic-scale details of the catalytic active phase will be presented, showing that NiFe LDHs are oxidized under applied anodic potentials from as-prepared α-phases to activated γ-phases.[3] The interlayer and in-plane lattice parameters of the OER-active γ-phase were obtained by performing wide angle X-ray scattering (WAXS) measurements on NiFe LDH nanoplatelets during operating electrochemical conditions and were characterized by a contraction of about 8%. Operando WAXS was then performed for other selected catalysts belonging to the transition metal LDH family of materials. Structural similarities of the catalytically active phases will be highlighted. In addition, the structural transformations of β-$Ni(OH)_2$ will be discussed, as potential host structure for novel multi-element catalysts. Also for $Ni(OH)_2$, the γ-phase is found to be the catalytically active phase. However, the structural transformations are more complex, involving multiple limiting phases. Their structural stability is presented and the discussion supported by density functional theory calculations.

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Liquid TEM Study of Cu and CuPd Thin Films for Nitrate Electroreduction

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ABSTRACT

Liquid phase transmission electron microscopy (LP-EM) enables the study in real time of the transformations of nano-materials in solvated reactive conditions, at the local scale of few nanometres (≤ 5nm).[1,2] The introduction of electrical connections and micro-electrodes within the sample holder liquid cell allows following the evolution of nanomaterials under the effect of an applied electrochemical potential (EC-TEM). This technique is particularly relevant in the field of nanomaterials for energy. [3,4]

In this talk, I will present our recent results about the synthesis and electrocatalytic stability of Cu and CuPd thin films for nitrate electroreduction (NO_3^- RR). NO_3^- RR from alkaline waste waters is an environmentally relevant reaction not only for depollution purposes, but also because it allows to produce an industrially relevant compound, NH_3, usually produced with the Haber-Bosch process, which requires high temperature and pressure.[5,6] Both the synthesis by electrodeposition and the electrocatalytic behaviour of Cu and CuPd films where characterized *ex-situ* with traditional 3-electrodes cells, and *in situ* by EC-TEM. CuPd films show improved activity and selectivity towards NH_3 compared to pure Cu. However, the lack of stability of these films, which delaminate when the cathodic potential is applied, hinders their application. In situ EC-TEM investigations during NO_3^- RR show that the films alloying, morphology, and crystalline phase are quite stable under working conditions. However, movies recorded during chronoamperometric measurements reveal that, when the cathodic potential is applied, the whole CuPd film contracts and shifts, a behaviour that might be at the origin of film stress, resulting in delamination in the H-cell. These results show the importance of in situ TEM for identifying the reasons behind the dynamic behaviour of electrocatalysts, and guide the design of new electrocatalyst with improved stability and activity

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ABSTRACTS

Thursday, April 4th, 2024

Thursday, April 4th

Session 2: Model systems

Chair: ***Nathaly Ortiz***

IT-02	Electrochemistry in the light of in situ Bragg coherent diffraction imaging ***Marie-Ingrid Richard***
OC-07	Amine-mediated electroreduction of CO_2 to formic acid and CO by COFbpyMn single-site catalyst in aqueous media ***Changwei Liu***
OC-08	Spectro-electrochemical examination of Pt electrocatalysis using in-situ NAP-XPS ***Hassan Javed***
OC-09	Towards operando transmission electron microscopy in aqueous electrolytes: optimized liquid flow configuration ***Marco Fontana***
ET-02	Resolving the gold-electrolyte interface using in situ X-ray photoelectron spectroscopy ***Sheena Louisia***
OC-10	The charge distribution at electrochemical interfaces probed with in situ surface resonant X-ray diffraction ***Yvonne Soldo-Olivier***
OC-11	Operando XAS study of Fe incorporation effects on Ni-Fe Prussian blue analogue for electrocatalytic water oxidation ***Guixiang Huang***
OC-12	Seeing inside palladium hydrides with X-rays ***Frédéric Maillard***

Thursday, April 4th

Session 3: Emerging techniques and challenges: where are we going?

Chair: ***Ovidiu Ersen***

IT-03	Bridging the nanoscale and the ensemble through correlated operando electron and X-ray microscopy experiments ***See Wee Chee***
OC-13	In situ studies of copper catalysts for electrochemical CO_2 reduction by soft X-ray spectro-microscopic characterization ***Chunyang Zhang***
OC-14	In situ hydration study of proton conductor electrolytes using a high-throughput approach ***Giulio Cordaro***
OC-15	Unraveling the oxidation behavior of phosphorus impurities in HT-PEMFCs via in situ tender X-ray spectroscopy at the Pt|aqueous H_3PO_3 interface ***Romualdus E. Wibowo***
ET-03	Tracking the evolution of Ni-based single atom catalysts for the CO_2 electroreduction reaction: an operando XAS/XES study assisted by machine learning techniques ***Andrea Martini***

Electrochemistry in the Light of *In Situ* Bragg Coherent Diffraction Imaging

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ABSTRACT

The advent of the new 4th generation x-ray light sources represents an unprecedented opportunity to conduct *in situ* and *operando* studies on the structure of nanoparticles in reactive liquid environments. I will illustrate how Bragg coherent x-ray imaging [1] allows to image in three dimensions (3D) and at the nanoscale the strain and defect dynamics inside nanoparticles during an electrochemical reaction [2,3]. First, we successfully imaged the morphology, the lattice displacement and the strain of an individual Pt nanoparticle in electrochemical environment [2]. Secondly, we will show how *in situ* and *operando* Bragg coherent x-ray imaging allows to study the structural evolution of single Pd nanocrystals at various electrode potentials typical of H adsorption, H absorption, and H_2 evolution. Open questions remain regarding the maximal quantity of H that can be inserted into a Pd nanocrystallite, the mechanism and kinetics of hydride (PdHx) nucleation (preferential sites for nucleation or homogeneous nucleation at the whole particle surface) and growth (α/β sharp transition or two-phase coexistence).

We acknowledge funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement CARINE No. 818823 and HERMES No. 952184.

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Amine-mediated Electroreduction of CO_2 to Formic Acid and CO by COFbpyMn Single-site Catalyst in Aqueous Media

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ABSTRACT

Decoration on molecular bipyridine-based ligands with alkyl amines in the vicinity of catalytic Mn center shows an improvement in selectivity toward FE_{CO} and TOF_{CO}, while they are normally used in organic electrolytes with additional organic proton donors. Here, we show a heterogeneous mechanically constrained Mn-based Covalent Organic Frameworks (COFbpyMn) as electrocatalyst for selective electroreduction of CO_2 into formate ($HCOO^-$) and formic acid (HCOOH) in an aqueous solution giving more advantages in terms of reusability, stability and practicality compared to molecular counterparts. With selected amines added into 1 M $NaHCO_3$ (pH 8.1), the catalyst can reach TOF_{HCOO^-} (h^{-1}) of 10900 and FE_{HCOO^-} of 90% with a current density of 13 mA/cm^2 in homemade H-cell at an overpotential of 420 mV *vs* RHE. COFbpyMn can maintain high activity and selectivity from CO_2 reduction to $HCOO^-$ at pH 6.1, pH 4.1 and even HCOOH at pH 2.4 with FE_{HCOO^-} of 80% and TOF_{HCOO^-} (h^{-1}) of 7200 at an overpotential of 336 mV *vs* RHE. Conversely, CO can be the main product with FE_{CO} of 98% and TOF_{CO} (h^{-1}) of 2300 in aqueous solutions by adding selected amines possessing higher pKa and proper molecular length. These results show that product selectivity can be tuned by adding inferred amines in aqueous media, tuning intermediates to COFbpyMn-H or manganese adduct anion ($COFbpyMnCO_2^-$), therefore boosting products to $HCOO^-$/HCOOH or CO selectively. Spectroelectrochemistry of the COFbpyMn/VuI (ATR-IR-SEC) was conducted using a customized three-electrode ATR-IR-SEC cell. The structural information on catalytically relevant species of the COFbpyMn/VuI can be obtained by analysing CO stretching vibrations (υ(CO)) in active manganese complexes under applied negative potentials, as well as be helpful in deducing metal oxidation state. Successfully, Mn hydride as a key intermediate for $HCOO^-$ and H_2 was deduced from spectroelectrochemical measurements.

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Spectro-electrochemical Examination of Pt Electrocatalysis using *In-situ* NAP-XPS

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ABSTRACT

X-ray based spectroscopy techniques are one of the most powerful characterization techniques regarding interfacial and bulk characterization[1]. To this end, different experimental arrangements have attempted to explore electrode-electrolyte interface spectroscopically. However, the X-ray based techniques rely on the vacuum inside the experimental chamber, limiting their applications[2]. In this work, we examine the Pt based electrochemical reactions using the electrochemical NAPXPS setup commissioned recently at Leiden Institute of Chemistry. We employ a special cell arrangement, in which the Pt electrocatalyst is deposited on a porous polycarbonate membrane and covered by graphene, enabling the *in situ* examination of the electrochemical reactions under wet conditions. We show that our setup allows us to investigate changes in oxidation states of involved species and electrostatic potential as well as gauge the proximity of a certain specie to the working electrode by examining its binding energy shift as a function of applied potential.

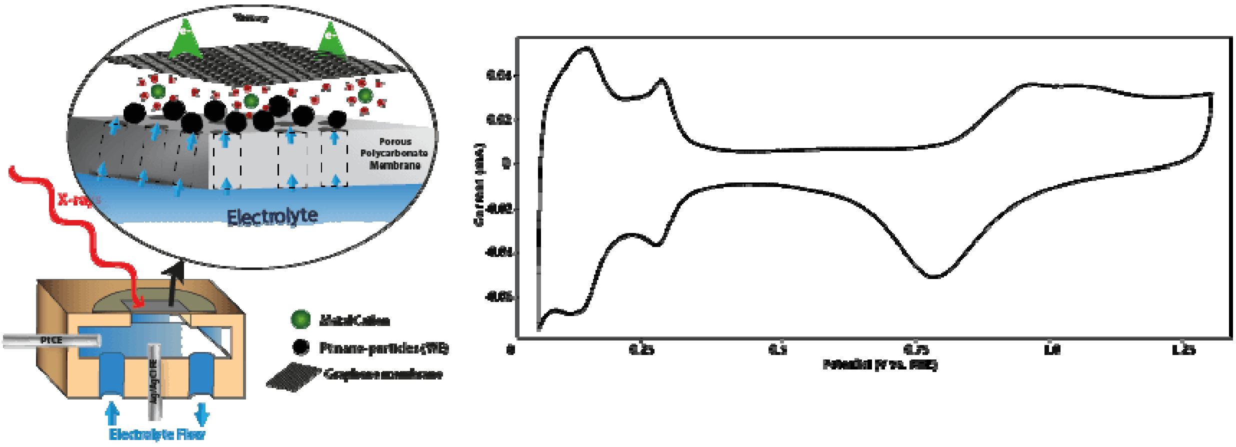

Figure 1: Schematic diagram and functioning of the in situ XPS cell

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Towards Operando Transmission Electron Microscopy in Aqueous Electrolytes: Optimized Liquid Flow Configuration

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ABSTRACT

Electrochemical catalytic reactions for the energy transition (hydrogen evolution reaction (HER), carbon dioxide (CO2RR), oxygen reduction reaction (ORR), oxygen evolution reaction (OER)) are attracting considerable interest from the scientific community, especially in the context of the ongoing global energy crisis. In order to design efficient catalysts with high activity, selectivity and stability, it is important to understand the fundamental mechanisms involved in the electrochemical processes. In this context, *in situ* / *operando* characterization techniques provide insight into the correlation between physical-chemical properties and the electrochemical performance. Specifically, electrochemical liquid phase transmission electron microscopy (EC-LPTEM) yields temporally and spatially resolved morphological, structural and chemical information regarding catalytic materials under electrochemical stimulation [1]. EC-LPTEM experiments are typically carried out in miniaturized liquid cell TEM holders with controlled liquid flow, where the electrochemical functionality may be provided with different technological approaches. One commonly encountered experimental set-up relies on MEMS-based technology to obtain a three electrode configuration (working electrode WE, counter electrode CE, reference electrode RE). The requirements for electron-transparency and the compatibility with the high vacuum conditions in the TEM column have a direct influence on the liquid cell geometry. As a result, EC-LPTEM experiments inevitably differ from the macroscopic counterparts and it is currently under scientific debate how to improve the experimental design in order to reach relevant *operando* conditions. One major challenge in the previously mentioned experimental set-up is the saturation of the miniaturized liquid cell by gaseous products from the reaction under study at the WE or by side reactions at the WE and at the CE, especially in aqueous electrolytes. Once the cell is saturated with gas, the electrolyte-electrode interface is dramatically affected, resulting in uncontrollable experimental conditions and elusive data interpretation.

In this work, we show that by properly optimizing the liquid flow configuration, it is possible to minimize the formation of gas bubbles in the liquid cell and to concurrently remove the gaseous products more efficiently in electrochemical conditions relevant for *operando* studies in aqueous electrolytes. Specifically, the standard geometry of the liquid cell in a commercial EC-LPTEM holder (*Poseidon Select*, Protochips, Inc.) is compared with a rationally optimized cell geometry which improves the liquid flow configuration [2]. Comparative electrochemical experiments are carried out under the optical microscope (with *ad hoc* glass chips) and inside the TEM column, to investigate the benefits of the optimized geometry. It Is shown that with the optimized geometry it is possible to perform electrochemical experiments with the cell fully filled with liquid (no gas saturation) in conditions (voltage window, current) which were previously not accessible [3] with the standard geometry. Finally, two examples of newly accessible experiments in aqueous electrolyte are shown: the electrodeposition of Zn nanostructures for energy storage applications and the dynamical evolution of a copper-based catalyst for CO2RR applications.

