

Supercharging the clean energy transition:
How can LEAPS facilities collaborate in battery
research?

Book
of
Abstracts

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1 Towards multi-dimensional operando spectroscopy for battery materials at BESSY II

Philipp Hönicke, HZB

Keywords: *Operando spectroscopy, X-ray absorption spectroscopy, electrochemical impedance spectroscopy, X-ray emission spectroscopy*

In the framework of various projects, we work on the establishment and characterization of measurement protocols for operando X-ray absorption (XAS), X-ray emission (XES) and electrochemical impedance spectroscopy (EIS) of cycling battery cells. X-ray absorption and emission spectroscopy are widely applied experimental techniques to gain insights into the chemical species present within the sample and can also be applied for quantitative operando battery characterizations [1,2]. Electrochemical Impedance Spectroscopy (EIS) is a widely applied technique in energy storage research [3]. It allows to gain valuable insights into electrochemical processes. By combining EIS and quantitative XAS/XES measurements and by performing both during charging/discharging conditions, one can reveal structure performance relationships with unprecedented detail and in a traceable manner.

In addition, a dedicated beamline for such multi-dimensional operando studies for battery materials is being planned in the framework of the BESSY II+ project. The SoTeXS (Soft-to-Tender X-Ray Spectroscopy) beamline will utilize a Cryogenic Permanent Magnet Undulator to provide a high photon flux in the targeted soft-to-tender photon energy regime between 500 eV and 5000 eV. This energy range will be ideally suited to investigate almost all elements relevant for battery applications and their evolution during cycling. The SoTeXS beamline will be designed for metrological investigations together with the Physikalisch-Technische Bundesanstalt, making it highly attractive for industrial research. It completes the battery portfolio to facilitate IR spectroscopy, X-ray emission and absorption (UPS, XPS, HAXPES, NEXAFS, EXAFS), Resonant Inelastic Scattering (RIXS), small and wide angle scattering (SAXS, ASAXS, WAXS), imaging and tomography.

References:

- [1] C. Zech, P. Hönicke, Y. Kayser, S. Risse, O. Grätz, M. Stamm and B. Beckhoff, *J. Mater. Chem.A* **9**, 10231 (2021)
- [2] C. Zech, M. Evertz, M. Börner, Y. Kayser, P. Hönicke, M. Winter, S. Nowak and B. Beckhoff, *J. Anal. At. Spectrom.* **36**, 2056 (2021)
- [3] A.Ch. Lazanas and M.I. Prodromidis, *ACS Meas. Sci. Au* **3(3)**, 162 (2023)

2 Traceable operando battery characterization using calibrated x-ray spectrometric instrumentation – quantitative analysis of the polysulfide driven degradation in lithium-sulfur batteries during cycling

Burkhard Beckhoff, PTB

Keywords: *Operando spectroscopy, X-ray absorption spectroscopy, electrochemical impedance spectroscopy, X-ray emission spectroscopy*

Characterization methods, traceable to the SI units, allow for the accurate correlation of the functionality of nano- or energy materials with the underlying chemical, structural or physical material properties. These correlations are required for the directed development of such materials to reach target functionalities such as specific capacities. The traceability of analytical methods revealing information on chemical material properties often relies on reference materials or qualified calibration samples, the spatial elemental distributions of which must be very similar to the material of interest. At the nanoscale, however, there exist only few well-known reference materials. An alternate route to establish traceability lays in the physical calibration of the analytical instrument's response behavior and efficiency in conjunction with a good knowledge of the various interaction probabilities and cross sections. This approach has been established by Germany's metrology institute PTB. For the elemental analysis, speciation, and coordination of nano- or energy materials the physical traceability can be achieved. This requires the radiometric calibration of energy- and wavelength-dispersive x-ray spectrometers as well as the reliable determination of atomic x-ray fundamental parameters using calibrated instrumentation. In different operational configurations the information depths, discrimination capability and sensitivity of x-ray spectrometry can be considerably. Time-resolved and hybrid approaches provide access to analytical information on different kind of batteries (Na, LiS, NMC) under operando conditions.

The improved understanding of degradation mechanisms is essential to developing next generation batteries. The provision of operando characterization techniques on realistic batteries is essential for an advanced mechanistic understanding in battery chemistry and, therefore, can contribute to their further performance improvement. Quantitative operando Near-Edge X-ray Absorption Spectroscopy (NEXAFS) has been employed during multiple charge–discharge cycles on both electrodes of lithium–sulfur (Li/S) coin cells. This enables the absolute quantification of dissolved polysulfides (PS) with no need for any calibration samples or reference materials with respect to both the local polysulfides concentration and average chain length. These investigations revealed during the charging process that the PS movement from the negative to the positive electrode is inhibited. This leads to a steady increase of dissolved PS at the anode side and, therefore, is one of the main reasons for capacity fading. Quantitative NEXAFS could track the polysulfides dissolved in the electrolyte and correlate for the first time their evolution

with the capacity fading of the cell. The appearance of PS during cell operation at the cathode and anode side was analyzed to characterize the transport mechanisms of the PS shuttle phenomena and to reveal quantitative information about their evolution at different states of charge and states of health.

The above operando analytical techniques and procedures have been transferred to the operando characterization of other materials such as NMC batteries suffering from SEI modification due to transition metal dissolution.

References:

- [1] B. Beckhoff et al., Anal. Chem. 79 (2007) 7873
- [2] B. Pollakowski et al., Anal. Chem. 85 (2013) 193
- [3] P. Hönicke et al., Phys. Rev. Lett. 113 (2014) 163001
- [4] T. Fischer et al., Anal. Chem. 87 (2015) 2685
- [5] B. Pollakowski, B. Beckhoff, Anal. Chem. 87 (2015) 7705
- [6] P.M. Dietrich et al., Anal. Chem. 87 (2015) 10117
- [7] V. Soltwisch et al., Nanoscale 10 (2018) 6177
- [8] P. Hönicke et al., J. Vac. Sci. Technol. A 37 (2019) 041502
- [9] R. Unterumsberger et al., J. Anal. At. Spectrom. 35 (2020) 1022
- [10] A. Wählich et al., J. Anal. At. Spectrom. 35 (2020) 1664
- [11] P. Hönicke et al., Nanotechnology 31 (2020) 505709
- [12] P. Hönicke et al., Spectrochim. Acta, Part B 174 (2020) 106009
- [13] M. Wansleben et al., J. Anal. At. Spectrom. 35 (2020) 2679
- [14] C. Zech et al., J. Mater. Chem. A, 9 (2021) 10231
- [15] C. Zech et al., J. Anal. At. Spectrom. 36 (2021) 2056
- [16] I. Holfelder et al., Rev. Sci. Instrum. 92 (2021) 123105.
- [17] P. Hönicke et al., Small 18 (2022) 2105776
- [18] B. Beckhoff, Nanomaterials 12 (2022), 2255
- [19] A. Wählich et al., Small 19 (2023) 2204943
- [20] European Partnership on Metrology, "Operando metrology for energy storage materials" project 21 GRD01 , <https://opmetbat.inrim.it/>

3 Advances in operando soft X-ray spectroscopy for battery research

Andrey Shavorskiy, MAX IV

Keywords: XPS, XAS, Operando, Synchrotron

HIPPIE is a high-flux, high-resolution soft x-ray beamline at MAX IV Laboratory (Sweden) with a new dedicated experimental platform for operando studies of electrochemical interfaces.[1] The demand to access this instrumentation at HIPPIE has been growing rapidly in recent years, which is a trend mirrored at facilities worldwide. These experiments utilize the dip-and-pull method to form a thin liquid meniscus on the surface of the working electrode in a three-electrode cell with a liquid electrolyte solution. Both the liquid film itself and the electrode-electrolyte interface can then be probed using X-ray photoelectron spectroscopy (PES) and X-ray absorption spectroscopy (XAS) whilst maintaining full electrochemical control. Such PES and XAS provide a detailed probe of oxidation state changes, chemical shifts, electronic structure and electrochemical potentials in-situ. This therefore a highly relevant method for understanding the chemistry at interfaces in batteries.

In this talk we will discuss status of spectroelectrochemical XPS/XAS using soft X-rays, including an overview of different approaches to cell design. We will primarily aim to introduce the method to those interested in this genre of advanced operando characterization. Focussing on the dip-and-pull setup at HIPPIE, we will outline the experimental realities and challenges that any potential new user should consider before applying for beamtime to conduct an experiment.

The HIPPIE beamline operates in the 250-2000 eV range, providing access to the L absorption edges of many transition metals and the K edges of most light elements. The dip-and-pull XPS/XAS experiments are realized with an ambient-pressure hemispherical electron analyzer allowing measurements in vapor pressures up to 25 mbar. Electrochemical cells can therefore use aqueous electrolyte solutions as well as many organic solvents, including many of those common in batteries (carbonates etc). An argon/nitrogen atmosphere glove box can be attached to the measurement chamber allowing air sensitive electrodes and electrolyte solutions to be easily studied. This apparatus therefore provides an incredibly flexible platform for operando studies of battery interfaces using soft-X-ray spectroscopy.

References:

[1] S. Zhu et al., HIPPIE: a new platform for ambient-pressure X-ray photoelectron spectroscopy at the MAX IV Laboratory, *Journal of synchrotron radiation*, **28**, 624-636 (2021)

4 Battery research at Diamond Light Source: Current status and opportunities

Sofia Diaz-Moreno and Elizabeth Shotton, DIAMOND

Keywords: *Spectroscopy, diffraction, imaging*

In this presentation we will provide some highlights of battery research which has been carried out at Diamond.

Examples will include:

- Huge demand for expensive lithium-ion batteries has stimulated the search for cheaper and more abundant source materials. Potassium is a promising alternative and red phosphorus has shown strong theoretical application as an anode material; however, it has severe limitations. A team from the University of Oxford studied a new composite of red phosphorus with graphite using Ptychographic XCT on I13's Coherence branchline (I13-1) to demonstrate early good electrochemical performance and effectiveness as a novel anode material.
- Detailed understanding of the structure and underlying processes in lithium-ion batteries and their cathode materials to improve their longevity and performance is a key area of research at Diamond. Although nickel-rich cathode materials are some of the most promising candidates for lithium-ion batteries their degradation mechanisms are still poorly understood. A team from the University of Cambridge worked on Diamond's High Resolution Powder Diffraction beamline (I11) to identify a mechanism responsible for battery fatigue and for producing a lowered accessible state of charge.

In addition, we will present an outlook for future opportunities in battery research that will be enabled by the upgrade of Diamond, planned for late 2027. In particular, we will describe the additional capabilities that the new spectroscopy flagship beamline SWIFT (Spectroscopy WithIn Fast Timescales) will bring.

5 Spatially resolved XPS for operando studies of materials, reactions and devices

Luca Gregoratti, ELETTRA

Keywords: *Near ambient pressure XPS, spectromicroscopy, nanomaterials, surface science, operando*

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). To monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones, for instance, is of crucial importance to shed light on the running processes. However the possibility to investigate chemical reactions with X-ray photoelectron spectro-microscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. Such developments expand the capabilities of SPEM which 30 years ago have been designed to perform exclusively characterizations at ultra-high vacuum regimes. One of the most recent developments is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 0.1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 μm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

Recent developments in PhotoEmission Electron Microscopy (PEEM), a powerful surface technique for dynamic imaging of surface processes, made possible the construction of the first NAP-PEEM enabling pressure gap capabilities also for this technique [2].

An overview of the current performances and of the future challenges of the spectro-microscopy tool will be addressed.

References:

[1] Sezen, H. et al. Spatially Resolved Chemical Characterization with Scanning Photoemission Spectromicroscopy: Towards Near-Ambient-Pressure Experiments *Chem. Cat. Chem.* 7(22), 3665-3673 (2015)

[2] Ning, Y. et al. A near ambient pressure photoemission electron microscope (NAP-PEEM), *Ultramicroscopy*, 200, 105-110, (2019)

6 Development of operando techniques in zero-excess solid-state batteries

Miguel Angel Nino, ALBA

Keywords: *Solid-electrolyte, anode free, zero excess Li, Synchrotron radiation, imaging, operando*

The zero-excess solid-state batteries, where the anode is formed in situ at the interface between the solid-state electrolyte (SE) and the anode current collector, have emerged as a promising new generation of environmentally friendly batteries with high energy density, improved safety, material and cell production cost reduction and recycling simplification, but still solutions for non-uniform anode formation which limits the battery performance must be found. The OPERA project (EU – GA. 101103834) is a consortium of research institutions, synchrotron radiation facilities and technological companies, from complementary research fields such as batteries, surface and material science or multiscale modelling. The consortium propose a strategy to face the current challenges of this technology through the development of novel operando experimental techniques at the ESRF, ALBA and DESY synchrotrons, and at the lab-scale, providing complementary information on multiaxial stress fields, chemical composition, nucleation and growth kinetics, structural defect formation and degradation of well-defined model cells with a resolution down to the atomic scale.

Inside the OPERA project, the PEEM at Circe BL-24 beamline at ALBA synchrotron is developing operando techniques based in a combined electron microscopy (LEEM) and photoemission microscopy (PEEM) to study the in-situ anode nucleation and growth in zero-excess solid state batteries using lithium based and sodium based solid electrolytes. In this talk we will present the scope and possibilities of the OPERA project and then, centering in synchrotron experiments, we will review the capabilities of LEEM and PEEM at ALBA focused on the possibilities and challenges of the development of this technique applied to the solid state batteries field.

