BOOK OF ABSTRACTS

European Workshop on Battery Interfaces

High-Resolution Techniques and Multiscale Modelling.

3rd & 4th April 2025. Córdoba, Spain.

Co-funded by
the European Union

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Keynote Lectures
Jeff Sakamoto, University of California, USA
Claire Villevielle, LEPMI, Grenoble, France

Invited Talks
Ainara Aguadero, ICMM-CSIC/Imperial College London, UK
Erik Berg, Uppsala University, Sweden
Alexandre Roelens, Vrije Universiteit Brussel, Belgium

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Daniel Rettenwander, Norwegian University of Science and Technology, Norway

Thursday 03 April	
08:30-09:00	Registration
09:00-09:15	Welcome and Introduction to the Workshop: María José Polo (UCO) Patrik Johansson (Uppsala University) Celia Polop (UAM-IFIMAC) and Santhana Eswara (LIST)
09:15-10:00 Keynote	First Morning Session Keynote lecture, Claire Villevielle, **Operando monitoring of batteries: Understanding transport limitations** Chair: Santhana Eswara Moorthy
10:00-10:30	Coffee Break
	Second Morning Session Chair: Rafael Trócoli
10:30-10:50	Hung Quoc Nguyen, Juraj Todt, Dora Zalka, Alexey Maximenko, Dragos Stoian, Norbert Schell, Wouter van Beek, Jozef Keckes, and Daniel Rettenwander, **Studying solid-state batteries during operation using X-rays**
10:50-11:10	Akarsh Sudheendra Bharadwaj, Andrés Miranda Martínez, Santhana Eswara Moorthy, Tim Dahmen, **Sampling and Reconstruction Algorithms for low-dose high-speed Acquisition of FIB-SEM/SIMS Images**
11:10-11:30	Valentina Diolaiti, Marco Ricci, Alfredo Andreoli, Fabio Rossi, Leonardo Sollazzo, Remo Proietti Zaccaria, and Donato Vincenzi, **Preliminary investigation of interface evolution in Ge-based lithium ion batteries**
11:30-11:50	Oliver Lohrberg, Jonas Schlaier, Kristian Nikolowski, Alexander Michaelis, **Operando Electrochemical Dilatometry to Study Li-Deposition in liquid and solid electrolyte Systems**
11:50-12:10	S. Trabesinger, N.E. Asres, P. Boillat, S. Eswara, J.M. Lopez Del Amo, S. Sharma, L. Skarjan, M. Strobl, X. Zhang, **Isotope-Enhanced Battery Interface Characterization**
12:10-12:30	Jesús M. Blázquez-Moreno, Álvaro Bonilla, Ana L. Páez Jerez, Almudena Benítez, Alvaro Y. Tesio, Álvaro Caballero, **Using X-ray nanotomography to understand the improved performance of Li-S battery with binders based on cheese shell waste**
12:30-14:30	Group photo and Lunch
	First Afternoon Session Chair: Peter Siffalovic
14:30-15:00 Invited	Erik Berg, Neeha Gogoi, Robin Lundström, Tim Melin, Kristina Edström, **Revisiting Interfacial Reaction Mechanisms of Li-ion Electrolyte Additives with Operando Characterization**
15:00-15:20	H.-G. Steinrück, X. Ge, D. Kopljar, B. Larrarte-Lizarralde, Á. Doñoro, A. Blázquez, L. Haneke, E. Esen, E. Ayerbe, M. Nojabaee,

	Experimental charge transport characteristics for interface and interphase modelling
15:20- 15:40	A. Galindo, N. Xavier, N. Maldonado, J. Díaz-Sánchez, C. Morante, G. García, C. Polop, Q. Cai and E. Vasco, **Lithiation behavior of metal components for Li-ion batteries by ion beam analysis**
15:40- 16:00	Eva del Campo Ortiz, Marek Marcinek, Grazyna Zofia Zukowska, Laurence J. Hardwick, Alex R. Neale, **Operando Raman Microscopy for $LiNiO_2$ electrodes: Data processes advances with PRISMA app**
16:00- 16:30	Coffee Break
	Second Afternoon Session Chair: Qiong Cai
16:30- 17:00 Invited	Alexandre Roelens, Annick Hubin, Mesfin Haile Mamm, **Multiscale Modelling of Electrode/Electrolyte Interface in All-Solid-State Battery**
17:00- 17:20	Lukas Köbbing, Manuel Lopez, Diego del Olmo, Beñat Larrarte-Lizarralde, Elixabete Ayerbe, Arnulf Latz, and Birger Horstmann, **Interface and Interphase Modelling Approaches Within OPINCHARGE**
17:20- 17:40	Rafael Klee, **An Approach to Studying Interfaces in Sodium-Ion Batteries (SIBs): Application of Characterization Techniques**
17:40- 18:00	Neubi F. Xavier Jr, and Qiong Cai, **Interlayer Metals for Zero-Excess Solid-state Batteries: A Multiscale Approach Combining Machine Learning Potentials and DFT**
18:00- 18:20	Antonio J. Fernández Romero, V. García Caballero, M. Cano, Florencio Santos, José Abad, María Vila, Germán R. Castro, Antonio Urbina, **In situ synchrotron X-ray diffraction study of Zn/Bi_2O_3 electrodes prior to and during discharge of Zn-air batteries: Influence on ZnO deposition**
18:30- 20:00	Poster Session
20:30	Dinner

Friday 04 April	
09:00- 09:45 Keynote	First Morning Session Keynote lecture, Jeff Sakamoto, **Next Generation Electrochemical Technologies Enabled by Solid-State Electrolytes** Chair: Celia Polop
09:45- 10:15	Coffee Break
	Second Morning Session Chair: Daniel Rettenwander
10:15- 10:45	A. Aguadero, E. Querel, I. Seymour, R. Brugge, A. Cavallaro, F. Pesci, Nick Williams,

Invited	**Understanding interface chemistries to optimize ion dynamics in all solid-state batteries**
10:45-11:05	R. Trocoli, V. Carnero, A. Licari, A. Lopez, A. Fernandez, C. Frontera, A.P. Black, R. Houdeville, G. C. B. Alexander, I. Roy, P. Parajuli, R.F. Klie, M. E. Arroyo-de Dompablo, S. Vincent, J. M. Garcia Lastra, J. Cabana, M.R. Palacín, **Operando synchrotron X-ray diffraction for multivalent cations intercalation**
11:05-11:25	Peter Siffalovic, Erik Simon, Eva Schlautmann, Karol Vesgo, Simon Micky, Juraj Todt, Peter Nadazdy, Poongodi Ayyanusamy, Jozef Keckes, and Wolfgang Zeier, **Monitoring Kinetics of Structural Changes in Solid-State Batteries**
11:25-11:45	Rajmohan Rajendiran, Ivan T. Lucas, **Real-time monitoring of transition metal dissolution and cross contamination in operating Lithium-ion batteries**
11:45-12:05	J. Díaz-Sánchez, P. Hernández-Martín, E.G. Michel, C. Polop, N. Kwiatek-Maroszek, M.A. Niño, M. Foerster, H.R. Bratlie, D. Rettenwander, R. Anton, A. Lowack and K. Nikolowski, **Nucleation and early-stage growth of Li and Na anodes in ZESSBs at the nanoscale by synchrotron-PEEM and AFM**
12:05-12:25	W. Corts, F. Bertram, S. Frücht, X. Ge, M. Lippmann, T. Matar, H.-G. Steinrück, H. Stöcker and T. Weigel, **A Fast-X-Ray Reflectivity Setup for Sub-Second Operando Studies of Electrochemical Interfaces**
12:25-12:40	Closing Remarks
	Afternoon visit of the Mosque for interested participants

Contributions

Operando monitoring of batteries: Understanding transport limitations

Claire Villevieille1*
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All-solid-state batteries have been presented as the ideal solution to address i) the safety limitations of conventional Li-ion batteries by suppressing the flammable organic electrolytes and ii) the problem of insufficient energy densities if coupled to Li metal. To date, two types of solid Li-ion electrolytes have been mainly studied, namely, thiophosphate materials and ceramic-based materials. As they are easy to process and they offer a high ionic conductivity in the range of 1-20 mS/cm, thiophosphate electrolytes such as e.g. thio-LISICONs and argyrodites are therefore regarded as suitable candidates to be used in lithium all-solid-state batteries.

Despite the progress in the development of superionic conductor, many aspects regarding their chemical and mechanical issues remain unsolved especially during electrochemical activities where the electrolyte is heavily decomposed. If the electrode engineering i.e. composite electrode (mixture of electroactive material, conductive agent and solid electrolyte) is under intense investigation, the role of the solid electrolyte used as separator is so far poorly studied. Quite often, the electrochemical fading mechanisms observed with ageing are solely ascribed to the conventional fading parameters (cycling, temperature, interfacial reaction, chemo-mechanical degradation), but it might be that most of those parameters are happening prior any electrochemical activities during the sintering process.

As an example, if the sintering (even cold sintering) is not properly performed, voids will appear in the solid electrolyte pellet, and during charge/discharge, the same voids could then evolve and propagate into cracks causing mechanical failure.

In this work, two different microstructure & morphological evolution will be monitored.

- The first one will focus on the relationship between the sintering parameters (time/pressure) of the thiophosphate materials and the pore network percolation[1]
- The second one will be based on an in-depth operando investigation of the microstructure evolution of the solid electrolyte and of the composite electrode[2]

Operando XRD-CT, XCT and FIB-SEM were selected as techniques of choice to establish the correlation between electrochemistry, microstructure, morphology, and electrochemical fading. The results obtained here should serve as a preliminary basis to develop better solid-state batteries.

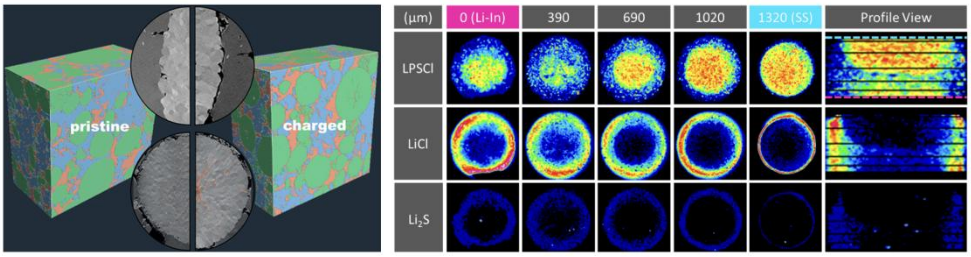

Figure 1. Left) Microstructure of LSPCl/NMC622 composite electrode investigated by operando FIB-SEM; Right) XRD-CT investigation (performed at ID15a, ESRF) of a half-cell LPSCl/Li-In aged for 20 cycles.

1. Perrenot P, Fauchier-Magnan A, Mirolo M, Lecarme L, Jouneau P-H, Boulineau A, *et al.* Room-Temperature Sintering of Amorphous Thiophosphate Solid Electrolyte (Li$_3$PS$_4$): Coupling Morphological Evolution to Electrochemical Properties. *Advanced Functional Materials* 2024, **34**(2)**:** 2310739.
2. Perrenot P, Bayle-Guillemaud P, Villevieille C. Composite Electrode (LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$) Engineering for Thiophosphate Solid-State Batteries: Morphological Evolution and Electrochemical Properties. *ACS Energy Letters* 2023, **8**(11)**:** 4957-4965.