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Resolving the Gold-electrolyte Interface using in situ X-ray Photoelectron Spectroscopy

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ABSTRACT

For pivotal reactions in the energy transition, such as CO_2 reduction[1] or the hydrogen evolution reaction (HER)[2] it has been observed that the choice of cations and anions in the electrolyte have a significant impact on the electrocatalytic performance. Resolving the distribution of these ionic species at the electrode-electrolyte interface is key to explaining this observation. The need for experimental insights into the interface is even more so important given the models so far employed to predict the physical behavior at the double layer are still incomplete according to recent reports[3]. To access the interfacial ion distribution experimentally, we present a case study showing how in situ X-ray photoelectron spectroscopy (XPS) can serve as a powerful tool for the investigation of the electrical double layer (EDL) formed at an electrode-electrolyte interface. By carrying out the measurements in a dip-and-pull geometry, we enable the formation of an ultrathin electrolyte film on the working electrode that is necessary to characterize the EDL in situ. While other works have previously employed this approach[4], our study does not rely on large concentrations of electrochemically inactive spectator molecules, e.g., pyrazine, in the electrolyte. Instead, we show that interfacial ions can be detected, even in a dilute 50 mM $KClO_4$ electrolyte. Due to the absence of specifically adsorbing ions, this electrochemical system is also ideal to tease out what forces besides electrostatics, featured alone in traditional double-layer models, might be contributing to the ionic distribution in the EDL. Using in situ XPS, we ascertain the potential dependent distribution of K^+ cations and Cl^- anions across the EDL. Our work reveals that complex behavior is observed even for this highly idealized system.

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The Charge Distribution at Electrochemical Interfaces Probed with *In Situ* Surface Resonant X-ray Diffraction

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ABSTRACT

Electro-catalysts make it possible to accelerate electrochemical reactions, with important applications in several fields, such as energy storage, chemical synthesis, biosensors, water electrolysis.

The electro-catalytic activity is largely influenced by the charge distribution at the electrochemical interface, the few Ångstrom thick metal-liquid interface region where the exchange of charges takes place. Understanding the involved mechanisms is of paramount importance. It is above all a question of being able to characterize the structural and electronic properties of the catalyst surface and of the charge distribution in the solution. Nevertheless, unlike for the atomic structure characterization, there is currently no experimental method to specifically probe the electronic structure at this interface.

We present here a new approach, which allows the direct experimental measurement of the charge distribution at the electrochemical interface. This was achieved by combining experimental and theoretical approaches, i.e. coupling *in situ* experiments of Surface Resonance X-Ray Diffraction (SRXRD) with first-principle simulation of the measured spectra. FDMNES code, recently extended for the simulation of surface resonant diffraction experiments[1], has now been developed for the electrochemical interface description, to consider the presence of the electrolyte facing the crystal and the effect of the applied external electric field.

We succeeded here in measuring for the first time the spatial charge distribution at the electrochemical interface of the archetypal system Pt(111) in acidic solution[2].

In the potential region where no adsorbed molecules are present, we could determine the charge distribution on each of the metal surface layers. Charge is actually distributed over the two last surface Pt layers, corresponding to an electric dipole over the two outermost platinum planes. We could also determine the position of the positive counter ionic plane at with a quite good sensitivity, despite its disordered structure.

Our results[2,3] demonstrate the potential of this original way to unveil the electronic densities at the electrochemical interfaces, a challenging topic for the understanding of the electrochemical reactivity and to validate the theoretical predictions.

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Operando XAS Study of Fe Incorporation Effects on Ni-Fe Prussian Blue Analogue for Electrocatalytic Water Oxidation

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ABSTRACT

Electrochemical water splitting is a key reaction in chemical energy conversion. One bottleneck of water electrolysis arises from the high overpotential required for anodic oxygen evolution reaction (OER). Over the past decades, researchers have made great efforts in developing new catalysts, especially nickel/cobalt-based materials, to improve the OER performance[1]. Ni-Fe Prussian blue analogues (PBAs), a cyanide-bridged coordination polymer, are receiving increasing interest because of their ability to lower the OER overpotential in alkaline media. It has been reported that Ni-Fe PBAs will be converted into metal (oxy)hydroxide species over the course of OER[2]. However, there is still great controversy over the real catalytic active sites of PBA catalysts under the turn-over conditions. Furthermore, some potential synergistic mechanism between Ni and Fe still remains unclear.

Herein, we modified the Ni-Fe PBA by replacing one cyanide group in the ferricyanide ion ($[Fe(CN)_6]^{3-}$) with a nitroso group (-NO), which can accelerate the conversion process of PBAs under alkaline OER conditions[3]. Meanwhile, we substituted part of the Ni^{2+} sites with Fe^{2+} or Fe^{3+}, and the obtained NiFe-Fe PBA catalysts exhibit dramatically higher catalytic performances, decreasing the OER overpotential from 353 to 254 mV at 10 mA cm^{-2}. We carried out the operando X-ray absorption fine structure (XAFS) spectroscopic research to probe the geometric and electronic structures of the Ni and Fe sites over the course of OER. The results combined with the ex-situ XPS suggest that, under the turn-over conditions, all the PBA catalysts can only be converted into metal (oxy)hydroxides in the outer layer, while the internal structure remains unchanged. For the Ni-Fe PBA, its surface will be converted into pure γ-NiOOH with the $[Fe(CN)_5(NO)]^{2-}$ dissolving out of the working electrode. For the NiFe-Fe PBA, however, both the Ni and Fe cations that initially coordinated with the $[Fe(CN)_5(NO)]^{2-}$ can retain to form the (oxy)hydroxide species, in which the potential Ni-Fe synergism accounts for the boosted OER performance. Notably, no further oxidation of the Ni and Fe into tetravalent species was observed in the operando XAFS experiments with applied potential up to 1.9 V *vs.* RHE, ruling out the previously reported Ni^{4+}/Fe^{4+} dominant catalytic mechanism. This work sheds light on the active phases of electrocatalyst that are generated in-situ under the applied bias, opening up the possibilities for exploring new reaction mechanisms under turn-over conditions.

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Seeing Inside Palladium Hydrides with X-rays

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ABSTRACT

Palladium hydrides (PdH_x) are a model system for understanding phase transition mechanisms, as well as the mechanisms of absorption and storage of hydrogen (H) in materials. Thoroughly examined in the gas phase, this system is also of interest for electrochemistry, especially electrocatalysis. Indeed, by applying a modest overpotential, the concentration of molecular hydrogen (H_2) in the solution and the H:Pd ratio can effectively be controlled. PdH_x hydrides exhibit a slightly expanded lattice at low H content ($x < 0.05$), referred to as the α-phase. As the H loading increases, the α-phase undergoes a complete transformation into a lattice-expanded β-phase.

Using WAXS, we recently monitored *in situ* the absorption of H into commercial Pd nanoparticles (NPs) 3.6 nm in size [1]. Similar to observations on bulk Pd, we identified two PdH_x phases with distinct strain characteristics in both acidic and alkaline electrolytes. Additionally, we observed the trapping of H within the Pd NPs. However, crucial aspects of the mechanism and kinetics of PdH_x formation could not be captured. Specifically, it remained unclear whether the Pd NPs are isotropically saturated (following a core@shell model) or if preferential H absorption pathways exist (according to a spherical cap model). Moreover, the small sizes of the facets made it challenging to discern the distribution of strain fields at different facets and at the edges and corners atoms.

In this study, employing Bragg Coherent X-ray Diffraction Imaging, we obtained information on the morphology, projected strain, 3D displacement fields, and *d*-spacing of 300 nm Pd nanocrystallites at various electrode potentials relevant to H adsorption, H absorption, and H_2 evolution, all without undesirable 'beam effect' [2]. We examined changes in lattice constants for both α and β phases and reconstructed the Pd NPs in each individual phase. The reconstructions revealed a continuous increase in the Pd lattice parameter, indicating homogeneous strain. Additionally, we observed heterogeneous strain in the reconstructed Pd NPs, with tensile strain accumulating on the {111} and {100} facets, while the lattice in the edges and corners of the atoms appeared compressed. This heterogeneous strain was found to be reversible when transitioning from one phase to the other.

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement HERMES N° 952184.

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Bridging the Nanoscale and the Ensemble through Correlated Operando Electron and X-ray Microscopy Experiments

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ABSTRACT

Electrocatalysts can restructure during reaction and create structural motifs that are only stable under working conditions. Therefore, we need insight into the morphology and chemical state of electrocatalysts within the electrolyte and under applied potential to elucidate their structure-function relationships. While there have been significant advances in *operando* methods for probing the structure and chemistry of catalysts during reaction, each technique has its own strengths and weaknesses. For example, *operando* X-ray absorption spectroscopy (XAS) provides valuable information about the catalyst's structure and chemistry but using it to rationalize the subtle changes on a catalyst's surface is more challenging since XAS is a bulk-sensitive method and averages over the entire ensemble. Conversely, electrochemical liquid cell electron microscopy (EC-EM) can provide catalyst morphology at nanoscale spatial resolution, but the images have limited chemical specificity. In this presentation, I will discuss recent work in my group using liquid cell EC-EM holders inside a transmission X-ray microscopy (TXM) to probe the chemical state of individual electrocatalysts and how such EC-TXM experiments allow us to bridge the insights obtained from TEM and XAS experiments.

In Situ Studies of Copper Catalysts for Electrochemical CO_2 Reduction by Soft X-ray Spectro-microscopic Characterization

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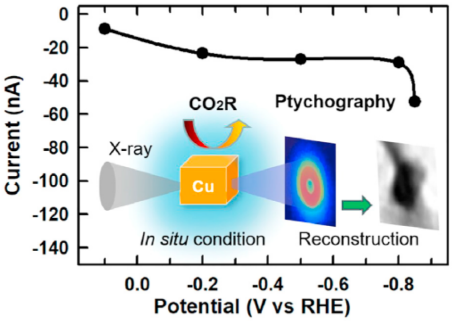
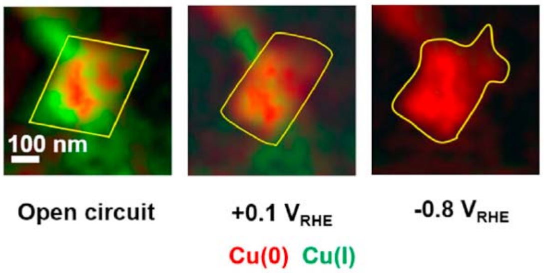
ABSTRACT

Carbon dioxide electroreduction (CO_2R) is a promising route to generate valuable feedstocks through the electrochemical conversion from CO_2 with electricity generated by renewable energy resources, thereby reducing greenhouse gas emissions and protecting the environment. [1] One of the critical challenges for developing practical CO_2R electro-catalysts is determining their structure and chemistry under operating conditions. Such results can then be used to optimize improved, high-performance electrocatalysts.

In this work, synchrotron-based scanning transmission X-ray microscopy (STXM) and X-ray spectro-ptychography were used for *in situ* studies of Cu CO_2R electrocatalysts. These methods provided spectroscopic characterization and quantitative oxidation state imaging during sample generation by *in situ* electrodeposition, and under CO_2R conditions. The *in situ* STXM studies of Cu catalysts [2] showed that electrodeposited Cu_2O particles were converted to metallic Cu at applied potentials less negative than that for initiation of CO_2R. Under CO_2R conditions, both *in situ* STXM [2] and *in situ* spectro-ptychography [3] showed metallic Cu is the active catalyst for CO_2 reduction. The ~3x better spatial resolution of *in situ* spectra-ptychography was used to follow morphological changes of a single Cu catalytic particle in the electrochemical regime of CO_2R. The results [3] showed that the initial cubic structure of the Cu particle changed to form irregular dendritic-like structures during the CO_2R process (see figure). Research performed at the SM beamline at CLS [2] and the Hermes beamline at Synchrotron SOLEIL [3].





In-situ Soft X-ray Spectro-Ptychography

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In Situ Hydration Study of Proton Conductor Electrolytes using a High-throughput Approach

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ABSTRACT

Discovering efficient and innovative materials for protonic ceramic cells requires the characterization of countless compositions. The knowledge of hydration thermodynamics and electrochemical performances is essential for understanding the proton conduction mechanisms and selecting the most promising electrolyte materials. However, traditional measurements are performed on individual samples and require extremely long stabilization times. A high-throughput approach was chosen to evaluate the electrochemical performance of hundreds of compositions inside the $Ba(Ce,Sn,Zr)_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCSZYY) ternary system. Thin film combinatorial libraries were produced by pulsed laser deposition on 100 mm diameter wafers. The composition gradient is obtained through alternate depositions of $BaCe_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCYY), $BaSn_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BSYY), and $BaZr_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZYY) centered on three opposite edges of the substrate to recreate the ternary diagram. XY-resolved characterization techniques were performed to map the elemental, structural, and hydration properties of each composition inside the BCSZYY ternary system.