7 Standardisation of control, data and metadata provision of in-situ and operando measurements via the Sample Environment Communication Protocol (SECoP)

Klaus Kiefer, HZB

Keywords: *Sample environment, SECoP, control, metadata, operando*

The integration of sample environment (SE) equipment in x-ray and neutron experiments is a complex challenge both in the physical world and in the digital world. This is especially true for setups with in-situ and in operando capabilities. The control of the SE equipment and the data and metadata format have to be adapted to the interfaces of the specific experiment control software. Therefore, it is time-consuming to integrate new SE or to share SE equipment between facilities. And in many cases, data and metadata for in-situ and operando SE equipment are not recorded by the experiment control software and have to be synchronised afterwards.

To tackle this problem, the International Society for Sample Environment (ISSE) [1] developed the Sample Environment Communication Protocol (SECoP) to standardize the communication between experiment control software and SE equipment [2,3].

SECoP offers, on the one hand, a generalized way to control SE equipment. On the other hand, SECoP holds the possibility to transport SE data and metadata in a well-defined way. In addition, SECoP provides machine readable self-description of the SE equipment which enables a fully automated integration into the experiment control and into the processes for data storage. Thus, SECoP supplies a well-defined and simple to use interface for user-provided SE equipment, for equipment shared by different research facilities and for industry.

This presentation will show how SECoP can help to facilitate the control of in-situ and operando measurements as well as the recording of the relevant data and metadata.

References:

[1] <https://sampleenvironment.org>

[2] K. Kiefer, et al. (2020). An introduction to SECoP – the sample environment communication protocol. *Journal of Neutron Research*, 21(3-4), pp.181–195

[3] <https://github.com/sampleenvironment/secop>

8 Full field tomography for battery research at Hereon beamlines at PETRA III

Fabian Wilde, DESY/HEREON

Keywords: *Tomography, Imaging, Beamline*

The Helmholtz-Zentrum Hereon operates two beamlines at the DESY / PETRA III synchrotron facility. Beamline P05 operates at energies between 5-45 keV and is dedicated full-field micro- and nano-imaging [1][2]. The Beamline P07 operates at energies between 30-200 keV and contains a full-field micro-imaging end station very similar to the one at P05 [3]. At both beamlines battery research is conducted, often in close collaboration with the Helmholtz-Zentrum Berlin [4]. Here, we will report on the current capabilities of the beamlines with respect to battery research.

References:

- [1] F. Wilde et al., "Micro-CT at the imaging beamline P05 at PETRA III," in AIP Conference Proceedings, 2016, vol. 1741, p. 030035. doi: 10.1063/1.4952858.
- [2] I. Greving et al., "Nanotomography endstation at the P05 beamline: Status and perspectives," J. Phys.: Conf. Ser., vol. 849, p. 012056, Jun. 2017, doi: 10.1088/1742-6596/849/1/012056.
- [3] F. Beckmann, J. U. Hammel, J. Moosmann, L. Lottermoser, G. F. Gunnell, and J. Habersetzer, "Optimization of high-energy microtomography using synchrotron radiation at PETRA III," in Developments in X-Ray Tomography XII, Oct. 2019. doi: 10.1117/12.2530001.
- [4] F. Sun et al., "Advancing knowledge of electrochemically generated lithium microstructure and performance decay of lithium ion battery by synchrotron X-ray tomography," Materials Today, Dec. 2018, doi: 10.1016/j.mattod.2018.11.003.

9 Soft X-ray Scanning Transmission Microscopy at MAX IV

Igor Beinik, MAX IV

Keywords: *STXM, batteries, NEXAFS, microscopy, spectroscopy*

The SoftiMAX beamline and its Scanning Transmission X-Ray Microscopy (STXM) end-station, commissioned in 2020, now offer a range of STXM-based measurement techniques for users in various fields, including catalysis and battery materials research. With the ability to achieve high spatial resolution, typically down to 20-30 nm in size, STXM enables detailed observation and analysis of thin samples at the meso- or nanoscale. For higher resolution needs, the available 2D detectors allow for ptychography measurements [1], capable of resolving features below 10 nm, this technique is suitable for samples that may tolerate higher beam exposures, e.g. magnetic thin films, or other inorganic thin film materials. Operating in the soft X-ray range (275-2500 eV), the measurements can be performed on samples from 0.1 to 5 μm thick, with the optimal thickness dependent on the photon energy and sample composition.

As a spectro-microscopy technique, STXM offers exceptional chemical sensitivity. It enhances the capabilities of Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy towards imaging by allowing for the acquisition of local absorption spectra through energy-dependent image stacks, which provide detailed spatially resolved chemical information. In catalytic and battery materials this is crucial for distinguishing various chemical states and elements down to the nanometer scale and following chemical changes during battery charge and discharge cycles, gas exposure, or electrochemical reactions. The information can be extracted normally via relatively straightforward image stack data processing. Importantly, STXM is generally considered to be non-destructive, making it an ideal tool for examining delicate battery materials, whilst also offering a possibility for in-situ studies. Previously, its use has been demonstrated for studying e.g. intercalation pathways of lithium iron phosphate (LFP) in the positive electrode of a lithium-ion battery, and current and state-of-charge induced transitions in the LiFePO_4 particles [2, 3]. Even in dynamic processes, like ion movement within batteries during operation [4], STXM can provide insights into battery degradation and potential improvements in battery performance, and has been applied to track the reaction dynamics of an electrode material, LiFePO_4 , by measuring the relative concentrations of Fe(II) and Fe(III) ions [5].

In this presentation, the capabilities of the SoftiMAX STXM will be demonstrated, with an emphasis on its utilization in battery materials research. Our instrument was built in-house and its design, which has undergone some modifications and adaptations at MAX IV, follows earlier conceptual designs with an interferometric sample positioning control scheme [6, 7]. Its characteristics as well as details regarding the in situ set up will be shown, which may be of particular interest to the battery research community. Information about the sample preparation

and data analysis routines will also be provided, along with the first results on the Zn/MnOx battery system from the Hitchcock group.

References:

- [1] Shapiro, D., Yu, YS., Tyliszczak, T. et al. Chemical composition mapping with nanometre resolution by soft X-ray microscopy. *Nature Photon* 8, 765–769 (2014)
- [2] William C. Chueh, et al. Intercalation Pathway in Many-Particle LiFePO₄ Electrode Revealed by Nanoscale State-of-Charge Mapping. *Nano Letters* 2013 13 (3), 866-872.
- [3] Li, Y., El Gabaly, F., Ferguson, T. et al. Current-induced transition from particle-by-particle to concurrent intercalation in phase-separating battery electrodes. *Nature Mater* 13, 1149–1156 (2014).
- [4] Ohmer, N., Fenk, B., Samuelis, D. et al. Phase evolution in single-crystalline LiFePO₄ followed by in situ scanning X-ray microscopy of a micrometre-sized battery. *Nat Commun* 6, 6045 (2015).
- [5] Lim, J., Li, Y., et al. Origin and hysteresis of lithium compositional spatiodynamics within battery primary particles. *Science*, 353(6299), 566-571 (2016).
- [6] Kilcoyne, A. L. D. et al., *J. Synchrotron Rad.* 10, 125-136 (2003).
- [7] J. Schwenke et al., *Microsc. Microanal.* 24, 2, 232-233, (2018).

10 TOMCAT 2.0: multiscale, multimodal dynamic tomographic microscopy

Federica Marone, PSI

Keywords: *Tomographic microscopy, time resolved, multimodal, multiscale, operando*

Before the Swiss Light Source at the Paul Scherrer Institute went into the dark-time for the SLS 2.0 upgrade project, the TOMCAT beamline has been providing during more than a decade cutting-edge multiscale, multimodal dynamic tomographic microscopy to a heterogeneous international scientific community including the energy field and battery research specifically.

To maintain and strengthen our role in this field as well as fully profit from the new diffraction limited storage ring, we are currently also undergoing a beamline upgrade project (TOMCAT 2.0) featuring a significant refurbishment of the current instrument (S-TOMCAT), which will include a new high-field superconducting bending magnet and a brand-new beamline (I-TOMCAT) based on an insertion device of latest generation.

Starting in summer 2025, TOMCAT 2.0 will offer to the wide academic and industrial community improved dynamical, high-throughput multidimensional and multimodal imaging capabilities, with a broad range of spatial resolutions (from 100 nm up to 10 μm) and energies (from 8 up to 50-80 keV). TOMCAT 2.0 on SLS 2.0 will profit from a smaller source size and a higher photon flux at most energies, leading to a general enhancement of image quality. The generalized increase in photon flux, depending on the energies also up to a factor 1000, will enable to simultaneously profit from both higher spatial and temporal resolutions, pushing different flavours (in-situ, operando, in-vivo and in-fieri) of dynamic tomographic imaging towards unexplored frontiers. High throughput capabilities without compromises on image quality or spatial resolution, for the (semi-) automatic analysis of hundreds of specimens will also become available. Photon hungry chemistry revealing techniques like fluorescence imaging are currently mostly limited to the 2D (radiographies or in the best case selected tomographic slices) case. The increased photon flux coupled to improved X-ray hyperspectral interpolating detectors will pave the way to rapid 3D chemical imaging, which might routinely complement the sample microstructure with spectroscopic information.

In this contribution, we will present the capabilities of the upgraded and new TOMCAT 2.0 instruments focusing in particular on the features most relevant for the battery community. A general increase in flux, but also specifically at higher energies, can be very beneficially for different aspects of energy research. Higher flux at higher energies will widen the static and dynamic investigation possibilities to denser materials as well as of larger and more realistic commercial systems (e.g. containing stainless steel and transition oxide metals), in a multi-scale zoom-in and in-line fashion, down to the sub-micrometer range in larger samples. At the same time, higher energies also mean smaller interaction of the X-ray probe with the samples and

therefore less invasive analyses, with reduced radiation damage and systems closer to their native state. A high photon flux over an extended spectrum of energies could give access to (operando) 3D comprehensive chemical characterization covering a broader range of elements than possible so far.

11 Research opportunities for battery characterization at EuXFEL

Ulrike Boesenberg, EUXFEL

Keywords: *X-rays, FEL, Instrumentation*

The European X-ray Free-Electron Laser facility (EuXFEL) offers unique possibilities for materials characterization using X-ray radiation [1]. With its high repetition rate of up to 4.5MHz, the ultrashort pulses of less than 50fs and typical sets of pump probe environments it enables unique experiments to probe the ultrafast time scales. In addition, a wide range of X-ray wavelengths are available at dedicated instruments to probe different types of dynamics and processes. This contribution will provide a brief overview of currently available instruments at EuXFEL highlighting the opportunities most suitable for battery investigations. Instrumentation and X-ray parameters at EuXFEL enable experiments to probe fundamental processes on the ultrafast timescale in battery materials. Most experiments at the Materials Imaging and Dynamics (MID) instrument make use of the exceptional coherence properties of the XFEL beam in the photon energy range of 6 to 25keV [2]. Typical experiment techniques include holography, (Bragg-) Coherent diffraction Imaging (CDI) and X-ray scattering investigating the dynamics via XPCS as well as ultrafast diffraction. Optical and electrical pumps are available and a flexible environment allows for the samples to be measured under a variety of conditions. For the SA2 beamline where both the MID and the High Energy Density (HED) instrument [3] are located, an increase in available photon energies above 25keV is foreseen for the future which enables time resolved pair distribution function (PDF) measurements. Application of this technique to EuXFEL and preparation work for this is in progress [4]. Femtosecond X-ray experiments (FXE) instrument has a focus on time resolved spectroscopy (XES, XANES, EXAFS or RIXS) and diffraction (XRD, XDS, WAXS) in the photon energy range of 4.9-20keV, making the transition metal K-edges available [5]. It offers an ultrafast, tunable laser, allowing excitation wavelengths from the UV to the IR to be used as a primary trigger for the reactions.

The Single Particles, Clusters, and Biomolecules & Serial Femtosecond Crystallography (SPB/SFX) instrument of the European XFEL is primarily concerned with three-dimensional diffractive imaging, and three-dimensional structure determination, of micrometer-scale and smaller objects, at atomic or near-atomic resolution with a particular emphasis on biomolecules [6].

The beamline also allows MHz X-ray Microscopy experiments to resolve fast dynamics at micrometer scale [7], and is developing a set-up to record 3D movies at MHz rate. In addition, EuXFEL operates 3 instruments in the soft X-ray regime (with a photon energy below 2keV) offering a suite of spectroscopy (XAS, XES, RIXS) techniques and as well as imaging [7–10]. The low photon energy enable access the i.e. to the O k-edge for spectroscopy as well as the

Ledges of transition metals (Mn, Co, Fe, Ni, Cu). The low photon energies are prone to probe surfaces and interfaces and imaging experiments make use of the exceptional degree of coherence in the XFEL beam.

References:

- [1] Tschentscher, T. *et al.* Photon Beam Transport and Scientific Instruments at the European XFEL. *Appl. Sci.* **7**, 592 (2017).
- [2] Madsen, A. *et al.* Materials Imaging and Dynamics (MID) instrument at the European X-ray Free-Electron Laser Facility. *J. Synchrotron Radiat.* **28**, 637–649 (2021).
- [3] Zastra, U. *et al.* The High Energy Density Scientific Instrument at the European XFEL. *J. Synchrotron Radiat.* **28**, 1393–1416 (2021).
- [4] Casalbuoni, S. *et al.* Superconducting undulator activities at the European X-ray Free-Electron Laser Facility. *Front. Phys.* **11**, (2023).
- [5] Galler, A. *et al.* Scientific instrument Femtosecond X-ray Experiments (FXE): instrumentation and baseline experimental capabilities. *J. Synchrotron Radiat.* **26**, 1432–1447 (2019).
- [6] Mancuso, A. P. *et al.* The Single Particles, Clusters and Biomolecules and Serial Femtosecond Crystallography instrument of the European XFEL: initial installation. *J. Synchrotron Radiat.* **26**, 660–676 (2019).
- [7] Vagovič, P. *et al.* Megahertz x-ray microscopy at x-ray free-electron laser and synchrotron sources. *Optica* **6**, 1106–1109 (2019).
- [8] Gerasimova, N. *et al.* The soft X-ray monochromator at the SASE3 beamline of the European XFEL: from design to operation. *J. Synchrotron Radiat.* **29**, 1299–1308 (2022).
- [9] Grychtol, P. *et al.* The SXP instrument at the European XFEL. *J. Phys. Conf. Ser.* **2380**, 012043 (2022).
- [10] Mazza, T. *et al.* The beam transport system for the Small Quantum Systems instrument at the European XFEL: optical layout and first commissioning results. *J. Synchrotron Radiat.* **30**, 457–467 (2023).
- [11] Zhou Hagström, N. *et al.* Megahertz-rate ultrafast X-ray scattering and holographic imaging at the European XFEL. *J. Synchrotron Radiat.* **29**, 1454–1464 (2022).