Next Generation Electrochemical Technologies Enabled by Solid-State Electrolytes

Jeff Sakamoto[a]

[a] *Materials Department, UC Santa Barbara, Santa Barbara, CA, USA*

The recent emergence and discovery of new ceramic ion conductors (CICs) with fast ionic conductivity at near-ambient temperatures creates the opportunity to push the frontiers of electrochemical energy conversion and storage. The ability to replace traditional liquid electrolytes with ceramics has the disruptive potential to improve safety and enable next generation technologies including solid-state batteries with metal anodes and impermeable membranes to prevent crossover in redox flow batteries for long-duration energy storage (LDES). Enabling the next generation of electrochemical conversion and storage, however, requires fundamental research to understand and control the emergent mechano-chemical environments that arise when CIC materials are interfaced with other dissimilar materials.

The underlying physics that control the stability and kinetics of all solid-state interfaces are fundamentally different from interfaces in state-of-the-art Li ion technology. Moreover, the mechano-electrochemical phenomena that occur during discharge and charge at the Li-CIC interface are considerably different. For example, during charging at higher rates Li metal filaments can initiate at defects and propagate through relatively hard ceramics. During discharge, if the Li stripping rate is sufficiently high and the pressure and temperature is sufficiently low, voids form at the interface causing current focusing and eventual permanent degradation.

The United States Department of Energy is supporting the collaborative and interdisciplinary project Mechano-chemical Understanding of Solid Ion Conductors (MUSIC – Figure). The overarching scientific mission of MUSIC is *to reveal, understand, and model, and ultimately control the chemo-mechanical phenomena underlying the processing and electrochemical dynamics of CICs for clean energy systems*. This presentation will consist of highlights from MUSIC to include topics such as anode-free manufacturing and *operando* impedance spectroscopy to analyze mechano-electrochemical phenomena at the Li-CIC interface.

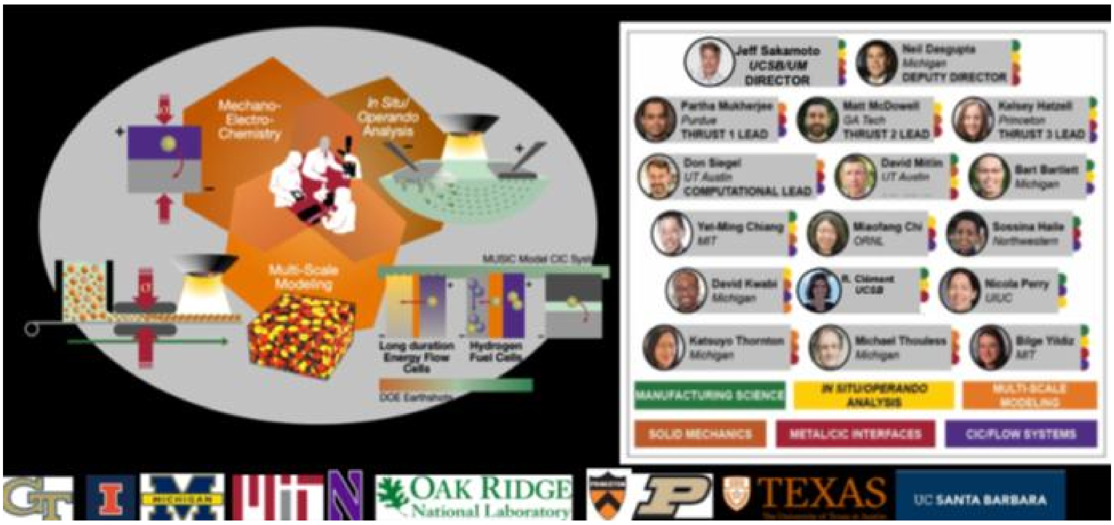

Figure. US DOE Energy Frontier Research Center, Mechano-Chemical Understanding of Solid Ion Conductor (MUSIC).

Revisiting Interfacial Reaction Mechanisms of Li-ion Electrolyte Additives with Operando Characterization

Erik Berg, Neeha Gogoi, Robin Lundström, Tim Melin, Kristina Edström

Department of Chemistry – Ångström Laboratory, Uppsala University Sweden

The performance and lifetime of Li-ion batteries are critically influenced by the choice of electrolyte additives. Many additives form electrode passivation layers, a.k.a. solid electrolyte interphases (SEI), during the battery formation process. Despite the recognized importance, their reaction mechanisms and impact on electrode stability and impedance remain debated. Herein, a series of studies of electrolyte decomposition and additive layer-forming mechanisms are presented. Focus is on a few of the most popular layer-forming molecular additives applied in Li-ion batteries, e.g. vinylene carbonate (VC), ethylene sulfate (DTD), and Propanesultone (PS), but a few less explored alternatives such as Lithium bis(oxalato)borate (LiBOB) will also be discussed.

Our findings derive from *operando* chemical characterization of the additives as they react. By combining analytical techniques, such as Online Electrochemical Mass Spectrometry (OEMS), Electrochemical Quartz Crystal Microbalance (EQCM), and Infrared spectroscopy (IR), we observe that layer-forming additives stepwise react and generate products with unique properties – each according to their respective chemical formulae and decomposition mechanism. For example, the reduction of the LiBOB salt is observed by IR to set in at relatively high electrode potentials of 1.8 V vs. Li^+/Li with solid lithium oxalate and oxalatoborates as the main products (Figure) [1]. Both products contribute to the layer that forms on the electrode, which in turn suppresses further electrolyte decomposition in later cycles. The integration of these experimental techniques allows for a comprehensive understanding of the dynamic processes governing electrolyte stability, which is crucial for the development of more robust Li-ion electrolyte formulations.

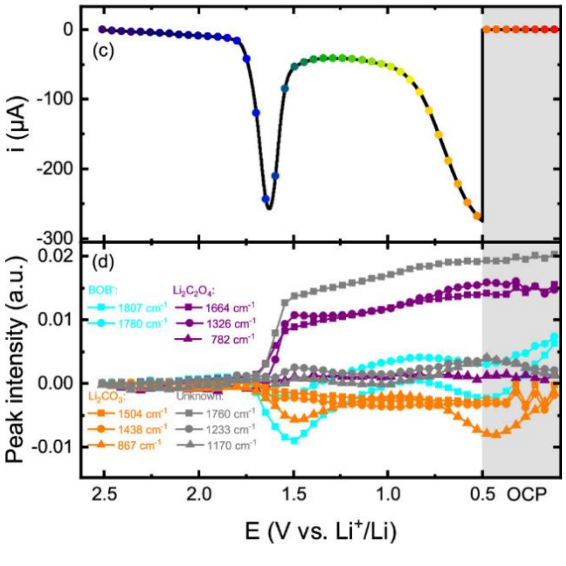

Figure. Current and IR peak intensities of selected molecular bond-environments during reduction of LiBOB at a carbon electrode (Cyclic voltammetry 0.1 mV/s, 2.6-0.5 vs. Li^+/Li).

References.

[1] *J. Phys Chem Lett*, 15 (2024) 2537, DOI: 10.1021/acs.jpclett.4c00328

Understanding interface chemistries to optimize ion dynamics in all solid-state batteries

A. Aguadero[a,b] E. Querel[a], I. Seymour[a], R. Brugge[a], A. Cavallaro[a], F. Pesci[a], Nick Williams[a]
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The need to develop safer batteries with enhanced energy densities is promoting the development of non-flammable solid electrolytes and their integration with alkali metal negative electrodes. A major challenge is the optimization of the dynamic metal/solid electrolyte interfaces that lead to premature cell degradation specially at high current densities. A key parameter is the interfacial adhesion between the alkali metal and the solid electrolyte, which is affected by the kinetics of the stripping currents[1]. Whereas some of these problems can be solved by the application of high pressures or temperatures during operation, the integration of these systems requires optimization of performance in unpressurised systems at room temperature. This can be achieved by interface engineering[2] which requires a deep chemical and structural understanding of surfaces and interfaces affecting ion dynamics and their evolution upon cycling. In this work, we focus on the study of alkali metal/ solid electrolyte interfaces paying particular attention to the effect that surface chemistry has on the charge transfer resistance and stability under high current densities. The study brings a combination of surface sensitive techniques (ex situ and operando) including secondary ion mass spectrometry, low energy ion scattering and x-ray photoelectron spectroscopy with electrochemical and computational analysis. We prove that the surface chemistry of solid electrolytes has a dominant role on the design of stable, high-performance metal/solid electrolyte interfaces and that the tuning of the surface chemistry is a powerful tool to improve the performance of these devices at high current densities[3-5]

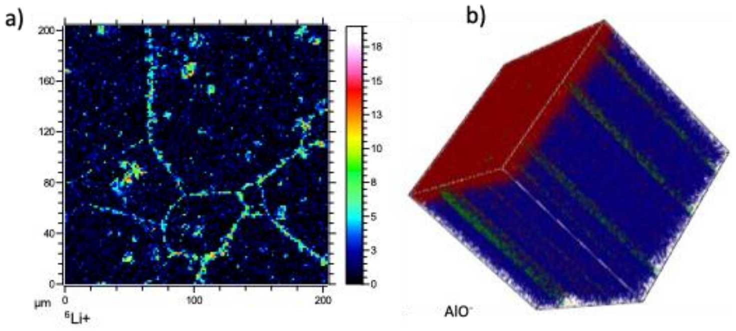

Figure. a) 2D Li^+ chemical map of garnet solid electrolyte and b) 3D reconstruction of AlO^- distribution along anode/solid electrolyte interface

References.