In particular, X-ray diffraction (XRD) was carried out to study the thin film structure. More than 300 diffractograms were collected on different positions of a single sample and analyzed through a custom-made code to calculate the pseudocubic cell parameter of the thin film. The resulting values of the *a* cell parameters range from 4.176 Å for the BSYY-rich part, to 4.251 Å for the BZYY area, up to 4.418 Å for the BCYY one, in good accordance with the values obtained by Rietveld refinement for reference powders of single materials.

In situ measurements were also performed at the DiffAbs beamline of the SOLEIL synchrotron by simultaneously collecting X-ray diffraction and fluorescence signals. XRF allowed the evaluation of the elemental distribution of the BCSZYY samples at room temperature and gave insight into thickness variation, complementary to spectroscopic ellipsometry. A custom-made furnace was specifically developed to perform *in situ* XRD measurements on wide surface samples at high temperatures in dry and wet conditions. The furnace consists of a hotplate and an X-ray transparent PEEK dome, allowing the control of temperature and atmosphere. Due to the large surface of the hotplate, a calibration of the radial thermal losses was performed through a platinum reference sample. With a setpoint of 735 °C, the distribution of the calculated temperature of the Pt deposition showed a maximum of 645 °C near the center and 40 °C lower at the edges. The BCSZYY sample was subsequently measured in dry and wet N_2 to calculate the unit cell expansion due to water incorporation and to extract some information about hydration thermodynamics for the entire BCSZYY ternary system. A custom-made setup for electrochemical impedance spectroscopy is under development to measure the electrochemical performance.

Unraveling the Oxidation Behavior of Phosphorus Impurities in HT-PEMFCs via *In Situ* Tender X-ray Spectroscopy at the Pt|Aqueous H_3PO_3 Interface

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ABSTRACT

High-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) with H_3PO_4-doped membranes are a viable choice for a stationary energy source [1,2]. However, during operation condition of HT-PEMFCs, the H_3PO_4 electrolyte may undergo reduction, leading to the formation of phosphorus impurities with lower oxidation states, such as H_3PO_3 [3,4]. Recent studies indicate that the H_3PO_3 may strongly adsorb on Pt, state-of-the-art electrocatalysts in HT-PEMFCs, adversely influencing the O_2 reduction reaction (ORR) [5,6]. Given that H_3PO_3 generated during HT-PEMFCs operation may strongly adsorb on the cathode, the resulting Pt catalyst poisoning will significantly limit the ORR and decrease the HT-PEMFCs performance. Hence, understanding the Pt-H_3PO_3 interaction and its oxidation behavior under conditions relevant to the HT-PEMFCs operation is crucial for optimizing HT-PEMFCs performance. Yet, such studies are currently extremely scarce.

Thus, our study aims to unravel the complex oxidation behavior of H_3PO_3 on Pt under conditions relevant to HT-PEMFCs operation via *in situ* synchrotron-based tender X-ray spectroscopies. For insights into the interactions at the Pt|aq.H_3PO_3 interface, "dip-and-pull" *in situ* ambient pressure hard photoelectron spectroscopy (AP-HAXPES) is conducted at room temperature and open circuit potential (OCP) conditions. Subsequently, *in situ* P *K*-edge X-ray absorption near-edge structure spectroscopy (XANES) is performed using a three-electrode flow cells at experimental conditions relevant to HT-PEMFCs operation, such as during positive potential applications similar to the potential of HT-PEMFCs' cathode and at elevated temperatures. This mechanistic approach is complemented with *ex-situ* characterizations, such as ion exchange chromatography (IEC), gas chromatography (GC), electrochemical characterizations, and XPS of aq.H_3PO_3 with and without Pt catalysts. The results reveal that Pt catalyzes the chemical oxidation of aqueous H_3PO_3 yielding H_3PO_4 and H_2 [7], which is enhanced upon heat application [8]. Furthermore, the study shows that under positive potential, aq.H_3PO_3 undergoes electrochemical oxidation to H_3PO_4 [8]. Both oxidation mechanisms involve a reaction with H_2O [8]. These findings highlight the complexity of Pt-H_3PO_x interactions and provide insights for potential adjustments in HT-PEMFCs operational conditions to mitigate H_3PO_3 catalyst poisoning.

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Tracking the Evolution of Ni-based Single Atom Catalysts for the CO_2 Electroreduction Reaction: An *Operando* XAS/XES Study Assisted by Machine Learning Techniques

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ABSTRACT

In the last decade, Ni and nitrogen co-doped carbons have attracted attention as promising catalysts for the CO_2 electroreduction reaction (CO_2RR) exhibiting high CO_2-to-CO conversion activities, comparable with those of noble metal catalysts [1]. In these systems, N atoms are incorporated in the carbon support forming a binding site for the singly-dispersed Ni species [2]. However, it is worth noting that a large number of different structural motifs can coexist in these systems and evolve during the CO_2RR process, making the identification of the actual active sites and interpretation of the CO_2RR reaction steps difficult to realize experimentally.

In this study, *operando* time-resolved XANES data were used to unveil the local structure around Ni sites in their *as prepared* states, but also under realistic working conditions during CO_2RR [3]. A multi-step approach has been used for the interpretation of the collected XANES data. First, we identified the number of different coexisting Ni species, their corresponding kinetic profiles and XANES spectra using unsupervised machine learning methodologies, such as the principal component analysis combined with a multivariate curve resolution technique [4]. In the second step, we deduced the atomistic structures for each of the identified species through a XANES fitting procedure, realized exploiting a supervised machine learning approach [5]. Afterwards, we validated the predicted structures processing the corresponding EXAFS spectra *via* Reverse Monte Carlo simulations [6], taking into account the structural disorder in the local environment around the identified Ni species. Finally, we simulated the related valence to core XES spectra and we compared the obtained results with the collected experimental profiles gaining additional information on the types of ligands appearing and evolving during reaction conditions

Our results confirm that the single Ni sites are the active species for the CO_2RR, but also reveal their dynamic, heterogeneous nature and adaptation to the reaction conditions. In particular, our data suggest that the local environment around Ni is directly affected by the interactions between the Ni site and CO adsorbates. We found that the initial state of our catalysts (before the CO_2RR), can be represented by a six coordinated model with four planar Ni-N bonds and two axial O atoms. The CO_2RR induces a local structural distortion of the Ni site in the N doped carbon matrix, with the progressive substitution of both the O atoms with a CO adsorbate. Overall, these results demonstrate the potential of XAS and XES spectroscopy in combination with advanced data modelling to access an unprecedented level of understanding of a complex multi-component catalytic system, yielding novel insights into the birth of Ni-active sites for the CO_2RR reaction.

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ABSTRACTS

Friday, April 5th, 2024

Friday, April 5th

Session 4: Applied and industrial systems

*Chair: **Clément Sanchez***

IT-04	Bridging discovery to application: Utilizing Synchrotron techniques in electrocatalysis	***Andrea Zitolo***
OC-16	Paradigm shift of platinum oxidation below fuel cell open-circuit voltage	***Raphaël Chattot***
OC-17	An operando zero-gap MEA cell for combined spectroscopy, diffraction, and imaging, applied to the study of ion effects in CO_2 electrolysis	***Matthew Mayer***
OC-18	Operando X-ray studies of gas evolving and consuming electrocatalysts	***Andrea Russell***
ET-04	Electrolyte distribution in silver gas diffusion electrodes for electrochemical CO_2 reduction measured by operando Synchrotron tomography	***Jens Osiewacz***
OC-19	Electrochemical and structural study of NiRux heterofunctional catalysts for the alkaline HER	***Marie-Sophie Fernandes-Diaz***
OC-20	Set-ups for in-operando X-ray absorption spectroscopy/electrochemistry in half-cell and fuel-cell configurations: The case study of palladium deactivation in direct alcohol fuel cells	***Enrico Berretti***
OC-21	Characterizing microstructure and gas transport properties of electrospun gas diffusion layers in proton exchange membrane fuel cells through high-resolution imagery	***Bertrand Roussillo--David de Beaufort***

Bridging Discovery to Application: Utilizing Synchrotron Techniques in Electrocatalysis

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ABSTRACT

Over the past few decades, studies in electrocatalysis have benefited from a growing development of *in-situ* and *operando* techniques based on the use of synchrotron radiation.[1] Indeed, the engineering of new complex materials necessarily involves a deep understanding at the atomic and molecular scale of their structural and electronic properties, and how these vary during the reactions they catalyze. Successfully conducting an electrochemical experiment under working conditions on a beamline requires a joint effort from experts in various fields: electrochemistry, engineering, and synchrotron science. Each system under examination requires the design of experimental environments that vary depending on the technique and the specific reaction under study, and must address the challenges arising from both the electrochemistry and synchrotron experiments.

Among the various *in-situ/operando* investigation techniques, X-ray absorption spectroscopy (XAS) has earned a prominent place in identifying the nature of active catalytic centers and their evolution over time.[2-4] The success of this technique is linked to its ability to extract structural and electronic information with a high degree of accuracy, and its applicability not only to ordered crystalline systems but also to disordered systems, including liquid phases, amorphous or dispersed systems. The aim of this talk is to provide an overview of the potential of the XAS technique, using examples such as reactions for CO_2 valorization or reactions occurring in fuel cell and electrolyzer devices, and to discuss possible technological applications. A significant effort on our part is indeed focused on understanding how synchrotron experiments can bridge the gap between discovery and application.

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Paradigm Shift of Platinum Oxidation below Fuel Cell Open-circuit Voltage

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ABSTRACT

The long-term stability of Pt catalysts is critical to the reliability of proton exchange membrane fuel cells (PEMFCs) [1], and receives constant attention. However, current knowledge of Pt oxidation is mostly restricted to that deduced from observations made in a PEMFC cathode environment under far-from-realistic conditions, which questions its practical relevance.

Herein, Pt oxidation is investigated directly in a PEMFC by means of stroboscopic *operando* high energy X-ray scattering. The onset potential for Pt surface atoms extraction through the place-exchange mechanism is observed far below the previously reported value, and most importantly, below the open-circuit potential of PEMFC cathode. Such early oxidation is shown to impact PEMFC performance and its role on Pt transient dissolution is verified by electrochemical on-line inductively coupled plasma mass spectrometry measurements above ambient temperature. By further demonstrating and resolving the limitations of currently employed accelerated stress test protocols in the light of place-exchange time constants, this new paradigm of Pt oxidation paves the way to new mitigation strategies against PEMFC degradation [2].

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An Operando Zero-Gap MEA Cell for Combined Spectroscopy, Diffraction, and Imaging, Applied to the Study of Ion Effects in CO_2 Electrolysis

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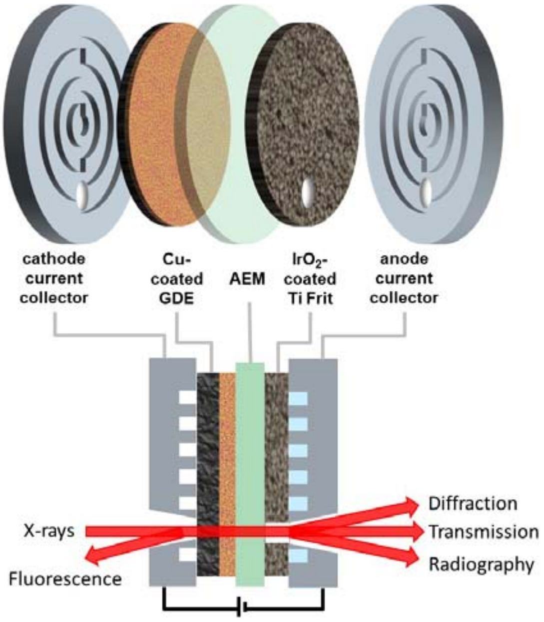
ABSTRACT

In situ and *operando* methods applied to electrocatalytic systems can provide important information about dynamics of catalyst structure and composition, transport processes, and degradation mechanisms. However, such methods are usually applied to specially designed cell geometries (i.e. small electrodes, thin electrolyte layers) and under test conditions (very low current densities, no product collection) which differ greatly from practical devices, putting the relevance of the results into question.

Here we report a zero-gap membrane electrode assembly (MEA) cell designed for electrolysis study under practical operating conditions. We demonstrate efficient high-rate CO_2 electrolysis (j > 200 mA/cm²) with a significant electrode area (8 cm²) using on-line product analysis, while simultaneously studying the system using a variety of X-ray based analytical methods, including X-ray absorption spectroscopy (fluorescence and transmission mode), imaging (radiography), and scattering. We demonstrate the methods on the study of phenomena relating to electrolyte ion effects in CO_2 electrolyzers, namely the unintended cation crossover through anion exchange membranes which can influence selectivity as well as lead to cell failure due to salt crystal precipitation.(1)



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Operando X-ray Studies of Gas Evolving and Consuming Electrocatalysts

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(b)

ABSTRACT

Electrolysis and electrosynthesis are becoming of increased importance in the transition to more environmentally friendly of energy and chemical production. For example, water electrolysers are used in the production of green hydrogen. Such electrolysers are limited by the activity and stability of the oxygen evolution reaction (OER). Similarly, the electrochemical conversion of carbon dioxide (CO_2) to useful chemicals and fuels is a promising route toward the achievement of carbon neutral and carbon negative chemical production. A better understanding the catalytically active sites and degradation mechanisms at current densities relevant for industrial application of these processes is paramount for further catalyst improvement

In this project we have developed a novel operando x-ray absorption spectroscopy (XAS) electrochemical cell, which aims to increase the mass transport limiting current density of gas evolving and consuming reactions through an improved three-phase interface between catalyst, electrolyte, and produced/consumed gas, whilst also ensuring near full utilisation of the electrocatalyst (see figure 1). Here we will illustrate the use of the cell for operando XAS studies of (1) an iridium oxide electrode in strongly oxygen evolving conditions and (2) copper oxide for CO_2 reduction.