Applied Research Talks

12 UltraBat: Capturing ultrafast electron and ion dynamics in batteries

Christopher Milne, EUXFEL

Keywords: *Battery dynamics, polarons, charge injection*

Batteries are attractive candidates for lightweight, high capacity, mobile energy storage solutions¹. Despite decades of research, a persistent fundamental knowledge gap prevents batteries from fulfilling their potential, because the atomistic mechanisms of charge and ion transfer across interfaces in batteries remain largely unexplored by experimental techniques. When charges move, the local arrangement of atoms changes in response to the new electronic configuration. How these changes occur has a significant impact on how efficiently and how far the charges can move, yet the time and length scales are still poorly understood. Conventional experimental probes used in battery research cannot provide the needed ultrafast time and atomic length scale resolution, nor sensitivity to changes in electronic configuration around specific atomic species. Hence, it is currently challenging to unravel the dynamic rearrangement of atoms and ions which accompany electron transfer, and in turn govern the charge transfer processes².

UltraBat (<https://ultrabat.dtu.dk>) has the goal of closing this knowledge gap by pushing further the latest development of ultra-bright and ultra-fast X-ray Free Electron Laser (XFEL) scattering³ and spectroscopy⁴ techniques together with visible and Raman ultrafast spectroscopy^{5,6} to study charge transfer between different redox centres in Li-rich layered intercalation compounds and at the solid/liquid interface. Advances in NMR spectroscopy will reveal local ordering and lithium interfacial dynamics on the nanometer scale. Coupled with predictions of experimental observables from a new framework for atomic-scale simulations^{7,8,9,10} of the electrochemical interface and transport mechanisms, we will probe phenomena driving diffusion of ions in complex electrode materials. This will provide the insight required for transformational approaches to control the redox reactions (e.g. electron transfer) that are common to many energy-related processes, including batteries, photovoltaics, and water-splitting systems.

References:

1. Tarascon, J.-M. Material science as a cornerstone driving battery research. *Nat. Mater.* **21**, 979–982 (2022). [doi: 10.1038/s41563-022-01342-x](https://doi.org/10.1038/s41563-022-01342-x)
2. Li, B. *et al.* Correlating ligand-to-metal charge transfer with voltage hysteresis in a Li-rich rock-salt compound exhibiting anionic redox. *Nat. Chem.* **13**, 1070–1080 (2021). [doi: 10.1038/s41557-021-00775-2](https://doi.org/10.1038/s41557-021-00775-2)

3. Kurta, R. P. *et al.* Exploring fingerprints of ultrafast structural dynamics in molecular solutions with an X-ray laser. *Phys. Chem. Chem. Phys.* (2023) doi:10.1039/d3cp01257c.
4. Milne, C. J. *et al.* Disentangling the evolution of electrons and holes in photoexcited ZnO nanoparticles. *Struct. Dyn.* **10**, 064501 (2023). doi: 10.1063/4.0000204
5. Pandya, R., Mathieson, A., Boruah, B. D., Aguiar, H. B. de & Volder, M. de. Interrogating the Light-Induced Charging Mechanism in Li-Ion Batteries Using Operando Optical Microscopy. *Nano Lett.* **23**, 7288–7296 (2023). doi: 10.1021/acs.nanolett.3c01148
6. Pandya, R. *et al.* Three-dimensional operando optical imaging of particle and electrolyte heterogeneities inside Li-ion batteries. *Nat. Nanotechnol.* **18**, 1185–1194 (2023). doi: 10.1038/s41565-023-01466-4
7. Tygesen, A. S., Chang, J. H. & García-Lastra, J. M. Dependence of polaron migration barriers on the fraction of Fock exchange in hybrid functionals: A systematic study of Vk centers in alkali halides. *Phys. Rev. B* **108**, 045120 (2023). 10.1103/physrevb.108.045120
8. Schaarschmidt, J. *et al.* Workflow Engineering in Materials Design within the BATTERY 2030+ Project. *Adv. Energy Mater.* **12**, (2022). 10.1002/aenm.202102638
9. Blasio, P. V. F. de, Jorgensen, P. B., Lastra, J. M. G. & Bhowmik, A. Nanosecond MD of battery cathode materials with electron density description. *Energy Storage Mater.* **63**, 103023 (2023). 10.1016/j.ensm.2023.103023
10. Bülle, F. T., Bhowmik, A., Vegge, T., Lastra, J. M. G. & Castelli, I. E. Automatic Migration Path Exploration for Multivalent Battery Cathodes using Geometrical Descriptors. *Batter. Supercaps* **4**, 1516–1524 (2021). 10.1002/batt.202100086

13 Exploring Li-ion Battery Safety Using Synchrotron High-Speed X-ray Imaging

Matilda Fransson, ESRF

Keywords: *Li-ion Battery Technology, Safety, Thermal Runaway, High-Speed X-ray Imaging, Synchrotron*

Understanding the engineering challenges associated with Li-ion batteries is of great relevance in the process of electrifying the transportation sector ¹ and enabling green energy storage in power-grid installations ². For efficient storage within these applications, energy-dense, high-capacity batteries are required for increased charge capacity³ and for simultaneous high-power output ⁴. Over the past years, impressive advances in Li-ion battery technology have been accomplished, however, one of the crucial challenges remaining is their explosive-like failures, referred to as thermal runaways (TR), that must be mitigated to avoid detrimental damages⁵. This matter is of particular importance since it is not expected to diminish; instead, it is likely to escalate with the increase in Li-ion battery capacity.

In order to ensure a safe battery market and aid in the development of battery TR mitigation mechanisms, battery safety tests of various kinds are employed. Here we incorporate simultaneous synchrotron high-speed X-ray imaging with battery safety testing for improved TR understanding ⁸. The employment of synchrotron high-speed radiography or fast tomography allows us to visualize the internal TR mechanisms and their coupled events. Spatiotemporal mapping and speed retrieval of the electrode layer delamination have been achieved through the application of Gabor filtering followed by image cross-correlation⁹. Further, we have studied TR propagation between electrically connected cells, sidewall breaches and ruptures ¹⁰, accessed information about the heat flux throughout the battery during TR, but also performed in-situ evaluation of implemented safety devices and systems ¹¹. This research emphasizes important information about TR and battery failure that can aid battery designers and manufacturers in improving battery safety.

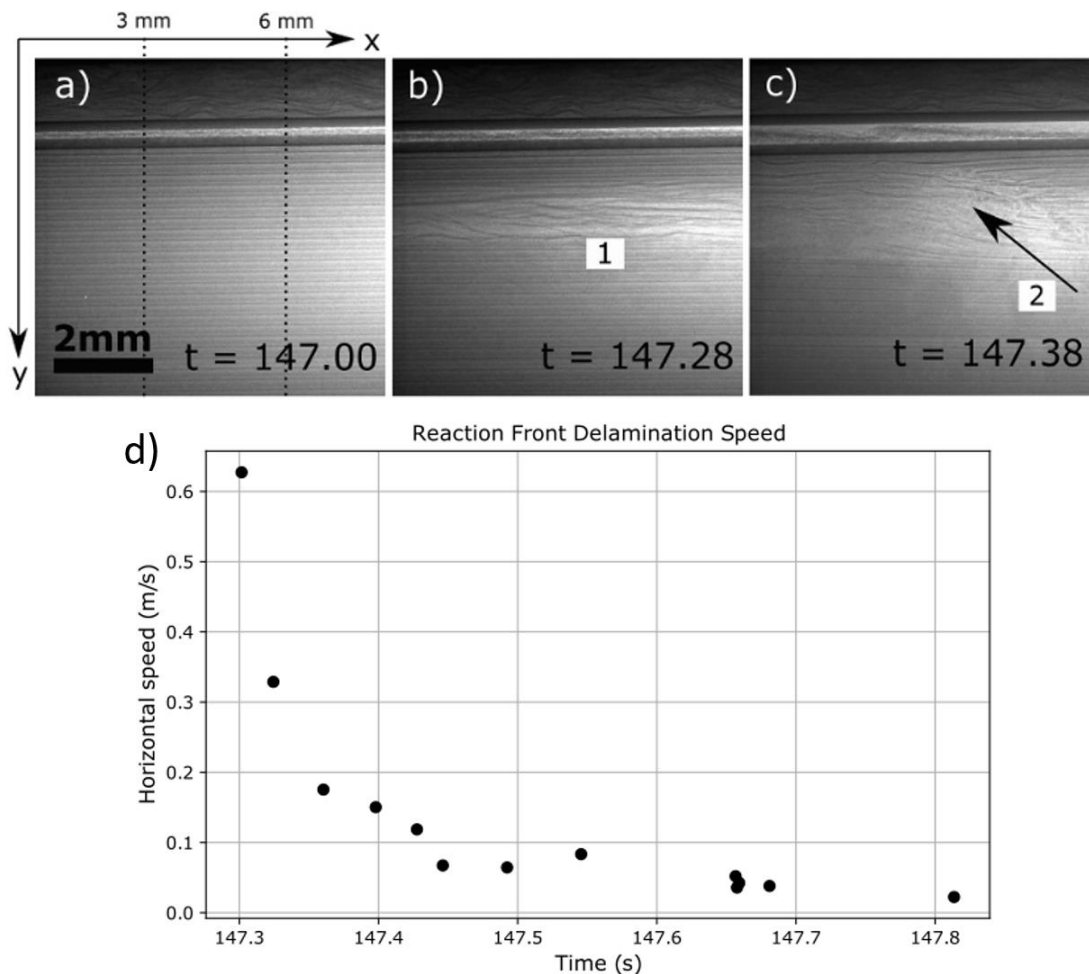


Figure 1: Radiography images during TR in a Li-ion cell initiated through external heating from TR in the neighboring cell; in the initial state in a), the start of electrode layer delamination (1) in b) and the continuation and electrode material displacement (2) in c). Retrieved reaction front speeds of the TR are presented in d), initiating at 0.64 m/s.

References:

1. Tamor, M. A. & Stechel, E. B. Electrification of transportation means a lot more than a lot more electric vehicles. *iScience* **25**, 104376 (2022).
2. Choi, D. *et al.* Li-ion battery technology for grid application. *J. Power Sources* **511**, 230419 (2021).
3. Feng, X., Ren, D., He, X. & Ouyang, M. Mitigating Thermal Runaway of Lithium-Ion Batteries. *Joule* **4**, 743–770 (2020).
4. Kim, J. S., Lee, D. C., Lee, J. J. & Kim, C. W. Optimization for maximum specific energy density of a lithium-ion battery using progressive quadratic response surface method and design of experiments. *Sci. Rep.* **10**, 1–11 (2020).

5. Finegan, D. P. *et al.* In-operando high-speed tomography of lithium-ion batteries during thermal runaway. *Nat. Commun.* **6**, 1–10 (2015).
6. Buckwell, M. *et al.* Failure and hazard characterisation of high-power lithium-ion cells via coupling accelerating rate calorimetry with in-line mass spectrometry, statistical and post-mortem analyses. *J. Energy Storage* **65**, 107069 (2023).
7. Pfaff, J. *et al.* In situ chamber for studying battery failure using high-speed synchrotron radiography. *J. Synchrotron Radiat.* **30**, 192–199 (2023).
8. Radhakrishnan, A. N. P. *et al.* Quantitative spatiotemporal mapping of thermal runaway propagation rates in lithium-ion cells using cross-correlated Gabor filtering. *Energy Environ. Sci.* **15**, 3503–3518 (2022).
9. Fransson, M. *et al.* Sidewall breach during lithium-ion battery thermal runaway triggered by cell-to-cell propagation visualized using high-speed X-ray imaging. *J. Energy Storage* **71**, 108088 (2023).
10. Pham, M. T. M. *et al.* Article Prevention of lithium-ion battery thermal runaway using polymer-substrate current collectors using polymer-substrate current collectors. *Cell Reports Phys. Sci.* **2**, 100360 (2021).

