



# **Emerging synchrotron techniques for characterization of energy materials and devices**

Grenoble – France – 23 – 25 September 2019

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# Aim, Scope and Format

The heterogeneous devices, which will play a role in the future green energy economy, such as batteries, solar cells, super-capacitors etc., rely on complex interactions over many length scales. This workshop focuses on the application of established and emerging synchrotron experimental techniques to understand problems from the energy sector, and investigate new experimental opportunities following the ESRF EBS upgrade.

Topics covered by the workshop include: hydrogen storage and hydrogen economy (fuel cells), gas separation and storage (porous materials), catalysis for energy related processes, electrochemistry and battery research, fuel efficiency and consumption, solar energy, thermoelectrics, piezoelectrics and supercapacitors.

The speakers will highlight scientific trends in their areas of expertise. Participants have the opportunity to be informed about the anticipated performance gains following the EBS upgrade, and therefore asked to identify new experiments, which will become possible as a result.

# Program

## Monday 23<sup>rd</sup> September – 12:00 → 20:30

<i>12:00 – 14:00</i>	<i>Registration at the ESRF Central building and lunch at the EPN Campus restaurant</i>	
14:00 – 14:10	Introduction by the organizers	
14:10 – 14:20	Introduction by scientific Director, J. Susini	
14:20 – 15:05	<b>Invited talk</b>	O. Oeckler
	New opportunities for the investigation of thermoelectric materials and devices with extremely brilliant high-energy synchrotron radiation.	
15:05 – 15:30	Piezoelectricity in centrosymmetric $Sr_{1-x}Pr_xTiO_3$ : a diffraction study under electric field	M. Scavini
15:30 – 15:55	Understanding lithium storage mechanism in nanostructured $MnO_2@CNT$ hybrid by <i>in-situ</i> synchrotron X-ray scattering study	M. Rana

### *15:55 – 16:25 Coffee break*

16:25 – 17:10	<b>Invited talk</b>	A. Beale
	Chemical imaging of catalytic materials under process conditions.	
17:10 – 17:35	Quantifying state of charge and Li plating heterogeneities during fast charging of Li-ion cells	D. Finegan
17:35 – 18:00	Emerging synchrotron techniques for thermodynamic characterization of metastable phases across electrochemical reactions	D. Bessas

### *18:00 – 20:30 Poster session and Wine & cheese*

## Tuesday 24<sup>th</sup> September – 9:00 → 17:40

9:00 – 9:45	<b>Invited talk</b>	D. Wragg
	XRD/PDF computed tomography and how to get the best possible <i>operando</i> data from ion batteries.	
9:45 – 10:10	Analysing operando spectroscopy data in battery studies: a chemometric approach	L. Stieviano

10:10 – 10:35 Probing inhomogeneous lithiation of graphite electrodes using *operando* micro X-ray diffraction S. Tardif

10:35 – 11:00 *Coffee break*

11:00 – 11:45 **Invited talk** W. L. Queen  
Understanding the structure-derived function of metal-organic frameworks and their application in separations.

11:45 – 12:10 Studying  $\text{In}_2\text{O}_3$  catalyst for  $\text{CO}_2$  hydrogenation to methanol at work: an *operando* XAS-XRD study P. M. Abdala

12:15 – 14:00 *Lunch*

14:00 – 14:45 **Invited talk** P. Shearing  
Developments in Synchrotron Techniques to Accelerate the Development of Electrochemical Devices

14:45 – 15:10 Operando investigation of the lithium/sulfur battery by coupled X-ray absorption tomography and X-ray diffraction computed tomography C. Barchasz

15:10 – 15:35 *Operando* synchrotron X-ray diffraction and Mössbauer spectroscopy of the cathode materials for Li-ion and Na-ion batteries O. A. Drozhzhin

15:35 – 16:05 *Coffee break*

16:05 – 16:50 **Invited talk** P. Hutchins  
High temporal and spatial resolution hard x-ray imaging for *in operando* study of real world fuel-based engineering systems.

16:50 – 17:15 Characterising evolving solid oxide fuel cell and electrolysis cell components with *ex-situ* and *in-operando* X-ray experiments J. R. Bowen

17:15 – 17:40 Probing water distribution and ionomer nanostructure in operating Proton Exchange Membrane Fuel Cells thanks to X-Ray synchrotron source A. Morin

*Free time*

19:00 *Transport to town by tram*

19:30 – 22:00 Workshop dinner in town, at "L'Epicurien", [www.lepicurien-grenoble.com](http://www.lepicurien-grenoble.com)

### Wednesday 25<sup>th</sup> September – 9:00 → 12:20

9:00 – 9:45 **Invited talk** J. Steele  
Straining to be Black: On the Metastability of Lead Triiodide Perovskite Thin Film Devices.

9:45 – 10:10 *In situ* and *operando* structural evolution of single metallic nanoparticle model catalysts under ambient pressure reaction conditions M.-I. Richard

10:10 – 10:35 Probing the electron density at electrochemical interfaces with *in-situ* surface resonant X-ray diffraction Y. Gruender

10:35 – 11:00 *Coffee break*

11:00 – 11:45 **Invited talk** B. C. Hauback  
Multifunctional metal hydrides for energy applications.

11:45 – 12:10 X-ray Raman Scattering study of energy storage materials based on metal hydride nanocomposites P. Ngene

12:10 – 12:20 Conclusions by the organizers

12:20 – 14:00 *Lunch and end of the meeting*

# Invited Talks





## New opportunities for the investigation of thermoelectric materials and devices with extremely brilliant high-energy synchrotron radiation

Oliver Oeckler<sup>1</sup>

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Thermoelectric (TE) materials are used to directly interconvert heat and electrical energy, both for Peltier cooling as well as for waste-heat harvesting, especially in remote places. In order to enhance the efficiency of such materials for energy conversion, research went a long way toward complex, often heterogeneous materials, including their electronic optimization and their structural characterization. Limited stability is still a major problem, and better understanding of structure-property relationships requires detailed analytics that is or will become available at ESRF.

According to the phonon-glass electron crystal concept, TE materials with nanoscale precipitates are very promising. They are often accessible by rapid quenching. So far, their formation cannot be traced in real time, but extremely brilliant beams and very fast detectors may enable this in the near future. In order to elucidate the crystal structure of nanoprecipitates, which are often present only in very small volume fractions, microfocused synchrotron radiation is an excellent tool to access single-crystal data for precise structure refinements. Crystallites with dimensions of less than one micron can be selected and pre-characterized by TEM and subsequently used for diffraction experiments at ID11.[1] In order to determine volume fractions and temperature-dependent phenomena like the dissolution of the precipitates in the matrix material or phase transitions as a consequence of diffusion-controlled compositional changes, extremely precise powder diffraction is required. As most materials exhibit high absorption coefficients, sampling parts of TE generators requires very short wavelengths.

As many TE materials decay upon heating, where a plethora of high-temperature phases play a crucial role, *in situ* analytics is essential. In mixed ionic-electronic conductors (MIECs), applied electrical currents may lead to electromigration of mobile atoms. This can change phase transition temperatures, the mixture of phases present, and their crystal structures. Concerning legs of TE generators, spatial and time resolution are highly desirable. ID15A offers excellent opportunities for 3D X-ray diffraction computed tomography, which yields high-quality powder diffraction data from voxels that are only a few microns in size. In the case of  $\text{Cu}_{2-x}\text{Se}$ , the microstructure of its cubic and monoclinic phases was obtained as a function of composition, time and sample position. Future *operando* experiments with even higher brilliance will offer much better time resolution and enable comparative studies of several materials, especially with respect to diffusion barriers that impede electromigration. Investigations may then extend to whole TE modules, using very high energies. The experimental setup needed for such studies resembles the one that is required for studies of battery materials.

From a more fundamental point of view, solid-state reaction mechanisms in thermoelectric materials may be tracked *operando* and new metastable phases may be discovered. Concerning electromigration, valence changes along sampled may be traced by space-resolved XANES studies and the evaluation of pair-distribution functions on a fast timescale may help to track changes in local structures. On an intermediate length scale, micro- and nanostructures may be traced by SAXS and ASAXS, especially at high temperatures, where the performance of the materials is most interesting.

The upgrade of ESRF will offer a plethora of exciting new possibilities, which can significantly contribute to a better understanding of thermoelectrics, from very fundamental aspects like crystal structures of new materials to *operando* studies with respect to the long-term stability of whole generators.

[1] F. Fahnbauer, T. Rosenthal, T. Schmutzler, G. Wagner, G. B. M. Vaughan, J. P. Wright, O. Oeckler, *Angew. Chem. Int. Ed.* **54** (2015) 10020.

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## Chemical imaging of catalytic materials under process conditions

Andrew M. Beale

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Chemical imaging is a term used to describe the mapping of the physico-chemical properties of materials in 2 and 3 spatial dimensions at the micro and nanoscale. With the developments of modern day X-ray sources and detectors, it is possible to perform a characterisation of a sample to a hitherto unprecedented degree, not only on samples pre and post mortem, but also during reaction. Ultimately this has led to the development of what is termed 5D imaging. It will be shown that these methods can be employed to study functional materials particularly catalytic materials under operational conditions to understand how they work or why they fail.

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## XRD/PDF computed tomography and how to get the best possible *operando* data from ion batteries

D.S. Wragg,<sup>1</sup> J. Sottmann,<sup>1,3</sup> A. Ruud,<sup>1</sup> Ø. Slagtern Fjellvåg,<sup>1</sup> M. Di Michel,<sup>2</sup> G. Vaughan,<sup>2</sup> H. Fjellvåg,<sup>1</sup> Oleg Lebedev<sup>3</sup>

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Energy storage is a crucial element of any renewable energy system. Balancing demand with supply from intermittent sources like wind and solar generation on a large scale and routine electrification of vehicles both require improved battery technology. Lithium batteries (LIBs) are a well-established technology and sodium ion batteries (SiBs), which have similar chemistry, are very promising for stationary storage applications at lower monetary and environmental cost than LIBs. Unfortunately, the standard anode for LIBs, graphite, has a poor capacity for sodium. The search for a high-capacity SIB anode which will maintain its capacity over many cycles and is safe, environmentally friendly and inexpensive, is an important focus in battery research.

To optimise anode performance, we use *operando* methods to study the chemical mechanisms and structural composition of the materials. Since many of the materials we are interested in become amorphous during battery cycling, total scattering analysis has become an important tool alongside conventional XRD, X-ray spectroscopy and calculations. The multiple (and sometimes mobile) components of a battery stack make the background corrections required for PDF analysis of total scattering data difficult when working in typical transmission and reflection *operando*-XRD battery cells [1,2]. To address this problem, we have applied the pair distribution function computed tomography (PDF-CT) method to SIB and LIB anodes at ESRF beamline ID15. By reconstructing the scattering data from the anode using tomographic methods we can zoom in on specific parts of the battery and extract PDF data without further background subtractions.

This talk will present our work [3] and suggest how the EBS could be employed to extend this approach with improved speed and spatial resolution coupled with improved data collection and processing to avoid beam damage.

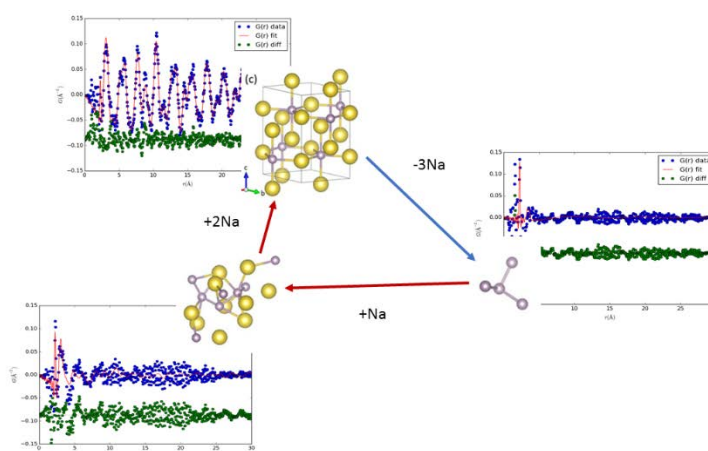


Figure 1. PDF-CT reveals the structures formed during sodium cycling in a phosphorus anode

[1] P. K. Allan, et al. *J. Am. Chem. Soc.* **138** (2016) 2352

[2] O. J. Borkiewicz, et al. *J. Appl. Cryst.* **45** (2012) 1261

[3] J. Sottmann, et al. *Angew. Chem. Int. Ed. Engl.* **56** (2017) 11385

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## Understanding the structure-derived function of metal-organic frameworks and their application in separations

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Currently, separation processes consume an estimated 10-15% of global energy. With this and the expectation that energy consumption will greatly increase with continued population growth and the implementation of large-scale carbon capture efforts, there is intensive scientific focus on the development of new adsorbents. The goal is to design new materials that might enable more energetically favorable separations compared to traditional distillation processes. This feat is not easy, as the differences in the molecules of interest, such as CO<sub>2</sub> and N<sub>2</sub>—the main components in a post combustion flue gas, are minimal. As such, these separations require tailor-made adsorbents with molecule specific chemical interactions on their internal surface.

Metal-organic frameworks (MOFs) have garnered much attention as next generation porous media for various applications, such as small molecule storage and separations. These materials, constructed by metal-ions or metal-ion clusters that are interlinked by organic ligands, offer unprecedented internal surface areas allowing the adsorption of large quantities of guest species. The molecular nature of the organic ligands within the hybrid organic/inorganic newcomers, induces structural versatility, allows the introduction of multifunctional properties, and permits a modular approach to their design. In these ways MOFs, which offer unmatched opportunities to achieve optimal efficiencies in many environmentally relevant applications, are unique relative to their all-inorganic counterparts. New MOFs are regularly reported; however, to develop better materials in a timely manner for specific applications, the interactions between guest molecules and the internal surface of the framework must first be understood. In this presentation, I will introduce metal-organic frameworks and show our results focused on understanding their structure-derived function. Particular emphasis will be placed on applying *in-situ* x-ray and neutron diffraction techniques to elucidate small-molecule interactions in several families of frameworks. I will also show that through the study of families of MOFs that undergo extensive chemical substitution, one can provide a platform to test the efficacy and accuracy of developing computational methodologies in slightly varying chemical environments, a task that is necessary for their evolution into viable, robust tools for screening large numbers of materials.

## Developments in Synchrotron Techniques to Accelerate the Development of Electrochemical Devices

Paul. R. Shearing

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Electrochemical devices for energy storage and conversion, such as batteries and fuel cells, are typically comprised of complex, porous electrodes which support a range of phenomena intrinsic to the performance of the device. There is an intrinsic link between the electrode microstructure and the performance of the device; for example, in a Li-ion battery, the packing density of active materials will determine its energy density, whilst the transport of Li-ions in the tortuous pore phase will determine its rate capability.

Over more than 10 years, the development and application of X-ray tomography tools has provided new insight into the rational design and optimisation of these electrode materials. Coupled with correlative microscopy and spectroscopy, and image based modelling, we now have a tool box to effectively engineer advanced materials for electrochemical devices, which may be expected to operate in extreme environments over many thousands of hours.

Increasingly, we are equipped not only to understand the morphology of these materials, but also through the application of advanced synchrotron methods, their chemistry and crystallography - this provides a richness of data which is unprecedented in the development and implementation of new materials. Moreover, owing to the inherently non-destructive nature of these experiments, our ability to extend these experiments to *in-situ* and *operando* investigations yields further insight into the materials in their native environment.

Here we will explore examples from of correlative synchrotron imaging applied to electrochemical devices, and consider how further developments in materials characterisation will enable future progress in the field.

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## High temporal and spatial resolution hard x-ray imaging for *inoperando* study of real world fuel-based engineering systems

Peter Hutchins

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One of the great challenges for high precision engineering, particularly within modern vehicle fuel systems, is direct observation of real systems in operation. The nature of such systems operating at extremely high pressure and temperature, very high time precision and repetition rates and constructed often of hardened steel, is such that direct observation of production systems behaviour is very challenging. As such, data is generated to inform engineering research and development either from idealised models, indirect measurements of secondary parameters and from observation of simplified and less challenging systems i.e. optical imaging of glass systems operated at ambient pressure and temperature.

Advances in hard x-ray imaging at the European Synchrotron Radiation Facility are allowing the combination of high spatial resolution 3D inspection, to be used in conjunction with high temporal resolution radiographic imaging, to drastically improve the data available from direct observation of real production systems and hence inform modelling. From the structure of fluid channels to the subsequent spray structure generated, to the direct observation of operation of complex moving part of engine systems, high flux hard x-ray imaging is allowing measurements previously not possible for such challenging systems.

In this study we demonstrate 1 micron resolved tomography of fuel injector sprayhole deposits, to allow accurate model generation of the impact of deposition on fuel spray structure, and conduct megahertz resolved imaging of fuel sprays for direct observation of the spray structure in situ. Additionally, we will show the use of 200kHz imaging at 2 microns spatial resolution through 5mm of hardened steel, to allow direct observation of production systems in real world operation. Though challenging, such experiments are now possible and can be quantified for data generation to inform real world engineering research and development.

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## Straining to be Black: On the Metastability of Lead Triiodide Perovskite Thin Film Devices

Julian A. Steele,<sup>1</sup> Johan Hofkens,<sup>2</sup> and Maarten B. J. Roeffaers<sup>1</sup>

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The all-inorganic CsPbI<sub>3</sub> perovskite offers the prospect of a more stable alternative to hybrid organic-inorganic perovskites. Unfortunately, like many other polymorphic perovskite systems, the metastability of its high-temperature black phase [1] stands in the way of realizing room-temperature (RT) stable optoelectronic devices. It is of interest to find ways to shift the energetics of CsPbI<sub>3</sub>, in order to secure RT black phase formation over its yellow non-perovskite phase [2]. In this presentation, we outline the role of glass substrate clamping and biaxial strain (induced by the large thermal expansion mismatch) to realize RT stable black-phase CsPbI<sub>3</sub> thin films. Employing synchrotron-based grazing incidence wide angle X-ray scattering with extremely fast acquisition time (~0.1 s), we track the introduction of crystal distortions and texture formation within black CsPbI<sub>3</sub> thin films as they are cooled from annealing temperatures. The thermal stability of black CsPbI<sub>3</sub> thin films are vastly improved by the strained interface, a response verified by ab initio thermodynamic modelling. This contribution introduces substrate clamping as an important parameter in the rational design of stable RT black inorganic halide perovskite thin films.

[1] R. J. Sutton et al., Cubic or Orthorhombic? Revealing the Crystal Structure of Metastable Black-Phase CsPbI<sub>3</sub> by Theory and Experiment. *ACS Energy Letters* **3** (2018) 1787–1794

[2] Y. Yang, J. You, Make perovskite solar cells stable. *Nature* **544** (2017) 155–156

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## Multifunctional metal hydrides for energy applications

B. C. Hauback

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Metal hydrides form large varieties of different types of materials. The traditional applications are related to hydrogen storage, but during the last decades it has found that these compounds are also important for batteries applications, smart windows, heat storage, magnetism and compressors.

During the last 10-15 years complex hydrides based on aluminum, boron and nitrogen, respectively, have been extensively investigated. Such materials have a much higher gravimetric hydrogen capacity than the traditional transition metal based hydrides, and thus potential candidates for hydrogens storage applications. Recently it has been found that boron-based complex hydrides, for example hexagonal  $\text{LiBH}_4$  has a high Li conduction, and thus such materials are also possible candidates as solid state electrolytes in Li-ion batteries.