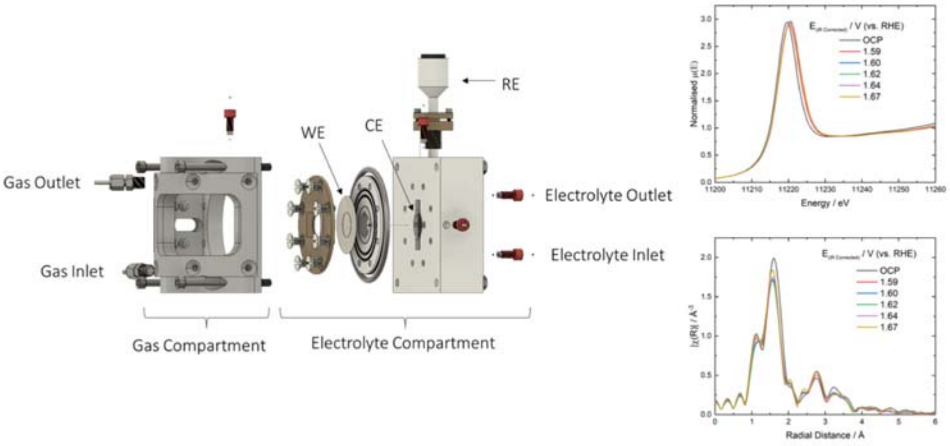

Figure 1: Schematic of the operando XAS electrochemical cell. Normalised Ir L_3 XANES (top) and EXAFS (bottom) collected in the operando XAS cell in 0.1 M H_2SO_4 under flowing N_2 at during the OER.

Electrolyte Distribution in Silver Gas Diffusion Electrodes for Electrochemical CO_2 Reduction Measured by Operando Synchrotron Tomography

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ABSTRACT

DIRECT MEASUREMENT OF ELECTROLYTE SATURATION INSIDE A SILVER-BASED GAS DIFFUSION ELECTRODE

Electrochemical CO_2 reduction (eCO_2R) stands out as a promising technology for steering the chemical industry away from fossil fuels. When integrated with renewable energies, it enables a carbon-negative process, utilizing CO_2 as a carbon source for producing essential chemicals. The efficiency of eCO_2R relies on gas diffusion electrodes (GDEs) with a substantial wetted surface area within the porous system, maintaining hydrophobicity for effective CO_2 mass transport. However, under high cathodic overpotential in eCO_2R, electrowetting reduces GDE hydrophobicity, causing excessive flooding and hindering CO_2 transport, leading to a decline in Faradaic efficiency due to the competing hydrogen evolution reaction (HER).[1]

Therefore, comprehending the flooding behavior of GDEs is crucial for advancing the eCO_2R process. Mathematical models play a pivotal role in describing the flooding state influenced by electrowetting and understanding its impact on gas transport through GDEs. Validating such models necessitates direct experimental measurements of electrolyte saturation during eCO_2R, achievable through synchrotron radiation.[2]

This study presents experimental results from direct measurements of electrolyte saturation during eCO_2R in sprayed silver GDEs. Operando synchrotron tomography experiments were conducted using high beam energy to penetrate the 3 mm diameter GDE in the in-plane direction. The results revealed increased beam absorption towards the gas side of the GDE, with higher absorption observed at elevated current density. Interpretation of these findings required distinguishing between concentration increase due to electric field-induced migration and the actual rise in electrolyte saturation.

These experimental outcomes were utilized to validate a continuum model for a sprayed silver GDE in eCO_2R. The model incorporated the effects of electrowetting on flooding behavior by introducing capillary pressure–saturation and contact angle–potential correlations.[3] A strong agreement between the model and tomography results was achieved, highlighting the interplay between concentration increase and flooding effects in eCO_2R.

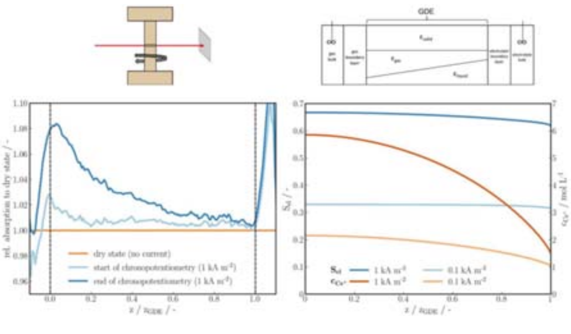

Fig. 1: Relative beam absorption coefficient over through-plane direction of GDE during chronopotentiometry (left). Model results for cesium concentration and electrolyte saturation over through-plance direction (right). z=0 corresponds to the gas side of the GDE.

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Electrochemical and Structural Study of NiRux Heterofunctional Catalysts for the Alkaline HER

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ABSTRACT

The alkaline water electrolysis is a promising method to store intermittent energy sources while producing green hydrogen efficiently. Among the different technologies available, anion exchange membrane (AEM) electrolyzers has the advantage of functioning with catalysts based on non-noble metals. Indeed, the use of alkaline medium provides suitable chemical stability for a large range of materials such as transition metals, which significantly reduces the AEM cost and allows a large-scale use. However, the performances and stability observed for AEM catalytic films are lower due to the sluggish water dissociation step occurring during the hydrogen evolution reaction (HER). Therefore, the concept of heterofunctional catalysts emerged as an efficient approach to combine the properties of active materials and create a synergy between them in order to promote the dissociation of water. To do so, members of our team developed a new family of heterofunctional catalysts based on large particles of nickel decorated by ruthenium nanoparticles. XPS results indicate that ruthenium is mostly observed on the nickel surface (see figure 1.a), which supports a heterogeneous structure. We carried out electrochemical characterizations (cyclic voltammetry measurements and electrolyzer test) and the results showed very high efficiencies for this family of materials (see figure 1.b), with performances similar to the platinum ones (60% Pt/C). The materials structure was also analyzed by *operando* X-Ray Absorption Spectroscopy (XAS) at the Ni and Ru K-edges to identify which metals are involved in the catalysis at low and high ruthenium content (see figure 1.c). In this presentation, the electrochemical and XAS results will be presented as well as the relationship between the structure and activity of these materials.

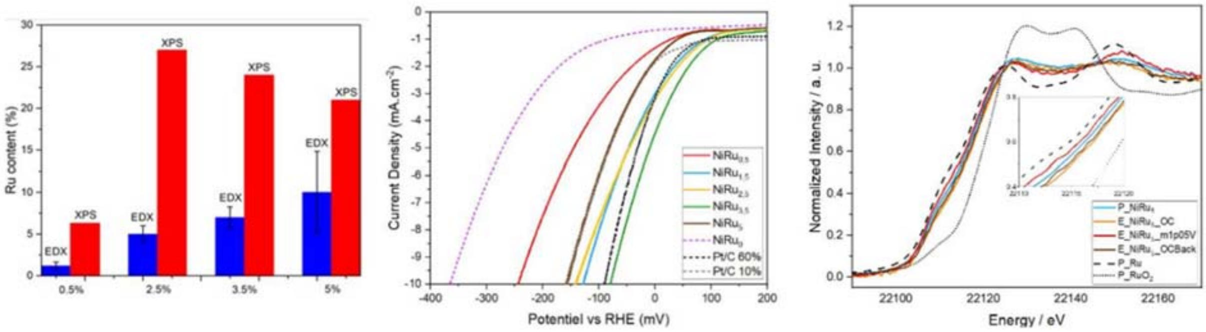

Figure 1: (a) The Ru content measured for the NiRux samples by XPS and EDX; (b) cyclic voltammograms of the NiRux and Pt/C 10% and 60% wt. references in 0.1 M KOH; (c) Operando XANES spectra registered for the NiRu5 and the references.

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Set-ups for In-operando X-ray Absorption Spectroscopy/Electrochemistry in Half-cell and Fuel-cell Configurations: The Case Study of Palladium Deactivation in Direct Alcohol Fuel Cells

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ABSTRACT

In recent times, palladium has been proposed as electrocatalyst for several applications, ranging from energy conversion to "green" processes to produce chemicals from renewable resources. Indeed, palladium-based electrodes have been successfully employed as anodes for alkaline Direct Alcohol Fuel Cells (DAFCs) and the electrolysis of hydro-alcoholic solutions. On the other hand, the main issue still preventing this element's large-scale adoption for the above-listed applications is its deactivation, whose origin has not yet fully understood. What is known so far is that Pd oxides' formation plays a significant role in the performance loss of electrochemical converters [1]. Moreover, recent studies showed some degree of palladium dissolution under operative conditions [2,3,5], which hinder the effectiveness of anode potential cyclic inversion in the catalyst's performance recovery.

A set of different experiments on the study of this particular deactivation phenomenon in alkaline DAFCs will be described in the present talk. All of them exploited the Fixed Energy X-Ray Absorption Voltammetry (FEXRAV) technique, an electrochemical X-Ray Absorption (XAS) technique, which permits to follow the speciation of an element during electrochemical stimulus [4]. Notably, studies on the palladium behavior in half cell [2,3] and complete fuel cell [5] configurations will be described. Lastly, the work done in order to prepare and characterize palladium model surfaces whit the same goal will be reported. This particular procedure's success could pave the road to the fundamental characterization of a vast array of different metallic catalysts.

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Characterizing Microstructure and Gas Transport Properties of Electrospun Gas Diffusion Layers in Proton Exchange Membrane Fuel Cells through High-resolution Imagery

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ABSTRACT

PEM fuel cells represent the future of electric vehicles. Improving performance, cost and durability of its components constitute key objectives for this technology. The gas diffusion layer (GDL) plays a critical role in the performance of the fuel cell. Indeed, it ensures gas transport, provides electrical and thermal conductivities, and must prevent cathode flooding while keeping the membrane well hydrated [1]. We investigate the fabrication and characterization of electrospun GDL (eGDL). Electrospinning allows for the creation of carbon fibers and pores in the range of hundreds of nanometers. This is two orders of magnitude smaller than the fibers and pores sizes of commercial GDL. Electrospinning has recently been used to design tailored porous media for PEMFC [2], [3]. We exploit the versatility of this innovative technique to fabricate eGDL with controlled microstructures, varying fibers and pores sizes [4]. We employ high resolution imaging (synchrotron X-Ray tomography, Fib-Sem) to analyse the microstructure of electrospun and conventional GDL. We also investigate a detailed characterization of gas transport properties from acquired 3D structures using GeoDict™ and ImageJ software [5]. Both monophasic and diphasic gas transport properties are calculated (diffusion, tortuosity, permeability, capillary pressure, relative permeability). Furthermore, we explore the influence of compression. We thus establish relationships between transport properties and microstructural parameters, evaluating the applicability of classical models such as Bruggeman and Karman-Kozeny. Finally, we relate our results to the actual performance of the studied GDL by performing fuel cell tests.

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POSTERS SESSION

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PO-24	Phase transfer analysis of BiOBr in BiOBr/MoS_2 heterojunction under photoelectrochemical environment ***M.Wang***
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PO-26	Making C-N bonds from carbon monoxide and nitrite Co-electroreduction ***S. Zhao***
PO-27	Interfacial synergy of iridium and titanium in model configurations for oxygen evolution reaction ***M. Zlatar***

Bio-inspired Carboxylate-polymer/metal Oxides Material for Electrocatalytic Water Oxidation

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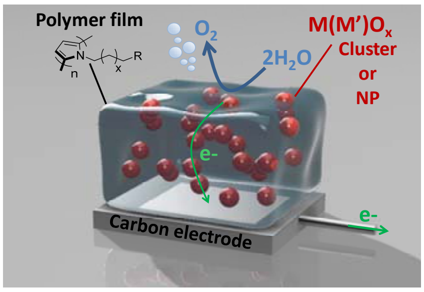
ABSTRACT

Water oxidation into dioxygen (OER) remains a bottleneck in the scale-up of water-splitting and CO_2-reduction electrolyzers due to slow kinetics and large overpotential. A key challenge is the development of efficient, robust and cheap OER catalysts based on earth-abundant elements. Heterogeneous metal oxides or (oxy)hydroxides are the most promising catalysts in terms of activity and robustness. Current research focuses on the development of oxides based on abundant metals (Co, Ni, Fe, Mn and Cu), which are less expensive than Ir and Ru oxides, and can be easily deposited on the surface of electrodes in the form of thin films to obtain efficient anodes.[1] A key factor in the performance of an electrocatalyst is its nanostructuration, the efficiency being significantly improved by increasing the active area/volume ratio while reducing the manufacturing cost. However, the reduction of the particles size for increasing the specific surface area of the catalyst leads to a decrease of their stability and can lead to aggregation. These limitations can be overcome by immobilizing the nanoparticles (NPs) in a polymeric or inorganic material.[2-4] In this context, we have recently designed bio-inspired nanocomposite electrode materials active and stable for water oxidation by a simple and versatile electrochemical method. These new materials consisting of (sub)nanosized earth-abundant (mixed) metal oxides $M(M')O_x$ clusters (M, M' = Ni, Co, Fe…) well dispersed into a polymer matrix substituted with anionic functions,[5] mimicking the carboxylates rich environment of the natural Mn_4CaO_5 cluster of PSII and its sub-nanosized structure, two essential features for an outstanding catalytic efficiency.