14 Beam effects in synchrotron radiation based operando characterization of battery materials: XRD and XAS study of $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ and LiFePO_4 electrodes

Ashley Black, ICMAB-CSIC

Keywords: *Beam damage, battery materials, x-ray diffraction, X-ray absorption spectroscopy*

Operando synchrotron radiation-based characterization techniques applied to energy storage materials are becoming a widespread characterization tool as they allow for non-destructive probing of materials with various depth sensitivities through spectroscopy, scattering, and imaging techniques. Moreover, they allow for faster acquisition rates, variable penetration depths, higher spectral or spatial resolution, or access to techniques that are only possible with a continuous tuneable source over a wide photon energy range. Compatibility between the electrochemical cell designs and the experimental setups may force some specific design features and care must be taken to ensure that these do not perturb the electrochemical response of the materials under investigation. The use of *operando* techniques has intrinsic advantages, as they enable the detection of metastable intermediates, if any, and ensure characterization under real conditions avoiding the risk of *ex situ* sample evolution during its preparation. However, they do not come with the extent of risks. The interaction between synchrotron radiation and samples, particularly within the intricate milieu of an operational electrochemical cell, can provoke anomalous behaviours in the sample at the measurement site, thereby jeopardizing the experiment's reliability. While beam-induced effects are well-recognized for their critical impact on characterizing biological samples, macromolecules, or soft matter, they have, until recently, received scant attention within the battery research community, being vaguely referenced and incompletely comprehended. This study aims to contribute to this ongoing debate by providing a systematic investigation into the occurrence of these phenomena and conducting a root cause analysis of beam-induced effects during the *operando* characterization of two widely commercialized cathode materials: $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ and LiFePO_4 . This examination spans diverse experimental conditions encompassing various cell types, absorption and scattering techniques. It seeks to correlation beam effects with factors such as radiation energy, photon flux, exposure duration, and other parameters associated with radiation dosage. Moreover, this study aims to offer a set of guidelines aimed at evaluating and mitigating the impact of beam-induced reactivity inhibition in battery *operando* experiments.

15 Understanding Battery Mechanisms through Operando Synchrotron Studies at BESSY II

Sebastian Risse, HZB

Keywords: *Operando battery analysis, silicon anodes, lithium/sulfur battery, imaging, spectroscopy*

This workshop contribution presents a series of operando studies at the synchrotron BESSY II, emphasizing the importance of such research for gaining mechanistic insights into battery systems. The studies are ordered according to the battery system, highlighting lithium-sulfur batteries and silicon electrodes.

Lithium-Sulfur Battery Insights:

- **Polysulfide Dynamics:** A joint work with PTB [1] employing operando Near-Edge X-ray Absorption Spectroscopy (NEXAFS) at the FCM beamline in the PTB lab at BESSY II [2] reveals crucial insights into polysulfide dynamics in lithium-sulfur batteries. The study highlights the restricted movement of polysulfides, impacting capacity fading and offering a deeper understanding of the polysulfide shuttle phenomenon.
- **Sulfur Crystal Evolution:** Another study [3] utilizes high-resolution synchrotron radiography at the BAMline [4] to examine α - and β -sulfur crystals' formation and dissolution. It uncovers the equilibrium between polysulfides and sulfur, with defects potentially reducing cell capacity. This research underscores the significance of visual monitoring in understanding sulfur crystal behavior.

Silicon-Based Electrode Research:

- **Morphological Evolution of Silicon Electrodes:** Another study at the BAMline [4] focuses on the morphological changes of a single-crystal silicon electrode in a lithium-silicon half-cell, observed via phase-contrast radiography.[5] The emergence of a cracking pattern and its implications on electrode stability and efficiency are central findings.
- **SEI on Silicon Anodes:** The final paper [6] presents a novel approach for X-ray Absorption Spectroscopy to study the Solid Electrolyte Interphase (SEI) on silicon anodes. Identifying key SEI constituents and aldehyde species, this study at the U49-2_PGM-1 beamline [7] contributes significantly to understanding SEI's role in battery performance.

These studies collectively highlight that operando synchrotron research is pivotal for a deep mechanistic understanding of battery systems. They also underscore the importance of sample

environment and cell design as critical factors for successful beamtime at synchrotrons, paving the way for future advancements in battery technology.

References:

- [1] Zech, C., Hönicke, P., Kayser, Y., Risse, S., Grätz, O., Stamm, M., & Beckhoff, B. (2021). Polysulfide driven degradation in lithium–sulfur batteries during cycling – quantitative and high time-resolution operando X-ray absorption study for dissolved polysulfides probed at both electrode sides. In *Journal of Materials Chemistry A* (Vol. 9, Issue 16, pp. 10231–10239). Royal Society of Chemistry (RSC). <https://doi.org/10.1039/d0ta12011a>
- [2] Krumrey, M. (1998). Design of a Four-Crystal Monochromator Beamline for Radiometry at BESSY II. In *Journal of Synchrotron Radiation* (Vol. 5, Issue 1, pp. 6–9). International Union of Crystallography (IUCr). <https://doi.org/10.1107/s0909049597011825>
- [3] Risse, S., Juhl, A., Mascotto, S., Arlt, T., Markötter, H., Hilger, A., Manke, I., & Fröba, M. (2020). Detailed and Direct Observation of Sulfur Crystal Evolution During Operando Analysis of a Li–S Cell with Synchrotron Imaging. In *The Journal of Physical Chemistry Letters* (Vol. 11, Issue 14, pp. 5674–5679). American Chemical Society (ACS). <https://doi.org/10.1021/acs.jpcllett.0c01284>
- [4] Markötter, H., Sintschuk, M., Britzke, R., Dayani, S., & Bruno, G. (2022). Upgraded imaging capabilities at the BAMline (BESSY II). In *Journal of Synchrotron Radiation* (Vol. 29, Issue 5, pp. 1292–1298). International Union of Crystallography (IUCr). <https://doi.org/10.1107/s1600577522007342>
- [5] Ronneburg, A., Osenberg, M., Dong, K., Hilger, A., Härk, E., Silvi, L., Manke, I., Ballauff, M., & Risse, S. (2020). Morphological evolution of a single crystal silicon battery electrode during lithiation and delithiation: An operando phase-contrast imaging study. In *Energy Storage Materials* (Vol. 32, pp. 377–385). Elsevier BV. <https://doi.org/10.1016/j.ensm.2020.06.007>
- [6] Schellenberger, M., Golnak, R., Quevedo Garzon, W. G., Risse, S., & Seidel, R. (2022). Accessing the solid electrolyte interphase on silicon anodes for lithium-ion batteries in-situ through transmission soft X-ray absorption spectroscopy. In *Materials Today Advances* (Vol. 14, p. 100215). Elsevier BV. <https://doi.org/10.1016/j.mtadv.2022.100215>
- [7] Kachel, T. (2016). The plane grating monochromator beamline U49-2 PGM-1 at BESSY II. In *Journal of large-scale research facilities JLSRF* (Vol. 2). Forschungszentrum Jülich, Zentralbibliothek. <https://doi.org/10.17815/jlsrf-2-75>

16 Charge state distribution in aged electrodes probed by 2D X-ray fluorescence imaging

Giuliana Aquilanti, ELETTRA

Keywords: *Charge state distribution, Prussian blue-based electrodes, X-ray fluorescence*

Synchrotron based 2D X-ray fluorescence is used to probe the spatial distribution of elements within an aged MnHCF-based electrode. In particular, using an excitation energy of 7200 eV the distribution of manganese and iron is evaluated. However, given the characteristic differences of Mn XANES spectra in the oxidized (Mn^{3+}) and reduced (Mn^{2+}) states and a DE = 5 eV between the edge maximum of Mn^{2+} and Mn^{3+} , an excitation energy can be found to highlight the redox of manganese within the electrode, and *redox selective fluorescence maps* are produced.

It is observed that inhomogeneities in charge state distribution is present especially in aged electrodes whose behaviour deviates from the ideal trend and for which the theoretical capacity and Coulombic efficiency have degraded after several electrochemical cycles. Detected charge state inhomogeneities of Mn are also confirmed by XANES analysis.

The rationale behind this work is to detect the difference in the oxidation state of the element throughout the whole surface of the sample directly through two-dimensional X-ray fluorescence by using the tunability of the excitation energy achievable at synchrotron sources.

References:

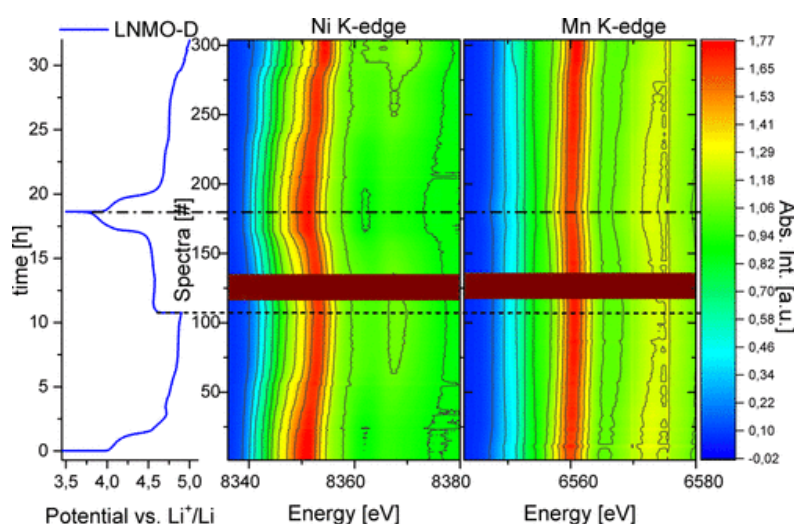
M. Maisuradze, I. Carlomagno, A. Mullaliu, M. Li, G. Aquilanti, M. Giorgetti, J. Phys. Chem. C 2023, 127, 44, 21498–21503

17 Elucidating the Influence of Transition-Metal Order and stoichiometry on the Reaction Mechanism of LNMO Cathode Spinel via a multi technique approach

Marcus Fehse, CICenergiGUNE

Keywords: High voltage cathode, operando XAS, solid state NMR, Lithium ion batteries

High voltage LNMO holds promise for high energy density, Co-free cathode material for Lithium-ion batteries. However, the influence of transition metal ordering on redox mechanism remains elusive. An *operando* dual-edge X-ray absorption spectroscopy on both transition-metal ordered and disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ during electrochemical delithiation and lithiation was carried out. The large data set was analyzed via a chemometric approach to gain reliable insights into the redox activity and the local structural changes of Ni and Mn throughout the electrochemical charge and discharge reaction. Our findings confirm that redox activity relies predominantly on the $\text{Ni}^{2+/4+}$ redox couple involving a transient Ni^{3+} phase. Interestingly, a reversible minority contribution of $\text{Mn}^{3+/4+}$ is also evinced in both LNMO materials. While the reaction steps and involved reactants of both ordered and disordered LNMO materials generally coincide, we highlight differences in terms of reaction dynamics as well as in local structural evolution induced by the TM ordering.



Evolution of operando XANES Ni and Mn K-edge during 1,5 electrochemical cycle vs lithium.

The structural properties of predominantly TM ordered LNMO with slight Ni deficiency were further investigated by applying complementary solid-state Li NMR as well as operando XRD. These techniques reveal that the lithiation reaction mechanism is more complex than the previously proposed simple sequence of two biphasic transitions. Both the local structural Li

NMR and long range XRD confirm the presence of extended solid solution region stretching well into the Ni^{2+/3+} region. Additionally intermediate species were identified which could be beneficial for bridging the miscibility gap, enabling faster phase transition.

References:

Fehse et al. Chem. Mater. 34 (2022) 14, 6529–6540

Asres et al. J. Mater. Chem. A, (2023), recently accepted

18 Oxygen Redox Assisted High-Capacity Sodium Transition Metal Oxides for Sodium-Ion Batteries

Seung-Taek Myung, Sejong University

Keywords: Oxygen; Redox; Cathode; Sodium; Battery

Oxygen-redox-based cathode materials for sodium-ion batteries (SIBs) have attracted considerable attention in recent years owing to the possibility of delivering additional capacity in the high-voltage region. However, they still suffer from not only fast capacity fading but also poor rate capability. P2- $\text{Na}_{0.75}[\text{Li}_{0.15}\text{Ni}_{0.15}\text{Mn}_{0.7}]\text{O}_2$ is introduced, an oxygen-redox-based layered oxide cathode material for SIBs. The effect of Ni doping on the electrochemical performance is investigated by comparison with Ni-free P2- $\text{Na}_{0.67}[\text{Li}_{0.22}\text{Mn}_{0.78}]\text{O}_2$. The $\text{Na}_{0.75}[\text{Li}_{0.15}\text{Ni}_{0.15}\text{Mn}_{0.7}]\text{O}_2$ delivers a specific capacity of $\approx 160 \text{ mAh g}^{-1}$ in the voltage region of 1.5–4.6 V at 0.1 C in Na cells. Combined experiments (galvanostatic cycling, neutron powder diffraction, X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, and nuclear magnetic resonance (7Li NMR)) and theoretical studies (density functional theory calculations) confirm that Ni substitution not only increases the operating voltage and decreases voltage hysteresis but also improves the cycling stability by reducing Li migration from transition metal to Na layers. In this work, we do not limit the TM element to Ni but extend to Co, to understand the difference in the oxygen chemistry behind the acceptable electrode performance. This research demonstrates the effect of Na-O-A (A: Li, Mg, Zn, or vacancy) in P2-type layered cathode materials.

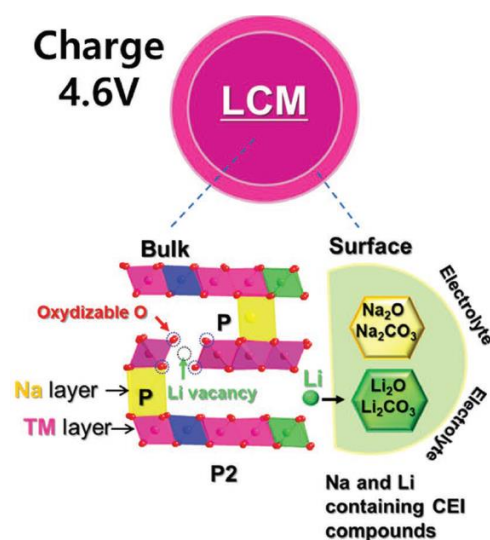


Figure 1. Structure and surface evolution in $\text{Na}_{0.6}[\text{Li}_{0.15}\text{Co}_{0.15}\text{Mn}_{0.7}]\text{O}_2$ material at charged state 4.6 V.