Hydrogen uptake and release are complicated in many of these compounds, with presence of several intermediate steps and phases that can be both crystalline and amorphous. Thus, synchrotron radiation X-ray diffraction in combination with neutron diffraction are the key methods for detailed structural characterization. Diffraction experiments during hydrogen desorption and absorption are important for clarifications of the intermediate phases and the processes for hydrogen uptake and release. Furthermore, catalysts and additives are important to promote the reactions, and therefore the combination of XANES/EXAFS and diffraction methods are needed to understand the effect of additives.

Selected examples of novel compounds, efforts to understand hydrogenation/dehydrogenation properties including effect of selected additives will be presented. The combination of neutron and synchrotron radiation X-ray scattering will in particular be emphasized. Furthermore, scientific trends in the area will be presented.

The Research Council of Norway, EU FP7 and H2020 are acknowledged for financial support.

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Oral

Contributions



## Piezoelectricity in centrosymmetric $\text{Sr}_{1-x}\text{Pr}_x\text{TiO}_3$ : a diffraction study under electric field

S. Checchia,<sup>1,2</sup> R. Cabassi,<sup>3</sup> M. Allieta,<sup>1</sup> M. Coduri,<sup>4,5</sup> C. Giacobbe,<sup>4</sup> M. Scavini<sup>1</sup>

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Crystallography under electric field has been recently applied to reveal macroscopic and microscopic structural response of ferroelectric materials to intense electric fields, and is especially important for application-ready (functional) polycrystalline materials. Here we focus on the effect of applied electric fields on the crystallographic structure of an occupationally disordered relaxor ferroelectric oxide. Basically, the centrosymmetric structure of relaxor ferroelectrics inhibits long-range polarization. On the one hand, this sets them apart from classic ferroelectrics, where clear signature of polar distortion instability allows straightforward interpretation of diffraction data in terms of increased electric dipole moment. On the other hand, their susceptibility to distortion under electric field points to local polar fluctuations and a host of possible structural changes.

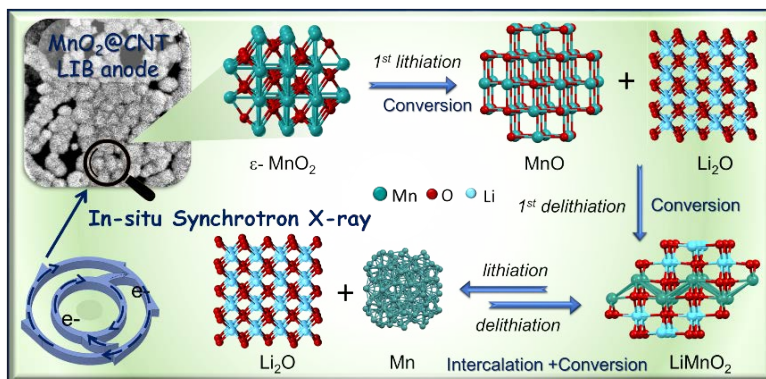
We present the case of Pr-doped strontium titanate perovskite ( $\text{Sr}_{0.85}\text{Pr}_{0.15}\text{TiO}_3$ ). Its structure shows high-temperature stabilization of the centrosymmetric antiferrodistortive (AFD) tetragonal phase observed in pure  $\text{SrTiO}_3$  below 105 K. The structural modifications induced by applied electric fields as large as 60 kV/cm were studied by synchrotron high-resolution diffraction combined with Pair Distribution Function (PDF) analysis. Under electric field, the bulk material shows anisotropic inhomogeneous strain and preferential orientation, their magnitude depending on the angle between the electric field vector and the scattering vector. Concomitant increases of tetragonal strain and octahedral  $\text{TiO}_6$  tilting angle do not break the initial long-range centrosymmetry. Conversely, PDF reveals that Ti is off-centered within its octahedral cage already at zero field, forming polar regions spanning up to 2 nm. The electric field enhances polarization within the polar nanoregions with no effect on their size, suggesting that they are pinned to charged defects introduced by Pr-doping. The large tetragonal strain found at the local scale may contribute to the ordering of the tilting angle at larger scales. This may imply a coupling between the local ferroelectric and the long-range AFD instabilities.

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## Understanding lithium storage mechanism in nanostructured MnO<sub>2</sub>@CNT hybrid by in-situ synchrotron X-ray scattering study

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Transition metal oxides (TMO) are gaining increasing attention for next generation, high performance, rechargeable lithium-ion battery anode due to their high theoretical capacity and electrochemical stability. Among them, MnO<sub>2</sub> is the most promising one due to its highest theoretical capacity and lower operational potential compared to other TMOs. Even though there are plenty of studies on exploring the electrochemical activity of nanostructured MnO<sub>2</sub>, their charge-discharge mechanism is not yet clear, and information about the lithium storage mechanism of MnO<sub>2</sub> is more insufficient with respect to other TMO based materials. In this work, for the first time, we have investigated the lithium storage mechanism in nanostructure MnO<sub>2</sub> anode using in-situ synchrotron X-ray scattering, electrochemical and Raman spectroscopy. Using electrochemical route, a high rate MnO<sub>2</sub>@CNT hybrid was synthesized, that exhibited specific capacity over 1100 and 500 mAh/g at a discharge current density of 25 mA/g and 5 A/g respectively with coulombic efficiency of 97.5%. The fraction of pseudocapacitive charge storage ranges from 27% to 83%, for current densities from 25 mA/g to 5 A/g. Detailed investigations reveal that, during the first charge-discharge cycle, the material undergoes an irreversible phase transformation to a lithiated form of manganese oxide. In the consecutive cycles, this structure undergoes a reversible phase transformation with metallic manganese and lithium oxide. Additionally, the high surface area of oxide nanostructures provides additional surface Li-storage sites, that leads to enhanced specific capacity, surpassing its theoretical value. This study provides a comprehensive understanding of possible Li-storage routes in nanostructured MnO<sub>2</sub>, and establishes a necessity to revisit the conventional concept of reversible lithium storage conversion mechanism in transition metal oxides.



- [1] Zheng et al. *Advanced Science* 2018, **5** 1700592.
- [2] Shen et al. *Advanced Materials Interfaces* 2018, **5** 1800362.
- [3] Chen et al., *Journal of Power Sources*. 2009,**189** 552.
- [4] Fang et al., *Electrochemistry Communications* 2010, **12** 1520.
- [5] Voskanyan et al., *Journal of Power Sources* 2019, **421** 162.

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## Quantifying state of charge and Li plating heterogeneities during fast charging of Li-ion cells

D Finegan

National Renewable Energy Laboratory, USA

The tradeoff between energy density and fast charging capability of Li-ion batteries is a principal impediment to widespread uptake of electric vehicles. High energy density is necessary for range, while fast charging is necessary for consumer convenience that is competitive with refueling a combustion engine. In this talk, the limitations of high-energy density electrodes for fast charging are investigated. Using a custom high-rate operando cell, high-speed (100 Hz) and high resolution (1  $\mu\text{m}$ ) XRD was used to conduct rapid depth profiling of a Li-ion graphite and NMC electrode during fast charging (6C or full charge in 10 minutes). Extreme gradients of state of charge over depth into the graphite electrode are observed, where full lithiation occurs near the surface while further into the electrode shows little activity. The high load witnessed by the surface region of the graphite leads to onset of lithium plating, the evolution of which is detected through XRD. The severe lithiation gradients and occurrence of Li plating are detrimental to performance and safety of cells, and can be linked to electrochemical measurements taken from commercially relevant cells in the lab.

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## Emerging synchrotron techniques for thermodynamic characterization of metastable phases across electrochemical reactions

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<sup>3</sup>Institut Charles Gerhardt Montpellier, Univ. Montpellier, CNRS, Montpellier, France

<sup>4</sup>Reseau sur le Stockage Electrochimique de l'Energie, CNRS, Amiens, France

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<sup>6</sup>Oak Ridge National Laboratory, Material Science & Technology Division, Oak Ridge, *Tennessee*,  
USA

Electrochemical reactions are fully explored mainly in battery materials for energy storage applications. The quintessential characteristic of electrochemical reactions is, however, the access to energetic - metastable - phases which do not exist *per se* in nature. The availability of such phases requires an otherwise serious investment in heavy infrastructure. The access to metastable phases is even hindered using first principle theoretical calculations.

In this pilot study, the electrochemical reaction of the model material NaFeO<sub>2</sub> against Na is followed *operando* using emerging synchrotron techniques such as Nuclear Forward Scattering, Nuclear Inelastic Scattering, and X-ray Diffraction. A full structural characterization, a <sup>57</sup>Fe hyperfine interaction characterization, and a <sup>57</sup>Fe complete vibrational characterization both in the pristine material as well as in a series of metastable phases along Na<sub>1-x</sub>FeO<sub>2</sub> is readily available.

Access to an arsenal of thermodynamic parameters such as the Fe vibrational density of phonon states (both eigenvalues and eigenvectors), the speed of sound in the material, the Fe interatomic force constant, the Fe atomic displacement parameters, the Fe vibrational entropy, *etc* is provided using Nuclear Resonance Scattering.

In this talk, an example of thermodynamic characterization of metastable phases across an electrochemical reaction will be discussed and further collaborations in the context of energy applications are going to be initiated.

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## Analysing operando spectroscopy data in battery studies: a chemometric approach

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Recently, a growing number of operando analyses have helped unraveling the electrochemical mechanism of lithium and post-lithium battery materials. The corresponding experiments usually lead to large amounts of data, requiring long and time consuming analyses. An alternative and innovating approach is using chemometric tools such as Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR).

PCA is used to discover the minimal particular structures in multivariate spectral datasets. In the case of operando experiments, it allows determining the number of independent components contributing to the whole dataset collected during electrochemical cycling. The number of principal components can then be used as the basis for MCR analysis, which permits the stepwise reconstruction of the “real” spectral components. A detailed description of MCR is given by Tauler et al. [1] who also proposed it for the analysis of in situ spectroscopic data, whereas its intrinsic limits are discussed by Ruckebush et al. [2]

In this presentation, we will show how such approach can be effectively applied to different techniques, such as Mössbauer and X-ray absorption spectroscopy (XAS), or transmission X-ray microscopy, for the comprehension of the electrochemical mechanisms in batteries.[3] In particular, the application of chemometrics to the study by XAS of the reversible sodiation of Sb-based negative electrode materials will show how, while one can gather important information for the reconstruction of the electrochemical sodiation paths in these compounds, it is intrinsically impossible to prove by XAS the formation of some of the reaction intermediates which are proposed in the case of Sb.[4]

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[3] M. Fehse, A. Iadecola, M.T. Sougrati, P. Conti, M. Giorgetti, L. Stievano, Applying chemometrics to study battery materials: Towards the comprehensive analysis of complex operando datasets, *Energy Storage Mater.* **18** (2019) 328–337. doi:10.1016/j.ensm.2019.02.002.

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## Probing inhomogeneous lithiation of graphite electrodes using *operando* micro X-ray diffraction

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Li-ion batteries are now ubiquitous and there is a strong demand for fast-charging, large-capacity devices which implies using large current densities and thick electrodes. In graphite, the most widely used anode material, this is expected to result in large Li gradients across the electrode, depending on the state-of-charge of the electrode [1, 2]. The heterogeneous intercalation of Li can be highly detrimental to the cell properties: some volumes of the electrode may cycle more and thus age faster, while others may not be used to their full capacity. In order to find the optimal cycling conditions, models have been developed but still need experimental validation and empirical parameter quantification.

We have performed for the first time an *operando* microdiffraction experiment to probe the lithiation state across the thickness of a graphite electrode during the cycling of the cell. We designed a bespoke electro-chemical cell and we recorded the powder pattern every few microns along the electrode thickness on a 2D Eiger detector on beamline ID13 at the ESRF (Fig.1a). After radial integration with the PyFAI software, we could evidence the distribution of graphite lithiation stages across the electrode (Fig.1b), at any point during the deintercalation of lithium. We could thus quantitatively retrieve the mean as well as the local Li content (Fig.1c). Our results show a sequence of homogeneous and heterogeneous distribution of the Li, as a function of the state-of-charge. Our observations are completely consistent with the predictions of the model, which could therefore be validated at the micro scale.

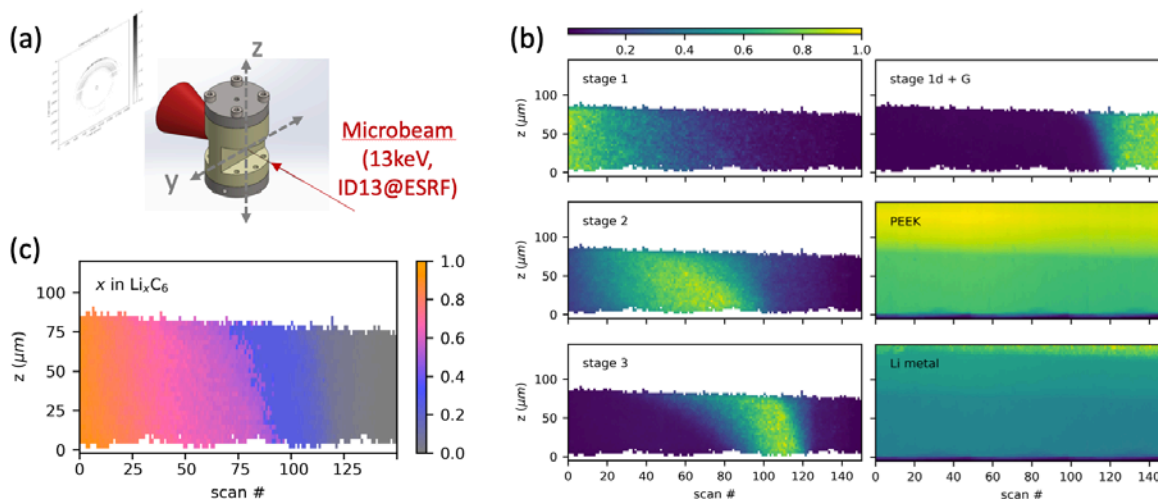


Figure 1: (a) Sketch of the experimental setup, (b) relative intensity distribution of the intercalation stages and (c) calculated corresponding local Li content, both across the electrode thickness and as a function of the Li deintercalation (scan #0 is almost fully lithiated, while scan #150 is fully delithiated).

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## Studying $\text{In}_2\text{O}_3$ catalyst for $\text{CO}_2$ hydrogenation to methanol at work: an *operando* XAS-XRD study

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The direct hydrogenation of  $\text{CO}_2$  to methanol allows converting one of the major greenhouse gases into a valuable energy carrier.  $\text{In}_2\text{O}_3$  has recently emerged as a promising catalyst for methanol synthesis via  $\text{CO}_2$  hydrogenation, exhibiting higher activity and selectivity than the benchmark  $\text{Cu-ZnO-Al}_2\text{O}_3$  catalyst [1]. The active sites of  $\text{In}_2\text{O}_3$  have been proposed to be oxygen vacancy sites formed on the catalyst's surface under reaction conditions [2]. Further developments of these catalysts require a detailed atomic level understanding of the structure (and changes thereof) under working conditions. Here, we report a structure-performance relationship study of  $\text{In}_2\text{O}_3$ -based methanol synthesis catalyst using combined *operando* X-ray absorption spectroscopy (XAS) at the In K-edge and X-ray powder diffraction (XRD).

The combined XAS-XRD experiment coupled with gas chromatography (GC) analysis allows relating the evolution of  $\text{In}_2\text{O}_3$  NPs to the activity in  $\text{CO}_2$  hydrogenation to methanol (Figure 1). The changes of the catalytic activity correlate with the changes in the In oxidation state, the local structure and the crystallinity of the catalyst during reaction. A multivariate analysis of the XANES data allowed to identify and quantify the formation of  $\text{In}_2\text{O}_{3-x}$  and  $\text{In}^0$  with time on stream (TOS) and correlate these changes with the three different catalytic stages: (i) Activation (ii) Steady state and (iii) Deactivation. During activation, the XANES analysis reveals a partial reduction of  $\text{In}^{3+}$ , while the EXAFS analysis shows a decrease in the In-O coordination number (while no significant changes are observed in the XRD data), indicating the formation of oxygen vacancy sites (i.e.  $\text{In}_2\text{O}_{3-x}$ ). During the catalytic steady stage, further reduction is observed leading at the end of this stage, to a decrease in both In-O and In-In coordination numbers. In the deactivation stage, a reductive amorphization of the  $\text{In}_2\text{O}_{3-x}$  nanocrystallites progresses with TOS ultimately over-reducing  $\text{In}_2\text{O}_{3-x}$  to molten  $\text{In}^0$  which is linked to the gradual deactivation of the catalyst.

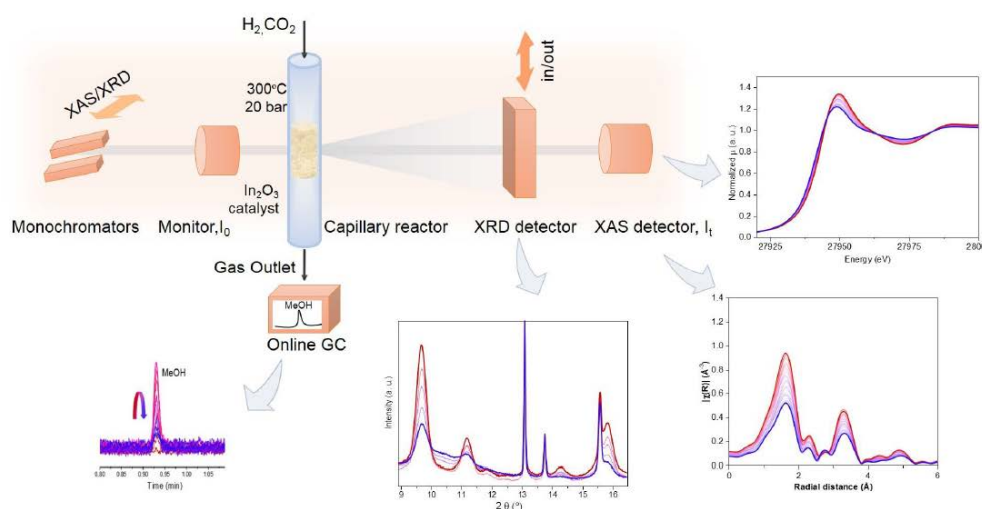


Figure 1: Schematic representation of the *operando*  $\text{CO}_2$  hydrogenation to methanol at SNBL, with the corresponding XAS, XRD and GC data collected [2].

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## ***Operando* investigation of the lithium/sulfur battery by coupled X-ray absorption tomography and X-ray diffraction computed tomography**

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High specific energy density sulfur electrodes are expected to serve in high performances low cost next generation lithium rechargeable batteries. However, contrary to conventional Li-ion batteries, Li/S cells transport charge via a series of complex chemical reactions involving solid and soluble sulfur species, which can cause severe morphological changes of the positive electrode upon cycling and lower practical performance. The use of a lithium metal negative electrode also introduces further cyclability issues. In particular, the high specific energy density means high areal capacity and high discharge rates for the lithium metal electrode during stripping/plating cycles. Consequently, morphology changes of both electrodes in the Li/S system upon cycling are still key parameters limiting the practical application of this technology [1-2].