These composite materials have been characterized by several methods, such as SEM, TEM, AFM and GIWAXS. More recently, in-situ and ex-situ XAS studies have also been performed to further the analysis of the composite material. The method of elaboration of the nanocomposites, their characterization by the several and complementary methods as well as their electrocatalytic performance for OER will be presented.

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In-operando XAS on Iron-phthalocyanine during Pyrolysis: The Evolution of the Active Sites of an Oxygen Reduction Reaction Electrocatalyst during its Synthesis

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ABSTRACT

The escalating demand for sustainable and cost-effective energy technologies has led to a paradigm shift in electrocatalysis, pivoting from platinum group metals (PGMs) to non-PGM alternatives. Among these, iron stands out as a promising candidate for the oxygen reduction reaction (ORR), a key cathodic reaction in fuel cell applications. Iron is abundant and significantly cheaper than PGMs, offering a sustainable solution for large-scale applications; when it is engineered at the nanoscale and combined with nitrogen-doped carbon supports, exhibits ORR activity approaching that of PGMs, thanks to the iron affinity towards oxygen. The electroreduction process is fostered particularly by the presence of Fe-N_x-C active groups, which facilitate the four-electron reduction pathway necessary for efficient ORR. Iron phthalocyanine is commonly used as base material to synthesize such electrocatalysts, blended together with a C filler and subjected to a pyrolysis process in non-oxidizing atmosphere at temperatures that could span between 500°C and 1000°C. Changes in process atmosphere and/or in temperature could lead to a dramatic change in the electrocatalyst performances, due to the variations occurring at the Fe-N_x-C active sites. In the present contribution we report ex-situ and in-operando X-Ray Absorption Spectroscopy (XAS) results acquired during pyrolysis of iron-phthalocyanine. Different processing atmospheres (completely inert 100% Ar and slightly reductive 95%/5% Ar/H2), and temperatures ranging between 200°C and 1000°C were used to prepare samples. The main aim of the XAS study was to correlate the synthesis parameters with the structure and functional properties of the electrocatalyst. A wide array of different characterizations such as TEM, EDX, XPS, XRD and Electrochemical tests were used, whose results were coupled with the XAS study. The set of collected enabled a novel insight into the evolution of Fe-N_x-C electrocatalysts during pyrolysis, fostering the capability to produce and design novel, top-performance and sustainable electrocatalysts for ORR.

Evaluation of Three Different Nano-catalysts for the Oxygen Reduction Reaction by Operando Photoemission Spectroscopy

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ABSTRACT

Since their discovery in the 1960s, proton exchange membrane fuel cells (PEMFCs) have been of great interest thanks to their high energy conversion and also because water is the only product of the reaction. In fact, within fuel cells, these are considered as the most promising technology for energy transport applications.[1] In PEMFCs the energy conversion takes place through the hydrogen evolution reaction (HER) at the anode and the oxygen reduction reaction (ORR) at the cathode. However, the ORR kinetics are various orders of magnitude slower than HER. In order to improve the efficiency, platinum nanoparticles (NPs) supported on carbon (Pt/C) are used as electrocatalyst at the cathode. Despite the high performance obtained through Pt, Its high-cost and low stability limits Its use in PEMFCs. In this context It is necessary to look for an alternative to Pt/C.[2]

In order to find a suitable substitute for Pt, the presented project aims to study the activity and stability of three different compounds which have shown previously a remarkable performance for ORR. In a first step, Pt_3Zn nanocatalyts will be tested. Pt-Zn intermetallic NPs have been proven as efficient catalyst for PEMFCs.[3] Also, It has been demonstrated that these NPs are unstable and tend to lose Zn.[4] For this reason, the study will be extended to Co_2P and NiCoP. Cobalt phosphides based materials are used as efficient electrocatalysts for hydrogen production and fuel cells, and as electrode material for baterries.[5]

To this end, the mentioned materials will be tested by cyclic voltammetry in different electrochemical systems. The evolution of the NPs will be first studied post-mortem with laboratory XPS. Operando investigation will be done by Near Ambient Pressure XPS (NAP-XPS) and X-ray Absorption Spectroscopy (XAS) using synchrotron radiation (SOLEIL).
Taking in account the information available in the literature, It is expected that the three compounds are going to show an activity comparable to Pt/C. However, in terms of stability, Co_2P and NiCoP are expected to surpass Pt/C and Pt_3Zn.

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Using X-ray Absorption Spectroscopy to Understand Electrocatalysts: Beamline B18

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ABSTRACT

The increased interest in electrochemical energy-storage/conversion systems such as metal-air batteries, fuel cells, and electrolyzers arising from the interest in electrification of energy supply and distribution has motivated many studies of oxygen reduction and evolution reaction (ORR and OER) electrocatalysts and CO_2 reduction electrocatalyst among other reactions. The development of more efficient and stable materials is a critical step for the final introduction of these devices in the market. Understanding the reaction mechanism at such complex materials requires direct information regarding the changes in the orbital occupancy of the metallic sites that can only be achieved using in situ characterization techniques. In situ X-ray absorption near-edge structure (XANES) studies enable identification of the oxidation states of the metal atoms, while the extended X-ray absorption fine structure (EXAFS) data enable the study of the accompanying change in the coordination environment.

B18 is the general purpose XAS beamline on Diamond, being part of the Spectroscopy Group, which includes I18 (microfocus beamline, 2-20 keV) and I20 (high flux beamline, 4-35 keV). B18 covers a wide energy range (2 to 35 keV covering K-edges from P to I and LIII-edges from Y to U), with a monochromator designed to carry out both conventional and Quick EXAFS (QEXAFS) measurements. The time resolution offered by B18, together with the possibility of combined use of XRD and XAS and a large and flexible sample space; make B18 a very attractive beamline for the study of in-situ/operando electrocatalysts.

I shall be introducing and discussing the capabilities of B18, as well as some of the most recent developments and scientific cases, to showcase how B18 can help the energy materials community to move forward.

Ligand-field/redox Potential Correlation in Co-Fe Oxides Investigated by 2p3d Resonant Inelastic X-ray Emission Spectroscopy

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ABSTRACT

Spinels are an essential class of minerals which serve as fundamental model structures for advanced functional materials. Fe loading into spinels can significantly alter the physical-chemical properties of the parent spinel.[1] BET, XRD, APT, HRTEM, SAED, EELS, Raman spectroscopy and Mössbauer spectroscopy have been widely used to explore the Fe role at the level of morphology, crystal structure, oxidation state, and geometric structure. Recently, 2p3d RIXS has been used as a site-selective technique to probe mixed-valence samples.[2] Here we used the 2p3d RIXS to directly probe the geometric and electronic environment surrounding a Co center in Fe-loaded Co-based spinels. $CoFe_2O_4$ (containing only $Co^{2+}{}_{Oh}$), $CoAl_2O_4$ (containing only $Co^{2+}{}_{Td}$), and $ZnCo_2O_4$ (containing only $Co^{3+}{}_{Oh}$) were chosen as references to study the spectral signatures of the different sites. Ligand-filed multiplet calculations were used to reproduce the L-edge XAS and 2p3d RIXS of the references.[3] The calculated Tanabe-Sugano diagrams allow for visualizing the ligand field modulations of the low-lying excited states. These electronic structure changes can then be correlated with the differences in Fe-induced electrocatalytic performance.

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Understanding the Activation of Hydroxide Perovskite Oxygen Evolution Reaction Catalysts

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ABSTRACT

More efficient and earth-abundant oxygen evolution reaction (OER) catalysts are required to enable a large-scale hydrogen economy. Ni- and Co-based oxides are among the leading candidates to displace precious metal OER catalysts. Their amorphous forms tend to deliver greater OER activity than their crystalline phases [1]. Under alkaline electrolysis conditions, the OER active phase for these classes of materials is a reconstructed (Co, Ni)-O-OH amorphous layer. Optimizing a perovskite surface's free energy of OH adsorption has been indicated as a way to boost the lattice oxygen evolution mechanism [2]; hence, directly incorporating hydroxide into the material lattice may lower this energy barrier. We observe large (>50 %) increases in activity due to (surface) amorphization of $CoSn(OH)_6$ ($BB'(OH)_6$) hydroxide perovskites. *Ex situ* thermal, *in situ* gavanostatic, and *in situ* cyclic voltammetry treatments yield differing activities [3-5]. Thus, $CoSn(OH)_6$ is a model material to investigate which parameters determine a highly active amorphous OER catalyst. Here we present *operando* X-ray diffraction and hard X-ray absorption spectroscopy (XAS), *ex situ* soft XAS, and *in situ* rotating disk electrode characterizations of the activation of $CoSn(OH)_6$. Initial data indicate that introducing oxygen defects can have a beneficial impact even greater than bulk amorphization. Future work towards identifying general amorphous OER activity descriptors is outlined.

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Operando Methods for Chemical Imaging during Electrochemical Processes in Solid-state: A Preview into the Recent Developments within the Horizon Europe Project OPINCHARGE

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ABSTRACT

Electrochemical processes underpin a variety of energy generation and storage technologies. To understand the performance degradation mechanisms of such energy materials, and to develop mitigation strategies, it is essential to observe the nanoscale structural and chemical changes that occur during electrochemical processes. However, such 'operando' analytical methods are not yet widely available. This is particularly severe for the case of Secondary Ion Mass Spectrometry (SIMS) imaging which is ideally suited for high-sensitivity chemical analysis and imaging of all elements (including isotopes) in the periodic table. Furthermore, for the analysis of light elements such as H and Li which play crucial roles in electrochemical technologies, conventional analytical techniques associated with electron microscopy such as Energy Dispersive X-ray spectroscopy are inadequate or even not suitable. In this context, the OPINCHARGE project [1] funded by the European Commission has been recently launched. One of the main goals of the project is to drive breakthrough innovations in *operando* analytical techniques for the study of solid-state interfaces in Li-ion batteries. The methods developed for that can be extended for applications in electrocatalysis investigations.

In our poster presentation, we will present an overview of the OPINCHARGE project and its major aims. We will also present our recently developed prototype instrumentation to enable operando SIMS imaging at sub-20 nm lateral resolution.

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The Combined Power of In-situ and Ex-situ Techniques: Stability and Decomposition Pathways of the NiOOH OER Active Phase of NiO_x Electrocatalysts at open Circuit Potential

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ABSTRACT

For water splitting, Ni based materials are highly researched. Various parameters are extensively studied, ranging from all kinds of sample preparation methods to huge variations in element combinations and stoichiometries.[1] Yet, most studies present results from ex-situ measurements. In our study[2], we deposited well defined model systems by DC magnetron sputtering to bridge the gap between ex-situ and in-situ measurements. For NiO, NiOOH is known to be the OER active phase.[4-6] However, the transformation from $Ni(OH)_2$ to NiOOH is reversible.[3] The transformation can either be potentially driven, or, at open circuit potential the NiOOH phase is decomposing to $Ni(OH)_2$ upon a potential drop. We studied this pathway in detail with in-situ Raman spectroscopy and ex-situ X-ray photoelectron spectroscopy. With Raman, the NiOOH phase is identified and the time evolution of the NiOOH decomposition is determined. These results emphasize the importance of in-situ techniques and a detailed knowledge of expected phases when performing ex-situ measurements. With this knowledge, we could show that NiOOH can be measured also ex-situ within a limited timeframe or if it is stabilized in vacuum. Such a vacuum stabilized sample was exposed to pure H_2O in a quasi in-situ approach and measured with XPS before and after exposure. The result was the restart of the decomposition of NiOOH. This reveals that the reduction of NiOOH requires protons and electrons, where the latter need to be generated by an oxidative reaction.

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Investigation of Ordering in High Entropy Alloy Nanoparticles after Glucose Electro-oxidation Reaction

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ABSTRACT

Multiple principal elements can provide a screening platform for the discovery of electrocatalysts.[1] The High Entropy Alloys (HEAs) are one of the kinds of metastable materials having different principal elements in the same lattice. They have chemical diversity on the surface along with an atomic size mismatch which consequences in lattice strain. These intrinsic properties in these disordered materials offer a range of adsorption energies for different molecules. Therefore, HEAs are being investigated to tune sensitivity, selectivity and stability in electrocatalysis.[2]

Glucose is an environmentally friendly molecule that when undergoes oxidation at C-1 anomeric carbon enables its direct conversion to electricity and value-added products. Gold surface is well explored for Glucose Electro-oxidation reaction (GOR) and is most active among other noble metals.[3] Interestingly, our preliminary experiments shows that noble metal-based HEA nanoparticles (NPs) are catalytically more active than both polycrystalline gold surface and gold NPs. However, we found that HEA NPs seem to undergo segregation after one hour of potentiostatic or potentiodynamic protocol in the presence of glucose. These segregations are important to track to understand electrochemical stability of HEA surfaces for GOR. One of the approaches to follow it is by detecting the origin of chemical short-range ordering (CSRO) and SRO due to defects in the HEA NPs.[2]

CSRO can be found by electron microscopy using diffraction and imaging in right crystallographic directions which provides local information from a few NPs.[4] While high energy X-rays from third generation undulators can be used to get Pair Distribution Function (PDF) in larger Q-space. Moreover, PDF from synchrotrons helps to get statistical data of the local structure. Hence combining advanced microscopic analysis from electrons and total scattering from X-rays can reveal the extent of SRO in HEA systems. The present work is therefore to understand the microstructural changes in noble metal based High Entropy Alloy (HEA) nanoparticles (NPs) after GOR with X-rays and electron probes.