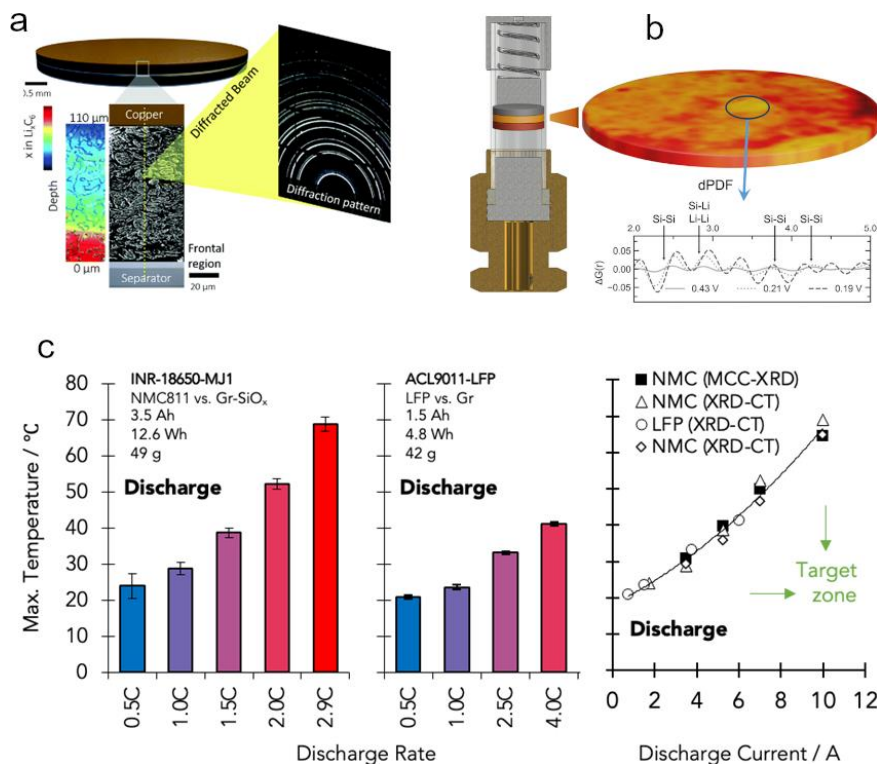
19 Understanding battery performance and degradation by means of spatially-resolved operando X-ray diffraction and X-ray diffraction tomography

Stefano Checchia, ESRF

Keywords: *Operando, in situ, X-ray diffraction, tomography, 18650, silicon electrodes*

Increasing energy demands and the planned electrification of several industrial sectors have made improving the performance and safety of Li-ion batteries during high-rate operation a necessity. Here we show the contribution of high-energy X-ray diffraction to addressing battery performance issues induced by fast charge/discharge and repeated cycling. In particular, we present high-speed, high-resolution diffraction-tomography methods used at beamline ID15A at the ESRF light source. Crystal structure information obtained with high spatial and temporal resolution during high-rate cycling exposes dynamic chemical/morphological inhomogeneities within batteries, and their relation to performance loss and potential failure. For example, Li concentration gradients across anodes leading to irreversible Li plating/stripping (Fig.1a), or leaching of d-metal ions from defective cathode particles upon repeated cycling. Determination of state of charge, strain and temperature inside large-format commercial cells (18650) through X-ray diffraction-tomography (XRD-CT) can reveal the pathways of heat accumulation for fast-charging protocols and in damaged batteries (Fig.1c). Using Pair Distribution Function (PDF) analysis allied to tomography (PDF-CT) we established 3D maps of silicon anode components combining crystalline, amorphous, active, and inactive materials (Fig.1c). The real-time, microscopic quantifications accessible through high-energy X-rays not only highlight the challenges faced by various type of cells, but can also inform more accurate computational models and help guide thermal management strategies for high-rate applications.

Figure 1: a) schematic of X-ray depth scanning of a graphite anode during 6C charge/discharge; b) schematic of operando PDF tomography measurements on amorphous silicon electrodes; c) peak operando temperatures measured inside commercial 18650 batteries during high-rate discharge.



References:

Finegan, D. P., et al, (2020). Spatial dynamics of lithiation and lithium plating during high-rate operation of graphite electrodes. *Energy & Environmental Science*, 13(8), 2570-2584.

Heenan, T. M. M., Mombrini, I., Llewellyn, A., Checchia, S., Tan, C., Johnson, M. J., ... & Shearing, P. R. (2023). Mapping internal temperatures during high-rate battery applications. *Nature*, 617(7961), 507-512.

Wragg, D. S., Skautvedt, C., Brennhagen, A., Geiß, C., Checchia, S., & Kozosov, A. Y. (2023). Tracking Lithiation of Si-Based Anodes in Real Time by Total Scattering Computed Tomography. *The Journal of Physical Chemistry C*.

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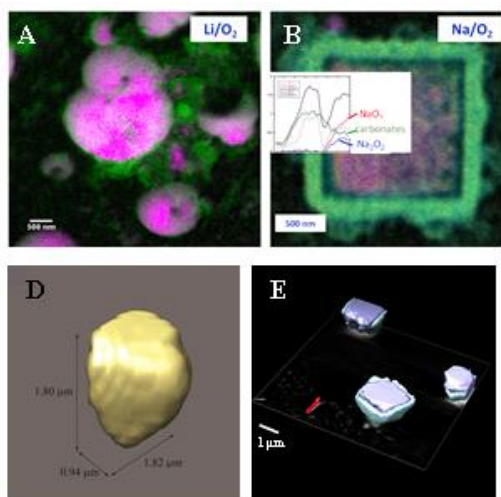
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12 Visualizing electrodes chemical states at the nanometer scale using Full Field Soft X-ray Transmission Microscopy at the Mistral beamline

Andrea Sorrentino, ALBA

Keywords: *Soft X-ray transmission microscopy, Spectromicroscopy, Tomography, Cathodes Imaging*

Synchrotron-based transmission soft X-ray microscopy (TXM) is able to deliver energy-dependent images, providing pixel-by-pixel absorption spectra with high spatial and energy resolution. By scanning the energy across the absorption edge of interest it is possible to discriminate and eventually quantify different chemical species, regardless of their crystalline state. When possible, the 2D chemical description can be extended to 3D performing tomography. We used TXM at the Mistral beamline of the Alba synchrotron [1] for the study of battery related materials. In this work the technique will be illustrated with few examples of application [2-4] and its limit will be addressed. Actual and future data acquisition and data treatment strategies, which may help to overcome these limits, will be also presented.



References:

- [1] A. Sorrentino, et al., J. Synchrotron Rad. 22, (2015) 1112.
- [2] M. Olivares-Marín, et. al. Nano Lett. 15, (2015) 6932.
- [3] I. Landa-Medrano, et. al. Nano Energy 37 (2017) 224–231.
- [4] M. Maisuradze, et.al., Small Methods 2023, 2300718.

13 In-Situ Measurements of Thin Film Model Systems for All Solid-State Batteries

Beatrice Laurenti, Catalonia Institute for Energy Research (IREC)

Keywords: *All-Solid-State-Batteries; Operando technique; Thin Film; Intercalation Mechanism; Reaction Processes Study*

The increase in energy consumption in the global age of digitalization has been increasingly demanding the development of efficient electrical-energy storage systems. Lithium-Ion Batteries (LIBs) with their high energy and power density, both gravimetric and volumetric, have enabled the development of light-weighted power sources present in every portable electronic device. However, the drive to develop more efficient and powerful LIBs has exposed the safety challenges of certain approaches. Conventional LIBs consist of highly flammable liquid electrolytes (LEs), which can be ignited under abuse conditions, leading to thermal runaways of LIBs. Hence, safe LIBs are a prerequisite for further accelerating the electronics field towards the implementation of the Internet of Things as well as in the global electric vehicle (EV) market. In this regard, all-solid-state batteries (ASSBs), in which non-flammable solid electrolytes (SEs) are used as substitutes for LEs, are increasingly regarded as very promising and safe next-generation battery systems. Better fundamental understanding of the complexity and operating mechanisms in LIBs, as well as ASSBs, is essential to addressing outstanding challenges, such as high energy and power density, safe to use, long cycle life, high efficiency, and special application requirements. Conventional electrochemical measurements reveal information about how a battery behaves and performs, but they cannot provide further explanation about the electrochemical mechanism and reactions involved. Facing the challenges of providing deeper insight into complex charge, mass transport and degradation mechanism under realistic operation condition, great interest has been taken in advancing in situ and operando techniques for the investigation of battery materials and devices (1,2,3,4,5). In this regard, thin film lithium-ion batteries that exclude both electrochemically inactive binder and conductive additives are excellent model systems to study cathode and anodes active material and solid-electrolytes, together with their interfaces, including grain boundaries.

Our focus lies on the development of optical technique with operando and in-situ capabilities such as spectroscopic ellipsometry (SE) are affordable and non-destructive options, well-known to operate accurately even at sub-monolayer dimensions with multilayer thin film systems. It allows to study not only the volume changes under operating condition, but also the changing of the optical parameters during operation (6,7). In-Situ TERS provides topographic images as well as nano-Raman mapping on the scanned area itself to study solid electrolyte interface (SEI) composition (8,9), phase changes as well as grain volume and grain boundaries behavior during intercalation/deintercalation processes (10).

References:

1. Dudney NJ, Nanda J, West WC: Handbook of Solid State Batteries. World Scientific; 2015.
2. Harks PPRML, Mulder FM, Notten PHL: In situ methods for Li-ion battery research: a review of recent developments. *J Power Sources* 2015, 288:92-105.
3. Nelson Weker J, Toney MF: Emerging in situ and operando nanoscale X-ray imaging techniques for energy storage materials. *Adv Funct Mater* 2015, 25:1622-1637.
4. Wang CM: In situ transmission electron microscopy and spectroscopy studies of rechargeable batteries under dynamic operating conditions: a retrospective and perspective view. *J Mater Res* 2015, 30:326-339
5. Jena, Z.Tong, B. Bazri, K. Iputera, H. Chang, S. Hu, R. Liu, *The Journal of Physical Chemistry C* 125, 16921 (2021)
6. Marta Cazorla Soult et al 2022. *J. Electrochem. Soc.* 169 040501
7. A. Morata, V. Siller, F. Chiabrera, M. Nuñez, R. Trocoli, M. Stchakovsky, A. Tarancón, Operando probing of Li-insertion into LiMn₂O₄ cathodes by spectroscopic ellipsometry, *J. Mater. Chem. A.* 8 (2020) 11538–11544.
8. Sirshendu Dinda et al. 2023, *Adv. Energy Mater.*, 2302176
9. Nanda et al. *Joule* 3, 2001-2019 (2019)
10. J.C. Gonzalez-Rosillo, B. Laurenti; A. Morata et al. Electrochemical Tip-Enhanced Raman Spectroscopy at grain boundaries. In preparation, 2024.

14 Insights in the effective rates and Buffer effect of Blended positive electrodes for Lithium ion batteries

Chatzogiannakis Dimitrios, ICMAB-CSIC, CIC energiGUNE

Keywords: Batteries, Electrodes, Operando, Cathodes, Blends

A seemingly promising route to improve battery cells is the utilization of blended electrodes, i.e. electrodes with more than one active materials. This provides an extra degree of freedom in tailoring the final product's properties but can potentially give rise to synergistic phenomena, witnessed in cases where the final product performs better than what is expected. Understanding the underlying phenomena that take place during normal operation of such systems is crucial and could enable us to predict and take advantage of such synergies for the design of next generation batteries.

One unique characteristic of such blends is that the rate they are cycled at (cell rate) can be different than the rate that each of the materials experiences (effective rate). This stems from the fact that during cycling, the activity of each active material varies making it take higher or lower share of current depending on the voltage/SoC. Another factor greatly affecting such behaviour is the ratio of the blending.

The aforementioned phenomena were studied using cell configuration where the complex (Blended) electrode is simulated using 2 simple (non blended) ones, slightly modified from the work of Heubner et. al². This configuration shows very interesting results regarding the effective rate that each component feels but could deviate from reality due to the lack of direct contact between the materials. For this reason, operando XRD and XAS were performed on the system of LiMn_2O_4 blended with $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ to validate the phenomena observed using a true blended electrode. Operando results were found to be in very good agreement with those derived from electrochemical tests (Fig. 1), added information to the mechanisms of reaction as well as highlighted the dramatic difference it makes to a material's rate of discharge when blended or not (Fig. 2).

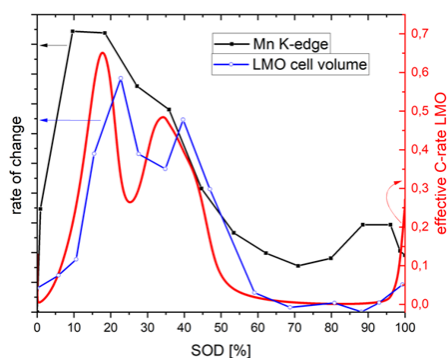


Figure 1: Comparison of the effective C-rate of LMO with the rate of change of the cell volume (from XRD) and Mn K-edge (from XAS).

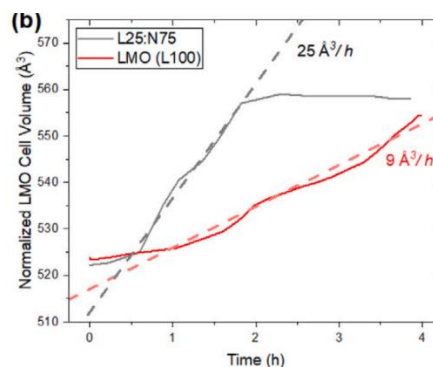


Figure 2: Comparison of the rate of change of the unit cell volume for LMO in a blend or pristine, showing the difference in the rate of discharge when blended.