In this work, operando absorption and X-ray diffraction computed tomographies were performed simultaneously to study the morphological evolution of electrodes and to probe the local modifications of chemical composition during cycling. Using a cell design with control of electrolyte quantity and pressure allowed the better understanding of the dynamics of sulfur dissolution and formation and lithium stripping with temporal and 3D spatial resolution. This combination of methods allows a unique insight into the details of the complex mechanisms involved in the Li/S cells, and provides tool to understand the limiting factors and to develop improved Li/S cells designs [3].

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## Operando synchrotron X-ray diffraction and Mössbauer spectroscopy of the cathode materials for Li-ion and Na-ion batteries

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Application of different diffraction and spectroscopic techniques to operando studies on the electrode materials became an integral part of the metal-ion battery research. Combination of novel operando electrochemical cell with sapphire windows [1], synchrotron X-ray diffraction (SXRDX) and Mössbauer spectroscopy (MS) has enabled us to study crystal structure evolution and phase transformation behavior during electrochemical cycling of several cathode materials for Li-ion and Na-ion batteries. Two examples are given below.

Li-rich iron-containing olivines  $\text{Li}_{1+\delta}\text{M}_{1-\delta}\text{PO}_4$  ( $\delta \sim 0.03-0.06$ ) prepared by solvothermal method via  $\text{Li}_3\text{PO}_4$  precursor demonstrate excellent electrochemical characteristics such as C-rate capability (140 mAh/g at 10C charge for the  $\text{Li}_{1.04}\text{Fe}_{0.96}\text{PO}_4/\text{C}$  material) and low voltage hysteresis (14 mV at C/300 rate for the same sample) between lithiation and delithiation. Phase transformations and evolution of the Fe cations coordination environment during  $\text{Li}^+$  (de)intercalation are studied in operando regime by means of synchrotron X-ray powder diffraction (SXPDX) and  $^{57}\text{Fe}$ Mössbauer spectroscopy (MS). Presence of a certain amount of  $\text{Li}^+$  in M2 position in the crystal structure of the initial phosphates leads to additional component in MS spectra of all studied compounds, corresponding to ferric ions in the M2 position with distorted second coordination sphere. Evolution of the MS spectra during charge/discharge reveals clear relationship between relative fraction of this component and the mechanism of  $\text{Li}^+$  (de)intercalation. Extended single-phase regions with large  $\text{Li}^+$  non-stoichiometry in triphylite and heterosite phases of  $\text{Li}_{1-x}\text{FePO}_4$  observed by means of SXPDX appear due to Li-Fe defects existing in Li-rich olivines and acting as a “diluting” agent preventing twophase spinodal decomposition. Increased thermodynamic stability of the intermediate  $\text{Li}_{1-x}\text{FePO}_4$  phases was also shown for Li-rich olivines by DFT calculations. These features can be regarded as an additional merit of Li-rich olivines rendering them promising cathodes for high-power Li-ion batteries.

Unusual phase transformation behavior was also observed for  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$  cathode material with NASICON-type structure by means of operando SXPDX. In contrast with other NASICON-type phosphates,  $\text{Na}_4\text{MnV}(\text{PO}_4)_3 \leftrightarrow \text{Na}_3\text{MnV}(\text{PO}_4)_3$  transition proceeds via single phase mechanism. The next step  $\text{Na}_3\text{MnV}(\text{PO}_4)_3 \leftrightarrow \text{Na}_2\text{MnV}(\text{PO}_4)_3$  is biphasic. Further desodiation results in appearance of additional voltage plateau at  $\sim 3.9$  V vs.  $\text{Na}/\text{Na}^+$ , associated with re-distribution of Na atoms over available positions and activation of Na1 site, which previously was considered as inactive. During reverse process, all extracted Na cations are introduced back via continuous solid solution region. The demonstrated behavior is in part similar with Li-ion monoclinic  $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$ , where fully deintercalated  $\text{Li}^+$  cations introduce disorder in the structure which leads to single-phase intercalation mechanism [3].

These and other examples will be discussed in more detail in the presentation.

This work was supported by the Russian Science Foundation (Grant No. 17-73-30006).

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[2] K.-Y. Park, I. Park, H. Kim, G. Yoon, H. Gwon, Y. Cho, Y.-S. Yun, J.-J. Kim, S. Lee, D. Ahn, Y. Kim, H. Kim, I. Hwang, W.-S. Yoong, K. Kang, *Energy Environ. Sci.*, 2016 **9** 2902-2915

[3] Zakharkin M. V., Drozhzhin O. A., Tereshchenko I. V., Chernyshov D., Abakumov A. M., Antipov E. V., Stevenson K. J., *ACS Applied Energy Materials* **1** (2018) pp. 5842-5846.

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## Characterising evolving solid oxide fuel cell and electrolysis cell components with ex-situ and in-operando X-ray experiments

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Microstructure has a strong influence the electrochemical performance and lifetime of solid oxide fuel cells and electrolysis cells. The origin of cell performance degradation is thus directly linked to microstructural change in their electrodes; in the electrolyte; and the interfaces between them and other cell components. Particle coarsening, interface reactions, phase changes, elemental diffusion and mechanical stress occurring at: high temperature, high electrical current density and harsh atmosphere drive these microstructure degradation mechanisms.

Due to these challenging operating conditions, accessing cell component microstructural information has typically been achieved with post-mortem type investigations. What remains challenging however is to track non-destructively the evolution of electrodes and electrolytes from before to after, or during processes to access the dynamics of degradation mechanisms [1–3] under realistic conditions and with sufficient resolution. So far “in-situ” type studies have mostly focused on mechanisms associated with the oxidation and annealing of Ni-yttria stabilized zirconia (Ni-YSZ) hydrogen electrodes [1–3].

Here we summarize recent work that capitalizes on unprecedented 3D data quality achieved by ptychographic X-ray computed tomography (PXCT) to quantify 3D microstructure evolution in a redox cycle and annealing phenomena in Ni-YSZ electrodes with ex-situ type experiments [4,5]; and a spatially resolved in-operando diffraction study of lattice strain associated with grain boundary oxygen bubble precipitation in a Sc doped YSZ electrolyte under high polarization [6] (see Figure 1). Limitations experienced and open questions will be discussed in terms of the expected EBS upgrade.

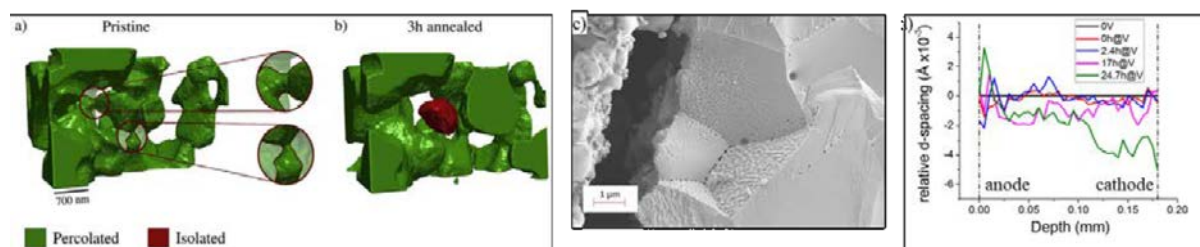


Figure 1: Microstructural evolution in the Ni network during annealing of a Ni-YSZ electrode revealing the formation of isolated Ni particles a) Pristine, b) annealed revealed by PXCT. c) SEM image of electrolyte grain boundary oxygen bubble formation at anode interface. d) change in the electrolyte lattice spacing profile in an operating symmetric LSM-Sc-SYZ cell. Reproduced with permission from Elsevier a) & b) [5] and c) & d) [6].

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## Probing water distribution and ionomer nanostructure in operating Proton Exchange Membrane Fuel Cells thanks to X-Ray synchrotron source

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Proton Exchange Membrane Fuel cells (PEMFC), as a highly efficient energy conversion technology, and hydrogen, as a clean energy carrier, have a great potential to reduce both carbon dioxide emissions and dependence on mainly imported hydrocarbons. Therefore, PEMFC is the predilection technology for automotive applications with a large deployment horizon by 2025-2030. However, in view of extending their use to a broad range of customers and to compete with existing technologies, progress has still to be done on current PEMFC stack technologies in terms of cost, performance and lifespan.

Nevertheless, degradation mechanisms are not clearly understood because of their coupling, and also due to the complex composition and intricate nanostructure of the PEMFC components. Moreover, our previous investigations [1-3] revealed that the degradation is strongly correlated to the local water content which is heterogeneous. Understanding the water distribution in PEMFC in correlation with the degradation mechanisms is particularly important to improve their performance reliability.

X-Ray Synchrotron sources, such as ESRF, are highly efficient tools to study the PEMFC during operation. Recently the water distribution has been probed with a spatial resolution of around 60 nm within 20 minutes thanks to nanocomputed tomography [4]. At CEA, we are developing for many years *Operando* studies on the evolution of water distribution and physical structure of the proton conduction polymer within the membrane during operation thanks to low energy (13 keV) Small Angle X-Ray Scattering (SAXS) (Figure 1) [5]. In 2018, we have been able to conduct similar studies within the electrodes after adapting the method to the use of microfocus beam on ID13 (ME-1496). In parallel, preliminary experiments of high energy (78 keV) SAXS tomography conducted at the end of 2017 on ID31 beamline demonstrate the possibility of having a complete picture of the heterogeneities in water distribution as well as micro structure of membrane (IN-1043). Improvements in the synchrotron source along with the beamline instrumentation, cell hardware and data analyses methods are expected to bring crucial information for PEMFC technology with unprecedented time and space resolutions in a near future.

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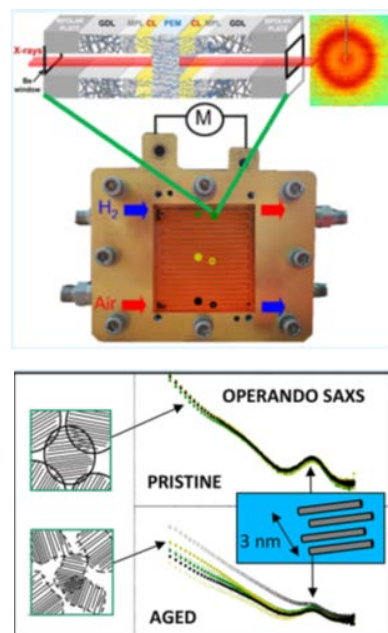
[2] L. Guétaz et al., *J. Power Sources* **212** (2012), 169.

[3] C. Robin et al., *J. Power Sources* **326** (2016), 417.

[4] S. J. Normile et al., *Materials Today Energy* **9** (2018), 187.

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(Top) Photography of the SAXS fuel cell, with a picture of the single serpentine gas flow channel and the six probed positions.

(Bottom) SAXS spectra for an aged and a pristine membrane depending on the position.

## ***In situ* and *operando* structural evolution of single metallic nanoparticle model catalysts under ambient pressure reaction conditions**

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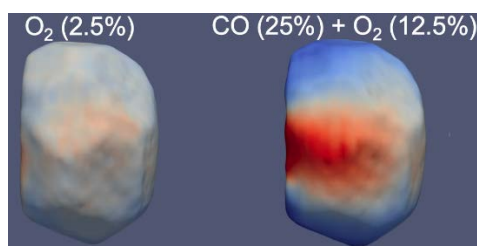
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 Characterising the structural properties (strain gradients, chemical composition, crystal orientation and defects) inside nanostructures is a grand challenge in materials science. Bragg coherent diffraction imaging (Bragg CDI) can be utilised to address this challenge for crystalline nanostructures. A resolution of the structural properties of less than 10 nm is achieved up-to-date [1]. The capabilities of the Bragg CDI technique will be demonstrated on single nanoparticles for enhanced catalysis.

As an example, the Bragg CDI technique allows understanding the interplay between shape, size, strain, faceting [2], composition and defects at the nanoscale. We will demonstrate that Bragg CDI on a single particle model catalyst makes it possible to map its local strain/defect field and directly image strain build-up close to the facets. We will also show results obtained during *in situ* [3,4] and *operando* Bragg CDI measurements during CO oxidation and H<sub>2</sub> hydrogenation: it was possible to track a *single* particle in liquid and gas phase environments (see Fig. 1), to monitor its facet changes and to measure its strain response to gas or electrochemical reaction.

This technique opens pathways to determine and control the internal structure of nanoparticles to tune and optimise them during catalytic and other chemical reactions. This technique should benefit from a unique opportunity: the ESRF **EBS** Upgrade. This should revolutionise imaging by making it possible to map evolving physico-chemical processes in a slow-motion movie.

Financial support to this work by ANR Charline (ANR-16-CE07-0028-01), ANR TERC (ANR-18-ERC1-0010-01) and a NOW TOP grant is gratefully acknowledged.



**Figure 1:** 3D Bragg coherent diffraction imaging reconstruction of both the shape and displacement field along the [111] direction of a faceted Pt nanocrystal (diameter of 150 nm) at 450°C during different gas mixtures: (left) in 2.5% of O<sub>2</sub> and (right) under stoichiometric conditions: in 25% of CO and 12.5% of O<sub>2</sub>.

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## Probing the electron density at electrochemical interfaces with in-situ surface resonant x-ray diffraction

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Electrochemical interfaces play a crucial role in many systems used for clean energy production, conversion and storage. Improving fundamental understanding of the electrochemical interface will thus help to solve current problems in these systems, e.g. the stability of the electrode and electrolyte and the charge transfer mechanism.

*In-situ* surface x-ray diffraction has enabled an atomic/molecular-level understanding of the interface under reactive conditions, including its potential and time dependence, to be developed. While information about the atomic structure of the electrode surface in electrochemical *in-situ* cells has been widely investigated, insight into the charge distribution and the structure of the electrolyte at the interface is still lacking. Advances in these directions offer possibilities in elucidating atomic scale models of the electrochemical interface and thus will help to establish structure-stability-reactivity relationships. [1]

A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry to better understand electrochemical processes and charge transfer during adsorption and deposition. [2] Thus combining x-ray spectroscopy and x-ray diffraction to gain site-specific information about the charge distribution at buried interfaces is a promising tool.[2,3] Examples of how the use of surface x-ray scattering techniques can help to characterise electrochemical interfaces in-situ in order to link, structure, reactivity and stability will be presented. [3,4] Application of the methodology to the understanding of electrocatalytic reactivity will be discussed.

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## X-ray Raman Scattering study of energy storage materials based on metal hydride nanocomposites

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Efficient energy storage is crucial for the use of renewable energy from intermittent sources such as solar and wind. Light-weight metal hydride have attracted much attention as a multifunctional energy materials due to their use in applications such as reversible hydrogen storage, rechargeable batteries (electrodes and electrolytes), ammonia storage/decomposition and heterogenous catalysis.[1-6] A common approach to improve the properties/performance of metal hydrides in these applications is by making nanocomposites with carbon or metal oxides. Characterization of light-weight metal hydride nanocomposites (e.g.  $\text{LiBH}_4/\text{C}$  and  $\text{LiBH}_4/\text{SiO}_2$ ) is often hampered by their lack of long-range crystallinity, the presence of mostly light (low Z) elements, and low concentration of the active phase(s). In this presentation, I will use examples from reversible hydrogen storage and all-solid-state Li ion batteries to demonstrate the efficacy of X-ray Raman Scattering (XRS) for the *ex-situ* and *in-situ* study of metal hydride nanocomposite materials in energy storage applications.[7-8] I will show that XRS is particularly ideal for probing the electronic (K and/or L edges) and structural changes in light elements such as Li, B, Ca, Na, Mg, N, K, Al, O and Si, which are often the main contents of metal hydride nanocomposite materials used especially for reversible hydrogen storage and battery applications

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# Posters



## Large anisotropic negative thermal expansion in Cu-TDPAT metal-organic framework: a combined *in-situ* X-ray diffraction and molecular dynamics study

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Understanding the underlying principles in the mechanism of Negative Thermal Expansion (NTE) in various materials is of great importance, as it can facilitate the design of materials with Controlled Thermal Expansion (CTE).<sup>[1,2]</sup>

Cu-TDPAT, a highly porous and stable metal organic framework with enhanced gas adsorption properties is found to show large anisotropic Negative Thermal Expansion (NTE). To investigate the NTE behavior of Cu-TDPAT framework, we employed synchrotron powder x-ray diffraction techniques (ESRF) combined with computational calculations. The lattice parameters and the volumes of the unit cells were determined by the sequential LeBail refinement conducted on the powder diffraction obtained from 100 K to 500 K and a heating the rate of 3 K per minute. The results reveal an anisotropic NTE behavior for Cu-TDPAT in all directions, a phenomenon that is not commonly seen in MOF materials. The lattice parameters  $a$  and  $c$  show 0.25 % and 0.28 % reduction upon heating. (Figure 1) The observed large NTE behavior encouraged us to determine the mechanism behind this rare behaviour. For this, *in-situ* single crystal x-ray diffraction experiments were carried out. The experiment reveals that there are three structural motions responsible for the pronounced NTE behaviour in this framework which include (Figure 2): (a) bending of the benzene rings around the central triazine ring (b) folding and twisting of the benzene rings around paddlewheel metal clusters (c) twisting of the paddlewheel clusters. In this presentation we will discuss this data in detail.

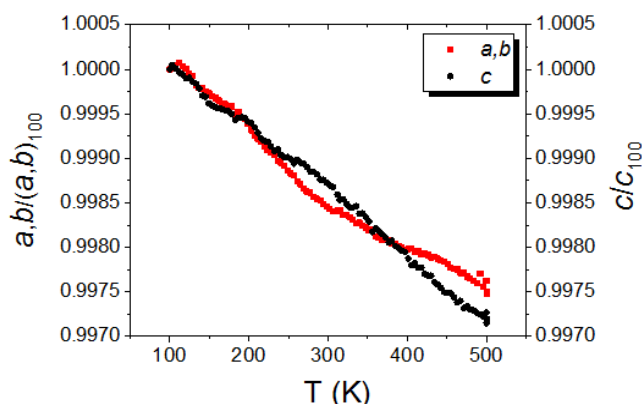


Figure 1- The evolution of lattice parameters ( $a, c$ ) as a function of the temperature normalized by their original value at 100 K. The standard deviations are smaller than the size of the points.

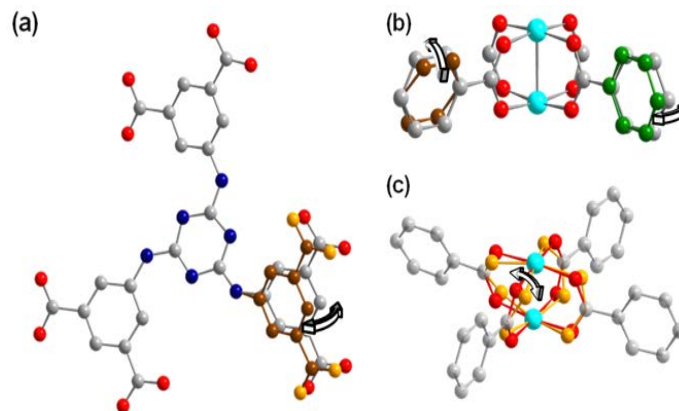


Figure 2- Structural motions in Cu-TDPAT responsible for the NTE effect

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## Long Duration Study of MOF Stability Towards Toxic Gases

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Although the use of fossil fuels for energy production must eventually be completely eliminated, sources predict that we will continue to burn them for many years to come.[1] In order to minimise the damage that this process is having on the planet, efficient methods of capturing harmful exhaust gases must be developed. Much work has been carried out on gas adsorption and separations in MOFs, however little is known about their long term stability towards toxic and corrosive gases.