1 I. D. Seymour, E. Quérel, R H. Brugge, F. M. Pesci, A. Aguadero, ChemSusChem, 16e202202215, 2023
2 I. Seymour and A. Aguadero Journal of Materials Chemistry A, 9, 19901, 202, 2021
3- R. Brugge, F. Pesci, A. Cavallaro, C. Sole..A. Aguadero, J. Mat Chem A 8, 14265, 2020
4- E. Quérel, I. D Seymour, A. Cavallaro, Q. Ma, F. Tietz, A. Aguadero, J. Phys. Energy, 3, 2021
5-R. Brugge R. Chater, J. Kilner, A. Aguadero, J. Phys. Energy 3, 034001, 2021
5- E.Quérel, N. J. Williams, I. D. Seymour, S. J. Skinner, A. Aguadero, Chem. Mater. 35, 3, 853–862, 2023

Multiscale Modelling of Electrode/Electrolyte Interface in All-Solid-State Battery

Alexandre Roelens, Annick Hubin, Mesfin Haile Mamme

Sustainable Materials Engineering Research group (SUME), Vrije Universiteit Brussel (VUB), Brussels, Belgium Nowadays the research for the next-generation batteries has intensified, driven by national and international policies. In this context, All-Solid-State Battery (ASSB) has gained in interest as a promising solution to make batteries safer while boosting their energy density. On top of the bulk properties of electrolyte and active materials, the stability of both cathode and anode interfaces is a key factor for long-term high performance. Nevertheless, characterizing heterogeneous interfaces at atomistic scale presents formidable challenges, particularly through experimental methods that necessitate specialized testing facilities (in-situ and/or operando techniques). (Ab initio and reactive) Molecular dynamics have emerged as a valuable tool to investigate buried interfaces. Recently, Relative Bond length Change (RBC) analysis was combined with AIMD simulations to study the long-term stability and compatibility of a broad range of Solid Polymer Electrolytes (SPEs) with key negative/positive electrode materials (graphite, silicon, lithium, LFP, NMC). The results highlighted how the functional groups interactions with electrodes affect their long-term stability and reactivity. Bond length distributions were found to respond to environmental changes and relate to the long-term reactivity. Furthermore, the balancing of the SPE polymer mobility and functional group–electrode surface attraction, respectively, kinetic and thermodynamic properties, further suggests a selective spatial orientation of functional groups when exposed to an electric field, which could have great implications for low-temperature and high-current-density environments. The obtained knowledge on how reactive key SPE polymer functional groups are and also how their reactivity changes in terms of the electric field orientation effect could provide new insights for designing new stable SPE polymers. Some of our findings will be discussed in this workshop.

Studying solid-state batteries during operation using X-rays

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Solid-state batteries are among the most promising energy storage technologies, offering high energy density and enhanced safety, making them ideal for next-generation electric vehicles.[1] However, their widespread adoption is hindered by critical challenges, including Li-dendrite formation, loss of interfacial contact due to electrode volume changes, and chemical incompatibilities between components.[2] Addressing these issues requires a deep understanding of the degradation mechanisms that occur during operation. Yet, studying solid-state batteries under realistic conditions remains challenging, primarily due to the necessity of applying high pressures.

In this talk, we will present our latest advancements in in-situ and operando X-ray studies of solid-state batteries. We will highlight the capabilities of our newly developed equipment, which enables cross-sectional high-energy XRD studies and simultaneous XRD and X-ray absorption spectroscopy (XAS) under controlled stack pressure and temperature. To demonstrate its potential, we will showcase our recent work on solid-state Na-S batteries, where we utilized spatially resolved operando cross-sectional high-energy XRD (spatial resolution <10 μm) in combination with XAS to unravel the polysulfide reaction mechanism and monitor phase and stress evolution in real time.

This study underscores how advanced diffraction and spectroscopy techniques, applied under realistic conditions, provide unprecedented insights into the fundamental processes governing solid-state battery operation.

References.

[1] *Adv. Energy Mater.* ***2023,*** *13, 2301886. https://onlinelibrary.wiley.com/doi/10.1002/aenm.202301886.*
[2] *Nat. Energy* ***2023****, 8, 230–240. https://doi.org/10.1038/s41560-023-01208-9.*

Sampling and Reconstruction Algorithms for low-dose high-speed Acquisition of FIB-SEM/SIMS Images

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We lay the foundation for sparse and adaptive Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) and Secondary Ion Mass Spectrometry (SIMS) imaging, specifically scanning modalities that exploit temporal coherence of time-dependent processes, as well as spatial and spectral redundancy in hyperspectral imaging. To this end, we formulate and test sampling and reconstruction algorithms, which will be implemented on the microscope hardware.

The critical factor studied is the effect of beam damage during image acquisition. To mitigate this, images can be taken at a lower dwell-time, which would result in a lower signal-to-noise-ratio (SNR) or a sparse scan can be implemented with a few pixels omitted [1]. This research focuses on the implementation and evaluation of various algorithms for sparse representation of images. These sparse images are reconstructed and is compared with the lower dwell-time images. It follows the work on adaptive sampling, where images are selectively dosed with varying dwell-times, and compressive sensing-based reconstruction algorithms for random sparse scans [2]. This work tests the effectiveness of random sampling in comparison with full raster scanning of equivalent electron dosage. Additionally, stratified random sampling is introduced, which is compared with random sampling. The goal of stratification is to avoid too many samples being close to each other leaving sparsely sampled areas.

Three reconstruction algorithms (nearest neighbour, linear, and cubic) are used as baselines for comparison. Two metrics, Peak Signal-to-Noise Ratio (PSNR) and Structural Similarity Index (SSIM), are used to assess the fidelity and structural similarity of the reconstructed images. Figure 1 shows PSNR and SSIM plots as a function of sparsity. Although the margin is small, the figures clearly indicate that stratified random sampling is an improvement over random sampling.

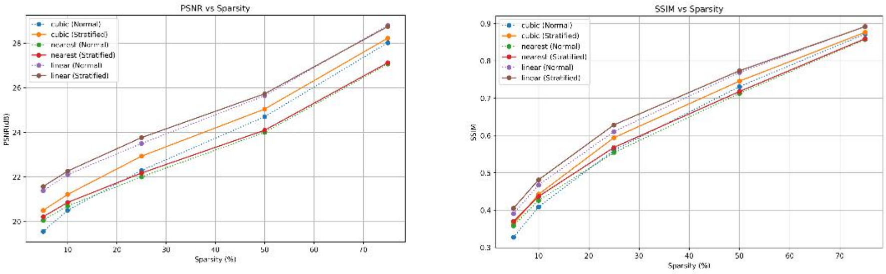

Figure. Evaluation of the sampling and reconstruction algorithms. Uniform random sampling is compared to stratified sampling for different reconstruction algorithms.

References.

[1] *Dahmen, Tim, et al. "Feature adaptive sampling for scanning electron microscopy." Scientific reports 6.1 (2016): 25350.*

[2] *Trampert, Patrick, et al. "Exemplar-based inpainting based on dictionary learning for sparse scanning electron microscopy." Microscopy and Microanalysis 24.S1 (2018): 700-70*

Preliminary investigation of interface evolution in Ge-based lithium ion batteries

Valentina Diolaiti[a], Marco Ricci[b], Alfredo Andreoli[a], Fabio Rossi[a], Leonardo Sollazzo[a], Remo Proietti Zaccaria[b] and Donato Vincenzi[a,c]

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The performance and longevity of lithium-ion batteries (LIBs) are critically dependent on the formation and stability of the solid electrolyte interphase (SEI) at the electrode-electrolyte interface. Germanium (Ge) has emerged as a promising alternative to silicon (Si). However, understanding the interfacial processes occurring at Ge-based electrodes remains an open challenge. To investigate the initial stages of interface formation, Ge-based thin-film electrodes were fabricated via plasma-enhanced chemical vapor deposition (PECVD) and subjected to electrochemical cycling in HF [1]. The fabricated Ge-based electrodes demonstrated an outstanding gravimetric capacity, four times higher than standard graphite [2]. The morphological evolution of the electrodes was monitored using *ex-situ* SEM and TEM, which provided critical insights into surface changes. Furthermore, XPS analysis was employed to determine the surface chemistry of the Ge electrodes before [3] and after cycling. This analysis is essential for understanding the chemical transformations that govern interfacial stability, as well as the impact of electrolyte decomposition products on the long-term electrochemical performance of Ge-based electrodes. The correlation between surface composition and morphological evolution provides a foundation for future optimization of interfacial properties.

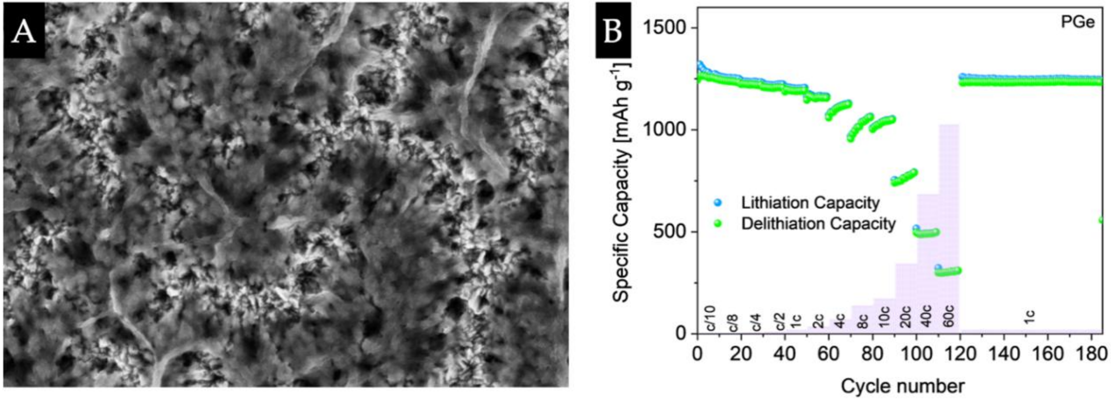

Figure. A) Nanostructured Ge-based electrode. B) Electrochemical tests performed at different C-rates for the porous Ge half-cell.

References.

[1] Diolaiti, V., et al. "Nanostructured germanium anode for lithium-ion batteries for aerospace technologies." *2022 IEEE 22nd International Conference on Nanotechnology (NANO)*. IEEE, 2022.
[2] Diolaiti, Valentina, et al. "Comparison of Porous Germanium Thin Films on SS and Mo as Anode for High-Performance LIBs." *IEEE Transactions on Nanotechnology* (2023).
[3] Fugattini, S., et al. "Binder-free nanostructured germanium anode for high resilience lithium-ion battery." *Electrochimica Acta* 411 (2022): 139832.

Operando Electrochemical Dilatometry to Study Li-Deposition in liquid and solid electrolyte Systems

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Zero-excess lithium metal batteries (ZELMBs) have received enormous attention for their potential to enhance energy density by eliminating additional anode materials, as well as simplifying production, therefore reducing costs, materials, and energy usage. In these batteries, lithium is plated in situ on the anode current collector during initial charging. However, challenges remain due to non-uniform lithium growth, leading to significant volume changes, battery degradation (due to "dead lithium" formation and continuous SEI layer growth), and safety risks from potential short circuits.

Efforts to address these issues focus on modifying current collectors (CC), electrolyte formulations, cycling protocols and the use of solid state electrolytes. Copper foil is a common CC material but suffers from poor lithium wettability, exacerbating non-uniform deposition. Applying thin lithiophilic layers, such as tin (Sn), improves lithium nucleation and adhesion, reducing nucleation overpotential and dead lithium generation. Additionally, designing optimized CCs with minimal inactive mass and volume helps maintain energy density. While these layers show promise, more characterization is needed to fully understand lithium plating and stripping behavior.

Advanced techniques, such as operando electrochemical dilatometry (OED), help monitor lithium deposition and dissolution, providing insight into morphology evolution and the quantification of dead lithium. These insights allow for better assessment of volume expansion, nucleation, and growth behavior during cycling. Herein the use of operando electrochemical dilatometry (OED) is presented to monitor the impact of lithiophilic coatings on the height evolution during Li deposition and dissolution compared to bare Cu, as well as in solid electrolyte systems.