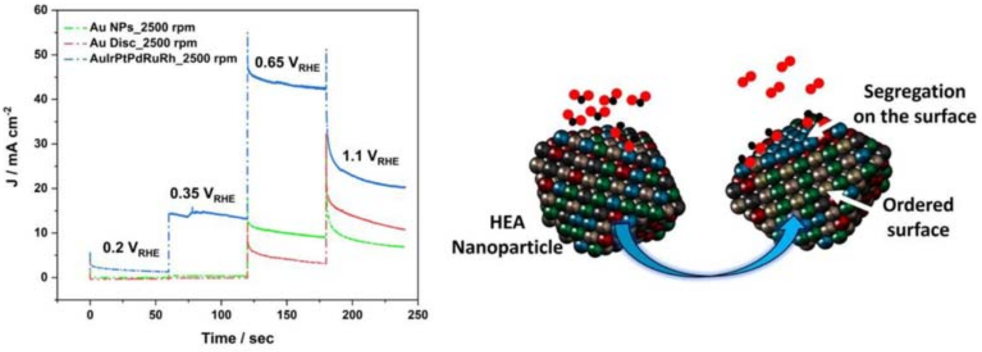

Figure: Plot shows potentiostatic steps of 60 seconds at 0.2VRHE, 0.35VRHE, 0.65VRHE and 1.1VRHE on Gold NPs, Polycrystalline Gold disc and HEA NPs (AuIrPtPdRuRh) in 50mM Glucose (0.1M NaOH + 0.1M NaClO4).

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Electrodeposition of Copper-based Catalysts for Carbon Dioxide Reduction

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ABSTRACT

The CO_2 electrochemical reduction (CO_2RR) is a most promising technologies to mitigate the effects of high CO_2 content in the atmosphere converting it into valuable fuels and chemicals under ambient conditions. In recent years, Cu-based electrocatalysts have attracted significant attention as they can produce multiple carbon (C_{2+}) products, however, there are still challenges such as wide distribution of reduction products, poor stability, and high overpotentials [1-3]. Among the diverse synthesis methods that have been proposed for the synthesis of Cu-based catalysts, the electrochemical method has the advantages of easy, low-cost preparation, controllable conditions and eco-friendly. Consequently, many efforts have been devoted to exploring different catalyst morphologies, such as foams, thin films and dendrites to investigate the structure-property correlation for CO_2 reduction over Cu-based catalysts [4].

Most of these investigations are typically performed in batch cell configurations (H-Cells) which are intrinsically limited (mass transport limitation, low liquid product concentration, electrolyte pH control). On the contrary a limited number of studies have been devoted to liquid flow cells and zero-gap Cells [5,6]. The aim of our work is to explore the electrochemical deposition of Cu and/or Cu-M onto gas-diffusion layers (GDLs) prepared under different electrochemical conditions to evaluate their potential as electrodes for CO_2 reduction. The selectivity of the synthesized catalysts towards the production of C_{2+} products was evaluated by analyzing the gaseous and the liquid products obtained using the catalysts as cathodes in flow and MEA Cells configuration. The morphology and the composition of the fabricated electrodes were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX). My presentation will aim to link the catalyst structure and the CO_2 reduction properties.

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Unveiling $Ba_{0.5}Sr_{0.5}Ni_{1-x}W_xO_{3-\delta}$ Catalyst Reconstruction during the Oxygen Evolution Reaction by Ex-situ and Operando X-ray Techniques

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ABSTRACT

Water electrolysis provides a means for long-term energy storage in the form of hydrogen gas, helping to offset seasonal variations in renewable energy production. Developing non-noble metal catalysts for the anodic oxygen evolution reaction (OER) is a key step in reducing the cost and increasing the energy efficiency and sustainability of this vital technology. Flame-spray synthesized perovskite oxides of the composition $Ba_{0.5}Sr_{0.5}Ni_{1-x}W_xO_{3-\delta}$ (BSNW) exhibit excellent OER activity in alkaline conditions. In particular, $Ba_{0.5}Sr_{0.5}Ni_{0.5}W_{0.5}O_{3-\delta}$, with a catalytic turn over frequency (TOF) five-times that of NiO, displays a competitive Tafel slope of 44.7 mV/dec. The perovskite structure, with its tunable ABO_3 formula, provides a unique opportunity to enhance the intrinsic activity of Ni sites with high-valence metal doping, and, in doing so, to define structure-activity relationships.

B-site W doping strongly influences the oxidation state of surface Ni sites, as revealed by ex-situ soft X-ray absorption spectroscopy (XAS) at the Ni L-edge. A higher concentration of W^{4+} increases the Ni^{2+}/Ni^{3+} ratio, enhancing the intrinsic activity of the Ni active sites. In addition, analysis of the O K-edge indicates a positive correlation between W content and oxygen vacancy concentration, activating $Ba_{0.5}Sr_{0.5}Ni_{0.5}W_{0.5}O_{3-\delta}$ for the lattice oxygen mechanism (LOM), whereby mobile oxygen atoms can move through vacant lattice sites to participate directly in OER catalysis.[1]

Akin to the the well-known surface reconstruction processes of NiO during alkaline OER ($Ni^{II}O$ - $Ni^{II}(OH)_2$ - $Ni^{III}OOH$), BSNW perovskites experience complex, electrochemically-induced transformations under OER conditions.[2] Therefore, catalyst 'pre-activation' using cyclic voltammetry (CV) is essential to develop their high-performance final state in-situ. Operando hard XAS at the Ni K-edge and W L_3-edge revealed that BSNW perovskites experience an irreversible Ni^{2+} - Ni^{3+} oxidation with CV cycling. However, both the extent and rate of this oxidation are greatly influenced by the B-site W concentration. Furthermore, operando X-ray diffraction revealed significant surface reconstruction that facilitates a strong growth in electrochemically active surface area, but this process is also heavily dependent on the W content. It is evident that the 'pre-activation' of $Ba_{0.5}Sr_{0.5}Ni_{0.5}W_{0.5}O_{3-\delta}$ catalysts is a function of the Ni:W ratio; elucidating the ways in which high valence metal doping influences the catalyst activation mechanism will guide the development of future Ni-based OER catalysts, for which this process is intrinsically coupled with OER activity.

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Influence of Crystallographic Structure on the OER Performance of Co & Ni-based Layered Hydroxides

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ABSTRACT

Water electrolysis stands out as one of the cleanest methods for hydrogen production; however, the oxygen evolution reaction (OER) involved in this process requires high voltages, posing an energetic efficiency challenge.[1] Efforts over the past decade have focused on developing cost-effective electrocatalysts, with earth abundant materials gaining prominence as non-precious metal OER catalysts.[2] Layered hydroxides (LHs) have proven excellent OER electrocatalysts, offering scalability, affordability, and composition with abundant elements. Despite their electrochemical prowess, fundamental aspects influencing OER, such as the role of LH crystalline structure, coordination environment, and cation distortions, remain understudied.[3] Here we study different Co & Ni-based LH phases by *in-house* physicochemical and electrochemical characterizations, followed by XAS measurements in ALBA Synchrotron of the samples previous and after the OER, revealing that the crystallographic structure significantly impacts OER performance. The α-LH phase, distinguished from layered double hydroxide (LDH), demonstrated superior catalytic behavior in the case of both Co and Ni, introducing a new chemical signature for the rational design of more efficient LH-based electrocatalysts.[4,5]

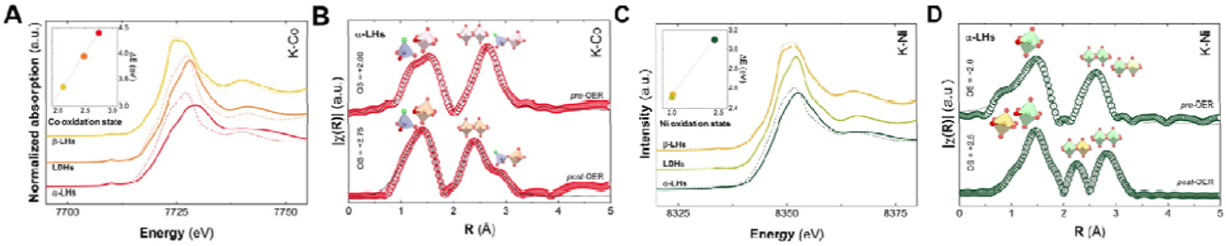

Figure 1. Normalised XANES in Co and Ni edge respectively A) C) and Fourier transform of the extracted κ2-weighted EXAFS oscillations B) D) for LHs samples pre and post-electrochemical performance.

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Investigating the Mechanism of the OER Core@Shell Fe_3O_4@$CoFe_2O_4$ Nanoparticles by *In Situ* and *In Operando* XAS

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ABSTRACT

The production of hydrogen via water splitting requires robust electrocatalysts to reduce the overpotential associated with the reactions occurring at the electrodes. The escalating interest toward transition metal oxides (TMO) answers an increasing demand in earth-abundant and noble-metal free anode catalysts, to offer an alternative to precious iridium and ruthenium oxides [1]. Recent advancements of the TMO-based catalysts have demonstrated remarkable activity for oxygen evolution reaction (OER) in alkaline medium, but those catalysts often lack the stability under the harsh operational conditions. Our study focuses on exploring how the activity of Fe_3O_4@$CoFe_2O_4$ core@shell nanoparticles, stable cost-effective OER catalysts [2,3], is influenced by the thickness and composition of the shell. In order to understand the influence of this element on the OER, electrochemical and X-Ray spectroscopic methods were applied.

Herein, we characterized three types of nanoparticles with different shell volumes, analyzing their structure and morphology. Evaluation of electrocatalytic performance revealed that shell thickness plays a pivotal role, with its optimum value around 0.65 nm. Notably, these core@shell structures demonstrated exceptional stability during extended electrochemical testing. *In situ* X-ray absorption spectroscopy (XAS) delved into the early stages of the OER mechanism, unveiling the impact of the shell thickness on the redox transformations of Co and Fe at the interface between the core and the shell. *In operando* XAS investigation in spectroelectrochemical cell enabled the acquisition of valuable information regarding the cation cooperative mechanism between core Fe(II) and shell Co(II) cations [4]. Overall, this study provides valuable insights into approaches for investigation of dynamic cations redox transformations by XAS technique for the TMO-based electrocatalysts.

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An Operando Zero-Gap MEA Cell for Combined Spectroscopy, Diffraction, and Imaging, Applied to the Study of Ion Effects in CO_2 Electrolysis

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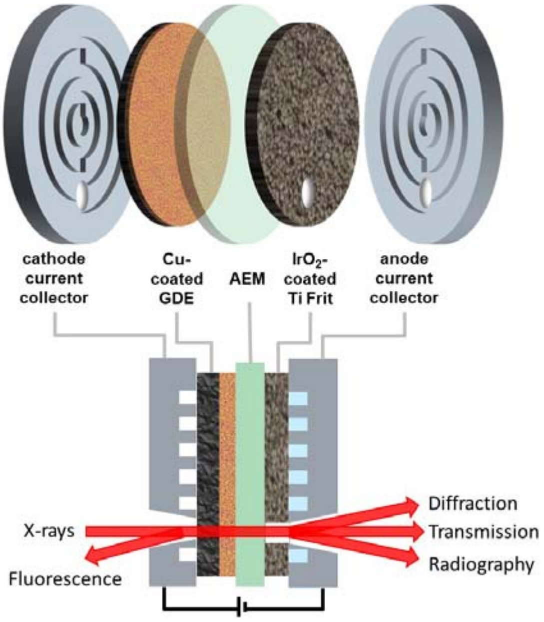
ABSTRACT

In situ and *operando* methods applied to electrocatalytic systems can provide important information about dynamics of catalyst structure and composition, transport processes, and degradation mechanisms. However, such methods are usually applied to specially designed cell geometries (i.e. small electrodes, thin electrolyte layers) and under test conditions (very low current densities, no product collection) which differ greatly from practical devices, putting the relevance of the results into question.

Here we report a zero-gap membrane electrode assembly (MEA) cell designed for electrolysis study under practical operating conditions. We demonstrate efficient high-rate CO_2 electrolysis (j > 200 mA/cm²) with a significant electrode area (8 cm²) using on-line product analysis, while simultaneously studying the system using a variety of X-ray based analytical methods, including X-ray absorption spectroscopy (fluorescence and transmission mode), imaging (radiography), and scattering. We demonstrate the methods on the study of phenomena relating to electrolyte ion effects in CO_2 electrolyzers, namely the unintended cation crossover through anion exchange membranes which can influence selectivity as well as lead to cell failure due to salt crystal precipitation.(1)



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Preparation of High-performance Materials for Overall Water Splitting and Zinc-based Batteries

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ABSTRACT

Developing high-performance and cost-effective electrocatalysts for metal-air batteries and water electrolysis is a desirable approach for moving toward a clean energy future. In this way, we have developed some advanced multifunctional electrocatalysts for next-generation energy storage and conversion systems. In one approach, the catalytic performance of the electrochemically synthesized pristine Ni-Co-Fe layered double hydroxide (LDH) toward the oxygen evolution reaction (OER) was studied.[1] In another study, the Ni-Co-Fe LDH film was electrochemically boronated to produce NiCoFeB. The amorphous tri-metal borate (TMB) exhibited excellent trifunctional electrocatalytic activities toward the hydrogen evolution reaction (HER), the OER, and the oxygen reduction reaction (ORR) with excellent durability in alkaline solutions.[2] A zinc–air battery based on the TMB dual oxygen catalyst cathode was also fabricated that outperformed the device based on the $Pt/C+RuO_2$ commercial noble metal benchmarks. In another approach, the metal-organic frameworks (MOFs) were tailored as high-performance and durable electrocatalysts.[3-4] In one study, a trilayer MOF in which Fe, Co, and Ni layers are epitaxially grown one on top of one another was electrosynthesized. The layer-by-layer assembled MOF exhibited outstanding trifunctional electrocatalytic activities toward the HER, the OER, and the ORR, along with the overall water splitting.[3] In another approach, a Fe-MOF was synthesized and then the MOF-derived Fe_2O_3/C was hydrothermally composited with N-doped reduced graphene oxide (MO-rGO).[4] The MO-rGO electrocatalyst displayed good bifunctional electrocatalytic activities toward the OER and the ORR, superior to the other similar-class electrocatalysts as well as the commercial α-Fe2O3-based one. The water-splitting cells and the Zn–air batteries based on the aforementioned electrocatalysts exhibited excellent energy conversion and storage performance compared to the commercial noble metal benchmarks. We hope these intriguing approaches to the development of advanced multifunctional electrocatalysts will inspire further advancement toward a more secure energy future.