In association with the I11 high resolution powder diffraction beamline at Diamond Light Source, we report the long duration (c.a. 4 years) study of the stability of the MOF MFM-300(Al) towards a series of harmful species. The MFM-300 family of MOFs has recently been reported to have high adsorption capacity and selectivity to the toxic gases NO<sub>2</sub>,[2] SO<sub>2</sub>,[3] and NH<sub>3</sub>. [3] Stability toward these gases has been monitored by weekly synchrotron powder x-ray diffraction collections and accompanied by extensive isothermal gas cycling experiments.

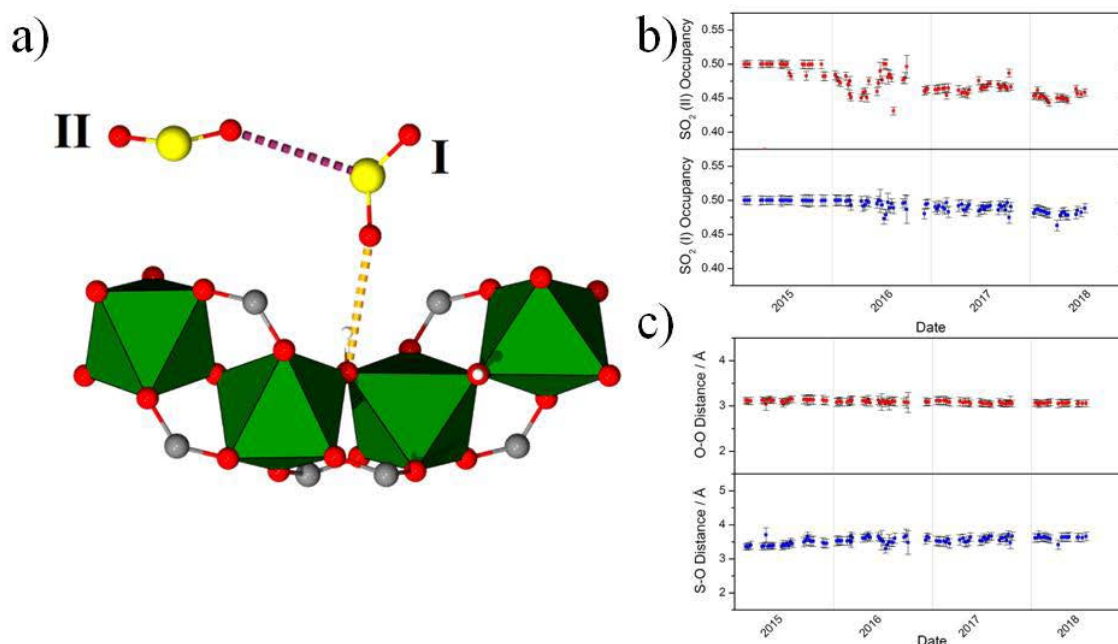


Figure 1: Results of Rietveld refinements of long duration SO<sub>2</sub> loaded MFM-300(Al) study; a) SO<sub>2</sub> binding positions b) Occupancies of SO<sub>2</sub>, c) host-guest and guest-guest interatomic distances

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## High pressure as a tool for engineering hybrid perovskites: an unprecedented pressure-induced band gap tuning

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The application of an external pressure is a fascinating and powerful tool to engineer the crystal and the electronic structure of photovoltaic perovskites. The most relevant interest of high pressure studies, together with the definition of the structural evolution with pressure, is the modulation, or engineering, of the optical band gap.

Here we report on the first structural and optical high-pressure investigation of  $\text{MASnBr}_3$  ( $\text{MA}=[\text{CH}_3\text{NH}_3]^+$ ) and  $\text{CsSnBr}_3$  halide perovskites. A massive red shift of 0.4 eV for  $\text{MASnBr}_3$  and 0.2 eV for  $\text{CsSnBr}_3$  is observed within 1.3-1.5 GPa from absorption spectroscopy, followed by a huge blue shift of 0.3 and 0.5 eV, respectively. Synchrotron single crystal diffraction allowed to correlate the upturn in the optical properties trend (onset of blue shift) with structural phase transitions from cubic to orthorhombic in  $\text{MASnBr}_3$  and from tetragonal to monoclinic for  $\text{CsSnBr}_3$ .

DFT calculations indicate different underlying mechanisms for the band gap evolution with pressure: a different key role played by metal-halide bond lengths for  $\text{CsSnBr}_3$  and cation orientation for  $\text{MASnBr}_3$  highlights the impact of a different A-cation on the pressure response. Finally, the investigated phases, differently from the analogous Pb-based counterparts, are robust against amorphization, showing defined diffraction up to the maximum pressure used in the experiments.

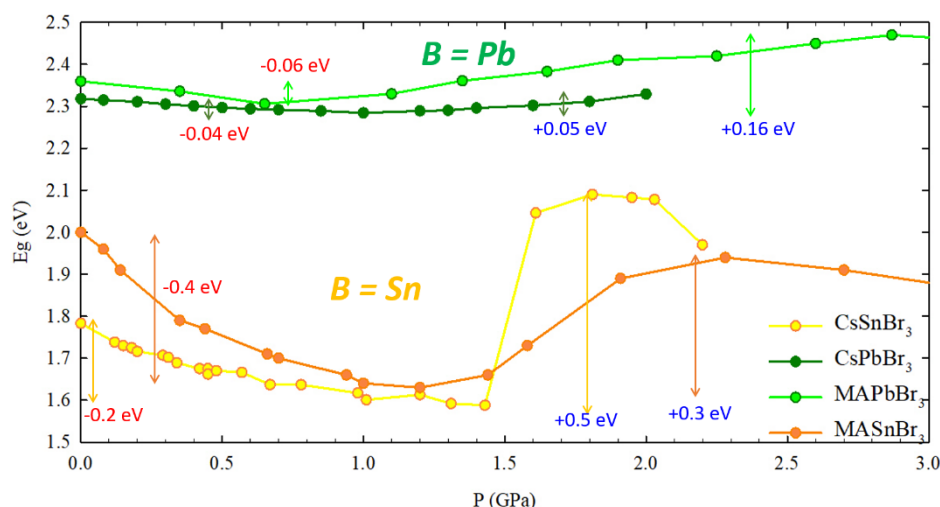


Figure 1: Band gap evolution with pressure of MA and Cs tin bromides compared to Pb counterparts from [2,3].

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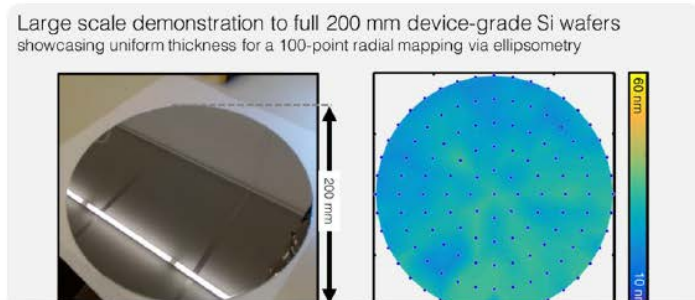
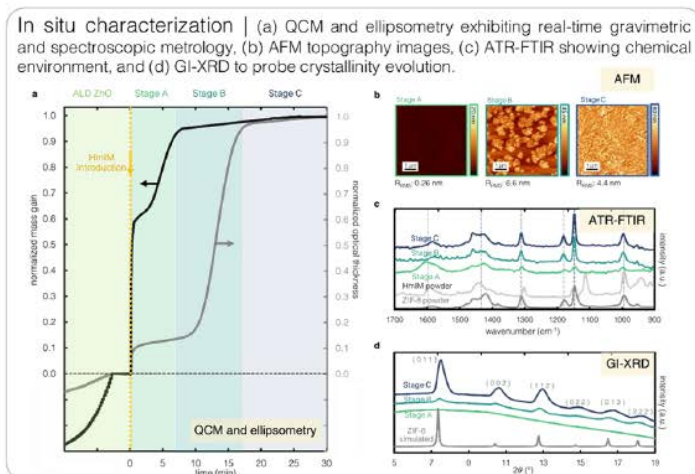
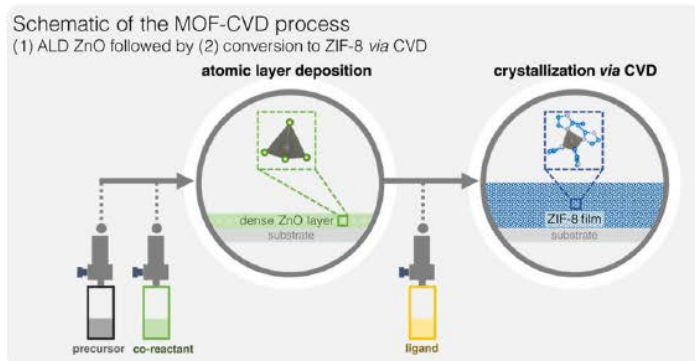
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## An integrated cleanroom process for the vapor-phase deposition of large-area metal-organic frameworks

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The integration of metal-organic frameworks (MOFs) in electronic devices requires the development of robust thin-film deposition methods. Eluding from the traditional solvent-based processes for the synthesis of MOFs, typically via powder preparation routes, we recently succeeded in the proof-of-concept demonstration of the chemical vapor deposition (CVD) of MOF thin films and subsequently optimized to 200 mm device-grade Si substrates. To further confirm the diversification of the CVD method for microporous crystalline materials and establish a new portfolio of formulations, various techniques using synchrotron radiation are essential. These measurements enable: 1) the identification of optimal growth conditions, 2) the understanding of the mechanism of the crystal growth and 3) the precise characterization of the epitaxial relationship between precursor and MOF. Successful elucidation of these various phenomena in CVD will enable the integration of MOFs in a wide array of energy-related applications such as gas sensing, gas storage, membrane separations, and batteries.

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## Transforming Co-imidazolate frameworks into amorphous Co-N-Se nanosheets for efficient water oxidation

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Herein, we demonstrate a mild, low temperature method to transform ZIF-67 into hierarchical porous, amorphous Co-N-Se nanosheets. Although various methods to fabricate transition metal selenides such as pyrolysis of single source precursors, chemical vapour deposition (CVD) etc. have been developed, these reactions require high temperatures ( $\sim 500$  °C) or the use of highly toxic/sensitive precursors which are avoided in the method developed in this work. By simply varying the reaction time an effective handle to regulate the degree of MOF-conversion was achieved and, thereby, fine tune the chemical composition and the porosity of Co-N-Se nanosheets. By the virtue of its abundantly exposed catalytically exposed sites and improved mass transport of the reactants/electrolyte, the amorphous Co-N-Se nanosheets were found to be a highly active and stable electrocatalyst for OER, even outperforming the state-of-art RuO<sub>2</sub>. Particularly, the Co-N-Se/3h sample achieved a current density of 10 mA/cm<sup>2</sup> at an overpotential of 352 mV with a small Tafel slope of 57.9 mV/dec. Mechanistic insights into the transformation of ZIF-67 into amorphous Co-N-Se nanosheets was obtained using x-ray absorption spectroscopy (XAS) which revealed that the OER activity is correlated to amount of Co<sup>3+</sup> active sites in the system. Information gained from structure-property correlation studies of these kind would be important to design efficient MOF-based electrocatalysts in future.

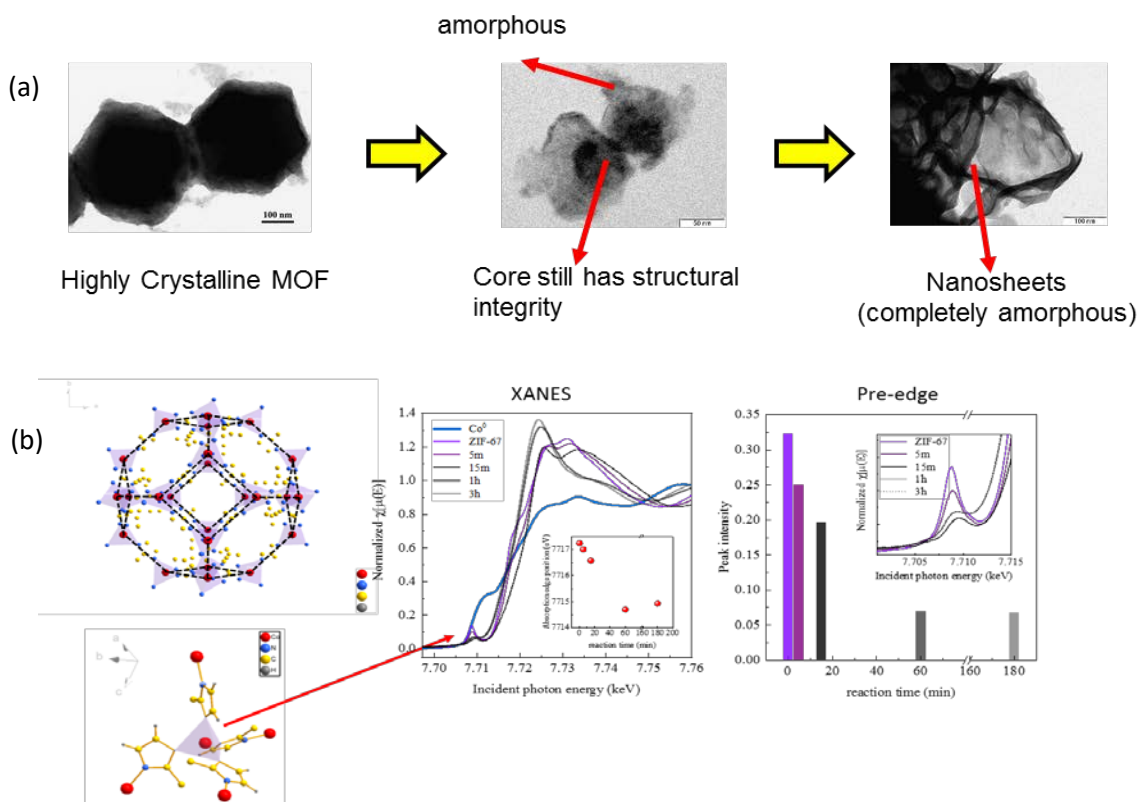


Figure 1. (a) TEM images and (b) Co K-edge XANES of the ZIF-67 through the evolution process

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## Combining a nine-crystal multianalyser stage with a hybrid CdTe photon counting detector for high-resolution X-ray powder diffraction

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The high-resolution powder diffraction beamline ID22 at ESRF combines a wide choice of photon energies with high brightness, allowing high-flux, high-resolution powder diffraction measurements at wavelengths down to  $\approx 0.3$  Å. In routine operation, a bank of nine scintillation detectors (channels  $2^\circ$  apart) is scanned to record the diffracted intensity versus  $2\theta$ , each detector preceded by a Si 111 analyzer crystal. Although the current system has operated very successfully for the past twenty years [1], recent developments in detector technology could be exploited to improve performance. With this in mind, the ID22 team borrowed a 2-dimensional Pilatus3 X CdTe 300K-W pixel detector from Dectris, which was mounted on the arm of the diffractometer, replacing the nine scintillator detectors. At each nominal  $2\theta$  value, a 2D image is recorded showing nine distinct regions of interest corresponding to the detection of the diffraction signals passing via each of the analyzer crystals. This arrangement offers major advantages in terms of data handling and processing. By varying the axial width of the region of interest considered as a function of  $2\theta$ , peak widths, peak shapes, and the statistical quality of the data, particularly at high  $2\theta$  angles, can be improved as compared to now. Parasitic scattering can be spatially separated from the diffraction signals, and bright spots from large grains identified and eliminated, if desired, thus improving the accuracy of the average, powder intensities [2]. In addition, an analyzer crystal maps a position in the sample directly onto a position on the detector, thus conferring spatial/depth resolution to the measurement, even allowing a sample to be distinguished from its container, or depth-mapping of a composite sample in high-resolution powder diffraction mode. We are planning to exploit this possibility to develop new form of powder-diffraction tomography.

Combining the versatility of a hybrid photon-counting area detector with the high angular resolution given by the analyzer crystals is an innovative approach to improving the overall performance of high resolution powder diffraction, as validated by the tests carried out using the borrowed detector. We will implement this new approach on ID22 at the restart of the ESRF in 2020, with the replacement of the scintillator detectors by an Eiger2 CdTe 2M-W pixel detector. Even greater improvements are expected by exploiting the smaller pixel size and the higher speed of the Eiger detector, as well as the increased flux provided by the new ESRF source, leading to a high impact and the possibility of 3-dimensional mapping of complex systems during in-situ and time-resolved experiments.

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## Defects and interface structure studied with High Energy X-rays: Towards the holistic understanding of electrochemical energy conversion and storage systems

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<sup>7</sup>University of Victoria, BC, Canada

Complete physico-chemical operando characterization of electrochemical devices in whole, or its constituent materials separately, is necessary to guide the development and to improve the performance. High brilliance synchrotron X-ray sources play a crucial role in this respect as they act as a probe with relatively high penetration power and low damage potential. These sources will undergo major upgrades in next decade and will provide even higher brilliance and, more importantly, coherence. These upgrades will be particularly advantageous for beamlines providing high energy X-rays as it will allow to use advanced scattering techniques with highly penetrating probe and therefore will bring the techniques typically used for ex-situ measurements to be used on materials in half-cells and operating electrochemical devices. In this contribution the new possibilities of using high energy, high intensity, coherent X-rays to probe model systems and whole electrochemical devices will be presented. The focus will be on defects tracking and local structure determination using advanced WAXS, SAXS and surface scattering techniques.

HESXRD (High Energy Surface X-ray Diffraction) [1] and TDS (Transmission Surface Diffraction) [2] provide ideal tools to study structural changes during reaction conditions on single crystal model electrodes. The main advantage of both techniques is the possibility to follow the surface structural changes precisely with atomic resolution. While HESXRD is ideally used to determine exact atomic position, the TSD is easier from experimental perspective and allows studies with high spatial resolution. Advantages and disadvantages of both approaches will be discussed and examples of measurements on ORR and OER catalysts will be given. The future possibility to use high energy coherent beams will open new opportunities for both techniques to study single defects and surface dynamics in operando conditions. Furthermore, local atomic and mesoscale structure, together with defect content, can also be determined for applied nanostructures by using Rietveld fitting, Pair Distribution Function (PDF) analysis and advanced SAXS theory. This in principle allows holistic investigations of interfaces at the device level, specification of defects' role in catalysis and determination of interplay between different phases during operation [3,4]. To study fuel cells or batteries at a device level, elastic scattering techniques coupled with the tomographic reconstruction (XRD-CT and SAXS-CT) allows spatial reconstruction of materials important atomic parameters in operando conditions. This will be demonstrated on imaging of standard 5 cm<sup>2</sup> PEM fuel cell during operation. We show that using advanced reconstruction algorithms allows to retrieve XRD peaks parameters normally inaccessible due to the parallax effect. This allow to obtain atomic scale information even for large objects which opens new opportunities with the EBS upgrade.