Isotope-Enhanced Battery Interface Characterization

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Studying interfaces, especially operando, is still one of the most challenging characterization approaches. Nuclear Magnetic Resonance (NMR) spectroscopy, neutron imaging, online electrochemical mass spectrometry (OEMS) and focused ion-beam with secondary ion mass spectrometry (FIB-SIMS) imaging constitute a complementary set of isotope-sensitive techniques that have the potential to provide profound insights into the interfacial reactions. While the basic principles of these techniques are rather well established, further development is required for seamless operando workflows with improved resolution and sensitivity, which is our focus within OPINCHARGE project.

In this talk we will discuss challenges and opportunities of these four isotope-sensitive techniques, our methodology developments, delivering exciting new insights (Figure 1) into the peculiarities of surfaces and interfaces of Li-based rechargeable batteries and further pathways for knowledge advancement.

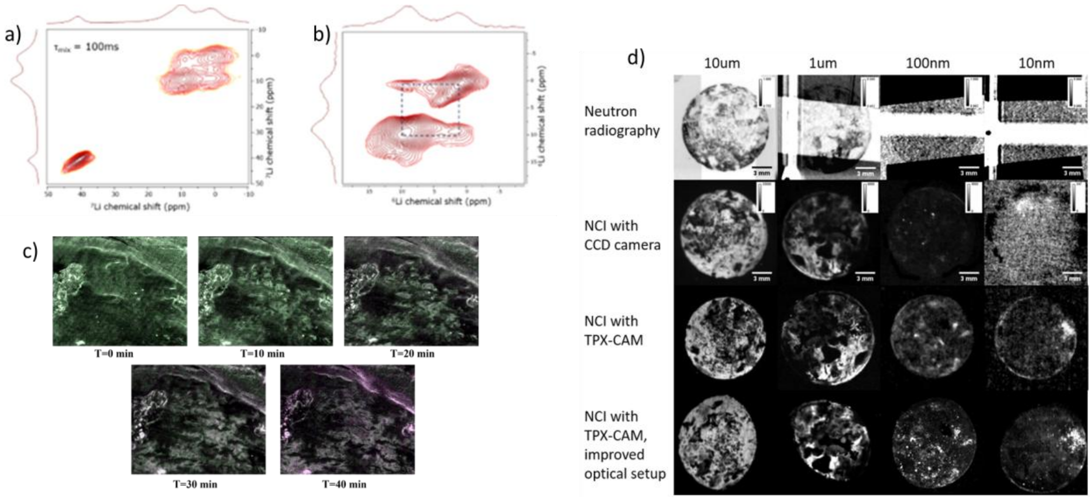

Figure 1. a) ^{7}Li-^{7}Li 2D EXSY NMR and b) ^{6}Li-^{6}Li 2D EXSY NMR experiments, demonstrating Li^{+} exchange between the SEI and Si particles. c) Time-series of overlay of ^{6}Li (Magenta) and ^{7}Li (Green) SIMS elemental maps of same ROI taken during charging. As charging proceeds, there is a relative increase in ^{6}Li counts. d) Images from ex-situ measurements of electrochemically plated ^{6}Li layers by using different neutron powered imaging techniques, and the four columns correspond to 10 um, 1 um, 100 nm, 10 nm average ^{6}Li thicknesses.

Using X-ray nanotomography to understand the improved performance of Li-S battery with binders based on cheese shell waste

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Lithium-Sulfur (Li-S) batteries have emerged due to their high energy density and potential as a promising alternative to lithium-ion batteries. However, addressing challenges such us the shuttle effect remains crucial for their development [1]. Among the key components of the Li-S battery cathode, the binder plays a critical role in maintaining the stability, structure and mechanical integrity of the electrodes during cycling [2]. Although polymeric binders (used in moderate amounts, approximately 10% of the working electrode) are usually non-conductive and electrochemically inactive, they can contribute to the electrochemical performance of the cell by interacting with the polysulfides, trapping soluble sulfur species, improving cathode particles interconnectivity, and preserving structural integrity [3].

In this work, a sustainable binder derived from the recycle cheese shell (RCS-b) for Li-S battery cathodes was studied. Its composition, similar to a wax, favors the particle interconnection within the cathode, achieving superior electrochemical stability during prolonged cycles, compared to commercial binders (STD-b). X-ray nanotomography analysis demonstrates that RCS-b minimizes electrode degradation, preserving the mechanical integrity and reducing active material loss over 1000 cycles These results highlight the potential of RCS-b as an eco-friendly and efficient binder for next-generation Li-S batteries.

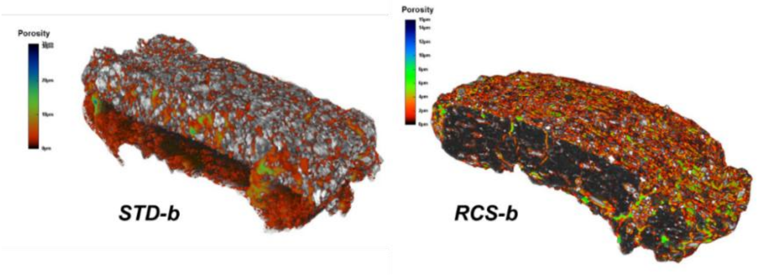

Figure. X-ray nanotomography of electrodes featuring commercial binder (STD-b) and recycled cheese shell binder (RCS-b).

References.

[1] *Adv. Energy Mater.* 7, (2017) 1700260, DOI: 10.1002/aenm.201700260
[2] *ChemElectroChem* 7, (2020) 4158–4176, DOI: 10.1002/celc.202000993
[3] *Adv. Energy Mater.* 8, (2018) 1802107, DOI: 10.1002/aenm.201802107

Acknowledgements

This research was funded by Spanish Ministry of Science and Innovation MICIN/AEI/10.13039/501100011033and the European Union “NextGenerationEU/PRTR” (Projects PID2023-147080OB-I00 & PID2020-113931RB-I00; “Juan de la Cierva – Incorporación” fellowship (IJC2020-045041-I). Iniciativa Federal para el Desarrollo de Materiales y Procesos Sustentables para el Almacenamiento de Energía, EX-2023-42139041–APN-DDYGD#MCT.

Experimental charge transport characteristics for interface and interphase modelling

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One of OPINCHARGE's goals is the development of mesoscale continuum models that predict solid electrolyte interphase (SEI) growth. For this purpose, we develop experimental scale-bridging methodologies to enhance the foundational understanding of SEI properties. Combined with modelling, this enables us to provide feedback to characterization techniques for tailoring measurements more specifically to the unknown quantities and improving their accuracy. In this contribution, we conceptualize OPINCHARGE's experimental efforts to reveal interface charge transport characteristics and summarize our first results.

To quantitatively elucidate electronic transport mechanisms and rates across the SEI, we use redox probe molecules (e.g., Fc/Fc^+ redox couple) to probe the mechanism and rate of electron transfer from electrode (e.g., Pt, Si) to the redox molecule. Complementarily, we probe the ionic transport properties and evolution of interfacial impedance using electrochemical impedance spectroscopy (EIS). We investigate the corresponding SEI's structural and chemical parameters using electrochemical quartz crystal microbalance (EQCM) and other *operando* techniques. Our initial results indicate unexpected and intriguing dynamic SEI behavior.

Moreover, we investigate chemo-mechanical phenomena of the SEI in silicon electrodes, with a focus on how the silicon shell and its mechanical properties govern electrochemical behavior. In our dedicated experiments, the electrode-electrolyte interface is modified by tailoring the electrolyte system and formation protocols while we monitor its evolution and the electrochemical response upon cycling. To deconvolute the intrinsic active material behavior from effects that are influenced by the electrode microstructure and the composition of the composite electrode, a single-particle measurements setup is developed and employed in addition to electrode-level studies.

Furthermore, we experimentally investigate the SEI layer forming on Si electrodes for various electrolytes. Besides differential capacity analyses to determine the reduction order of each electrolyte salt and solvent, contributions of each reduction product are compared in terms of resistivity. For this purpose, changes in cell resistances are monitored by EIS as a function of state-of-lithiation. Possible benefits and disadvantages of the expected SEI components will be discussed.

Finally, we aim at overcoming present problems of typical reference electrode materials (i.e., lithium metal, lithium alloys, etc.) related to measurement irreproducibility and potential drifts of steady-state potential. Towards this end, we employ intercalation compounds (i.e., LFP, LTO, etc.), which exhibit distinctive plateaus that may allow more accurate potential monitorization of cathode and anode. Specifically, we integrate a micro-mesh, coated with LTO, into the cell configuration with the possibility to activate and re-calibrate the reference electrode during cell operation.

Lithiation behavior of metal components for Li-ion batteries by ion beam analysis

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Metal components are widely used as current collectors, anodes, and interlayers in lithium-ion batteries. Proposals to integrate all these functionalities into a single metal component would significantly enhance the energy density of the cell and streamline its design. [1] However, this multifunctional component must also adhere to more stringent requirements, including a high and reversible Li storage capacity, rapid lithiation and delithiation kinetics to enhance rate performance, mechanical stability, and improved safety. The lithiation behavior of six single-atom metals (Al, Sn, Zn, Ag, Mg and Cu) was investigated to screen their capabilities to potentially be used as interlayers or anodic current collectors in Zero-Excess Li-Ion Batteries (ZELIB). [2] These metals were analyzed using ion beam analysis on electrochemically tested samples subjected to both weak and strong lithiation regimes. Three types of ions/projectiles were employed to thoroughly determine the Li depth profile: H^+ for measuring Li content via nuclear reaction $^7Li(\alpha,p)^4He$, He^+ for estimating how Li dilutes the metal host lattice through Rutherford backscattering, and Ga^+ to evaluate the impact of Li content on focused ion beam milling from the surface down to several microns in depth. The investigation revealed three distinct lithiation behaviors beyond the kinetic limitations of the weak lithiation regime: (i) Al, Sn, and Zn form pure intermetallic alloys with Li; (ii) Ag and Mg create solid solutions; and (iii) Cu acts as a lithiation barrier, resulting in rough Li plating. These findings are consistent with the binary Li-metal phase diagrams of the studied systems and fit well with ab—initio simulations.

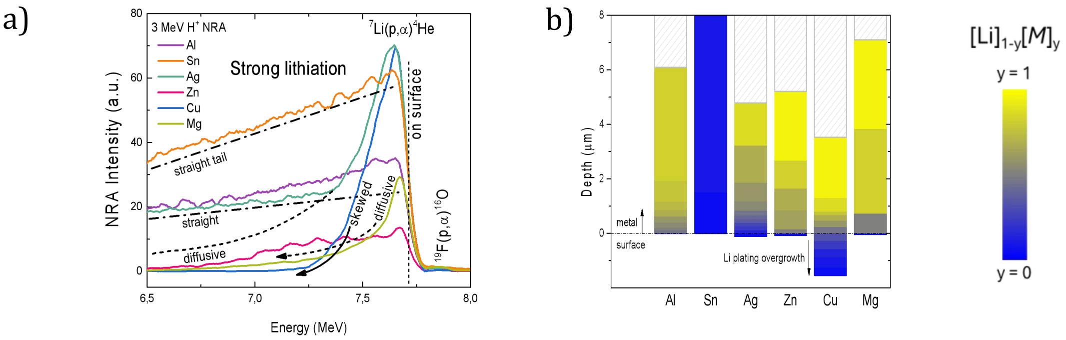

Figure. (a) Li NRA bands of the metal foil samples after strong lithiation, and (b) color gradient representation of their $[Li]_{(1-y)}$ $[M]_y$ composition profiles, where [ ] indicates atomic concentration.