References:

1. Chatzogiannakis et. al. Journal of Power Sources 591 (2024) 233804
2. Heubner et al. Journal of Power Sources 363, 311–316 (2017).

15 Advanced manufacturing processes of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) ceramic electrolyte for lithium-metal batteries.

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Keywords: *All-solid-state lithium batteries; 3D-printing; stereolithography (SLA); LAGP electrolytes; ultra-fast high-temperature sintering*

Currently commercialized Li ion batteries contain liquid-based electrolytes, which have high ionic conductivity at room temperature but still present drawbacks in terms of safety, durability and manufacturing or maintenance complexity. For this reason, All-solid-state lithium batteries (containing solid electrolytes) have gained attention in the last decades thanks to their increased safety, chemical and thermal stability [1,2].

The present study focuses on 3D printing of ceramic electrolytes for Li-metal batteries. Despite the advantages of additive manufacturing, only a few works have employed these techniques for the manufacturing full ceramic electrolytes [3,4]. Stereolithography (SLA) is a promising technique that enables the production of complex shapes impossible to reach with conventional ceramic processing techniques [5]. Here we present the employment of SLA to produce $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) ceramic electrolytes. One of the advantages introduced by SLA in the case of preparation of ASSBs is that power linearly increases with the increase in active area maximized by printing.

As the electrolyte material, here we use NASICON-type LAGP, which is suitable for ASSB thanks to its high ionic conductivity (10^{-4}S cm^{-1}) at room temperature, high chemical, thermal and electrochemical stability [4,6].

Self standing complex LAGP structures were printed, debinded and sintered. Crack-free LAGP electrolytes with conventional flat and corrugated geometries were successfully produced with high densification (>80% of the theoretical one), and uniform shrinkage in x y and z directions. The printed electrolytes demonstrated to have conductivities in good agreement with LAGP manufactured with conventional techniques (10^{-5} - 10^{-4}S cm^{-1})[7].

Moreover, preliminary results on ultrafast high-temperature sintering (UHS) of LAGP will be presented. UHS represents a promising debinding and sintering method that drastically reduces the manufacturing time and energy consumption, in addition to suppression of degradation phenomena and lithium losses [8-10]. UHS allowed to produce parts with ionic conductivities in the same order of magnitude of the ones obtained by conventional sintering.

References:

[1] A. Armand and J.-M. Tarascon, Building better batteries, Nature, 2008, 451, 652–657. <https://doi.org/10.1038/451652a>

- [2] X. Q. Zhang, C. Z. Zhao, J. Q. Huang and Q. Zhang, Recent Advances in Energy Chemical Engineering of Next-Generation Lithium Batteries, *Engineering*, 2018, 4, 831– 847. DOI: 10.1016/j.eng.2018.10.008.
- [3] D. W. McOwen, S. Xu, Y. Gong, Y. Wen, G. L. Godbey, J. E. Gritton, T. R. Hamann, J. Dai, G. T. Hitz, L. Hu and E. D. Wachsman, 3D-Printing Electrolytes for Solid-State Batteries, *Adv. Mater.*, 2018, 30, 1–7. DOI: 10.1002/adma.201707132.
- [4] A.G. Sabato, M. Nuñez Eroles, S. Anelli, C.D. Sierra, J.C. Gonzalez-Rosillo, M. Torrell, A. Pesce, G. Accardo, M. Casas-Cabanas, P. López-Aranguren, A. Morata, A. Tarancón, 3D printing of self-supported solid electrolytes made of glass-derived $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ for all-solid-state lithium-metal batteries, *J. Mater. Chem. A*. 11 (2023) 13677–13686. <https://doi.org/10.1039/d3ta01435e>.
- [5] S. Zakeri, M. Vippola and E. Levänen, A comprehensive review of the photopolymerization of ceramic resins used in stereolithography, *Addit. Manuf.*, 2020, 35, 101177. DOI: 10.1016/j.addma.2020.101177.
- [6] Rachel DeWees and Hui Wang, Synthesis and Properties of NaSICON-type LATP and LAGP Solid Electrolytes, *ChemSusChem* 2019, 12, 3713 – 3725. <https://doi.org/10.1002/cssc.201900725>.
- [7] D. Ferreira, A.G. Sabato, A. Morata et al. 3D printing optimization of NASICON solid-electrolytes with complex geometries. In preparation. 2024
- [8] Chengwei Wang et al., A general method to synthesize and sinter bulk ceramics in seconds, *Science* 368, 521–526 (2020). DOI: 10.1126/science.aaz7681
- [9] A. Curcio, A.G. Sabato, M. Nuñez Eroles, J.C. Gonzalez-Rosillo, A. Morata, A. Tarancón, F. Ciucci, Ultrafast Crystallization and Sintering of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ Glass and Its Impact on Ion Conduction, *ACS Appl. Energy Mater.* 5 (2022). <https://doi.org/10.1021/acsaem.2c03009>
- [10] J. Wu et al., Ultra-fast high temperature sintering (UHS) of $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ electrolyte: A rationalization of the heating schedule, *Ceramics International* 48 (2022) 6356–6362. <https://doi.org/10.1016/j.ceramint.2021.11.178>

16 Imaging the microstructural-chemistry of batteries during operation with synchrotron light

Dario Ferreira Sanchez and Chayene G. Anchieta, Paul Scherrer Institut

Keywords: *Operando Synchrotron Chemical Imaging*

I am pleased to take this opportunity to share some experiences on battery research, making use of the microXAS beamline facility at the Swiss Light Source (SLS), in order to ultimately understand the microstructural-chemistry of complete battery cells during operation by imaging it with synchrotron light.

Two recent examples will be discussed in more details: one on Solid State Battery, and a second on Lithium-Air Battery. In both cases, the structural and chemical features and reactivity were resolved in space and time by looking simultaneously at the micro- X-ray diffraction, X-ray fluorescence and X-ray absorption contrast signals.

Solid-state batteries hold the promise of addressing several limitations associated with conventional lithium-ion batteries, including safety and energy density. Within this context, the integration of High-Energy Nickel Cobalt Manganese (HE-NCM) cathodes into solid-state batteries has garnered significant attention. Understanding the dynamic changes within HE-NCM cathodes during operation is crucial for optimizing solid-state battery performance. The investigations we have conducted were focused on imaging/tracking the microstructural-chemistry of a solid-state battery system, composed of HE-NCM combined with LYC catholyte changes during the first cycle. The spatially resolved observed evolution of crystal structures and phase transitions during lithiation and delithiation processes will be discussed.

Li-air batteries attract significant attention due to their highest theoretical energy density among all existing energy storage technologies. Currently, challenges related to extending lifetime and long-term stability limit their practical application. To overcome these issues and enhance the total capacity of Li-air batteries, in this work, we have investigated on the effects of the application of NiO/ZrO₂ catalysts. Operando advanced chemical imaging with micrometer spatial resolution unveil that NiO/ZrO₂ catalysts substantially change the kinetics of crystalline LiOH formation and facilitate its rapid decomposition with heterogeneous distribution. Moreover, ex-situ combined neutron and X-ray computed tomography (CT) analysis, provide evidence of distinct lithium phases homogeneously distributed in the presence of NiO/ZrO₂.

In vision of the SLS upgrade, which already taking place, future perspectives on battery research will be presented. Particularly for the microXAS beamline, that includes: gain in spatial resolution by a factor of 5 to 10 (approaching to 100nm figure), significant increase of energy range, and, significant increase of 2 orders of magnitude in photon flux.

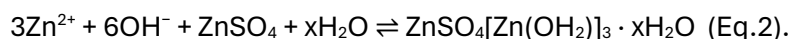
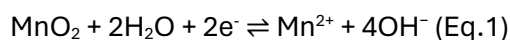
I am looking forward to have fruitful discussions with all the participants, do not hesitate in approaching me to chat.

17 Dissolution-deposition processes in aqueous Zn-MnO₂ batteries revealed by x-ray absorption

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Keywords: *zinc-ion batteries; hard x-rays; soft x-rays*

Zinc batteries have gained considerable attention over the past decade as a more sustainable and safe chemistry comparable to lithium and other high-energy systems, because Zn can be electrochemically plated and dissolved in aqueous electrolytes, with a still respectable capacity of 820 mAh g⁻¹_{Zn}. In addition, Zinc is more common and less expensive than lithium, which makes these batteries particularly suitable for large scale energy storage. Several cathode materials can be coupled with Zn, but the most common choice is MnO₂. Not only Mn can be considered among the least critical battery materials, its electrochemistry can involve two electrons if the Mn²⁺ state is reached. While in most alternative compounds for the positive electrode the main mechanism involves Zn²⁺ intercalation, in this case it has been demonstrated that MnO₂ is dissolved and Zinc Hydroxide Sulfates (ZnSO₄[Zn(OH₂)₃·xH₂O, ZHS) will form, induced by local pH increase:



Many details of the overall discharge and charge mechanism remain unclear. For instance, with many different initial MnO₂ phases and electrode architectures the first and second discharge profile are typically very different and present several steps that have not been well clarified. Most involved Mn compounds are poorly crystalline and air sensitive, and their exact composition has not been uncontroversely determined, yet.

X-ray absorption/emission (XAS/XES) is a versatile and effective technique for the determination of local chemistry and structure. We explored its potential to study mechanisms in the Zn/MnO₂ batteries. As a first step, we found that in operando experiments it is critical to limit beam interactions with the system. We then confirmed an almost reversible MnO₂ dissolution and ZHS formation during discharge and charge. We could not find any clear evidence of Zn-Mn mixed oxides or Mn(III) intermediate neither in discharge nor charge. However, we obtained indirect indication of Mn states between 3 and 4 by exsitu XES. Furthermore, we demonstrate that XAS data can be used to quantify evolution of the main Mn and Zn species and their distribution, which suggest possible bottlenecks that limit discharge capacity below the theoretical limits.

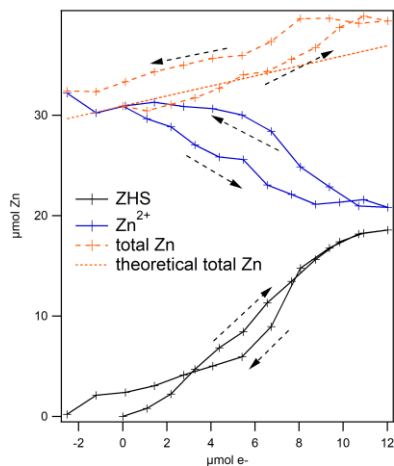


Figure 1. Quantification of ZHS in electrode and Zn cations in the electrolyte of a operando Zn/MnO₂ coin cell

References:

Wang, W.; P. Black, A.; Liu, C.; Martin-Diaconescu, V.; Simonelli, L.; Tonti, D. High Performance N-Doped Carbon Nanosheet/MnO₂ Cathode Derived from Bacterial Cellulose for Aqueous Zn-Ion Batteries. *J. Mater. Chem. A* **2023**, *11* (32), 17272–17281.
<https://doi.org/10.1039/D3TA01487H>.

18 Deciphering the Sodium-Ion Storage Mechanism within Hard Carbon Anodes and Handle Precipitation Mechanism in Lithium Sulfur Cathodes.

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Keywords: *sodium-ion batteries, lithium-sulfur batteries, carbonaceous electrodes; wide-angle and small-angle scattering*

Batteries play a pivotal role in advancing technologies that support the shift towards electromobility and the storage of renewable energy in grid systems. Emerging applications bring new requirements, such as enhanced energy density, rapid charging capabilities, a wide operational temperature range, and sustainability in raw materials and processing [1]. To address these demands, a global effort is underway to optimize and extend the capabilities of next-generation technologies like sodium-ion batteries (SIBs) [2-4] or lithium-sulfur batteries (LSBs)[5].

A common feature among these innovations is tunable carbonaceous electrodes (CEs). The energy storage potential of LSB cathodes and SIB anodes relies to a large extent on the morphology of CEs of different origins from the nanometer to angstrom length scales. [6] For example, the precipitation mechanism of LSB is not yet fully understood and the sodium storage mechanism in hard carbons remains uncertain, inspiring the detailed study of the structure of non-graphitized carbons.

Advanced characterization techniques play a crucial role in supporting the necessary advancements in battery technology [7]. Comprehending the functionality of new materials, the mechanisms of emerging chemistries, and various processes requires detailed characterization from the atomic scale to the cell level [2-6]. The rapid progress in synchrotron X-ray and neutron technologies presents new possibilities for addressing these challenges [7]. This LEAPS-INNOV battery research forum contribution explores recent breakthroughs in understanding processes at carbonaceous anodes and cathodes. It focuses on scattering methods to investigate them, from ex situ to real-time testing and state-of-the-art electrochemistry analysis and experiments at large-scale facilities.

References:

1. Critical Raw Materials for Strategic Technologies and Sectors in the EU A Foresight Study, (2020).
2. L. Kalder, A. Olgo, J. Lühns, R. Härmas, J. Aruväli, P. Partovi-Azar, A. Petzold, E. Lust, E. Härk, Interlayer Spacing of Hard Carbon as a Quantified Structural Parameter for Sodium-Ion Batteries. Combined Analysis by WAXS and SANS, Energy Storage Materials, Under revision.