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## Li<sub>3</sub>ClO based glasses for solid state batteries

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Discovering new chemistry and materials to enable rechargeable batteries with higher capacity and energy density is our priority. The novel inorganic and thermally stable oxides are potential substitutes for the toxic and flammable organic liquid electrolytes that are used in the Li-ion batteries. The oxyhalide solids are derived from the precursors of crystalline anti-perovskites of metal hydroxides and have the highest reported Li<sup>+</sup> and Na<sup>+</sup> conductivity,  $\sigma > 10^{-2} \text{ S cm}^{-1}$  at room temperature (25°C) [1].

Here we study Li- and Na –ion based oxides, with nominal composition:  $A_xM_{1-x}O_{1+y}Cl_{1-2y}$  (where A=Li, Na and M=Ba, Ca), which were prepared from commercial precursors: NaCl, LiCl, NaOH and Ba(OH)<sub>2</sub> etc, applied multi-step heat treatments.

The structure characterization is challenging, first of all we intend to understand the atomic structure of the new materials. Neutron diffraction experiments were carried out at the 10 MW Budapest research reactor using the PSD diffractometer,  $\lambda_0 = 1,069 \text{ \AA}$  [2].

Since electrode materials are inherently nano-scale materials, local observations of these materials at high resolutions can be helpful to understand the microscopic processes that occur inside nano-particles and their interfaces with the electrolyte. Transmission electron microscopy coupled with energy dispersive X-ray spectroscopy was used to visualize and study the structural morphologies and atomic distribution. The nano-domains were verified by high-resolution transmission electron microscopy.

Both Li and Na based compositions has a well-defined structure. Details of the structural characteristics will be presented.

Acknowledgement - This work was supported by the NKFIH, Nr. 2017-2.3.7-TÉT-IN-2017-00023.

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## Investigation of electrostrictive polymer efficiency for electromechanical energy harvesting

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Converting vibrations to a practical form of energy have been the subject of many late surveys. The concluding purpose is to convert ambient vibrations to achieve low-power consumption devices, such as microelectromechanical systems and wireless sensors, which have restricted existence duration that would need costly maintenance. The techniques used to convert vibrations into electrical energy comprise: piezoelectric elements, electromagnetic devices or electrostatic systems. Electroactive polymers have been most used as smart material for sensing in last year's. Electromechanical applications are actually concentrated on energy harvesting, including the development of wireless portable electronic equipment autonomous and specific actuators such as artificial muscles. The aim of this work is the identification of electromechanical conversion losses by electrostrictive polymers using the Fast Fourier Transform (FFT) analysis. These losses are due mainly to the variation of the electrical and mechanical parameters exciting the electrostrictive polymer. In order to estimate this dissipated energy, an evaluation by FFT has been performed. In this context, an analytical model will be detailed and the theoretical results will be compared with the experimental results. Good agreements have been found between the two approaches.

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## Hyperspectral Chemical Imaging in Space and Time using Synchrotron Light in the microXAS beamline at the Swiss Light Source

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Commonly in technological functional/engineered materials as well as in nearly all inorganic or biological materials in nature, pronounced physical and chemical heterogeneities are observed at various length and time scales. These complex hierarchical structures potentially dictate the macroscopic physical properties and chemical reaction pathways in space and time. Consequently, being able to unveil physicochemical properties at relevant spatial and temporal length scales is fundamental for the understanding of properties, function, and reactivity of materials. Imaging (in two-, three- and four-dimension) is frequently limited to morphological analysis; however, very often imaging disclosing physicochemical properties turns out to be essential (which may involve even more dimensions: 3D real-space, time, energy and 3D reciprocal-space). Therefore, the need for “chemical microscopes” is growing rapidly. Particularly, the development of standard methodologies to investigate the local structure and chemical/elemental composition in the micrometer and sub-micrometer range is critical.

In that regard, synchrotron-based techniques have been applied to provide, in a non-destructive manner, high-resolution imaging of chemical speciation for various complexes and heterogeneous systems. The use of several X-ray techniques providing chemical contrast such as X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS) or X-ray diffraction (XRD) in a simultaneous and/or combined manner allow the recording of multimodal and multidimensional/hyperspectral datasets. Among their advantages, it can be mentioned:

- (i) the potential to perform in situ experiments;
- (ii) the resolution that can be achieved down to the tens of nanometers;
- (iii) in addition to 2D scanning analysis studies (‘chemical images’) based on spectro-microscopy and XRD-imaging also, due to the considerable penetration power of (hard) x-rays, investigations in 3D (‘chemical tomography’) are also feasible. Combining computed tomography approaches with the afore mentioned chemical x-ray techniques provides means to derive local chemical information from within intact, undisturbed objects or materials;
- (iv) the ability to get depth resolved crystalline contrast by analyzing the XRD and chemical–elemental contrast by analyzing the XRF;
- (v) element-specific chemical sensitivity by tuning the X-ray energies around element-specific absorption resonances.

In this presentation, recent progress and achievements in the field of 2D/3D chemical imaging and speciation analysis using various synchrotron radiation x-ray microprobe techniques, as well as on full-field ones will be presented. Examples from a wide range of scientific disciplines, including materials science, environmental science, or biology, will be used to illustrate the potential of chemical imaging.

Future prospects will be addressed and arising new research opportunities will be outlined.

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## Debundling of Multilayered MoS<sub>2</sub> from 3D Nanoflower Architecture to Few Layer MoS<sub>2</sub> Nanoflakes in TiO<sub>2</sub> heterostructure: Efficient Dye Adsorbent and Enhanced Photocatalytic Activity under White LED Light

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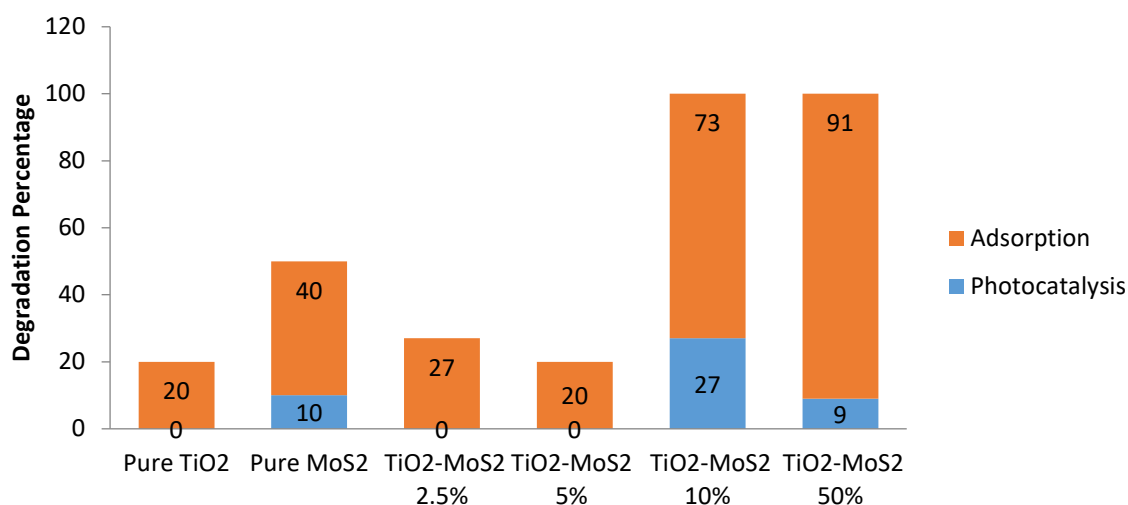
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TiO<sub>2</sub>-MoS<sub>2</sub> nanocomposites with different weight percentage of MoS<sub>2</sub> (0, 2.5, 5, 10, 50 and 100%) are synthesized by one-step hydrothermal method. Pure MoS<sub>2</sub> SEM images showed multilayered layers of MoS<sub>2</sub> aggregate to form 3D nanoflower-like structure, which is not seen in TiO<sub>2</sub>-MoS<sub>2</sub> nanocomposites. TEM image confirms the reduction in width of MoS<sub>2</sub> nanoflakes in TiO<sub>2</sub>-MoS<sub>2</sub> nanocomposites compared to pristine MoS<sub>2</sub> nanoflakes. Raman spectra obtained for TiO<sub>2</sub>-MoS<sub>2</sub> (50%) confirms the presence of TiO<sub>2</sub> anatase phase and also the peak position difference ( $\Delta k$ ) between E<sub>2g</sub> & A<sub>1g</sub> of MoS<sub>2</sub> is 20.5 which is lesser than pure MoS<sub>2</sub> (22.9), which suggest that the multilayer nanoflakes in pure MoS<sub>2</sub> got reduced to few-layer nanoflakes in the TiO<sub>2</sub>-MoS<sub>2</sub> nanocomposites. The samples showed an increase in adsorption co-efficient of methylene blue dye with respect to increasing in weight percentage of MoS<sub>2</sub> in TiO<sub>2</sub>-MoS<sub>2</sub> nanocomposites. The nanocomposites with 50% weight of MoS<sub>2</sub> showed higher adsorption rate compared to pure MoS<sub>2</sub>. The absorption spectrum of TiO<sub>2</sub>-MoS<sub>2</sub> (10% & 50%) showed broad absorption window including UV & visible region. This optical property of TiO<sub>2</sub> -MoS<sub>2</sub> nanocomposites shows enhanced photocatalytic activity even in low power visible white LED light.

**Decolorisation of Methylene Blue**



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### 3D characterization of ice particles in jet A-1 fuel

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Water in jet fuels is a big concern for the aeronautical industry, especially at low temperatures, for which ice particles form and may accumulate in the fuel feeding systems, generating high pressure drop and a potential restriction of fuel, causing risk of engine failure. This was e.g. the case in 2008 with the crash of the Boeing 777-GYMMM, for which two engine failures occurred at the Heathrow London airport. As a result, the Air Accidents Investigation Branch launched several studies in order to better understand and prevent such ice blockage situations [1]. For this purpose, IFTS has developed its own test loop [2] with a reproducible and repeatable method to generate ice particles from  $-40$  to  $-5^{\circ}\text{C}$  at the critical water content in jet fuel for emergency system operations, i.e. 260 ppm.

The main objective of this research work is to characterize the size and shape of ice particles produced in jet A-1 fuel through the ice clogging method of the IFTS at  $-20^{\circ}\text{C}$  (temperature believed to be critical in previous studies). The approach is twofold: (1) 3D image acquisition of ice particles to characterize their shape and size distributions. (2) direct dynamic observation of these particles inside a glass-section adapted to the pipes of the test loop by a high-speed camera and correlating these 2D results with those of the 3D method. In this work, we present the first results concerning the 3D ice characterization in jet A-1 fuel. For this purpose, we developed an experimental method to sample the ice particles within the fuel, transporting them under cold-stable conditions for storage in a cold room. Later on, we set up the ice samples in a specific cryogenic cell (CellStat) in order to keep them at a stable state (around  $-20^{\circ}\text{C}$ ) during X-ray tomography [3]. Then, an image processing method was developed to segment these samples, which were analyzed afterwards using several softwares [4-6]. To sum up, first results have shown repeatable and coherent particle size distributions and minor variations in their shape based on Gaussian and mean curvature distributions.

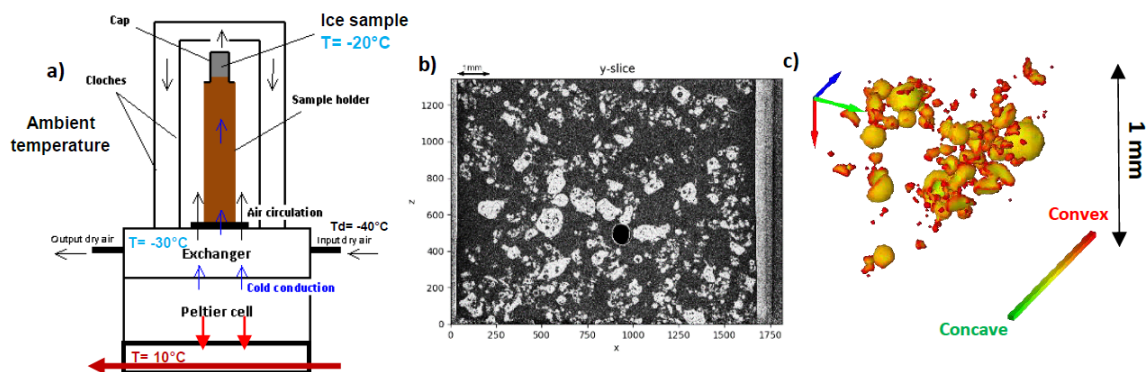


Figure 1: a) Schema of the cryogenic cell "CellStat"; b) Vertical slice of a typical sample (ice particles within fuel); c) 3D sub image of the ice sample.

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## Reversible adsorption of nitrogen dioxide within a robust porous metal–organic framework

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Nitrogen dioxide (NO<sub>2</sub>) is a major air pollutant causing significant environmental and health problems. We report reversible adsorption of NO<sub>2</sub> in a robust metal–organic framework. Under ambient conditions, MFM-300(Al) exhibits a reversible NO<sub>2</sub> isotherm uptake of 14.1 mmol g<sup>-1</sup>, and, more importantly, exceptional selective removal of low-concentration NO<sub>2</sub> (5,000 to < 1 ppm) from gas mixtures. Complementary experiments reveal five types of supramolecular interaction that cooperatively bind both NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> molecules within MFM-300(Al). We find that the in-situ equilibrium 2NO<sub>2</sub> ↔ N<sub>2</sub>O<sub>4</sub> within the pores is pressure-independent, whereas ex-situ this equilibrium is an exemplary pressure-dependent first order process. The coexistence of helical monomer–dimer chains of NO<sub>2</sub> in MFM-300(Al) could provide a foundation for the fundamental understanding of the chemical properties of guest molecules within porous hosts. This work may pave the way for the development of future capture and conversion technologies.

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## Two new diffractometers for single crystal and powder diffraction at BM20/ESRF

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The Institute of Resource Ecology / Helmholtz-Zentrum Dresden-Rossendorf operates since 20 years the Rossendorf Beamline (ROBL/BM20) at the European Synchrotron Radiation Facility (ESRF) [1]. Two new diffractometers will be installed at the beamline until July 2020. We discuss here their use for single crystal and powder diffraction.

The single crystal diffractometer is foreseen for small and large molecule crystallography, mainly for structures with heavy and very heavy metals. The second diffractometer allows the use of moderate high-resolution powder diffraction. Studies of complex intergrown crystals and electron density are possible. The energy range of 5-35 keV allows the use of anomalous dispersion. In-situ experiments on single crystals and powders are supported. Diffraction measurements can be combined simultaneously with X-ray emission and absorption spectroscopy. The experimental hutch is equipped for the use of radioactive material.

The single-crystal diffractometer is a duplicate of the diffractometer at SNBL/BM01/ESRF [2]. It is installed on an adjustable granite table. A stable metal frame carries a Pilatus3 X 2M detector. The detector can be tilted and the distance between sample and detector can be varied from 140 to 600 mm. Samples will be mounted on typically a kappa goniometer. A microscope for sample alignment is placed in a distance 170 mm from the crystal. A Vortex X90 CUBE silicon drift detector with a FalconX1 processor will be used to align small crystals. This detector can be used to determine simultaneously the chemical composition or the metal oxidation states. The setup comprises a cryo cooler (80-400 K) and a heater (up to 1200 K) which can be used at both diffractometers. The single-crystal diffractometer can be used also for powder diffraction. The resolution for powder diffraction can be increased by using the second diffractometer, a 6-circle Huber diffractometer, in combination with a Pilatus 100k detector with a typical sample-detector distance of 800 mm. This arrangement does not reach the resolution of synchrotron diffractometers with secondary analyzer crystals, but provides a magnitude better resolution than lab diffractometers [3].

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## Diffraction scattering computed tomography data analysis work flow: From raw data to Rietveld refinement

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Many advanced materials contain several phases organized in 3D. Examples include many energy materials and complex biological materials like bone. To unravel their internal structure, diffraction scattering computed tomography (DSCT or XRD-CT) is a very useful technique since it allows mapping powder diffraction information in each voxel within a 3D volume [1-5]. DSCT requires collection of large amounts of data, which in turn calls for efficient data analysis procedures. We have constructed a data analysis work flow facilitating DSCT analyses.

The software is built in MATLAB. First, the 2D diffraction images from the detectors are integrated. This is done using a new indexing method that is quite fast. To ensure proper mapping of coordinates from detector to polar ( $q$  and azimuthal angle), we use sub-pixel indexing in a manner that differs from other procedures [6] that allows full control over desired precision, which is especially useful for azimuthally resolved integration. The integrated data are tomographically reconstructed and can then be fed into automated Rietveld refinement procedures using an updated and more efficient version of our previous work [7]. Together, these procedures provide an easy-to-use and efficient platform for analysis of large diffraction data sets such as those encountered in DSCT.

We illustrate our procedure on DSCT data on bone, where we use the results to shed light on the complex structure of the human femoral head. We expect to broaden our use of DSCT to other classes of material including energy materials.

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## Numerical study of InGaN/GaN heterojunction PIN based solar cell

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The Indium Gallium Nitride (InGaN) alloy can lead to high efficiency solar cells. Indeed its band gap can cover the whole solar spectrum, including the visible region, solely by changing the Indium composition [1–3]. In this work, the calculation of characteristic parameters of GaN/InGaN heterojunction solar cell, such as: short-circuit current density, open-circuit voltage, and conversion efficiency by using two dimensional numerical simulations parameters taking into consideration the spontaneous and piezoelectric polarizations. The effects of indium content of the wells have been study, the thickness the barrier and the thickness of the quantum well in these parameters. We have shown that the Indium gallium nitride (InGaN) offer great potential for high-efficiency photovoltaics.

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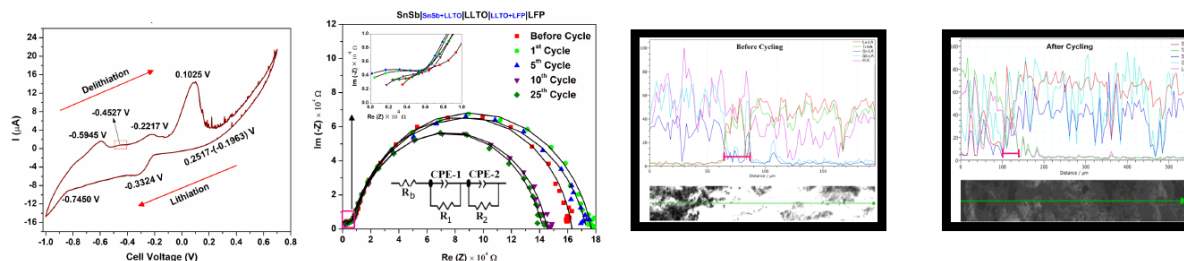
## Electrode-electrolyte interface modification and line profile analysis in all solid Li-ion battery

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An all solid Li-ion battery fabricated using tin antimony (SnSb) alloy anode, lithium lanthanum titanate (LLTO) solid electrolyte and lithium iron phosphate (LFP) cathode materials. Initially, the device assembly was carried out, only using the active counterparts without any add-ons to enhance the cell characteristics. The geometry of the assembled device is, SnSb|LLTO|LFP and the cell is fabricated in pellet conformation. Prior to the assembly, the compatibility of the active materials were ensured by HOMO-LUMO calculations and X-ray diffraction analysis of the electrode-electrolyte blends. Electrochemical analysis of the pellet conformation assembled as it is, were not successful to provide prominent redox peaks operated in the potential window, 2 V. However, simultaneous impedance analysis exhibit growth in charge transfer resistance/ solid electrolyte interface (SEI) of the device for each cycle and this scenario is observed for 25 cycles. Hence control over this interface and SEI formation may reduce such performance limiting passive activities of the cell. In this regard, application of a small coating between the electrode-electrolyte interfaces has been successful at minimizing interfacial impedances and interphase formation. In the present work, different interface layers have been attempted to bring out successful assembled ASSLIB. As a consequence of detailed interfacial modifications in ASSLIB, instead of three layers, a five layer assembly has been made with interface modification and one of the successful attempt is reported here.