References: [1] Jeong, W. J. et al, ACS Energy Letters **9** (2024) 2554–2563, DOI: 10.1021/acsenergylett.4c00915

[2] Genovese, M. et al, J. Electrochem. Soc. **165** (2018) A3321–A3325, DOI: 10.1149/2.0641814jes

Operando Raman Microscopy for $LINIO_2$ electrodes, data processes advances with prisma app

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The growing demand for high-performance Li-ion cells nowadays has encouraged researchers to deeply understand the evolution of the various battery's components over time. Ageing mechanisms have a great impact on the battery life performance; therefore, a better understanding of these complex processes may allow the prolongation of their useful cycle life. Monitoring the cathode material during battery operation is crucial since it represents the performance-limiting component in most of the LIBs [1]. Particularly, cobalt free lithium transition metal oxides are currently gaining interest as active materials for enabling higher energy density cells. Among them, $LiNiO_2$ presents relatively high capacity and long durability. However, this material suffers from fast capacity loss and thermal instability at highly deintercalated states due to its non-stoichiometric composition [2]. The mechanisms involved in the capacity fade remain still unclear making it crucial to understand these processes throughout cycling.

Among the methods available to perform *operando* measurements for Li-ion electrodes, Raman spectroscopy is well stablished to track structural evolution and chemical composition during charge and discharge [4,5]. With this work, an optimised electrode configuration [5] is presented which enables the monitoring of the different electrode phase transitions over several cycles. The developed methodology was applied for the investigation of $LiNiO_2$ active material as a benchmark to understand the evolution of lithium metal oxides among time. The spectra collection obtained was rapidly analysed via the analysis tool PRISMA [7]. Overall, the ability of *operando* Raman as a pertinent diagnostic tool to follow electrodes behaviour during commercially relevant cycling conditions is demonstrated.

[1] Matteo Bianchini et al. *Angew. Chem. Int. Ed.* (**2019**), 10434-10458, 58(31).
[2] Edgar Bautista Quisbert et al. *Small* (**2023**) 19 (30) 2300616.
[3] Hui et al. *J. Am. Chem. Soc.*(**2022**) 9434-9442, 144(21)
[4] Sole et al. *Faraday discussions* (**2016**) 223-231, 72
[5] Timothy E. Rosser et al, *J. Electrochem. Soc*. (**2021**), 070541 (168).
[6] Flores E et al. *Chemistry-methods* (**2022**) 2(10).

Interface and Interphase Modelling Approaches Within OPINCHARGE

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The OPINCHARGE modelling activities aim to generate an improved understanding of interfaces and interphases inside lithium-ion batteries. The DLR investigates the chemo-mechanical interaction between next-generation silicon anodes and the covering SEI layer. It was identified that the mechanical deformation of the shell in a core-shell setup causes the experimentally observed voltage hysteresis and slow voltage relaxation of silicon nano-anodes [1, 2]. Based on the chemo-mechanical knowledge, the DLR derived a simplified and easy-to-use voltage hysteresis model that preserves the physical information at the interface and captures voltage relaxation processes [2]. Recently, the study was generalized from a spherical symmetric setup to elliptical nanowires to identify the effect of asymmetric geometries. Therein, local changes in the surface-to-volume ratio of the anode lead to heterogeneous stress and lithium concentration distributions [3].

CIDETEC complements with research on the growth of SEI layer during formation process based on kinetic Monte Carlo (kMC) model interactions among electrode and electrolyte particles. Current improvements focus on the combination of kMC with a macroscale model, Single Particle Model (SPM), to be able to capture the voltage evolution during the entire SEI formation process. Further, to streamline feature extraction in experimental cells to parametrize and validate the models, CIDETEC is also creating Distribution of Relaxation Times (DRT) model based on ML to create an automatized methodology to analyze Electrochemical Impedance Spectroscopy (EIS) tests.

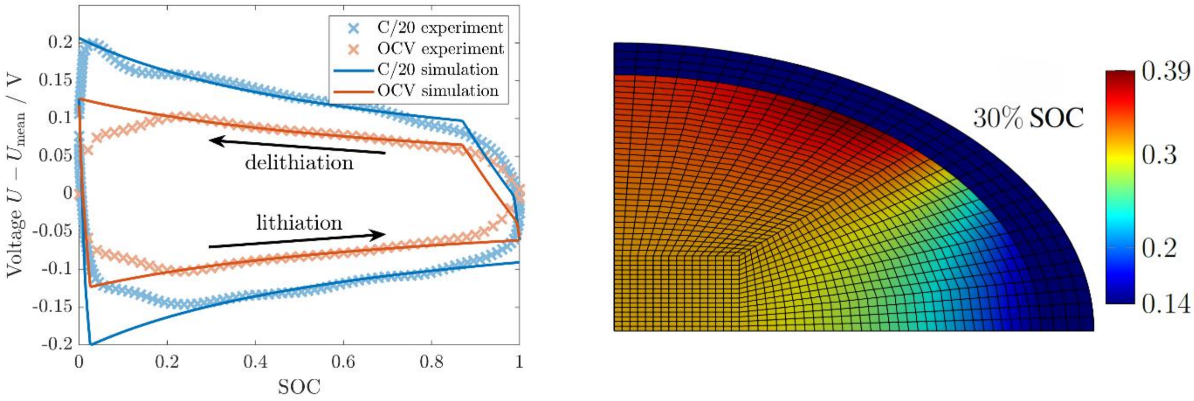

Figure. Voltage hysteresis of spherical silicon-SEI system in reduced model [2] and lithium concentration distribution in elliptical nanowire covered by SEI [3].

References.

[1] *Adv. Funct. Mater.* 34 (2024), 7, 2308818, DOI: 10.1002/adfm.202308818.
[2] *ACS Appl. Mater. Interfaces* 16 (2024), 49, 67609-67619, DOI: 10.1021/acsami.4c12976.
[3] *Batter. Supercaps* (2025), e202400604, DOI: 10.1002/batt.202400604.

An Approach to Studying Interfaces in Sodium-Ion Batteries (SIBs): Application of Characterization Techniques

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Sodium-ion batteries (SIBs) have gained significant attention as a promising alternative to lithium-ion batteries, particularly for large-scale energy storage applications due to the abundance and low cost of sodium. However, the performance and durability of SIBs are highly dependent on the complex physical and chemical processes occurring at the electrode-electrolyte interfaces. Despite their potential, a detailed understanding of these phenomena remains a key challenge for their development [1, 2].

This oral presentation offers an introduction to SIBs, focusing on the critical characteristics of the electrode-electrolyte interfaces and how advanced characterization techniques, such as TEM, XRD, SEM and EIS, have been helpful in studying these processes. The main challenges facing SIBs, including interface stability and the formation of solid electrolyte interphase (SEI) layers, will be approached by a discussion about how experimental tools have enabled the observation of material morphological evolution during charge/discharge cycles and the dynamics of electrochemical reactions.

Through examples from recent studies, it will be illustrated how those techniques have provided valuable insights into ionic transport mechanisms, SEI formation, and the interactions between the system components.

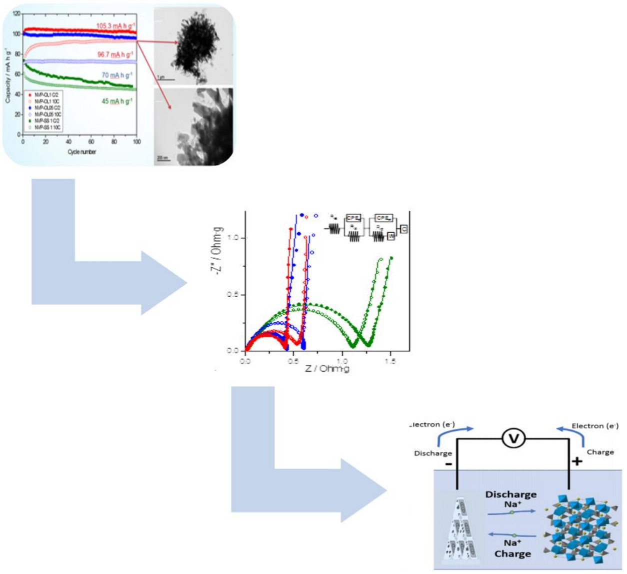

Figure 1. Approach to Studying Interfaces in Sodium-Ion Batteries.

References.

[1] *Future Batteries,* 4 (2024) 100010, DOI: 10.1016/j.fub.2024.100010
[2] *Nature Chem.* 7 (2015) 19, DOI: 10.1038/nchem.2085
[3] *EER,* 5 (Suppl 1), (2022) 20, DOI: 10.1007/s41918-022-00137-7

Interlayer Metals for Zero-Excess Solid-state Batteries: A Multiscale Approach Combining Machine Learning Potentials and DFT

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The concept of anode-free or zero-excess lithium batteries (ZELBs), has attracted a lot of interest as it simplifies the battery manufacturing process, improves safety, and could bring significant cost reduction.[1] However, the Li stripping/plating occurring on the surface of the commonly adopted Cu current collector, are one of the main disadvantages of ZELBs.[2] In this work, we present an efficient computational workflow to screen the performance of interlayer metals at the anode side, aiming to obtain stable deposition/stripping process of Li during operation. We performed density functional theory (DFT) calculations to investigate Li deposition on 14 interlayer metals, including those forming solid solutions with Li (Ca, Mg, Tl, Zn, Al, Sb, Ag, Au, Pt), those forming intermetallic alloys with Li (Sn, Si, Ge), and those non-alloying with Li (Cu, Ni). We evaluated the adsorption energy (E_{ads}), substitutional energy (E_{subst}), and Li diffusion barriers. For all materials that form solid solutions with Li, a more negative E_{subst} compared to E_{ads} was observed, indicating that at the specified concentration, Li more favourably replaces atoms in the interlayer through a substitution mechanism rather than surface deposition. The solid solution alloy layer increased the binding strength of Li on Ca, Mg, Tl, Zn, and Sb. Conversely, lithiated sites in the Al, Sb, Ag, Au, and Pt solid solution alloys surfaces reduced the energy barrier for Li diffusion. We compared the aforementioned properties to propose which alloys concentrations perform more efficiently during Li deposition. We conducted large-scale molecular dynamics simulations using machine learning interatomic potentials (MLIPs), trained with DFT data, for the Li-Cu, Li-Zn, Li-Mg, and Li-Sb systems, considering varying amounts of Li metal. For the Li-Cu interface, we observed that with low amounts of Li metal, Li atoms tended to adsorb on top of one another, forming clusters and leaving empty spaces on the Cu surface. At higher Li concentrations, Li metal did not retain its stable bcc structure at the Li-Cu and Li-Zn interfaces. Solid solution formation was observed at the Li-Zn and Li-Mg interfaces, with a larger presence of hcp lattice in the former and bcc lattice in the latter. Finally, we predicted that, instead of forming a solid solution, Li preferentially forms intermetallic alloys at the Li-Sb interface, based on the morphology and coordination analysis.