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Activity and Stability of Ir-Ru Bi-metallic Catalyst: Electrochemical and Structural Analysis

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ABSTRACT

For the large scale commercialization of proton exchange membrane water electrolysers (PEM-WE) it is necessary to find a stable, active and inexpensive catalyst for anodic oxygen evolution reaction (OER). RuO2 has high OER catalytic activity, but pure RuO2 is unstable in OER potential window [1]. IrO2 is stable during oxygen evolution reaction but we have to compromise in terms of activity. Additionally, high expense of Ir is preventing large scale utilization [2]. On the other hand, bi-metallic oxides of Iridium and Ruthenium are showing both activity and stability in OER potential range [3]. At the same time by substituting Ru with Ir, we can reduce the amount of expensive Ir in catalytic layer. In this work we are aiming to evaluate the activity and stability of bi-metallic Ir-Ru OER catalysts, and also trying to establish the connections between morphological, structural and compositional evolution of bi-metallic systems and their catalytic properties in PEM-WE.

To fully comprehend how the metallic ratio and catalytical properties are depended to each other, structural analysis of the samples were done using catalysts with ten different metallic ratios, from 100% Ir to 100% Ru. The analysis of the crystal structure, carried out on *post mortem* membrane electrode assembly (MEA), give a hint about the concentration-dependent interplay between Ir and Ru, affecting the alloy´s structure and chemical state. To fully understand this phenomenon and confirm that the different ratios of Ir and Ru indeed influences the electrochemical performance of the PEM-WE, we have conducted *operando* wide angle X-ray scattering (WAXS) measurements in a fully operational PEM-WE single cell. This measurement allows us to observe the structural evolution in real working condetion and correlate it with the actual electrochemical performance and degradation processes of the alloys [4].

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Determination of the D-band Center of Bimetallic Catalysts for Carbon-neutral Fuel Synthesis using X-ray Photoelectron Spectroscopy

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ABSTRACT

Renewable higher alcohols, particularly iso-butanol, present a promising alternative for transportation fuel, derived from green methanol and ethanol through methylation [1,2]. The catalytic activity of metal catalysts is intrinsically tied to the positioning of their d-band centers, influencing both reactant adsorption and subsequent reaction rates [3]. By adjusting catalyst composition, adsorption strength can be adjusted, thereby impacting the overall catalytic process. The theoretical framework investigates the intricate relationship between the d-band center position and the Fermi-Energy. This correlation significantly affects the strength of the interaction between transition metals and adsorbates, leading to a cascade of effects on antibonding states' energy, occupancy, surface-adsorbate interaction strength, and the number of activated molecules for the reaction [4]. Utilizing X-Ray Photoelectron Spectroscopy, we assess the d-band center values of carbon-supported bimetallic catalysts synthesized in our study. Calculating d-band centers involves the weighted average energy of Valence Bands (VBs), with background subtraction fixed at 10 eV. The introduction of Pt to the catalysts induces observable differences in VB geometry and d-band center values (-2.54 eV for 5% weight loading of Pt on activated carbon), closely comparable to existing literature [5]. The insights gained contribute to ongoing efforts in designing catalysts for efficient and sustainable iso-butanol synthesis, providing a pathway toward advanced renewable fuel solutions for the future of transportation.

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$La_{0.6}Sr_{0.4}Fe_{0.95}Pt_{0.05}O_{3-\delta}$ Bifunctional Catalyst for Low Temperature OER/ORR Applications

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ABSTRACT

Perovskites oxides (ABO_3) are arousing great interest as OER/ORR electrocatalyst in alkaline medium due to their unique structural and electronic properties [1].

Lanthanum strontium iron (LSF) oxide has been widely investigated as electrode for fuel cell applications because its flexible structure can be tuned by B-site doping [2, 3]. Noble metal doping (≤ 5%) has been recently proposed as an alternative way to highly boost the electrocatalytic properties while limiting the final cost of the electrode material [4, 5].

At high temperature and in reducing environment B-site doped LSF are prone to the exsolution of metallic nanoparticles (NPs), and, among transition metals, noble metals are energetically mostly favored [6]. The synergic effect of noble metal NPs exsolution and the formation of oxygen vacancies can have a remarkable impact on the OER/ORR activity, and promote a bifunctional oxygen activity preserving the use of reduced amount of dopant content.

Here, 5 mol% Pt was successfully doped at the B-site of LSF (LSFPt) through citrate-solution combustion method. The synthetized compound is investigated and then treated at 500 °C in H_2 to induce structural surface modifications and NPs exsolution. Structural and microstructural characterizations (XRPD, TGA, SEM) are carried out to evaluate both the Pt-doping and the reduction treatment effects on the structure and surface. The electrochemical activity for OER and ORR was assessed in alkaline media both for LSF and LSFPt untreated and treated in H_2.

Soft XAS measurements are carried out at the Phoenix beamline at the Swill Light Source (SLS) synchrotron on reduced and as-prepared LSFPt samples, to have a deep understanding on the role of reduction treatment on the catalytic activity.

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EC Cell for Operando XAS Investigations on X-ray Opaque Supports

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ABSTRACT

Investigating the electronic and structural dynamics of a catalyst in *operando* conditions has a crucial role in the development of more performant electrochemical devices. A special importance must be assigned to the catalyst/electrolyte interface, whose understanding enables the improvement of catalyst formulations. Several approaches are available. The stringent experimental requirement imposed by imaging methods or vibrational spectroscopies often makes the investigation challenging, with respect to the more straightforward approach allowed by x-ray absorption spectroscopy (XAS). However, if hard x-rays have a long penetration depth, probing an absorption edge below 10 keV in the presence of a layer of electrolyte can be quite challenging. In most setups, this obstacle is overcome by depositing the sample on a conductive and x-ray transparent support like graphite or a thin silicon nitrate membrane[1,2], then probing the sample from the substrate side. However, this geometry not only limits the sensibility to the electrode/electrolyte interface, but it precludes the study on non-transparent supports. Different electrochemical cells have been designed to reduce the absorbance of the liquid layer by shrinking its thickness[3], but (to the best of our knowledge) no XAS measurement at energies below the Cu K edge are known.

We will describe a novel electrochemical cell for *operando* XAS measurements in fluorescence mode. The thin layer of flowing electrolyte allows to probe energies as low as the Ti K-edge. As case study, we will report the operando XAS measurements at the Fe and Ni K-edges on thin Ni-doped maghemite films (111) epitaxially grown on Pt (001) single crystal substrates[4]. We will describe the role of Ni doping in the catalytic performances of maghemite for the oxygen evolution reaction. Preliminary results concerning the photocatalytic performances of these samples will also be shown. The described electrochemical cell is now available to the scientific community at the SAMBA beam line.

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Fuel Cell Catalyst Degradation Mechanisms – A Bimodal Catalyst Study

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ABSTRACT

This comprehensive operando X-ray scattering investigation focuses on bimodal benchmark Pt catalysts and their corresponding monomodal counterparts, aiming to elucidate the degradation mechanisms observed during Accelerated Stress Tests (AST). The primary objective is to gain deeper insight into degradation phenomena, such as electrochemical or classical Oswald ripening, nanoparticle desorption from the support, and coalescence. This research builds upon prior work on Pt catalyst degradation, encompassing both monomodal and bimodal catalysts[1,2].

The experimental approach employed a combination of Small and Wide Angle Scattering (SAXS and WAXS) along with Pair Distribution Function (PDF) analysis of Total Scattering. By integrating these diverse X-ray scattering techniques, we could track the degradation across various length scales.

SAXS enabled the observation of nanometer-scale degradation, specifically capturing the morphological and size evolution, aided by a Monte-Carlo analysis[3] approach for assessing the size distribution changes during degradation. Furthermore, SAXS provided insights into the volume fraction of scatterers, facilitating the monitoring of relative changes in Pt nanoparticle abundance pre-, during, and post-AST. Whereas WAXS and the PDF analysis furnished information on crystallite size and strain within the catalyst, enabling a closer examination of degradation phenomena, such as Pt catalyst coalescence.

The measurements were conducted at ID31, European Synchrotron Radiation Facility (ESRF), using an operando Gas Diffusion Electrode (GDE) in ambient air. The small beam size at the beamline allowed for tracking of degradation at different depths within the catalyst layer. By contributing to our understanding of fuel cell catalyst degradation, this study lays the foundation for the development of robust and resilient fuel cell catalysts.

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Single Atom Pt on Carbon Nanotubes for Selective Electrocatalysis

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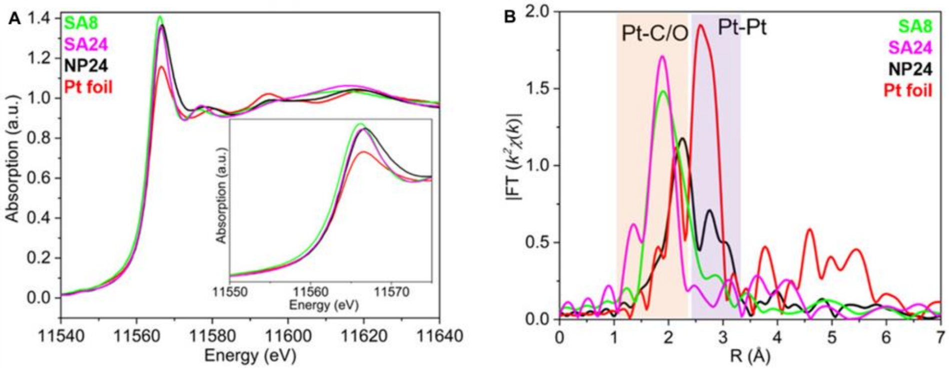
ABSTRACT

The electronic configuration and local co-ordination structure of Pt in the samples were investigated by X-ray Absorption Spectroscopy. X-ray absorption near edge structure (XANES) of the Pt L_3-edge samples, with Pt foil serving as a reference in Figure A. In the XANES spectra, a distinctive white line is observed just above the L_3-edge absorption edge, originating from a dipole transition from Pt $2p_{3/2}$ and $2p_{1/2}$ to the $5d_{5/2,3/2}$, and $5d_{3/2}$ bands. Notably, the intensity of the white line for the SA8, SA24, and NP24 samples exceeds that of Pt foil, suggesting a higher unoccupied density of states with $5d_{5/2}$ and $5d_{3/2}$ character. While SA24 and NP24 exhibit similar white line intensities, SA8 shows a higher intensity, indicating a reduction in electrons in the d orbital. The observed negative shift in E_0 dismisses oxidation as the cause, affirming that the species are nearly zerovalent.

The Fourier transforms of the extended X-ray absorption fine structure (EXAFS) are presented in Figure B. The SA samples only feature one major peak at 1.9 Å, whilst the region around 2.6 Å is notably low. This shows the lack of Pt–Pt bonding in the sample and hence the single-atom nature of the Pt

In situ/operando techniques is very crucial for understanding the dynamic changes in the catalyst's structure and composition during electrochemical reactions. It is essential for elucidating reaction mechanisms and understanding the changes in the catalyst's structure during electrochemical reactions helps identify active sites responsible for catalytic activity.



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Electrocatalytic Hydrogenation of Furfural at the Surface of Structured Copper Electrodes: A NAP-XPS Study

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ABSTRACT

Biomass-derived platform molecules like furfural are investigated as potential substitutes in the chemical and energy sectors in the context of the energy transition. The main valuable products of furfural reduction are furfuryl alcohol (FOH) and 2-methylfuran (2MF)[1]. In comparison to (thermo)catalysis, the electrocatalytic valorization pathway of furfural offers mild conditions, water as a proton source, direct use of electricity and modularity[2].

The main challenges today lie in achieving sufficient faradaic efficiency towards the furfural conversion (vs. H_2 production from water) and obtaining high selectivity towards FOH or 2MF. Using a self-templated copper electrode, we managed to obtain 100% selectivity towards either product by varying the pH, temperature and electrode potential.

To elucidate the origin of such performance, quasi-operando experiments of NAP-XPS in the lab and AP-XPS at the MAX IV synchrotron facility in Lund, Sweden (HiPPIE beamline) were performed. They revealed the beneficial coexistence of Cu(0) and Cu(I) under operating conditions (applied potential below -0.3 V vs. RHE) [3]. Furthermore, they gave an insight into the composition of the adsorbed organic layer thus providing valuable information regarding the electrocatalytic mechanism of furfural reduction.