\* (In series) Figure 1: Cyclic voltammetry of SnSb|electrode-electrolyte blend|LLTO|electrode-electrolyte blend|LFP full cell; Figure 2: Impedance of the cell before and after cycling; Figure 3, 4: Line profile analysis of anode|electrolyte interface before and after cycling the cell.

The pellet geometry made as SnSb|electrode-electrolyte blend|LLTO|electrode-electrolyte blend|LFP, is successful at resolving redox activity of the active materials (Figure 1) and cycleable up to 65+ cycles. Altogether, the cell provides a specific capacitance in the range ~33 mAh/g. Due to the inactivity of initial unsettled SEI formation at electrode-electrolyte interface, initial number of cycles delivers variable output capacitance. Owing to the intimate contact area facilitated by mixture powder of interface, the cell chemistry has been improved and the stability of the cell increases. This has been double verified with the impedance measurements after every subsequent cycle. The growth and decrease of SEI is observed at initial cycles and after 10<sup>th</sup> cycle the SEI/Charge transfer contribution fell down to a lower value than the impedance of the cell before cycling, (Figure 2). Hence the mixture interface layer is favorable to enhance the physical contact of electrode and electrolyte. The elemental charge distribution and line scanning analysis reveal the probable charge migrations and natural growth of interface layer from 25  $\mu\text{m}$  to 38  $\mu\text{m}$  after 65 cycles, (Figure 3, 4). However, such a growth is not performance limiting one which has been confirmed from the capacitance of the cell for higher number of cycles.

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## A look inside the structure of a single LMNO battery particle

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One major challenge in the field of lithium-ion batteries is to understand the degradation mechanism of high-energy Li- and Mn-rich layered cathode materials. The so-called voltage decay has been restricting their practical application for more than a decade, even though they can deliver 30 % excess capacity compared with today's commercially used cathodes. In order to unravel the nature of this phenomenon, we have investigated systematically [1] the structural and compositional dependence of Mn-rich compounds on the lithium content provided during synthesis. A coin cell battery (CR2032) of composition  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  (cycled 868 times) was targeted to confirm the anticipated morphology of an individual crystallite.

Bragg coherent diffraction imaging was used, on the ID01 beamline [2], to image the internal strain distribution in a single crystallite. A core shell structure was observed as anticipated from conclusions drawn from probes which extract average information from many crystallites (x-ray / neutron powder diffraction, x-ray absorption spectroscopy etc.).

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[2] S. J. Leake et al., *J. Synchrotron Rad.* **26** (2019) 571-584 <https://doi.org/10.1107/S160057751900078X>

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## Study of sulfur-based electrodes by coupled *in situ* synchrotron X-ray tomography and X-ray diffraction

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The Lithium-Sulfur (Li/S) battery system is one of the most promising candidates to become the successor of the current Li-ion battery. However, in spite of its high theoretical specific capacity (1675 mAh.g<sup>-1</sup>) and energy density (up to 500 Wh kg<sup>-1</sup>), it still suffers from a shortened cycle life resulting from the numerous complex processes occurring upon cycling. Hence the constant need for understanding of those mechanisms drives the use of innovative *in situ* characterization techniques. In the present study, *in situ* synchrotron X-ray tomography and diffraction are used to help better understand the optimization of sulphur-based electrodes for Li/S batteries.

X-Ray computed tomography (XRCT) is certainly one of the most powerful analytical tools enabling non-destructive 3D imaging of objects with complex and porous morphologies. Using appropriate image processing, segmentation and analysis procedures, quantitative parameters can be extracted such as the volume fraction, the particle size distribution, and dissolution kinetics of the constitutive phases of the Li/S electrodes. A spatial resolution of a few tens of nm can be reached with a synchrotron X-ray source compared to a few  $\mu\text{m}$  with a conventional laboratory X-ray source. This technique, coupled with *in situ* synchrotron X-ray Diffraction, enables to follow in great details the evolution of the different species inside the tested Li/S batteries and get invaluable information on their behavior and degradation mechanisms. Recently, *in situ* XRCT and XRD has been used to characterize Si-based anodes [1].

A first study demonstrated that AE could be used as an efficient tool to monitor the morphological degradation of S-based electrodes upon their cycling and offers relevant information for optimizing their formulation and architecture [2]. Further electrode optimization was investigated with the use of a poly-electrolyte binder (PEB) enhancing the performances of S-based electrodes by creating a ionic layer at the surface of the electrode which confines the polysulfide chains and prevents sulfur loss over cycling. *In situ* synchrotron X-ray tomography and diffraction were used at ESRF in France to study the behavior of those electrodes in comparison to classic CMC-binder based electrodes. The aim of this study was to get a better global understanding at the reduced capacity loss of PEB-based electrodes on Aluminum current collector. To do so, the morphology of the electrodes were compared, as well as the evolution of the different sulfur and lithiated species throughout the electrode and the electrolyte upon cycling. Batteries were studied again after 10 cycles to compare the evolution of their internal degradation.

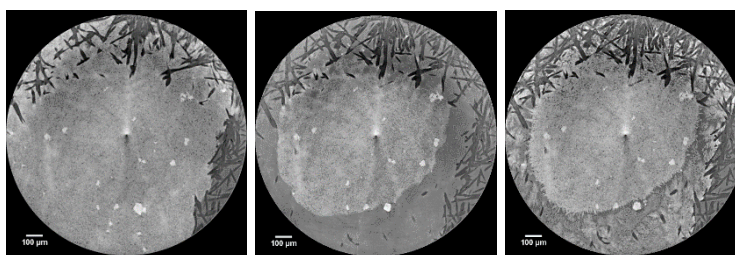


Figure 1 – X-ray tomography images of the surface of the PEB-based electrode during the 1st cycle at (a) 0% DOD, (b) 100% DOD and (c) 100% SOC

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## Probing the Chemical Environment of Single Pt Atoms in TiO<sub>2</sub>/carbon dots/Pt for Photocatalytic Hydrogen Evolution Reactions

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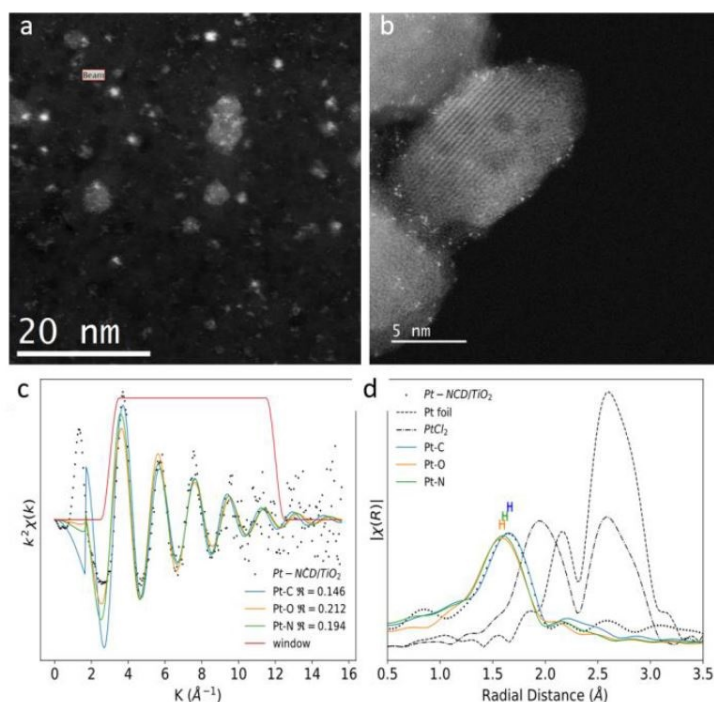


Figure 1. HR-STEM images of (a) Pt-NCDs and (b) Pt-NCDs/TiO<sub>2</sub>; (c, d) EXAFS data of Pt-NCDs/TiO<sub>2</sub>

Platinum group metals show a great potential in improving the efficiency of photocatalysts towards practical applications. However, the scarcity and high-cost of Pt remains a big challenge. Decreasing the Pt content by maximizing the atomic efficiency with retained excellent performance would bring the research one step closer to reality.[1] In this work, we report a novel approach of using nitrogen doped CDs (denoted as NCDs) as a support to fabricate highly stable and isolated single site Pt atoms as a form of co-catalysts. The Pt single site catalysts (SACs) with NCDs are then anchored on TiO<sub>2</sub> support, achieving a new, highly efficient and multi-scale structured photocatalytic system for H<sub>2</sub> evolution. STEM images (Figure 1) show the Pt exists as single atoms on CDs and TiO<sub>2</sub>, with XPS data indicate

the Pt stay mostly in the oxidized state of Pt<sup>2+</sup>. The XANES spectra from XAS experiments indicate that the NCDs have retained the Pt atoms in an oxidized form, consistent with the finding from XPS. FT-EXAFS fitting suggests that the Pt atoms are likely coordinated with carbon atoms, which has been proved to be stable after photocatalytic reactions. The activity towards hydrogen production has been evaluated under visible light irradiation. After decorating with Pt SACs and NCDs, the sample showed 7 times higher H<sub>2</sub> evolution rate compare to bare TiO<sub>2</sub>. The material benefits from optimal H\* absorption, lower energy barriers [2] and sufficient charge separation induced by the Pt SACs, which providing a promising way to reduce the high cost of noble metals in many fields and pave a new avenue for the development of highly efficient materials.

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## Lithium metal negative electrode: lithium oxydation and reduction characterized by X-ray tomography

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Lithium metal is considered as the most promising anode material thanks to it has a very high theoretical capacity and to the lowest electrochemical potential. Nevertheless, inhomogeneous lithium stripping and plating, leading to uncontrollable dendritic growth, dragged lithium metal batteries out of practical applications. Since the 1960s, many solutions have been proposed to suppress dendrite growth including the use of a solid electrolyte as a mechanical barrier [1].

Our research is based on the study of lithium-electrolyte-lithium cells, using a solid polymer electrolyte. These cells are polarized at a fixed current to move a chosen thickness of lithium through the electrolyte. Post-mortem characterizations are made by X-ray tomography, and the image analyses lead to a thickness variations mapping (see Figure 1). These qualitative and quantitative analyses give information on lithium behavior during stripping and plating. The advantage of using such symmetric cells is that oxydation and reduction can be simultaneously studied. The impact of different parameters have been analyzed, such as the influence of the moved thickness, the lithium microstructure or the first polarisation.

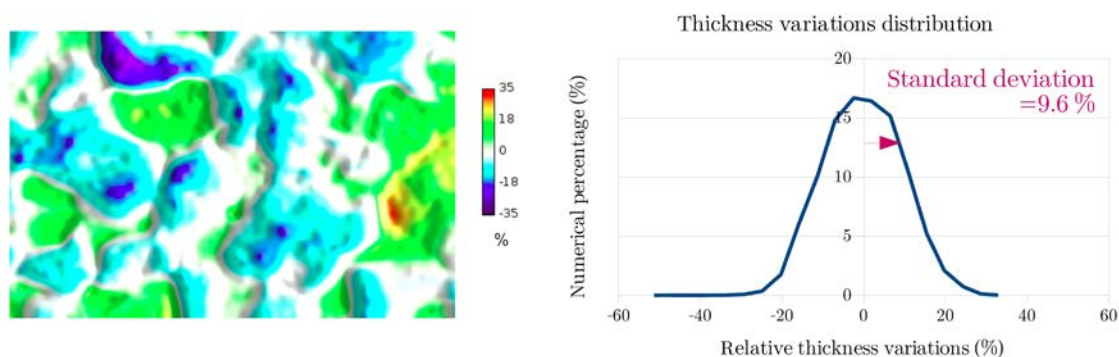


Figure 1: Image analysis of a cell after moving 22µm of lithium  
(left) 2D map of thickness variations (right) quantitative distribution of thickness variations

[1] W. Xu et al., *Energy Environ. Sci.* **7**. (2014) 513-537

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## New thermoelectric materials synthesised via microwave-induced heating in a single mode cavity to be probed in real time with neutrons

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Green technologies are vital to ensuring a global reduction in energy wastage and associated pollution. New materials and production methods are required to meet these demands and the use of microwave-induced synthesis works well within this framework. Microwave radiation instantaneously induces heating directly and volumetrically within a material, greatly decreasing both heating and cooling times and minimising the energy requirements per reaction cycle[1]. Thermoelectric generators produce a current in a circuit containing two types of thermoelectric semiconductors held between conducting plates of different temperatures[2]. The effectiveness of a thermoelectric material is quantified by the dimensionless figure of merit ( $zT$ ), defined by the thermal and electrical parameters as expressed in equation 1[3]. It is assumed that the electrical conductivity ( $\sigma$ ) and thermal conductivity ( $\kappa$ ) do not vary along the length of the material and so are independent of absolute temperature ( $T$ ), unlike the Seebeck coefficient ( $S$ ) which represents the voltage generated across the temperature gradient[4]:

$$zT = \left( \frac{S^2 \sigma}{\kappa} \right) T \quad (1)$$

This poster will discuss some of the thermoelectric materials that have been produced in our lab to date, along with the methods of synthesis using the single mode cavity microwave reactor (figure 1) that has been designed to operate within the POLARIS neutron diffractometer at the ISIS Rutherford Appleton Laboratory (RAL) facility in Oxford.

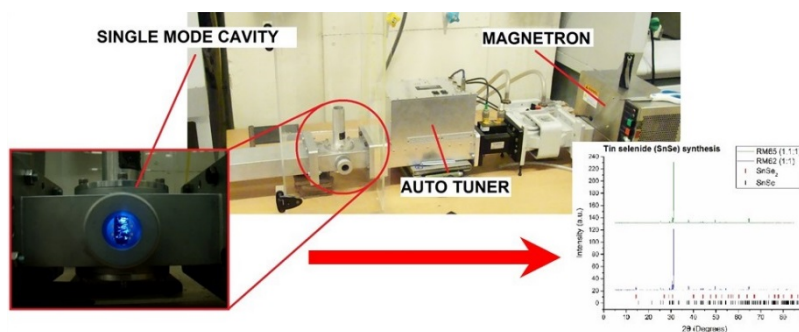


Figure 1: Single mode cavity microwave reactor initiating synthesis of tin selenide

POLARIS has previously been used to study structures over short timescales[5], therefore future work will involve carrying out microwave-induced reactions and collecting the neutron data *in-situ* to allow detailed analysis of microwave chemistry and synthesis pathways in real time.

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[4] H. S. Kim et al, *Proc. Natl. Acad. Sci.* **112** (2015) 8205.

[5] J. W. Makepeace et al, *Faraday Discuss.* **188** (2016) 525.

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## Using X-ray diffraction to detect Li metal deposition

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Li metal deposition onto anodes can be viewed negatively and positively. For graphite anodes, Li metal plating can occur under extreme fast charging (XFC) conditions where the anode potential can locally drop below the Li/Li<sup>+</sup> potential; this plating is thought to result in significant capacity fading and potentially shorting. On the other hand, for Li metal anodes, Li plating is a necessity. In both graphite and Li metal, *in situ* observation of Li metal has proven challenging. In this talk, I will discuss our work using X-ray diffraction to track Li metal deposition on graphite in full pouch cells and in Li metal anodes. To look at the origins of capacity loss in lithium metal anodes [1], we have developed a method of monitoring lithium metal in the anode via operando X-ray diffraction (XRD). Throughout cycling, we can understand through what mechanisms inefficiencies are occurring and how much they contribute overall. We observe that the contributions of chemical corrosion and ‘dead’ lithium to the overall Coulombic efficiency varies much more across electrolytes and cycling conditions than the SEI does. To detect the presence of Li metal during XFC [2], we have conducted two-dimensional XRD mapping for full pouch cells cycled under conditions up to 9C (in 6.67 minutes) for 450 cycles. I will describe the methodology we have adopted. We find considerable spatial heterogeneity correlated with the graphite staging, significant cell-to-cell variability and a strong correlation between Li metal quantity and capacity fade.

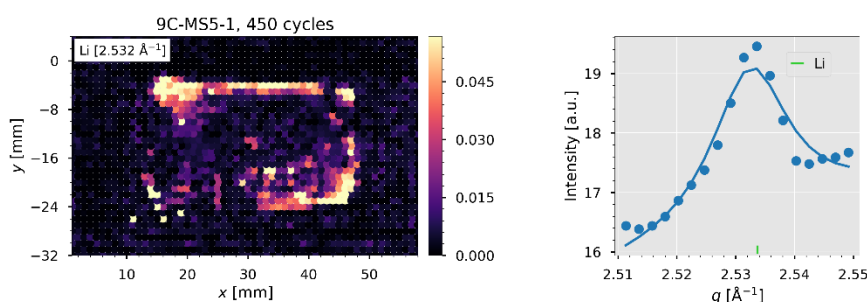


Figure 1: (left) image of Li metal XRD for full pouch cell cycled at 9C for 450 cycles. (right) example of I(Q) showing Li metal.

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[2] Dufek et al., *J. Pow Sour.* (2017) **367** 237-249

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## XAS operando degradation analysis on PGM-free ORR catalysts for PEMFCs: Fe-N-C vs. $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$

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Proton Exchange Membrane Fuel Cells (PEMFCs) have been, in recent years, successfully deployed in several small-scale production of vehicles. Unfortunately, mass commercialization of this technology is hindered by the relatively high cost, mostly due to the amount of Pt required at the cathode electrode, because of the sluggish Oxygen Reduction Reaction (ORR) kinetics. Alternatively, PGM-free catalysts can be employed to decrease catalyst cost due to their high abundance, despite their specific activity and stability being inferior to that of Pt. The most promising candidates so far contain N-coordinated Fe as active species, embedded in a carbon matrix [1]. Aiming at a higher stability in acidic medium, we prepared a ZrO<sub>2</sub>-based catalyst [2], whose ORR activity could be astonishingly boosted [3] by partially substituting Zr<sup>4+</sup> in the structure with Fe<sup>3+</sup>, very ORR-active by itself. The nanometric carbon-supported catalyst here considered, denoted  $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$ , was already characterized using XRD, Mössbauer spectroscopy and XPS, to get first information about phase and Fe coordination, and tested in a PEMFC (loading of 0.38 mg<sub>cat</sub>/cm<sup>2</sup><sub>MEA</sub>) [4]. Previous spectroscopic works investigated Fe-N-C materials by various *ex-situ* [1] and operando XAS in a liquid cell [1, 5, 6].