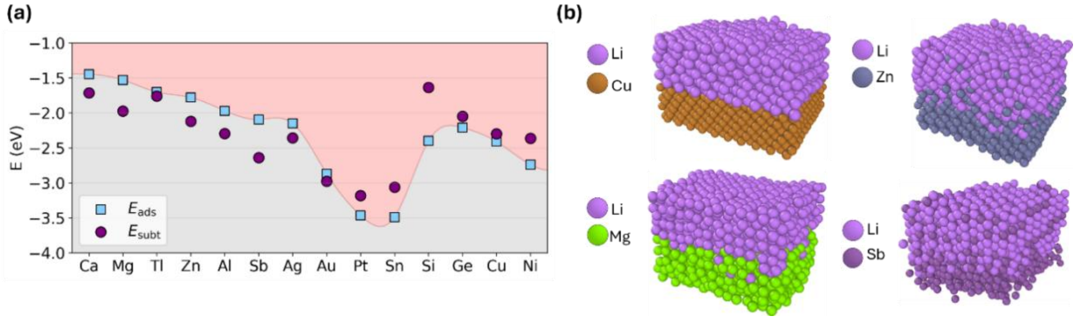

Figure. (a) Adsorption energy and substitional energu for the materials screened in this work. (b) Snapshots of the molecular dynamics simulations for the Li-interlayer interfaces studied here.

References.

[1] *Albertus, P. et al. ACS Energy Lett. 6 (2021) 1399, DOI: 10.1021/acsenergylett.1c00445*

[2] *Huang, W. et al. Adv. Energy Mater. 12 (2022) 2201044, DOI: 10.1002/aenm.202201044*

In situ synchrotron x-ray diffraction study of Zn/Bi_2O_3 electrodes prior to and during discharge of Zn-air batteries: Influence on ZnO deposition

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In this communication Zn-based electrodes containing different amount of Bi_2O_3 will be analyzed by synchrotron XRD during the discharging process of a real Zn-Bi_2O_3/air battery. Although Bi_2O_3 is clearly detected for pristine Zn-Bi_2O_3 based electrodes, when it was immersed in 6M KOH solution before starting the discharge resulted in the disappearance of Bi_2O_3 XRD signature in the pattern and the appearance of new peaks indicating the presence of metallic Bi, regardless of the amount of Bi_2O_3 initially included in the Zn-Bi_2O_3 electrodes. This behavior together with Open Circuit Voltage measurements points to a spontaneous reduction of Bi^{3+} to metallic Bi by the oxidation of Zn to Zn^{2+}. Irrespective of the amount of Bi_2O_3 present in the negative electrodes, Zn XRD peaks diminish as the discharge proceeds. However, the initial amount of Bi_2O_3 clearly affects ZnO and Bi metal XRD peaks. ZnO peaks do not appear in the XRD patterns obtained for higher quantities of Bi_2O_3 electrodes. Besides, in this case metallic Bi peaks are observed during all discharging processes, indicating that Bi remained in the electrode.

This work led us to the design of a new type of rechargeable alkaline battery composed by a Bi_2O_3 positive electrode and a Zn negative one, which will also be discussed.

Acknowledgements

The authors acknowledge funding for project PID2022-139191OB-C32 funded by MICIU/AEI /10.13039/501100011033 and FEDER, UE.

References.

[1] *F. Santos, J. Abad, M. Vila, G.R. Castro, A. Urbina, A.J. Fernández Romero.* Electrochimica Acta 281 (2018) 133, DOI: 10.1016/j.electacta.2018.05.138
[2] *S. Lorca, F. Santos, J. Abad, Y. Huttel, A. Urbina, A.J. Fernández Romero.* Sustainable Energy and Fuels 4 (2020) 4497, DOI: 10.1039/d0se00551g

Operando synchrotron X-ray diffraction for multivalent cations intercalation

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Notwithstanding the ubiquitous presence of Li-ion batteries (LIBs) in portable applications, research in alternative technologies based on abundant elements which could provide higher energy density is currently expanding. Amongst them, magnesium metal batteries have emerged as one of the most promising candidates. However, their practical deployment is plagued with diverse hurdles such as the sluggish Mg^{2+} solid-state diffusion caused by the strong coulombic interactions between Mg^{2+} and host material. Different cathodes materials have attracted great attention like Vanadium pentoxide. In contrast with the large number of studies devoted to α-V_2O_5, other polymorphs have deserved less attention. Herein, we present proofs of the feasibility of magnesium insertion and de-insertion in β-V_2O_5 polymorph as Mg-cathode. On the other hand, Prussian Blue Analogs (PBAs) have been proposed as versatile materials able to intercalate numerous multivalent cations, however, we demonstrate here that such claims are not always supported by rigorous analysis methodologies and structural characterization, proving that detail attention must be taken to avoid K^+ or Na^+ co-intercalation. Finally, battery recycling is also attracting great attention to reduce LIBs waste environmental footprint, ensure critical material supply and reduce third country dependency for LIBs manufacturing. We demonstrate also here, the possibility to use PBAs as Ni^{2+}/Co^{2+} intercalation electrodes to recover these valuable metals from batteries spent. The electrochemistry features were ascribed unequivocally to the intercalation/deintercalation of Mg/Ni/Co in the structure and the associated reduction/oxidation of transition metal by a deep structural study which includes among other techniques operando S-XRD or X-ray absorption spectroscopy.

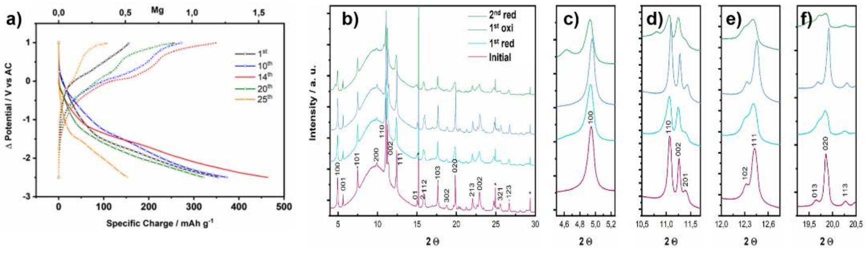

Figure. Selected cycles of β-V_2O_5, b – f) operando S-XRD diffraction patters obtained.

References.

[1] *ACS Appl. Energy Mater.*, 5 (2022) 11964, DOI: https://doi.org/10.1021/acsaem.2c02371

[2] ChemSusChem. (2023) e202301224, https://doi.org/10.1002/cssc.202301224

Monitoring Kinetics of Structural Changes in Solid-State Batteries

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Optimizing the performance of solid-state batteries (SSBs) requires a comprehensive understanding of structural parameters, including phase transformations and chemo-mechanical stresses [1] . This presentation provides a concise overview of the capabilities of scanning high-energy X-ray diffraction (HR-XRD) in addressing these critical aspects. We will begin by emphasizing the significance of monitoring residual stresses arising during SSB fabrication, particularly those induced during the die-pressing of the separator and cathode powders. Subsequently, we will examine the evolution of the spatial distribution of the stress field within the SSB during cycling. Finally, we will demonstrate the importance of simultaneously evaluating phase and stress evolution, particularly in understanding the lithiation/delithiation processes in high-capacity cathode layers. A focus will be on spatially-resolved mapping of Li diffusion within the cathode material.

This work was funded by the European Union’s Horizon Europe research and innovation program under grant agreement No. 101103834 (OPERA). The authors acknowledge the financial support of project APVV-20-0111

References.

[1] J. Janek, W. G. Zeier, *Nature Energy 2023 8:3* **2023**, *8*, 230.

Real-time monitoring of transition metal dissolution and cross-contamination in operating Lithium-ion batteries

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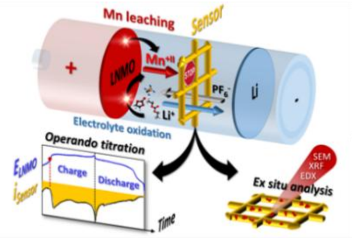
Chemical crosstalk in functioning batteries, which describes the shuttling of electrolyte soluble reactive species through the separator and the disruption of the electrode operation, is a major concern, which impacts the development of new electrode generation for lithium or sodium ion/metal batteries and therefore needs to be addressed urgently. The development of crosstalk sensing techniques that operate under conditions as close as possible to those of functional battery cells and that offer a trade-off between cumber-some/ costly implementation and powerful analytical resolution is the subject of intense research efforts. (operando RRDE[1], SECM[2], fluorescence microscopy[3], XAS4,[5] OEMS[6], NMR/EPR[7]).

In the Opincharge project, a powerful and relatively simple cross-talk sensing technique based on the electrochemical trapping of redox shuttles is developed and applied to different positive electrodes. Leaching and transport of transition metal species from the positive composite electrode and of electrolyte oxidation products could be evidenced, quantified and tracked by our group upon cycling of a LNMO/Li battery system[8]. Ongoing work aims to improve the capture efficiency, sensitivity and selectivity of the sensor, while minimizing its electrochemical footprint on battery operation.



Operando crosstalk sensing. A polarized Pt mesh (constant voltage: 1 V vs Li/Li^+) is positioned between the two electrodes of a battery system (T-shape Swagelok cell) to detect and trap transition metals (Mn, Ni, Co…) leaching from the positive electrode and migrating toward the negative electrode upon cycling of the battery.

References.
[1] J. Electrochem. Soc. 150 (2003), A905, doi.org/10.1149/1.157754
[2] J. Electroanal. Chem. 687 (2012), 30, doi.org/10.1016/j.jelechem.2012.08.021
[3] Electrochem. Commun. 34 (2013), 29, doi.org/10.1016/j.elecom.2013.04.007
[4] J. Mater. Chem. A 4 (2016), 18300, doi.org/10.1039/c6ta08865a
[5] J. Electrochem. Soc. 166 (2019), A378, doi.org/10.1149/2.1151902jes
[6] J. Electrochem. Soc. 165 (2018), A3304, doi.org/10.1149/2.0511814jes
[7] Mater. Au 3 (2022), 3, 88, doi.org/10.1021/acsmaterialsau.2c00060
[8] J. Pow. Sources (2025), 630, 236031, doi.org/10.1016/j.jpowsour.2024.236031

Nucleation and early-stage growth of Li and Na anodes in ZESSBs at the nanoscale by synchrotron-PEEM and AFM

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Zero-Excess Solid-State Batteries (ZESSBs), where the anode forms in situ during charging, have gained attention for their potential to enhance energy density and simplify manufacturing, reducing costs and resource use. However, practical implementation faces challenges due to uneven alkali metal anode growth. Despite various strategies for uniform anodes, the microstructural evolution during nucleation and early growth remains largely unknown [1].