3. A. Adamson, R. Väli, M. Paalo, J. Aruväli, M. Koppel, R. Palm, E. Hark, J. Nerut, T. Romann, E. Lust, A. Jänes, Peat-Derived Hard Carbons for High Capacity Sodium-Ion Batteries: Synthesis and Characterization, ECS Meet. Abstr., MA2020-02 (2020) 78.
4. K.Schutjajew; P.Giusto, E.Härk, M.Oschatz, Preparation of Hard Carbon/Carbon Nitride Nanocomposites by Chemical Vapor Deposition to Reveal the Impact of Open and Closed Porosity on Sodium Storage Carbon 2021, 185, 697-708, 10.1016/j.carbon.2021.09.051
5. S. Risse, E. Härk, B. Kent, M. Ballauff, Operando Analysis of a Lithium/Sulfur Battery by Small-Angle Neutron Scattering. ACS Nano, 13(9), 10233–10241 (2019)
6. E.Härk, M. Ballauff, Carbonaceous Materials Investigated by Small-Angle X-ray and Neutron Scattering. C Journal of Carbon Research. C 2020, 6(4), 82; <https://doi.org/10.3390/c6040082>.
7. E. K. J. Allan-Cole, I. Arčon, M. Bianchini, C. Didier, R. Dominko, M. Fehse, Z. Gao, M. Guizar-Sicairos, E.Härk, K. Hatzell, T. Jousseume, M. Kavčič, Z. Lu, F. Marini, J. Mata, V. K. Peterson, E. Principi, M. Sadd, A. Senyshyn, P. R. Shearing, S.Tardif, M. F. Toney, C. Villeveille, A. Vizintin, A. Iadecola, S. Lyonard, A. Matic, L. Stievano. Roadmap to operando analyses of batteries at large scale facilities: 2. Small Angle Scattering (SAXS/USAXS/SANS/USANS) (2023) – Journal of Physics: Energy - under revision manuscript.

19 Towards rapid thermal processed all-phosphate solid-state thin film batteries

Fernanda Monteiro Freitas, Catalonia Institute for Energy Research (IREC)

Keywords: *All-solid-state batteries; ultra-fast high-temperature sintering; thin-films*

Solid-state batteries (ASSBs) have gained significant attention as a superior alternative to conventional liquid electrolytes in Lithium-Ion Batteries (LIBs). The employment of solid electrolytes not only addresses safety concerns but also introduces a transformative paradigm shift for smaller high-power devices, such as consumer electronics and IoT devices, through the implementation of thin-film geometry enabling shorter charging times and prolonged battery lifespans in comparison to conventional bulk liquid-filled LIBs [1]. However, despite their considerable potential, ASSBs face challenges that impede their widespread adoption, particularly in the context of fast-charging capabilities. The intricate solid-solid interfaces forming between electrodes and the solid electrolyte present issues during battery operation, involving structural, chemical, and electronic alterations at these interfaces. Notably, many of these challenges manifest formerly during the heat treatment processing stage of the fabrication of ASSBs, where the elevated temperatures (>1000 °C for bulk systems) and extended processing durations inherent render these interfaces susceptible to degradation, significantly impacting battery performance [2-4].

A previous investigation conducted by our group successfully optimized thin $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) solid electrolytes produced by pulsed laser deposition (PLD) at 700 °C, achieving high ionic conductivities of 0.1 mS.cm⁻¹ through conventional annealing (800 °C, 5h dwell and 3 °C.s⁻¹) [4]. In response to the above-mentioned challenges, our research group leads now investigations into the Rapid Thermal Process (RTP) as a pivotal breakthrough together with low temperature fabrication of LATP. These processes facilitates the crystallization of LATP/Lithium Iron Phosphate (LiFePO₄) cathodes, with rates ranging 10-50°C/s. Notably, the combination of these approaches eliminates the need for traditional long processing times exceeding 10 hours at high temperature, currently addressing issues related to lithium losses and the appearance of secondary phases.

Leveraging the Rapid Thermal Process (RTP) in combination with low temperature PLD fabrication at Catalonia Institute for Energy Research (IREC), our work not only contributes to overcoming challenges associated with processing thin LATP solid electrolytes but also enhances chemical and structural compatibility at the interface between LATP and LFP cathode. This dual-focused effort ensures the successful integration of these components into the next generation of solid-state thin-film batteries.

References:

[1] M. Balaish, J.C. Gonzalez-Rosillo, K.J. Kim, Y. Zhu, Z.D. Hood, J.L.M. Rupp, Processing thin but robust electrolytes for solid-state batteries, *Nat. Energy*. 6 (2021) 227–239.
<https://doi.org/10.1038/s41560-020-00759-5>.

[2] V. Siller, J.C. Gonzalez-Rosillo, M. Nuñez Eroles, M. Stchakovsky, R. Arenal, A. Morata, A. Tarancón, Safe extended-range cycling of Li₄Ti₅O₁₂-based anodes for ultra-high capacity thin film batteries, *Mater. Today Energy*. 25 (2022) 100979.

<https://doi.org/10.1016/j.mtener.2022.100979>.

[3] V. Siller, J.C. Gonzalez-Rosillo, M. Nuñez Eroles, F. Baiutti, M.O. Liedke, M. Butterling, A.G. Attallah, A. Wagner, A. Morata, A. Tarancón, Nanoscaled LiMn₂O₄ for Extended Cycling Stability in the 3 V Plateau, *ACS Appl. Mater. Interfaces*. 14 (2022) 33438–33446.

<https://doi.org/https://doi.org/10.1021/acscami.2c10798>.

[4] V. Siller, A. Morata, M.N. Eroles, R. Arenal, J.C. Gonzalez-Rosillo, J.M. López del Amo, A. Tarancón, High performance LATP thin film electrolytes for all-solid-state microbattery applications, *J. Mater. Chem. A*. 9 (2021) 17760–17769.

<https://doi.org/10.1039/d1ta02991f>.

20 Interfaces in solid-state batteries: From model systems to industrial scenarios

Juan Carlos Gonzalez-Rosillo, Catalonia Institute for Energy Research (IREC)

Keywords: *All-solid-state batteries; operando characterization; ultra-fast high-temperature sintering; 3D-printing; thin-films*

All-solid-state batteries (ASSBs) have emerged as a cutting-edge energy storage solution, presenting numerous advantages over conventional liquid electrolyte-based batteries. Enhanced safety, higher energy density, and improved cycling stability are among the key benefits of ASSBs, positioning them as a reliable option for applications with stringent safety requirements. [1] Nevertheless, despite their potential, ASSBs encounter challenges that hamper their widespread adoption, particularly regarding fast-charging capabilities. A pivotal factor contributing to this challenge is the complex solid-solid interfaces that form between the electrodes and the solid electrolyte. These interfaces are dynamic regions that can undergo significant transformations throughout battery operation, including structural, chemical, and electronic changes at these interfaces, potentially resulting in growing interfacial resistance, undesirable side reactions, and even the formation of dendrites. However, many of the problems arise earlier during the processing stage, where the high temperatures and long processing times usually involved in the fabrication of ASSBs can make these interfaces susceptible to degradation that profoundly influence battery performance.

To unleash the full potential of ASSBs and enable efficient and commercially viable fast-charging technologies and solutions, a comprehensive understanding and optimization of these interfaces are imperative, which becomes particularly challenging in bulkier systems. Here, the aid of well-controlled model systems to gain a comprehensive understanding of the underlying interfacial dynamics becomes essential [2-4].

At the Nanoinoics group at IREC (Spain), we aim to use our large expertise in ceramic processing and operando characterization to push the commercialization of ASSB at different lengthscales. In particular, during this talk we will briefly discuss the following points regarding during this talk:

- 1) Operando characterization techniques developed at IREC and industrial partners based on non-destructive optical methods (Operando Spectroscopic Ellipsometry, Electrochemical Tip-Enhanced Raman Spectroscopy). [2,3,5,6]
- 2) 3D printing of functional ceramics for complex shaped, free-standing ASSB with engineered architectures. [7,8]
- 3) Ultra-fast sintering techniques for interfaces optimization: Rapid Thermal Processing (RTP) for thin film model systems and Ultra-fast High-temperature Sintering (UHS) for 3D-printed ceramics. [9,10]

This talk aims to generate discussion regarding some of the current hot topics in the community, specially regarding ultra-fast sintering techniques and fast charge and discharge ASSB, and the possibility to have time and spatial resolution in operando conditions to characterize the dynamic nature of the several interfaces involved in the electrochemistry.

References:

- [1] M. Balaish, J.C. Gonzalez-Rosillo, K.J. Kim, Y. Zhu, Z.D. Hood, J.L.M. Rupp, Processing thin but robust electrolytes for solid-state batteries, *Nat. Energy*. 6 (2021) 227–239. <https://doi.org/10.1038/s41560-020-00759-5>.
- [2] V. Siller, J.C. Gonzalez-Rosillo, M. Nuñez Eroles, M. Stchakovsky, R. Arenal, A. Morata, A. Tarancón, Safe extended-range cycling of Li₄Ti₅O₁₂-based anodes for ultra-high capacity thin film batteries, *Mater. Today Energy*. 25 (2022) 100979. <https://doi.org/10.1016/j.mtener.2022.100979>.
- [3] V. Siller, J.C. Gonzalez-Rosillo, M. Nuñez Eroles, F. Baiutti, M.O. Liedke, M. Butterling, A.G. Attallah, A. Wagner, A. Morata, A. Tarancón, Nanoscaled LiMn₂O₄ for Extended Cycling Stability in the 3 V Plateau, *ACS Appl. Mater. Interfaces*. 14 (2022) 33438–33446. <https://doi.org/https://doi.org/10.1021/acsami.2c10798>.
- [4] V. Siller, A. Morata, M.N. Eroles, R. Arenal, J.C. Gonzalez-Rosillo, J.M. López del Amo, A. Tarancón, High performance LATP thin film electrolytes for all-solid-state microbattery applications, *J. Mater. Chem. A*. 9 (2021) 17760–17769. <https://doi.org/10.1039/d1ta02991f>.
- [5] A. Morata, V. Siller, F. Chiabrera, M. Nuñez, R. Trocoli, M. Stchakovsky, A. Tarancón, Operando probing of Li-insertion into LiMn₂O₄ cathodes by spectroscopic ellipsometry, *J. Mater. Chem. A*. 8 (2020) 11538–11544. <https://doi.org/10.1039/C9TA12723B>.
- [6] J.C. Gonzalez-Rosillo, B. Laurenti; A. Morata et al. Electrochemical Tip-Enhanced Raman Spectroscopy at grain boundaries. In preparation, 2024.
- [7] A.G. Sabato, M. Nuñez Eroles, S. Anelli, C.D. Sierra, J.C. Gonzalez-Rosillo, M. Torrell, A. Pesce, G. Accardo, M. Casas-Cabanas, P. López-Aranguren, A. Morata, A. Tarancón, 3D printing of self-supported solid electrolytes made of glass-derived Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ for all-solid-state lithium-metal batteries, *J. Mater. Chem. A*. 11 (2023) 13677–13686. <https://doi.org/10.1039/d3ta01435e>.
- [8] D. Ferreira, A.G. Sabato, A. Morata et al. 3D printing optimization of NASICON solid-electrolytes with complex geometries. In preparation. 2024
- [9] F. Monteiro, J.C. Gonzalez-Rosillo, A. Morata et al. Towards rapid thermal processed all-phosphate solid-state thin film batteries. In preparation, 2024.
- [10] A. Curcio, A.G. Sabato, M. Nuñez Eroles, J.C. Gonzalez-Rosillo, A. Morata, A. Tarancón, F. Ciucci, Ultrafast Crystallization and Sintering of Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ Glass and Its Impact on Ion Conduction, *ACS Appl. Energy Mater*. 5 (2022). <https://doi.org/10.1021/acsaem.2c03009>

21 Demystifying mysterious time and space evolution in state-of-the art graphite-silicon composite battery electrodes

Marta Mirolo, ESRF

Keywords: *Li-ion batteries, composite electrodes, silicon-graphite, charge dynamics, scattering*

The reaction processes in Li-ion batteries can be highly heterogeneous at the electrode scale, leading to local deviations in the lithium content or local degradation phenomena. To access the distribution of lithiated phases throughout a high energy density silicon-graphite composite anode, we apply correlative operando small- and wide-angle X-ray scattering (SAXS and WAXS) tomography.

In-plane and out-of-plane inhomogeneities are resolved during cycling at moderate rates, as well as during relaxation steps performed at open circuit voltage (OCV) at given states of charge. Lithium concentration gradients in the silicon phase are formed during cycling, with regions close to the current collector being less lithiated when charging compared to their counterpart close to the separator. On the other hand, graphite does not show any strong gradient in lithiation state across the electrode.

In relaxing conditions, the multi-phase and multi-scale heterogeneities vanish to equilibrate the chemical potential. In particular, Li-poor silicon regions pump lithium ions from both lithiated graphite and Li-rich silicon regions. Our findings are corroborated by modeling of the chemical potential of graphite and silicon, taking into account that the chemical potential of silicon depends not only on the lithiation state (as the graphite component), but also on internal stress due to volume changes during (de-)lithiation.

This charge redistribution between active materials is governed by distinct potential homogenization throughout the electrode and hysteretic behaviours. Such intrinsic concentration gradients and out-of-equilibrium charge dynamics, which depend on electrode and cell state of charge, must be considered to model the durability of high capacity Li-ion batteries.