In this contribution we report an XAS operando analysis conducted at the FAME ESRF beamline BM30b in a H<sub>2</sub>/O<sub>2</sub> PEMFC on a commercial Fe-N-C (Pajarito Powder, USA) and on  $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$  (both 4 mg<sub>cat</sub>/cm<sup>2</sup><sub>MEA</sub>). The data enable a correlation between catalysts operation/degradation at various potentials and XANES results at the Fe K edge. Further, Zr K edge XAFS data on  $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$  show changes upon operation (related to Zr valence/coordination, under investigation).

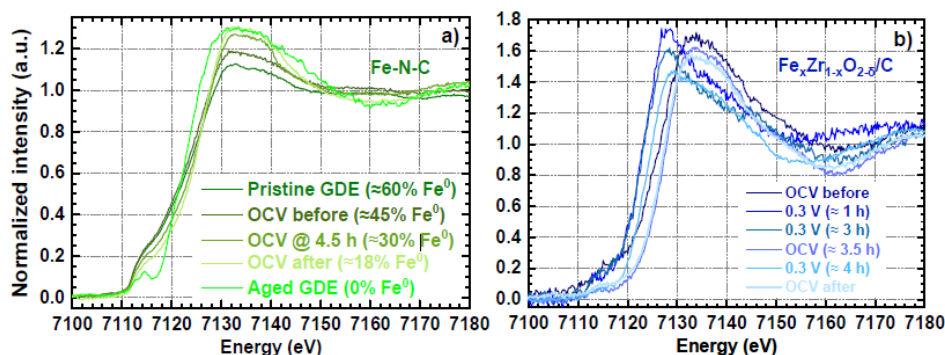


Figure 1: *Ex situ/in situ/operando* XANES data collections ( $\approx 25$  min., fluorescence yield) in H<sub>2</sub>/O<sub>2</sub> PEMFC on a) Fe-N-C and b)  $\text{Fe}_x\text{Zr}_{1-x}\text{O}_{2-\delta}/\text{C}$  before, during and after tests at 0.3 V<sub>cell</sub>. (GDE= Gas Diffusion Electrode)

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## Fuel Injector Nozzle Geometry and its Effect on Internal Flow and the External Spray

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Cavitation is an important phenomenon in fuel injectors that can lead to nozzle damage, increased emissions, and decreased efficiency over the life of an engine. Modern injectors are designed to suppress cavitation, but this is achieved using slow, expensive trial-and-error because cavitation is poorly understood. As engine designers demand ever-higher pressures from their fuel injection systems, the problems of cavitation become ever more important.

A series of measurements have tracked the fuel flow inside a diesel injector and quantified its impact on the fuel distribution outside the injector. First, high precision measurements of the injector geometry were captured using X-ray tomography [1]. Next, high-speed X-ray imaging revealed that flow over a sharp corner caused a low-pressure region to form, resulting in streams of cavitating fuel [2]. Time-resolved X-ray tomography of the spray quantified the density distribution of the fuel as it emerged from the nozzle [3]. This highly accurate ( $\pm 3\%$ ) measurement revealed that cavitation inside the nozzle generated a highly asymmetric fuel spray, with a low-density region corresponding to the location of strongest cavitation. Finally, tomographic reconstruction was applied to a series of X-ray phase contrast images to build a 3D map of the boundary between the liquid and gas inside the steel injector nozzle.

These capabilities reveal a complete picture of cavitation, from its geometric inception, flow through the injector, and its manifestation in the external spray. Typically, simulations of cavitation are tested against data acquired in oversized plastic nozzles at lower pressures. These in situ data allow cavitation models to be tested at engine-relevant conditions, and will lead to a better understanding of injector flow. This accomplishment can enable the design of injectors capable of higher pressures and improved performance, improving efficiency and reducing emissions over the lifetime of the engine.

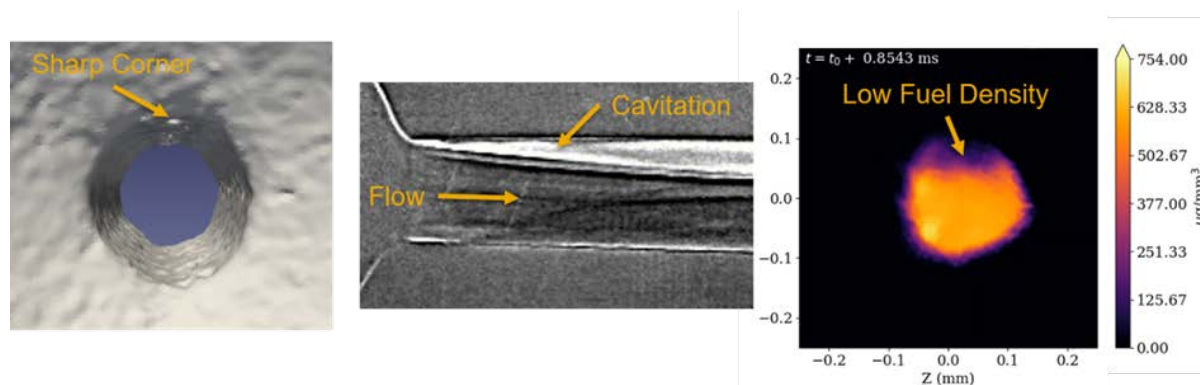


Figure 1: High precision X-ray tomography reveals the internal geometry of the injector (left), while X-ray imaging (center) captures the bright signature of cavitation produced by the sharp inlet corner and continuing downstream. This flow separation persists to the nozzle exit, and causes a low-density region in the fuel distribution (right) just outside the nozzle.

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## All-inorganic metal halide perovskite for X-ray detector: reducing dark current by light soaking effect enhances sensitivity

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The ease of solution processability, earth abundant cheap precursors and superior performance metal halide perovskites (MHPs) in solar cell and LED devices led to exploration of alternative application prospects for this novel class of materials.[1] All-inorganic MHPs offer novel prospect of chemically stable emergent alternative of hybrid organic-inorganic perovskites possessing analogous electronic configuration.[2,3,4] Currently, medical X-ray imaging uses a very high dose of X-ray, which might cause DNA damage and cancers to the patients, which is undesirable.[4] Recent finding shows that MHPs can be use as potential medical X-ray detector for direct X-ray to current conversion material with very high sensitivity, very low dose detection limit, low operating bias voltage compared to the conventional materials (HgI<sub>2</sub>, amorphous Se, CdTe). MHPs based X-ray detector is highly promising as they are composed of heavy Pb atom and have relatively high absorption coefficients for X-ray radiation and use of Pb in X-ray imaging can be accepted in diagnostic equipment as Pb is already used there in X-ray diagnosis system.[5] MHPs X-ray detector utilizes hybrid organic-inorganic metal halide perovskites (MAPbI<sub>3</sub>, where MA is methylammonium) which is relatively less susceptible to moisture and heat compare to the all inorganic counterparts due to the volatile nature of organic cations.[5] At KU Leuven, we focus on ambient stable all-inorganic MHPs alternatives for X-ray detectors (in collaboration with AGFA, Belgium). We have found that CsPbBr<sub>3</sub> microcrystals shows prominent X-ray induced photocurrent. Experimental observations reveal that a precise stoichiometric control tunes the morphology and monodispersity of CsPbBr<sub>3</sub> microcrystals, which is crucial for high performance X-ray detection. A special device fabrication technique by employing additive has been employed to make a uniform >500 um thick film to increase the attenuation of X-Ray absorption. Surprisingly we observe a huge photoinduced dark current reduction and large enhancement of photocurrent (X-Ray) on these microcrystals. This indicates that in CsPbBr<sub>3</sub> microcrystals photoinduced defect repairing or structural modifications happen, which is found to be stable for a longer period of time. The light soaking effect on the crystals structure deformation of MHPs needs high resolution Synchrotron in situ XRD measurement (e.g. GIWAX) to unravel the detail understanding of the dark current reduction process. Hence, there is a substantial room for the development of MHPs based high sensitive, ultralow dose detection X-ray detectors towards commercialization.

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## Local structural distortions in doped lead tellurides and their thermal evolution

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Thermoelectric (TE) materials are extremely technologically important as an alternative solution for increasing global energy demand, owing to their capability to convert heat into electric power and vice versa. Lead telluride-based semiconductors are leading materials for thermoelectronics applications in intermediate temperature range (400–900 K) due to high carrier mobility, direct narrow band gap and intrinsically low thermal conductivity [1]. Even though they were one of the first materials used for TE power generation, their potential to convert heat into electricity (TE efficiency) has not been fully exploited and it is still a subject of intense research activity [2–4]. In recent years, SnTe became attractive as an environmentally friendly alternative to PbTe for mid-temperature TE power generation. However, a major drawback of SnTe is in its high hole density which leads to poorer Seebeck coefficient, higher thermal conductivity and lower thermoelectric figure of merit. Tin and lead tellurides have similar physico-chemical properties, namely, the same rock salt crystal structure, narrow energy gap and similar band structure, and thus their TE properties can be presumably improved by using similar techniques [5]. One of the most effective and widely used strategies for high performance thermoelectrics is to reduce lattice thermal conductivity by introducing local structural distortions. In this work we review our most important findings on local structural properties of doped PbTe:A (A=Cr, Mn, Ni, Yb) systems obtained by using X-ray Absorption Fine Structure (XAFS) [2,3,6,7] and discuss their impact on improvement of materials' TE properties.

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## In operando resonant X-ray diffraction spectroscopy on layered Li-rich cathode materials for high-energy Li-ion batteries during cycling

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Despite the success of secondary lithium-ion batteries (LIBs) in portable devices, many challenges still remain for large energy storage systems such as electric vehicles (EV).[1] High-energy Li-excess 3d transition-metal (TM) layered oxides (LLOs,  $\text{Li}(\text{Li}_x\text{TM}_{1-x})\text{O}_2$ , TM = Ni, Co and Mn) are considered to be promising candidates as cathode materials for next generation high-energy LIBs due to their low toxicity, low cost and high capacity.[2,3] In previous work, we synthesized Co-free lithium-excess oxides, i.e.  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ . During synthesis, the precursor material undergoes phase transitions from spinel phase ( $Fd-3m$ ) to rock-salt phase ( $Fm-3m$ ) and finally to a monoclinic layered phase ( $C2/m$ ). The layered  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  cathode materials shows state-of-the-art electrochemical performance. During cycling, a solid solution reaction was observed which is associated with Li removal from the Li as well as the TM layer. An oxygen redox reaction and a TM migration induced phase transformation occur in the layered LLOs during the charge–discharge process, making the mechanism of charge compensation in these materials very complex. The TM migration usually triggers a phase transition from original layered structure to rock-salt/spinel structure and results in a decrease in capacity and operation potential, reducing the device lifetime. The changes in crystal structure due to irreversible release of Li/O during cycling are not quite understood. In particular, it is not clear which crystallographic sites are involved in TM migration, since Mn and Ni can hardly be discerned by X-ray diffraction. In X-ray absorption spectroscopy, on the other hand, contributions from different sites and phases are superimposed.

In this work, we tackle the ambiguities in site occupation in the involved phases of the material by in-operando diffraction anomalous fine structure (DAFS) measurements on a Li-ion battery cell during charge and discharge. DAFS provides X-ray absorption-like information selectively for those atoms that contribute to diffraction and, hence, allows to discriminate different crystallographic phases and sites. The measurements have been carried out at the “*in-situ* and nano X-ray diffraction beamline” P23 at DESY using a coin cell with aperture for X-ray transmission. Using the LAMBDA area detector in small distance to the sample, we recorded intensity spectra at Mn-K as well as Ni-K edges for several Bragg reflections. At the same time, the transmitted intensity was monitored using a PIN diode in order to perform an absorption correction for the diffracted intensities. The data allows to conclude about preferred site occupation of the TMs and to assess their valence state and local chemical environment. Therefore, DAFS has a great potential for application on battery materials.

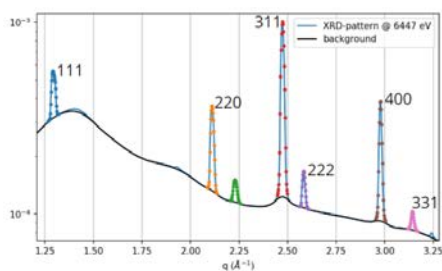


Fig. 1: Typical diffraction pattern for the spinel phase obtained via azimuthal integration of detector images.

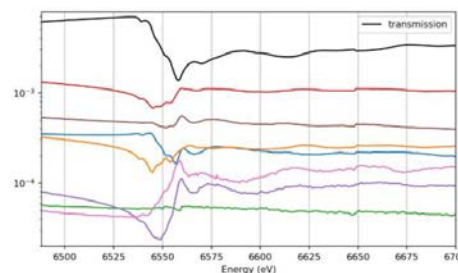


Fig. 2: Absorption corrected energy dependencies of integrated intensities of each reflection in Fig. 1.

[1] B. Kang and G. Ceder, *Nature* (2009) **458** 190–193. DOI: 10.1038/nature07853

[2] M. Sathiya, et al., *Nat. Mater.* (2015) **14** 230–8. DOI: 10.1038/nmat4137

[3] W. Hua, et al., *J. Mater. Chem. A* (2017) **5** 25391–25400. DOI: 10.1002/aenm.201803094

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## Small angle x-ray study of hybrid organic-inorganic diblock copolymer electrolytes

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Lithium metal anodes offer higher energy density than their graphite counterparts, yet suffer due to lack of stability against liquid electrolytes as well as failure by short circuiting due to dendritic growth.<sup>1,2</sup> Diblock copolymer electrolytes offer highly tunable nanostructures containing both soft, ion-conducting domains and mechanically rigid non-conducting domains to counteract lithium dendritic growth. The diblock copolymer structure greatly affects the ion transport in the system.<sup>3,4</sup> However, there are few studies on the effects of added salt to the morphology of diblock copolymers containing both organic and inorganic constituents. The phase behavior of poly(ethylene oxide) *-block-*polyhedral oligomeric silsesquioxane acrylate (PEO-POSS) mixed with lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt is systematically studied by varying volume fraction, temperature, and salt concentration. Using small angle X-ray scattering (SAXS), the morphology and segment-segment interaction parameter is obtained to quantify the thermodynamic interactions within the system and develop a phase diagram. This study shows that PEO-POSS without salt exhibits a classical order-*to*-disorder transition. Adding salt dramatically changes the phase behavior and a disorder-*to*-order transition is observed upon heating. Upon further salt addition, a transition from lamellae to coexisting lamellae and hexagonally packed cylinders is observed. Our results suggest that the addition of salt plays a more complicated role in hybrid organic-inorganic electrolytes compared to traditional all organic diblock copolymer electrolytes.

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[3] Ganesan, V., et al. *ACS Macro Lett.* **1**, 513–518 (2012).

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## Understanding the voltage and capacity fade in Li Rich NMC electrodes

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Li-rich layered transition metal oxides  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$  are attractive electrode materials providing high energy densities, relatively good cycling stability with reduced environmental costs [1]. However, their utility in many applications suffers from both voltage and capacity fade, most likely related to structural transformations and not yet fully understood [2].

We investigated the manganese oxidation and spin states which are linked to the Mn size and magnetic interactions, resulting key parameters in defining the possible phases in which this cation may be involved [1, 3], and then in controlling the reversibility of the reactions along cycling. The Mn redox-state, constantly in opposition to the expected charge compensation, and spin-state resulted correlated with Ni oxidation/reduction, also spatially, suggesting that strain induced on the Mn–O sublattice by Ni oxidation triggers Mn reduction [3].

To elaborate design strategies that can be used to control the structure, for instance, hindering the spinel formation at the benefit of the electrode cycle life, it results then fundamental to address quantitatively how the strain controls the Mn oxidation and spin state.

Here we report about the local structural and electronical transformations during electrochemical cycling of a  $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}]\text{O}_2$  cathode, combining several complementary techniques: X-ray absorption (Mn, Ni, and O K-edge) and X-ray emission spectroscopy (Mn K $\beta$  emission line).

We focus mainly on the first charge and discharge cycle, identifying few key states of charge: the pristine state, the beginning and the end of the high voltage plateau, and the fully charged and following discharged states.

The reported results unravel the role of strains in controlling the electrochemistry of Li-rich cathodes.

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## Formation of formamidinium-based hybrid perovskite during spin coating: *In situ* GIWAXS study

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Organic-inorganic lead halide perovskites have very interesting optoelectronic properties and have been applied in light emitting diodes, photodetectors and photovoltaics. The first solar cell was reported in 2009 by Kojima *et al.*[1] and achieved efficiency higher than 20 % after only six years.[2] The current certified record (24.2 %) is close to the well stabilized monocrystalline silicon solar cells (27.6%). The most efficient perovskites are based in formamidinium (FA) cation and halide mixture (Br<sup>-</sup> and I<sup>-</sup>). Cs<sub>y</sub>FA<sub>y-1</sub>Pb(I<sub>x</sub>Br<sub>1-x</sub>)<sub>3</sub> and MA<sub>y</sub>FA<sub>y-1</sub>Pb(I<sub>x</sub>Br<sub>1-x</sub>)<sub>3</sub> (MA:methylammonium) are promising candidates to application in tandem solar cells due to band gap adjustment by controlling the composition. The preparation of this material is carry out by spin coating deposition of a perovskite precursor in DMF/DMSO mixture and an antisolvent is dropped under rotation to remove the excess of solvents and promote its formation. Consequently, a better understand of the phases and its evolution during spin coating preparation is desired to improve the efficiency of FA-based hybrid solar cells. In this work we studied the perovskite formation during spin coating using *in situ* grazing incidence wide angle X-ray scattering (GIWAXS) in Cs<sub>0.17</sub>FA<sub>0.83</sub>Pb(I<sub>0.83</sub>Br<sub>0.87</sub>)<sub>3</sub> and MA<sub>0.17</sub>FA<sub>0.83</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> under different relative humidity (rH) and ratio between perovskite and DMSO.[3] The higher amount of DMSO prolonged the duration of the colloidal gel. The presence of this gel at the time of antisolvent dropping is crucial to obtain homogenous and pinhole free films appropriate to achieve good performance in devices. The MAFA perovskite formation takes place through the conversion of the 2H-4H-6H polytypes, and a thermal annealing is required to complete conversion to perovskite. In high rH we observed the formation of the intermediate MA<sub>2</sub>Pb<sub>3</sub>I<sub>8.2</sub>DMSO and after the thermal annealing of the film, 4H and 6H polytypes are not complet converted to perovskite impacting negatively in the performance. Interesting, when MA is replaced by Cs, the formation takes place through 2H-4H polytypes to perovskite without thermal annealing independ of the rH and DMSO amount. Besides, the high rH condition lead to the heterogeneous morphology of the films and the impaired device performance. In summary our results reveals the complexity of the perovskite formation that depends on the antisolvent method, relative humidity and composition.