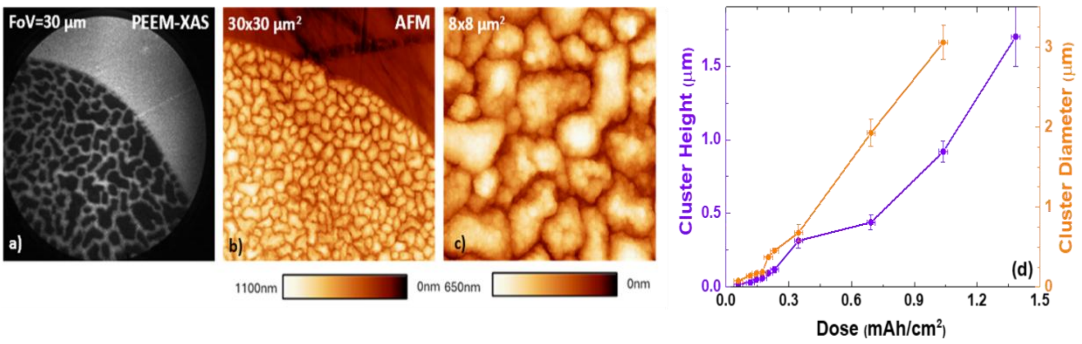

Figure. Images of the Na anode grown on NaGdSiO electrolyte taken by a) PEEM-XAS (hν=1057 eV, Na K-edge), for 30 µm Field of View (FoV) and AFM for b) 30x30 µm^2 and c) 8x8 µm^2. Anode was grown for 60 min with Ie=0.3 µA and E_e=6 eV what results in D_e=0.69 mAh/cm^2 d) Cluster mean height and diameter evolution with electron irradiation dose.

We investigated the initial stage of Li and Na anode formation in ZESSBs by mimicking the current collector with a virtual electrode (Figure). Analysis at the nanoscale of the chemical composition, oxidation state and morphology of the anodes were anaysed in-situ by synchrotron Photoemission Electron Microscopy (PEEM) and Atomic Force Microscopy (AFM) in glovebox. We have determined a constant grain aspect ratio during growth, and that anode growth in ZESSBs is not determined by electrolyte grain boundaries or by physical current collectors.

Our findings highlight the virtual electrode method as a powerful tool for investigating the nucleation and early-stage growth of anodes at the nanoscale, revealing how experimental conditions such as temperature, current or conditions at electrolyte interface can significantly influence the growth efficiency.

References.

[1] *Nat. Mater. 23, 1678-1685 (2024)* DOI: 10.1038/s41563-024-02006-8

A Fast-X-Ray Reflectivity Setup for Sub-Second *Operando* Studies of Electrochemical Interfaces

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A fundamental understanding of atomic scale processes occurring at electrochemical interfaces is crucial for advancing the development of energy-related electrochemical systems such as batteries or fuel cells. For this purpose, *operando* experiments are imperative. X-ray reflectivity (XRR) is a non-destructive technique that enables *operando* analysis of buried structures at electrochemical interfaces with atomic resolution [1,2]. However, the time-resolution of typical XRR setups of minutes per XRR scan is limited by diffractometer motor motion (and detector read-out times). In many cases, this is too slow to observe the interfacial phenomena of interest [1,2].

To overcome these limitations, we developed a novel fast-XRR (fXRR) setup, which employs a fast quasi-continuous rotation stage in combination with a stationary, high frame rate area detector. With this setup, the sample can be rotated with a frequency of up to 10 Hz, yielding sub-second time resolution for an individual XRR scan. In contrast to complementary fXRR setups [3,4], our fXRR setup can be straightforwardly combined with complex and relatively large/heavy sample environments, such as electrochemical cells including housing.

In this contribution, we present the concept and data reduction pipeline of our fXRR setup and show results obtained at PETRA III beamline P08 at DESY using 18 keV and a Dectris Eiger 1M detector. We reached a time resolution below one second for an incident angular range of 0° – 6° ($\triangleq 0 – 0.9$ Å^{-1}). We measured several multilayer samples and benchmarked the results to “standard” XRR measurements, where the measurements took several minutes. Exemplary results are shown in Figure 1, where two fXRR measurements (5 s and 0.5 s per scan) are compared to measurements of the same sample with standard setups, where the measurements took 10 min and 13 min, respectively. We find good agreement and conclude that our novel setup provides significant XRR data in less than one second, demonstrating its usability for *operando* XRR measurements. Finally, we will show first results from *operando* fXRR of silicon interfaces relevant to lithium-ion batteries with a focus on the initial lithiation mechanism and the nucleation and growth of the solid electrolyte interphase.

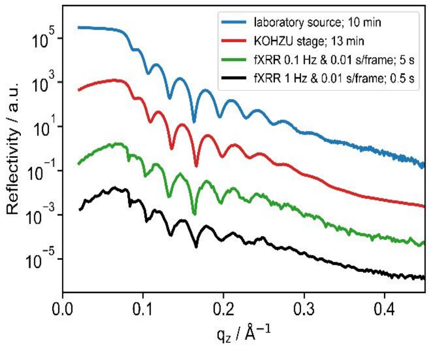

Figure 1: Comparison between two fXRR measurements and two standard XRR scans.

References.
[1] C. Cao, H.–G. Steinrück, *Encyclopedia of Solid-Liquid Interfaces.* (2024) 391, DOI: 10.1016/B978-0-323-85669-0.00105-7
[2] C. Cao, H.–G. Steinrück et al., *Nano Letters*, 16, (2016) 7394, DOI: 10.1021/acs.nanolett.6b02926
[3] M. Lippmann et al., *Review of Scientific Instruments*, 87, (2016), 113904, DOI: 10.1063/1.4967239
[4] H. Jorres et al., *Applied Physics Letters*, 114, (2019), 081904, DOI: 10.1063/1.5085063

POSTER SECTION

Structure-dependent electromechanical properties of epitaxial $LiCoO_2$ cathodes

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The all thin-film lithium-ion batteries (LIBs) attract considerable attention as model systems to investigate at micro and nanoscale the physical mechanisms underlying the operation of commercial batteries and other microelectronic devices [1]. Among the cathodes suitable for solid state LIBs, $LiCO_2$ stands out for exhibiting a distinctive negative chemical expansion coefficient β (i.e. its volume shrinks upon lithiation) which can be used to offset for the typical volume expansion of the rest of the commercial cathodes. This property makes $LiCO_2$ an excellent candidate for creating "zero-strain" cathode blends. However, since lithiation/delithiation in $LiCO_2$ occurs through the movement of boundaries between coexisting domains, namely, insulator $\mathrm{Li_{x>0.93}CoO_2}$ and metallic $\mathrm{Li_{x<0.75}CoO_2}$, it is essential to reinterpret macroscopic β in terms of the balance between local β.

In this work, we investigate the microstructure and the local map of β coefficients in epitaxial $LiCO_2$ cathodes deposited by pulsed laser deposition (PLD) on single-crystal (100) $SrTiO_3$ substrates, which was previously coated with a thin-film $SrRuO_3$ electrode (Figure). For this purpose, the individual layers of the system are microstructurally analyzed by SEM and EDX [2]. The crystalline phases presented in the epitaxial LCO structures are identified using Raman spectroscopy and XRD. The local map of the coefficient β is analyzed by cAFM [3],[4]. Some preliminary results are shown below:

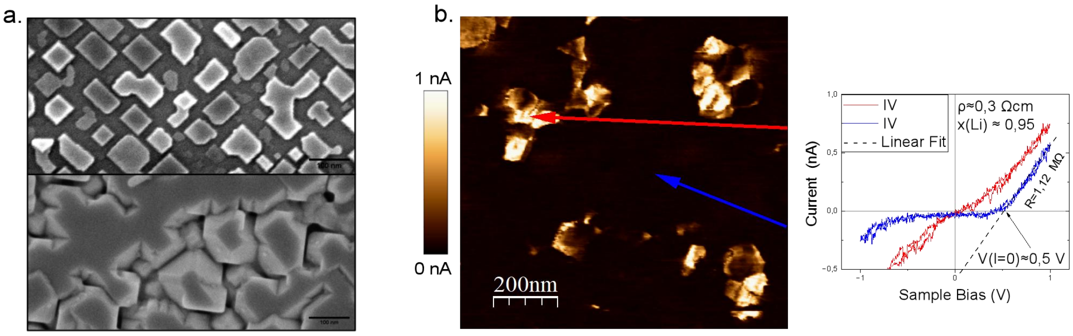

Figure. (a) Different growth stages of epitaxial LCO by SEM; (b) Electrical response at nanoscale of LCO by cAFM.

References.
[1] E. J. Fuller, et al. ACS Nano 16 363-371, (2022). DOI: 10.1021/acsnano.2c05594.
[2] Z. Li, et al. Thin Solid Films. 612, 472-482, (2016). DOI: 10.1016/j.tsf.2016.05.017.
[3] V. A. Smirnov, et al. Tech. Phys. 63, 1236–1241 (2018). DOI:10.1134/S1063784218080182.
[4] A. Milewska, et al. Solid State Ionics. 263, 110-118 (2014). DOI: 10.1016/j.ssi.2014.05.011.

Optimizing Acquisition Parameters to Minimize Beam Damage for Battery Materials

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In high-resolution STEM EELS studies of battery materials, long acquisition times and high electron doses may degrade sensitive interfaces. To address this issue, it is important to control total dose and dose rate. These factors can be adjusted through parameters such as beam current, dwell time, pixel size, sampling number, and probe size [1-3]. A recent study also emphasizes the role of scan patterns in reducing beam-induced damage [4]. Currently, determining the optimal settings relies on extensive trial and error and is highly dependent on the microscopist's experience.

In this work, we present a systematic approach to optimize acquisition parameters, thus mitigating beam damage while maintaining the highest possible spatial resolution. We first experimentally measure the critical dose from a series of diffraction patterns (Figure 1a). This value gives an average electron dose the sample can tolerate before damage occurs [5]. In the modelling part, we predict the beam influence on the sample beyond the area of the initial beam location. Combining the experimental measurements and modelling, our method recommends the best acquisition parameters for a battery sample under given conditions.

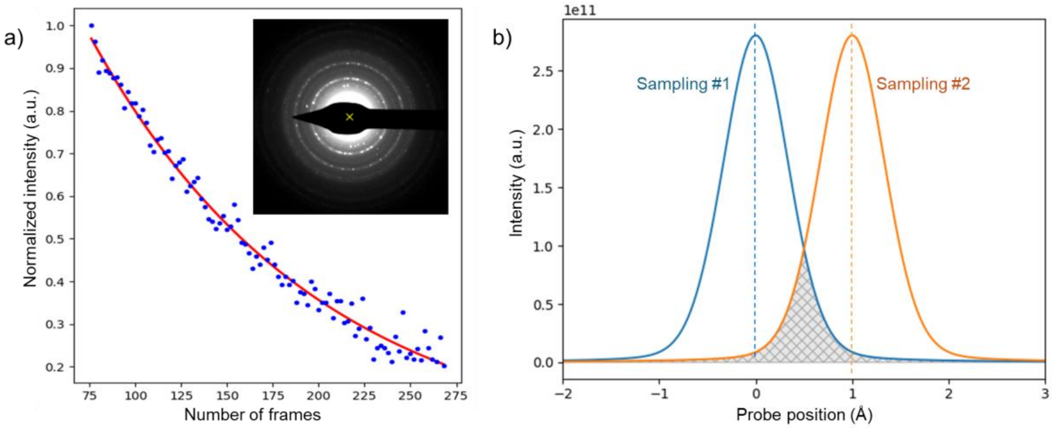

Figure 1. (a) Calculation of the critical dose from the decay rate of the normalized intensity in electron diffraction patterns. (b) Modeling of electron-beam broadening at consecutive sampling points.