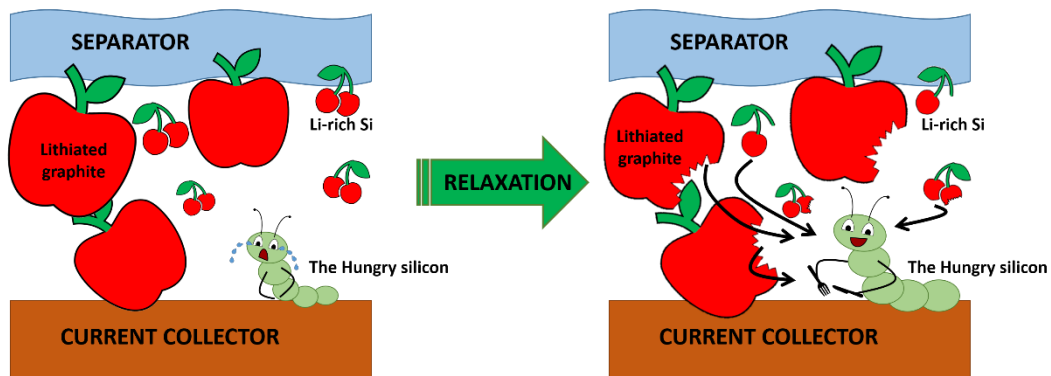


Figure 1: At the end of lithiation, the state of charge of graphite is homogeneous across the electrode. On the other hand, silicon is more lithiated close to the separator than close to the current collector. During relaxation however, the charges redistribute in the electrode to homogenize the lithiation state between graphite and silicon.

References:

Charge Dynamics Induced by Lithiation Heterogeneity in Silicon-Graphite Composite Anodes, Christopher L. Berhaut, **Marta Mirolo**, Diana Zapata Dominguez, Isaac Martens, Stéphanie Pouget, Nathalie Herlin-Boime, Marion Chandesris, Samuel Tardif, Jakub Drnec, and Sandrine Lyonnard, *Adv. Energy Mater.* **2023**, 13, 2301874, DOI: 10.1002/aenm.202301874

22 Operando XAS study of $\text{Li}_{1.2}\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_2$ towards Co-free batteries materials

Oleg Usoltsev, ALBA

Keywords: *Co-free Li-rich cathodes, XAS spectroscopy, Li-ion batteries*

Thanks to the operating high voltages and delivered capacities, Li-rich transition-metal-oxide cathodes are still the most promising materials for next-generation lithium-ion-batteries. In addition to the need of higher power densities and increased energy, the satisfaction of additional requirements such as safety, sustainability, cost-effectiveness, and large-scale manufacturing is becoming a key. Co-free Li-rich cathode join the reduced costs with higher performances. However, their cycle-life remains limited, and individual roles of the transition-metals are still not fully understood. The investigation of the chemical species evolution along the first charge is here reported for the $\text{Li}_{1.2}\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_2$ system (for $x = 0.56$, $y = 0.16$, $z = 0.08$ and $x = 0.6$, $y = 0.2$, $z = 0$). The local electronic and structural properties around the transition metals have been accessed by means of an operando multi-edge XAS as a function of charge. The charge compensation mechanism and on the effects induced by lowering the Co content has been revealed, allowing to address fundamental electronical and structural aspects that define the functional properties of Li-rich NMC cathode materials for Li-ion batteries. The investigation of structural parameters evolution obtained by first shell Fourier analysis of EXAFS data simultaneously with the application of multi curve resolution approach to the XANES spectra allowed highlighting $\text{Li}_{1.2}\text{Mn}_x\text{Ni}_y\text{Co}_z\text{O}_2$ system transformation during charge/discharge cycling.

23 Using the FELIX free electron lasers for green technology-enabling fundamental research

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Keywords: *Free electron laser, infrared spectroscopy, hydrogen adsorption, CO poisoning, water splitting*

The free-electron lasers of the HFML-FELIX Laboratory in Nijmegen, The Netherlands, provide unique access to high power and tunable laser light in the far- and mid-infrared spectral range, allowing a variety of fundamental research in e.g. solid-state physics and surface science [1], astrochemistry [2], nanoscience, chemistry and even clinical research [3]. HFML-FELIX houses 11 beam stations with a variety of experimental instruments and operates as a user facility, hosting experiments of national and international researchers, in addition to strong in-house research programs.

In this contribution, I will introduce the HFML-FELIX research facilities, summarizing the variety of experimental techniques available for experiments in gas and condensed phases. The heart of the talk will be devoted to the use of infrared spectroscopy to characterize fundamental chemical processes relevant for materials research for energy-related applications, such as methane activation [4,5], hydrogen splitting [6] and storage [7], fuel cell catalyst materials [8], and water splitting reactions [9].

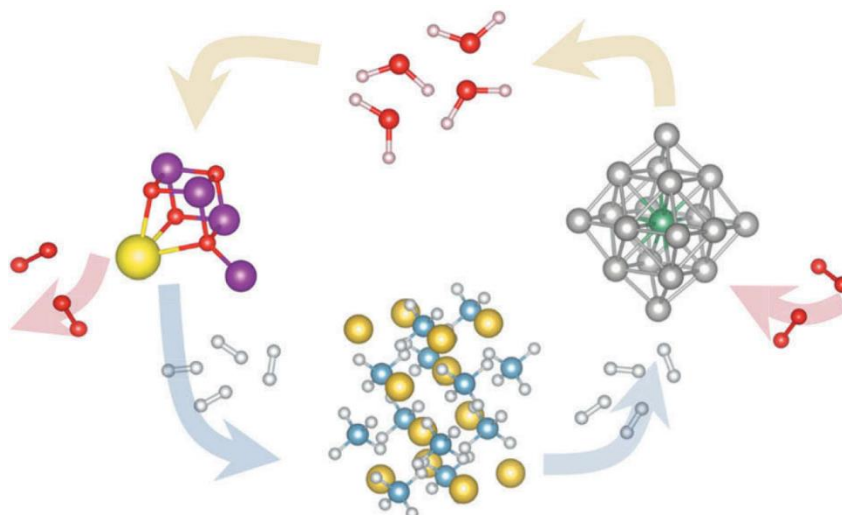


Figure 1. Schematic representation of the hydrogen economy cycle, with the involvement of gas-phase research to uncover detailed chemical process. Hydrogen is generated via electrolysis of water, after which the hydrogen is stored for later re-electrification in a fuel cell. Extracted from Ref. [7].

References:

- [1] A. Stupakiewicz, C. S. Davies, K. Szerenos, D. Afanasiev, K. S. Rabinovich, A. V. Boris, A. Caviglia, A. V. Kimel & A. Kirilyuk, *Nat. Physics*, 17, 489–492, 2021.
- [2] D. B. Rap, J. G. M. Schrauwen, A. N. Marimuthu, B. Redlich, and S. Brünken, *Nat. Astron.* 6, 1059–1067, 2022.
- [3] M. C. Huigen, L. A. Kluijtmans, T. M. Peters, H. H. Al-Shekaili, et al. Untargeted metabolomics and infrared ion spectroscopy identify biomarkers for pyridoxine-dependent epilepsy. *J. Clin. Invest.*, 131, 15, 2021.
- [4] S. M. Lang, T. M. Bernhardt, V. Chernyy, J. M. Bakker, R. N. Barnett, U. Landman, *Angew. Chem. Int. Ed.*, 56, 13406-13410, 2017.
- [5] J. Lengyel, N. Levin, F. J. Wensink, O. V. Lushchikova, R. N. Barnett, U. Landman, U. Heiz, J. M. Bakker, M. Tschurl, *Angew. Chem. Int. Ed.*, 59, 23631-23635, 2020.
- [6] P. Ferrari, H. T. Pham, J. Vanbuel, M. T. Nguyen, A. Fielicke, E. Janssens, *Chem. Commun.*, 57, 9518-9521, 2021.
- [7] J. Vanbuel, P. Ferrari, E. Janssens, *Adv. Phys: X*, 5:1, 1754132, 2020.
- [8] P. Ferrari, L. M. Molina, V. Kaydashev, J. A. Alonso, P. Lievens, E. Janssens, *Angew. Chem. Int. Ed.* 55, 11059–11063, 2016 .
- [9] G.-L. Hou, T. Yang, M.-Y. Li, J. Vanbuel, O. V. Lushchikova, P. Ferrari, J. M. Bakker, E. Janssens, *Angew. Chem. Int. Ed.* 60, 27095–27101, 2021.

24 Holistic Energy Storage Materials Research with Synchrotron-based Spectroscopies at the Energy Materials In-situ Laboratory Berlin

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Keywords: *Synchrotron, XAS, HAXPES, operando, buried interfaces*

Energy storage devices contain multiple buried interfaces that determine long-term performance stability and power density of the device. To date, the structural, electronic and electrical properties of energy storage materials, interfaces, and devices are predominantly investigated as ex-situ and/or post-mortem samples, and correlations made from these studies rely on the assumption that the employed experimental procedures result in meaningful, device-relevant findings. Although this is often true, it is imperative to develop skills and methodologies to characterize interfacial structures under operating conditions to probe transient and metastable effects to fully understand and overcome performance-limiting mechanisms.

In this contribution, we report on the diverse experimental infrastructure available at the Energy Materials In-situ Laboratory Berlin (EMIL) at HZB for probing solid/solid and solid/liquid interfaces under operating conditions. The wide energy range of the soft x-ray UE48-PGM branch (80 – 2000 eV) and the hard x-ray U17-DCM branch (2 – 10 keV) of EMIL's two-color beamline allows x-ray absorption spectroscopy (XAS) of both light and heavy elements, as well as, photon-energy-dependent (and, thus, depth-dependent) photoelectron spectroscopy measurements. The probing depths of these techniques allow for access of the buried (solid/liquid and solid/solid, respectively) interfaces of the devices, and the EMIL undulators provide sufficiently high fluxes to collect high-signal-to-noise data on the timescale relevant for device operation. In addition to the far-reaching complementary x-ray analytic capabilities, the access to the sample preparation infrastructure in the EMIL facility makes it uniquely suited for *in-system* fabrication and analysis of complete energy storage devices. These highly integrated set-ups, including *in-situ* and *operando* sample environments, combined with sample/device preparation and diagnostic control available at EMIL provide unprecedented holistic experimental capabilities for energy storage materials research.

25 Going Operando: Probing interfaces in anode-free Li-ion batteries with polymer electrolyte by operando synchrotron-based X-ray spectroscopies

Zora Chalkley, HZB

Keywords: Anode-free, XAS, HAXPES, operando, SEI

Anode-free solid-state lithium metal batteries with composite polymer electrolyte (CPE) are promising replacements for current lithium (Li) ion batteries due to higher energy densities and mitigation of safety issues. In the anode-free design, Li metal (Li^0) is deposited (plated) from the cathode on the anode current collector (CC). Plating of Li results in degradation of the CPE and formation of a thin (~ 100 s of nanometers) solid electrolyte interphase (SEI). Poor performance of the SEI is a common reason for premature cell failure and capacity loss over cycling. Therefore, unambiguous identification of SEI chemical components is necessary for rational design of longer lasting and more efficient anode-free batteries. It is vital, then, that the SEI be analyzed in the realistic operating (*operando*) conditions.

In this presentation, we introduce a cell sample environment to probe buried SEI. Initially designed for the HIKE endstation located at the KMC-1 beamline of BESSY II, the *operando* cell permits us to directly probe the Li/CPE interface and monitor the SEI formation by synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES) and X-ray absorption spectroscopy (XAS) during electrochemical conditioning of the cell (Figure 1a). A view of the SEI is achieved through penetration of a thin (~ 5 nm), electron transparent CC deposited on the CPE via electron beam deposition (Figure 1b,c). To demonstrate the efficacy of the technique, we plated/stripped lithium in small steps (dosages) at predetermined negative/positive potentials vs Li/Li⁺, respectively. Selected Li 1s spectra, collected during cell open circuit, confirm the successful cell cycling via the appearance of a Li^0 plasmon peak with plating and its subsequent decreased intensity with partial stripping (Figure 1d). The validity of the cell environment will be demonstrated through example CPE systems and many benefits of the cell design – including SEI composition and thickness extraction – will be shown through HAXPES and XAS data.

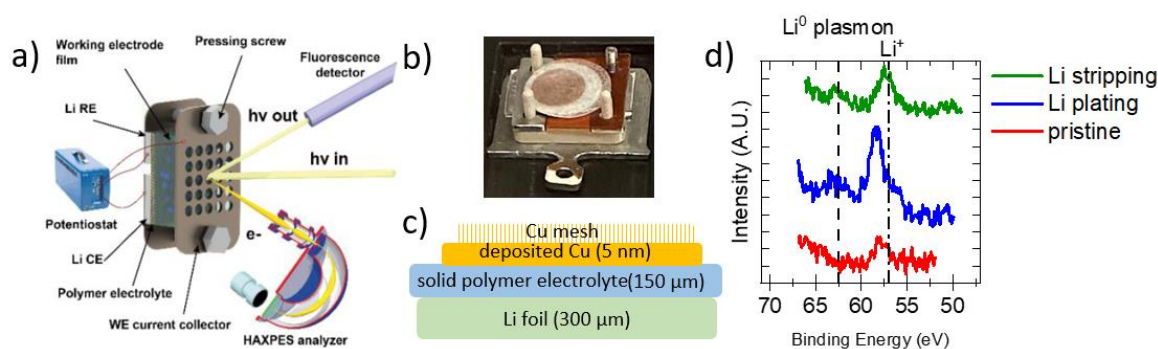


Figure 1 a) *Operando* cell sample environment developed for HIKE at BESSY II. b) Photograph of the partially assembled cell, showing Cu current collector directly deposited on a solid polymer electrolyte, placed on Li foil. c) Schematic of the fully assembled cell. d) Li 1s spectra acquired at $h\nu = 2.1$ keV of a pristine sample, after Li plating, and subsequent Li stripping. Li^+ appears at ~ 57 eV and Li^0 plasmon peak at 62.5 eV.