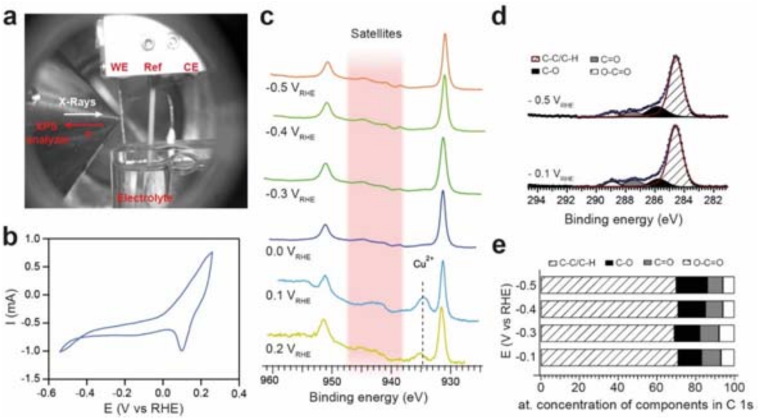

Figure 1. a) Picture of the experimental three-electrode setup inserted inside the XPS chamber on the HIPPIE beamline at the MAX IV light source facility. b) Cyclic voltammetry acquired with the setup pictured in a, on a copper foil immersed in a 1 M H_3PO_4 electrolyte containing 0.01 M of FAL. c) In-situ Cu 2p spectra acquired at different potentials for a copper foil immersed in 1 M H_3PO_4. d) In-situ C 1s spectra acquired at – 0.1 V and – 0.5 V vs. RHE at the surface of a copper foil immersed in a 1 M H_3PO_4 + 0.01 M FAL electrolyte. e) Atomic percent of C 1s components extracted from in-situ C 1s spectra acquired on copper foil at different potentials in 1 M H_3PO_4 + 0.01 M FAL electrolyte.

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Efficient Strategies to Optimize Hematite-based Photoanodes Photoelectrochemical Activity

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ABSTRACT

In the framework of hydrogen production as means for renewable energy storage, hematite photoanodes (Fe_2O_3) have received renewed interest, owing to their absorption spectrum compatible with sunlight, and abundance in nature, allowing cost- and resource-efficient production of hydrogen by solar water splitting [1].

Pure hematite photoanodes exhibit poor photoelectrochemical (PEC) activity, related mainly to short charge carriers mean free path (of about 4 nm) and sluggish water oxidation kinetics. First, we demonstrate that Ti doping not only increases charge mobility, as expected, but most importantly acts on the density of available, unoccupied electronic states, in the conduction band through formation of benefic surface states [2]. In this manner the charge transfer rates are strongly improved at the interface with the electrolyte resulting in overall enhanced PEC activity. Second, we demonstrate additional PEC activity improvement replacing standardly used air atmosphere during the hematite phase transition up to 600 °C from the incipient akaganeite phase, with Nitrogen. A Ti-rich phase (pseudo-brookite) occurs at the surface of the Ti-doped hematite particles offering additional unoccupied states in the conduction band, as demonstrated by the O K-edge X-ray absorption-based measurements [3].

For all these findings we correlate PEC macroscopic characterization (photocurrent, Electrochemical Impedance Spectroscopy) of the hematite-based photoanodes synthesized by ACG (Aqueous Chemical Growth), with synchrotron spectromicroscopic studies and electron microscopy.

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Phase Transfer Analysis of BiOBr in BiOBr/MoS_2 Heterojunction under Photoelectrochemical Environment

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ABSTRACT

BiOBr is a promising material in various photoelectrocatalytic reactions.[1] However, its instability under photoelectrochemical environment has become a drawback for BiOBr as a photoelectrocatalyst.[2] To solve this problem, MoS_2 is induced to form a Van der Waals heterojunction to attract the extra electrons inside BiOBr to avoid the reduction of BiOBr.[3] However, different BiOBr/MoS_2 ratios can result in different structure tolerance of BiOBr: heterojunction with 1% MoS_2 can increase the stability while 50% MoS_2 even accelerate the reduction of BiOBr. By performing the in situ wide-angle X-ray diffraction (WAXD) on BiOBr/MoS_2 with 1% and 50% of MoS_2, respectively, we managed to monitor the phase transfer speed of BiOBr during the hydrogen evolution reaction. It is known that both the negative voltage and UV light can prompt a reduction of BiOBr to Bi. Interestingly, the reduction speed of BiOBr under both negative potential and UV light is even slower than under only negative potential.

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Operando X-ray Absorption Spectroscopy of Nickel-based Catalysts for OER

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ABSTRACT

Catalysts are usually metastable in their active state. A phase transition triggered by the reaction conditions is kinetically frustrated in the presence of catalytic reactions proceeding on their surface.[1] Consequently, operando methods are the most suitable way to understand the interaction between catalytically active surfaces and reaction intermediates. Iron doped nickel hydroxides are the state-of-the-art catalysts for alkaline oxygen evolution reaction (OER). They become transformed into the oxyhydroxide phase under catalytic conditions, where an adsorption-dissolution equilibrium of Ni and dopant species like Fe is maintained at the surface.[2,3] We apply operando X-ray absorption (XA) spectroscopy at the Ni-edge as well as the O K-edge to characterize the electronic structure and local coordination of the active oxyhydroxide phase in detail. Additionally, the absorption signals at the Na and B K-edges facilitate to observe intercalated ions remaining from preparation. The combination of potentiostatic XA-spectra measured at selected potentials and potentiodynamic absorption measured at fixed photon energies during cyclic voltammetry allows us to study phase transitions of the material under catalytic conditions in the OER-regime. Element specific absorption changes can be tracked and intercorrelated based on the high resolution in electrode potential our methods offer.[4] While our recent results were obtained in 0.1 M KOH at 25°C, on potentials close to the onset of the OER, we will expand our measurements also to more alkaline conditions, higher temperatures (~ 80°C) and higher current densities. Our approach will help to elucidate the role of iron and interlayer-ions in OER catalysis on nickel-based catalysts under conditions relevant for industrial hydrogen electrolysis.

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Making C-N Bonds from Carbon Monoxide and Nitrite Co-electroreduction

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ABSTRACT

Electroreduction of CO_2/CO [1-3] has been widely investigated as it holds a promising route for energy storage and the production of chemical products in a sustainable way. Driven by renewable energy such as solar, wind and nuclear energy, electrochemically convert greenhouse gases to value-added chemical products such as methanol [4], ethanol [5] is an efficient way to synthesize products that are indispensable in chemical industry. Beyond simple carbon species, the synthesis of nitrogen containing compounds is also highly-demanded [6]. Recently, electrochemical building C-N bond reactions [7] have been intensely studied because of their simplicity, low cost and extensive substrate scope. However, the modest selectivity and poor mechanistic understanding remain a challenge. In our study, we utilized CO and NO_2^- as reactants to generate C-N coupling products in aqueous solutions with a cobalt molecular electrocatalyst (Co phthalocyanine) deposited at a carbon paper electrode. Notably, through modulation of the concentration of KNO_2 and pH of the electrolyte, critical factors influencing C-N products yield rate, we achieved extraordinary faradaic efficiency of 50 % for CH_3NH_2 and CH_2NOH at an applied potential of -1.6 V vs. SCE. Our investigation pinpointed the chemical reaction between hydroxylamine and formaldehyde, originating from NO_2^- and CO partial electroduction, respectively, as a pivotal step in C-N bond formation. This work provides an effective way to synthesize methylamine via C-N coupling and holds promise for the production of diverse value-added organonitrogen products such as ethylamine, formamide and beyond.

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Interfacial Synergy of Iridium and Titanium in Model Configurations for Oxygen Evolution Reaction

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ABSTRACT

Iridium-based catalysts on the anode side of the proton exchange membrane water electrolyzers (PEMWEs) are crucial for efficient green hydrogen production, yet the high demand for iridium significantly hampers scalability.[1] A viable strategy to mitigate iridium utilization involves using oxide support materials,[2] traditionally viewed solely as passive carriers. Contrary to this, our research emphasizes the vital role of dynamic catalyst-support interactions (CSIs) in enhancing both the activity and durability of Ir-TiO_2-based oxygen evolution reaction (OER) electrocatalysts.[3, 4]

To elucidate the underlying mechanisms of these interactions, we employed a range of advanced synchrotron-based analytical techniques. These include X-ray photoemission electron microscopy (XPEEM) for elemental mapping, near edge X-ray absorption fine structure (NEXAFS), low energy electron microscopy (LEEM), and X-ray photoemission spectroscopy (XPS) for depth profiling. In combination with synchrotron-based techniques, we also used in situ inductively coupled plasma mass spectrometry (ICP-MS) to study potential-dependent dissolution of both catalyst and support.[5]

Through these methods, we unravel the complex electronic interplay between iridium and titanium sites in various Ir-TiO_2 model catalysts, leading to a better understanding of their synergistic behavior and resulting in improved OER performance, corrosion resistance and the electronic structure of involved materials.

Our study not only advances the fundamental understanding of CSIs but also offers a blueprint for designing next-generation electrocatalysts with optimized performance and reduced precious metal reliance. This leap forward presents significant progress in the sustainable and economical generation of green hydrogen.

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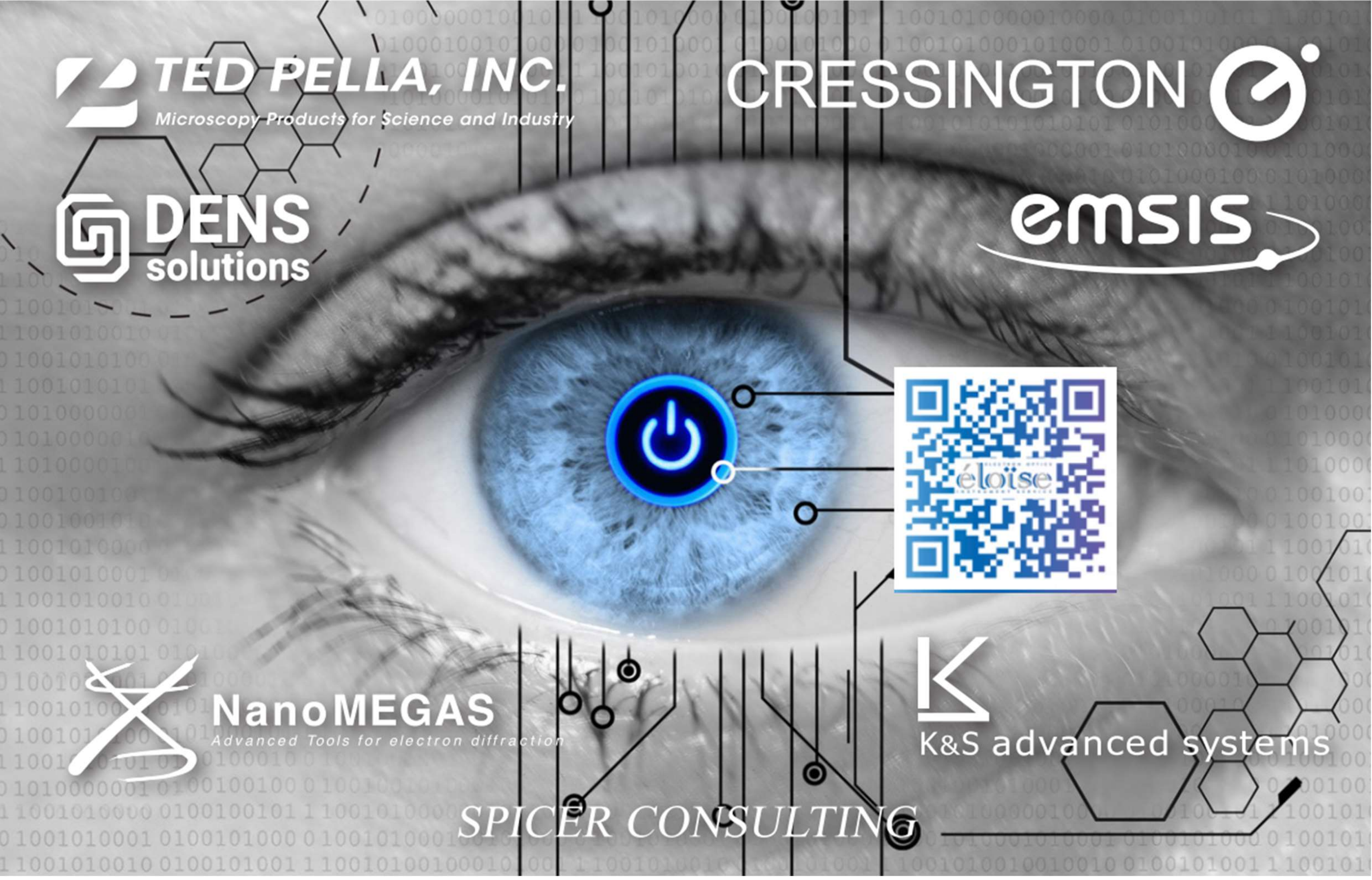

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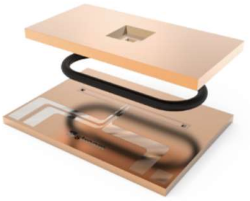

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