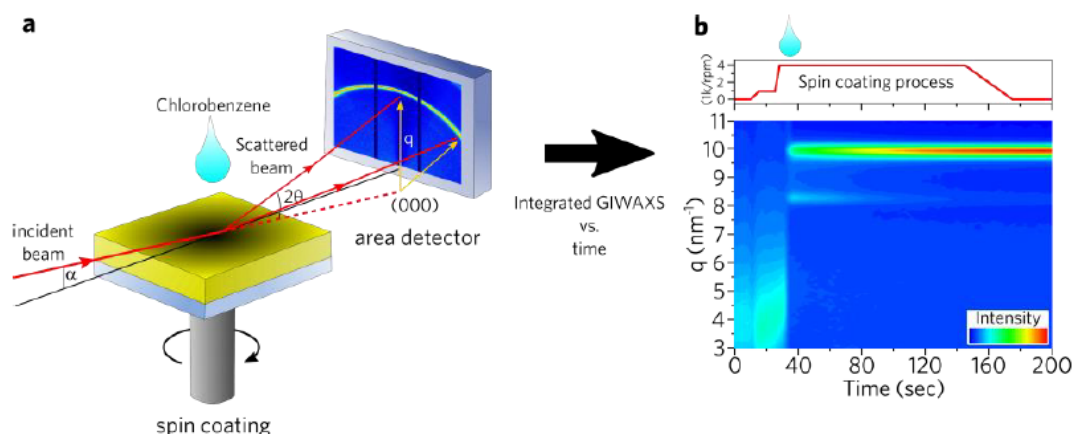


Figure 1: (a) Schematic representation of the *in situ* measurements and (b) 2D intensity maps versus time.

[1] A. Kojima *et al.*, *J. Am. Chem. Soc.* **131** (2009), 6050-6051.

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[3] R. Szostak *et al.*, *Sustain. Energy Fuels* (2019)

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## Low-temperature catalysts based on ceria supported ultra-small Pd, Au and PdAu nanoparticles: synthesis and characterization

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Supported noble-metal nanoparticles (NPs) are well-known catalysts for a wide range of chemical reactions, particularly, for CO oxidation. A number of attempts were made to develop catalysts with high performance and stability [1, 2]. However, there are some difficulties due to a various factors influence on catalytic activity such as composition, size and shape of the NPs, the material and functionalization of the support, dispersion and distribution NPs over the surface.

In this study, we used wet impregnation and reduction in an H<sub>2</sub>/Ar flow to synthesize Pd, Au and PdAu NPs on modified matrix surfaces of ceria. The samples demonstrated high catalytic activity in the CO oxidation reaction: the 100% of CO conversion was achieved at ~50 °C for Pd NPs. It was determined that the catalytic activity of the samples decreased in row Pd/CeO<sub>2</sub>>Au/CeO<sub>2</sub>> PdAu/CeO<sub>2</sub>, which indicated the absence of a synergistic effect in the case of a bimetallic sample.

The obtained NPs demonstrated a high dispersion according to SEM/EDS analysis, but their small size (1.5–2 nm) made it difficult to analyze them by conventional techniques such as TEM or XRPD. DRIFT spectroscopy with CO probe molecules was used to investigate the size and morphology of NPs and the ceria support. On the basis of the area ratio under the peaks attributed to bridged (B) and linear (L) carbonyls (Figure 1a), high-dispersion Pd NPs were corroborated. These results were in good agreement with data of XANES analysis (Figure 1b) and CO chemisorption measurements.

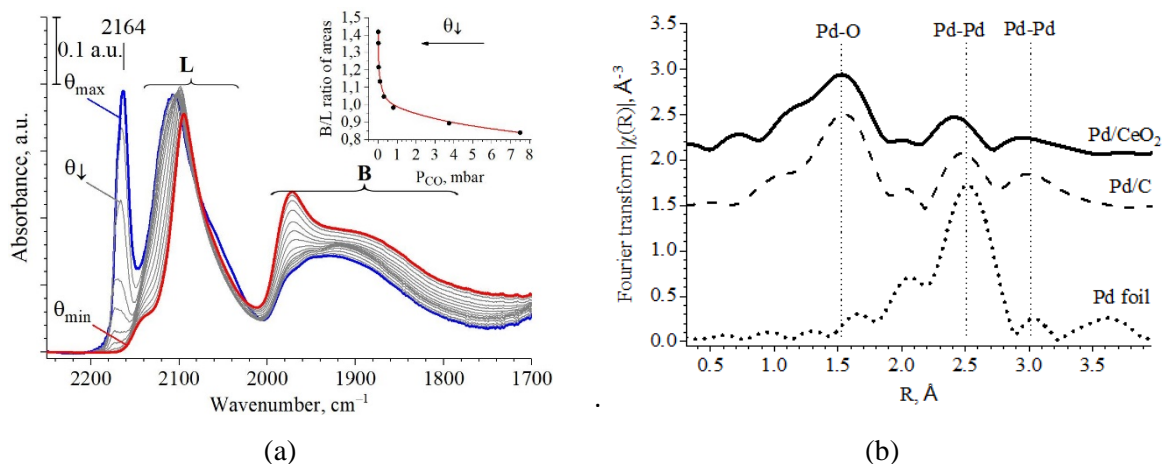


Figure 1 (a): DRIFT spectra of Pd/CeO<sub>2</sub> (reduced at 200 °C in a 5% H<sub>2</sub>/Ar mixture) during CO desorption at –140 °C from the highest CO coverage (red line) to the lowest coverage (blue line). Intermediate spectra are shown in grey color. The dependency of the area ratio under the peaks related to linear (L) and bridged (B) carbonyls from the CO pressure is shown in the inset; (b) Fourier transformed Pd K-edge XANES spectra. Spectra of Pd/CeO<sub>2</sub>, commercial Pd/C and Pd foil are shown in bold, dashed and dotted lines, respectively.

[1] G. Spezzati et al., *Appl. Catal. B Environ* **243** (2019), 36–46.

[2] E.M. Slavinskaya et al., *Appl. Catal. B Environ.* **166** (2015), 91–103.

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## SNBL BM31: Towards multi probe operando XRD + XAS + PDF

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The availability of experimental methods that probe a material's structure, often complex and dynamic, at different length and time scales is key to obtain fundamental insight in technologically relevant materials and environmental geochemistry. Indeed, progress in sustainable technologies relies on the development of innovative materials utilizing an in-depth understanding of the interplay between a material's structure and its macroscopic properties. To this end, there is a need for advancing current X-ray based facilities allowing the study of materials with multiple techniques at their working state (i.e., *operando* methods).

The BM31 station of the Swiss Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), offers the possibility to combine X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XRD) in an alternating fashion, quasi-simultaneously, in the same experimental setup. SNBL aims at extending these capabilities, by upgrading the current setup with a new CdTe area detector and focusing capabilities. This equipment will allow to i) implement pair distribution function analysis (PDF) of total scattering data, enabling combined XRD-PDF-XAS experiments and ii) enhance appreciably both the temporal ( $\sim 1$  s for XAS,  $\sim 100$  ms for XRD-PDF) and spatial resolution (utilizing a beam size of  $\sim 100 \times 100 \mu\text{m}^2$ ) of the experiments.

The combined XRD-PDF-XAS measurements will allow the acquisition of complementary information of a material under the relevant working conditions: covering the length-scale from short to mid-range atomic arrangements viz.  $\sim 1 \text{ \AA}$  to several nm by PDF, the average structure by XRD, as well as the electronic state, and geometry around the element of interest by XAS. All these data can be acquired in a temporal and spatially resolved manner in a single experiment. This will constitute a unique tool allowing the detailed study of materials for a wide range of applications, for instance: heterogeneous and electro-catalysis, CO<sub>2</sub> capture, gas separation, batteries and trace element reactions in environmental studies.

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## Nano X-ray imaging for materials science: A solid Oxide Fuel Cells study at ID16B

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ID16B beamline is a multi-modal beamline [1] offering a combination of nano X-ray imaging techniques based on X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray absorption spectroscopy (XANES) and phase contrast tomography allowing for the characterization, of heterogeneous materials, in a non-destructive way.

Solid Oxide Fuel Cells (SOFC) are high-performance electrochemical devices for energy conversion made of a complex multilayered and poly-phased structure including various ceramics and metals. They are considered as potential candidates to provide a solution to the quest for clean energy. In order to develop efficient, durable and reliable devices, a deep understanding of the nano-scale degradation processes occurring during elaboration and operation is strongly needed. In this talk, the novel insights brought into these degradation phenomena by the nano X-ray imaging will be detailed. The study of nickel agglomeration, poisoning, elemental diffusion (Figure 1) [2] and mechanical failure into the SOFCs using various nano X-ray imaging methods available at ESRF will be presented.

Moreover, *in situ* measurements at the highest time and spatial resolutions are required to follow precisely real-time degradation. In that respect, a new *in situ* high temperature nanotomography stage has been successfully developed on ID16B beamline [3]. The first results will be described, showing unambiguously the important input of *in situ* investigation on the study of nanoscale dynamics in materials. Finally, the new opportunities offered by the techniques for energy materials and devices such as solar cells and batteries will be shown.

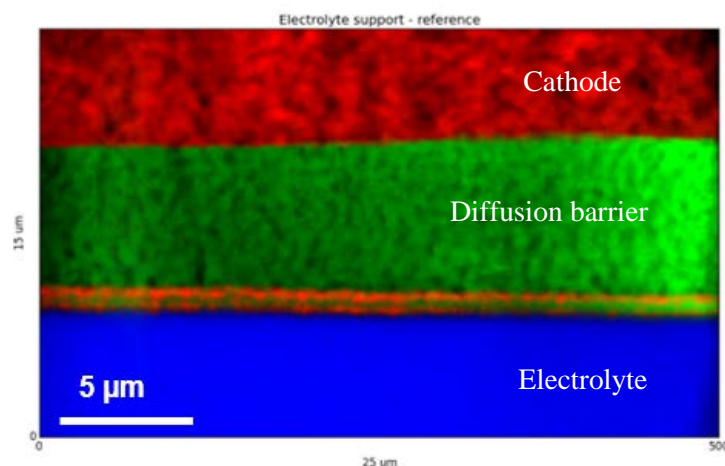


Figure 1: Fluorescence map scanned across SOFC layers (step size: 50nm-dwelltime:100ms). Blue is Zirconia found in the dense electrolyte, green is Cerium found in the diffusion barrier and Red is Strontium found in the cathode layer. It can be seen that at the interface between the electrolyte and the diffusion barrier, thin (~150nm thick) layers of Strontium has been formed by diffusion of the Strontium from the cathode layer despite the diffusion barrier.

[1] G. Martínez-Criado, et al. *J. Synchrotron Radiat.* **23** (2015) 344

[2] J. Villanova et al., *J. Power Sources* **421** (2019) 100

[3] J. Villanova et al., *Materials Today* **20** (2017) 354

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## Dual functional self-regenerative Cr-substituted Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub>

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Brownmillerite-type Ba<sub>2</sub>In<sub>2</sub>O<sub>5</sub> is a well-known high-temperature oxygen ion and proton conductor with mixed ionic-electronic conductivity [1]. This kind of materials are interesting as ceramic membranes in oxygen gas separation [2]. Additionally, the yellow color of the materials suggests a potential application as photocatalyst for the activation of small molecules such as H<sub>2</sub>O and CO<sub>2</sub> [3, 4]. The partial substitution of In<sup>3+</sup> by Cr<sup>3+</sup> altered the crystal structure and changed the optical band gap. The crystal structure changes are of vital importance for membrane applications, while the induced band gap variations are particularly relevant for photocatalysts.

The addition of Cr<sup>3+</sup> resulted in a crystal structure change from *Ibm2* to *I4cm* caused by an enhanced disorder of the oxygen vacancies in the Brownmillerite-type structure. This is clearly recognizable by the increased FWHM of the reflections along the *c*-axis. An increased degree of disorder resulted in a reduced activation energy for the oxygen transport *via* oxygen vacancies. However, more than 10 % Cr substitution for In caused a shrinkage of the unit cell resulting in a reduced self-diffusion coefficient of the oxide ions. As a consequence, Ba<sub>2</sub>In<sub>1.8</sub>Cr<sub>0.2</sub>O<sub>5</sub> exhibited the highest oxygen permeability with  $P(\text{O}_2) = 1.4 \text{ mL} \cdot \text{cm}^{-1} \cdot \text{min}^{-1} \cdot \text{mm}$  at  $T = 1223 \text{ K}$  (Fig. 1) by a careful adjustment of both: degree of disorder of oxygen vacancies and unit-cell volume [2]. Thermochemical studies also showed the application potential as oxygen gas separation membrane in a CO<sub>2</sub>-fueled plasma for CO generation [5].

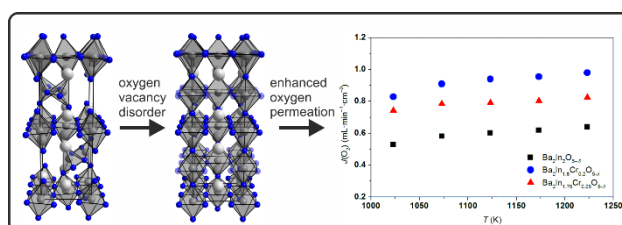


Figure 1: Crystal structure change / oxygen vacancy disorder (left) and oxygen permeability (right) [2].

Furthermore, increasing Cr<sup>3+</sup> substitution reduced the optical band gap and improved the photocatalytic conversion of CO<sub>2</sub> in presence of H<sub>2</sub>. The nominal composition Ba<sub>2</sub>In<sub>1.4</sub>Cr<sub>0.6</sub>O<sub>5</sub> revealed a compatible photoactivity with that of P-25 (TiO<sub>2</sub>) (Fig. 2), even though its BET surface area is smaller by a factor of 250 [4]. However, the materials are readily deactivated due to surface reconstruction mainly caused by an altered surface structure during the photocatalytic tests. Combined *in operando* XANES/DRIFTS/MS studies will provide insights into the reaction mechanism of CO<sub>2</sub> conversion and deactivation mechanisms that have not been fully understood due to limited technical capabilities of the beam lines before the EBS upgrade.

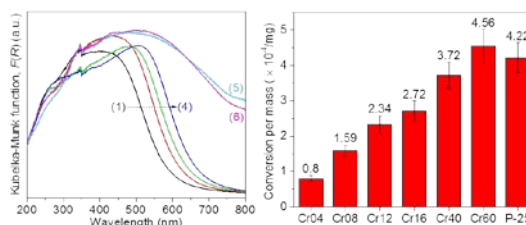


Figure 2: Optical band gaps of Ba<sub>2</sub>In<sub>2-x</sub>Cr<sub>x</sub>O<sub>5</sub> (left;  $x = 0.04$  (1),  $0.08$  (2),  $0.12$  (3),  $0.16$  (4),  $0.4$  (5),  $0.6$  (6)) and photocatalytic CO<sub>2</sub> conversion compared with P-25 as reference material (right) [4].

[1] J. Goodenough et al., *Solid State Ionics* **52** (1992), 105.

[2] M. Widenmeyer et al., *J. Mem. Sci.* (2019) submitted.

[3] S. Yoon et al., *Solid State Sci.* **73** (2017), 1.

[4] S. Yoon et al., *Solid State Sci.* **78** (2018), 22.

[5] M. Widenmeyer et al., *Thermochim. Acta* (2019) submitted.

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## The Materials Science Beamline ID11

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The Materials Science beamline, ID11 at the ESRF, is dedicated to high-energy X-ray diffraction and imaging applications [1]. Over the years, ID11 has been used for a wide range of materials science research with applications to energy materials. These include in-situ measurements on various battery and fuel cell materials, as well as fundamental research to determine structures of new compounds.

Three different end stations are available to adapt to different sizes of sample and sample environment. In the EH1 hutch, a heavy duty Huber stage can host experiments up to ~150 kg in weight and has space for large sample to detector distances. The 3DXRD station is located at 96 m from the source and offers beam sizes from ~2x1 mm down to ~2x1 microns. This station can be used for tomography as well as diffraction and is well adapted for imaging based diffraction contrast (DCT) and topo-tomography experiments.

A “nanoscope” end station has been commissioned in order to exploit very small X-ray beams that can be focussed down to ~100 nm in size. This instrument has extremely good mechanical performance (~40 nm run out) and can be used for determining structures from extremely small crystallites as well as using scanning methods to map out microstructures.

All three of the end stations at ID11 will see the full benefit of the EBS upgrade with an increase of the flux on sample in the range 10-40 X. This will be complemented by a new detector (Eiger4M CdTe) which is planned for use with the 3DXRD and nanoscope stations. These beam and detector upgrades will allow us to use DCT and XRDCT methods to follow systems as they evolve during in-situ experiments.

[1] Vaughan, G.B.M., Wright, J.P., Bytchkov, A., Curfs, C., Grundlach, C., Orlova, M., Erra, L., Gleyzolle, H., Buslaps, T., Götz, A. and Suchet, G., 2010. Challenges in Materials Science and Possibilities in 3D and 4D Characterization Techniques: *Proceedings of the 31st Risø International Symposium on Materials Science*. Roskilde: Riso National Laboratory for Sustainable Energy, Technical University of Denmark, pp.457-476.

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## Why Metal-Organic Frameworks can be considered as promising solids for mechanical energy storage?

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Before the last decade mesoporous silica and zeolites were considered as the most promising porous solids for mechanical energy storage applications [1]. Since the last 5 years the mechanical behaviour properties of several families of flexible MOFs have been intensively investigated by coupling experimental (compression assisted by mercury porosimetry, in-situ powder X-ray diffraction,...) and computational (force field and quantum-based) approaches. This systematic exploration emphasizes the possibility to design flexible porous solids with a pressure-induced structural transition between its initial structure towards a more contracted pore form associated with tunable mechanical energy works, some of them [2-5] exceeding the performance of standard porous materials reported so far for such application [1, 6].

Amongst the MOFs considered so far, owing to a pressure-induced contraction we have evidenced three types of pressure-induced structural contraction behaviours: irreversible, reversible with or without hysteresis loop. These behaviours are associated with the following potential applications: nano-shock absorber, nano-damper and nano-spring respectively. In addition we have evidenced either crystalline/crystalline or crystalline/amorphous structural transition.

The family of the isorecticular MIL-53, MIL-47 (MIL stands for Materials of Institut Lavoisier) and Basolite A520 have been shown to be very promising materials to store energy mechanically. [1-9] showing crystalline/crystalline pressure-induced contraction between a large pore form (orthorhombic or monoclinic system  $V_{LP}$ : 1200-1500 Å<sup>3</sup>) and a contracted pore form (monoclinic system,  $V_{CP}$ : 800-900 Å<sup>3</sup>), We demonstrated that varying the nature of the metal centre: Al, Cr, Ga and V and of the organic linkers; benzene dicarboxylate (BDC, grafted or not) [2], thiophene dicarboxylate (TDC) [3] or fumarate (FA) [4] allows a tuning of the volume change ( $\Delta V/V_0 \sim 25-40\%$ ) and the pressure of transition ( $15 < P < 280$  MPa) associated with this structural transition leading to a range of work energy ( $W = P \times \Delta V$ ) stored during a cycle of compression/decompression  $7 < W < 100$  J.g<sup>-1</sup> [2-4]. More recently the mechanical behaviour of DUT-48/49 (DUT: Dresden University of Technology) and a series of isorecticular microporous MOFs have been investigated. The DUTs appear as promising nano-shock absorbers showing an amorphization of their structures during the pressure induced contraction with the following characteristics:  $35 < P < 65$  MPa,  $64 < \Delta V/V_0 < 72\%$  and  $85 < W < 106$  J.g<sup>-1</sup> [5]. The other series of flexible MOFs present a fully reversible contraction of the structure at a highest pressure ever observed  $\sim 380$  MPa ( $\Delta V/V_0 \sim 20\%$ ) giving a work energy about 60 J.g<sup>-1</sup>.

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