References

[1] Demers H, et al. *Microsc Microanal*., 2012, 18(3), 582-590.
[2] Verbeeck J, et al. *Ultramicroscopy*, 2012, 120, 35-40.
[3] Nicholls D., et al. *Nanoscale*, 2020,12, 21248-21254.
[4] Velazco A., et al. *Ultramicroscopy*, 2022, 232, 113398.
[5] Jain N., et al. *Micron*, 2023, 169, 103444.

Acknowledgement: The authors thank the OPINCHARGE project, which received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101104032.

Improving the Electrochemical Performance of Metal-Sulfur Batteries through Magnetism and Sustainability

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Metal-sulfur batteries are regarded as one of the most promising technologies for energy storage, owing to their high energy density and sustainable characteristics [1,2]. Nevertheless, their commercialization is impeded by several challenges, including slow reaction kinetics and the shuttle effect. Among the various approaches proposed to address these obstacles, a novel alternative, the introduction of an external magnetic field in ferromagnetic materials, has recently garnered significant attention [3].

This study introduces an innovative approach that combines recycled ferrite with an external magnetic field generated by a permanent magnet, achieving significantly improved reaction kinetics and polysulfide adsorption, thus improving electrochemical stability. Under the effect of the magnetic field, the cells show lower polarization, higher Li^+ diffusion coefficient and up to 40% higher retention capacity. In addition, capacities close to 500 mAh g^{-1} are obtained at charge and discharge rates of only 6 minutes and an areal capacity of 3 mAh cm^{-2} with ultra-high sulfur loading of 13 mg cm^{-2}. Beyond its outstanding electrochemical performance, this approach is also more environmentally sustainable, as it uses recycled electronic waste processed through dry milling, removing the reliance on fossil-based carbon.

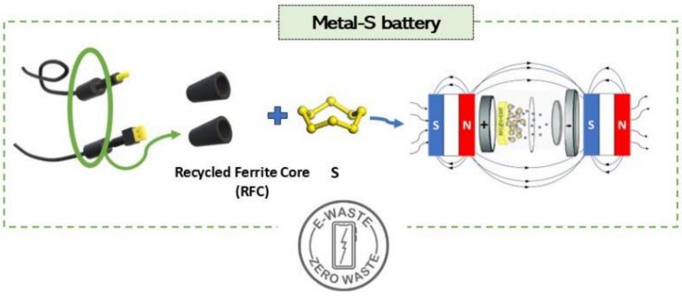

Figure. Illustrative diagram of this study.

References.
[1] *Adv. Mater.* 31 (2019) 1901125, DOI: 10.1002/adma.201901125
[2] *J. Power Sources.* 608 (2024) 234613, DOI: 10.1016/j.jpowsour.2024.234613
[3] *Angew. Chem. Int. Ed.* 61 (2022) e202211570, DOI: 10.1002/anie.202211570

Acknowledgements.
This research was funded by Ministerio de Ciencia e Innovación MCIN/AEI/10.13039/501100011033 (Projects PID2020-113931RB-I00 & PID2023-147080OB-I00), European Union “NextGenerationEU”/PRTR (Project PDC2021-120903-I00), Junta de Andalucía (FQM-175) and Navarra Government (project PC003-04 3D-MAGNET). Alvaro Bonilla gratefully acknowledges Spanish Ministry of Universities the granting of aid for predoctoral contracts (FPU20/02673).

Investigating the impact of SEI characteristics on electrochemical behaviour of silicon anodes for Li-ion cells through single particle- and electrode-level measurements

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Silicon is one of the most promising anode materials for Li-ion batteries with a theoretical capacity more than 10 times higher compared to the commercially used graphite electrodes. It is also highly abundant, environmentally friendly and exhibits a low working potential [1]. However, like other alloying anodes, silicon experiences a large voltage hysteresis related to high volume changes of its particles during cycling. This can cause a difference of up to 350 mV between the charging and discharging curves, affecting accurate SOC monitoring, energy efficiency and thermal management [2].

Recently Köbbing et al. [3] proposed, that the visco-elastoplastic behavior of the silicon shell is the origin of the voltage hysteresis. Its mechanical properties affect the lithium transport and concentration within the particle, leading to deviations in the measured electrochemical potential during cycling. To validate this hypothesis, we perform an experimental study to investigate the impact of the SEI (Solid Electrolyte Interphase) properties on the electrochemical behavior of the battery, by tailoring the formation protocol and the electrolyte composition while using a silicon electrode. Electrochemical measurements such as galvanostatic cycling, dynamic relaxation behaviour, galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS) were performed at both the electrode- and particle-level. The latter was done in a specialized single-particle measurement setup to differentiate the intrinsic active material behavior from microstructural and compositional effects of the composite electrode.

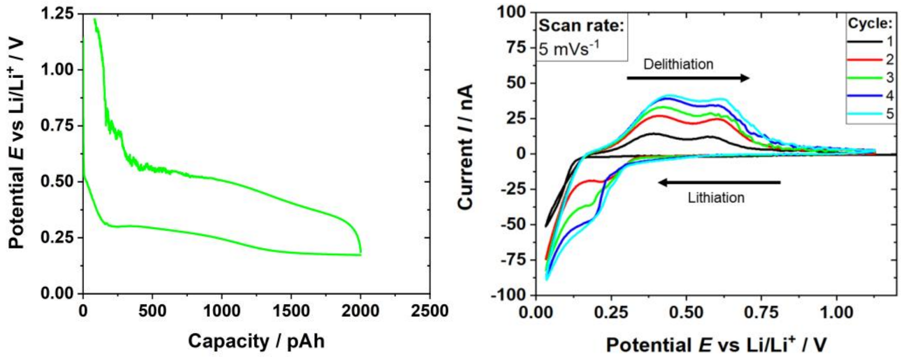

Figure 1 Voltage hysteresis and cyclic voltammetry of an investigated silicon particle.

References.
[1] L. Sun, Y. Liu, R. Shao, and J. Wu, Energy Storage Materials, vol. 46, pp. 482-502, 2022
[2] J. Lyubina, Applied Physics Letters, vol. 118, no. 9, 2021.
[3] L. Köbbing, A. Latz, and B. Horstmann, Advanced Functional Materials, vol. 34, no. 7, p. 2308818, 2024

ROBIN: A case of study how coatings could improve cycling-life in SIBs

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NASICON-type phosphates are a promising cathode material for sodium-ion batteries (SIBs) due to their 3D architecture, which is effective for sodium-ion insertion. This structure offers advantages like high voltage, cyclability, stability, and conductivity at a low cost [1]. These materials show promise as SIB electrodes, but their limited electronic conductivity remains a challenge.

Various strategies have been proposed to address this issue, such as ionic substitution [2], composites with carbon conducting phases [3], and optimizing the morphology of the active materials [4].These modifications have improved the electrochemical properties by reducing the particle size, increasing the specific surface area, and optimizing the electrode-electrolyte interface. However, these modifications have drawbacks, including reduced gravimetric density, highlighting the need for more effective alternatives.

Study of NASICON materials' surfaces and interfaces is crucial to understanding degradation phenomena affecting electrode performance and lifetime. Surface engineering offers a novel strategy to enhance conductivity and structural stability while protecting electrodes from aggressive electrolytes such as $NaPF_6$. [5].

The ROBIN project is an initiative that aims to explore and develop new surface modification strategies, with a focus on the incorporation of advanced coatings such as anionic conductors, electronic-conducting polymers, and inert oxides [6]. These synthesis routes are designed to minimize environmental impact while ensuring good contact between electrodes and modifiers. The resulting materials will undergo advanced characterization techniques to select the most promising cathode for integration into a complete sodium-ion battery.

Figure 1. ROBIN scheme of work

References.

[1] *Adv. Energy Mater.* 3 (2013) 156, DOI: 10.1002/aenm.201200558
[2] *J. Power Sources,* 313 (2016) 73, DOI: 10.1016/j.jpowsour.2016.02.066
[3] *JEAC,* 784 (2017) 47, DOI: 10.1016/j.jelechem.2016.11.064
[4] *ACS Appl. Mater. Interfaces,* 8 (2016) 23151, DOI: 10.1021/acsami.6b07950
[5] *EER,* 5 (Suppl 1), (2022) 20, DOI: 10.1007/s41918-022-00137-7
[6] *ACS Appl. Mater. Interfaces, 9* (2017) 1471, DOI: 10.1021/acsami.6b12688

Lithium Loss Mechanisms in PVD-Deposited $LiCoO_2$ Cathodes and Their Effect on Battery Performance

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This study investigates the impact of Li loss during the physical vapor deposition (PVD) process on the electrochemical performance of $LiCoO_2$ cathodes for lithium-ion batteries (LIB) [1]. The research identifies the primary Li-loss mechanisms inherent to PVD, including Li evaporation and diffusion effects, and their influence on the cathode's structural and electrochemical properties. Li deficiency resulting from these mechanisms leads to structural distortions, phase inconsistencies, and reduced electrochemical performance, characterized by lower capacity retention and increased impedance.

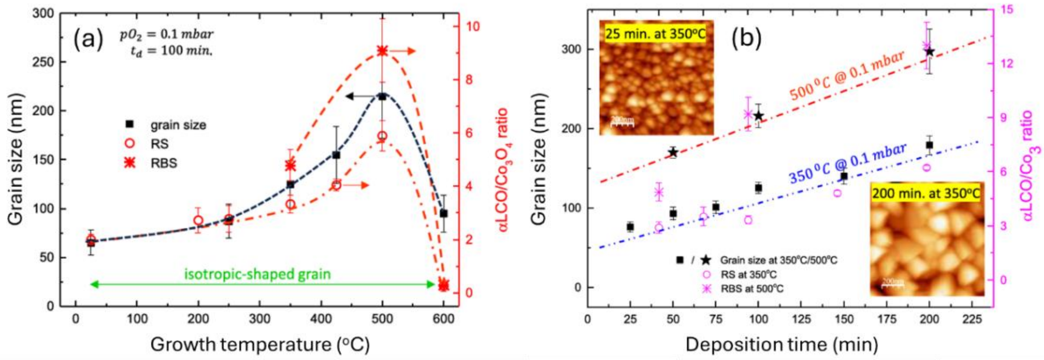

Figure. a) Evolution of grain size (left) and the $\alpha LCO/Co_3O_4$ ratio (right) as functions of growth temperature. The $\alpha LCO/Co_3O_4$ ratio is determined using Raman spectroscopy (RS, empty circles) and Rutherford Backscattering Spectroscopy (RBS, filled circles). b) Evolution of grain size (left) and $\alpha LCO/Co_3O_4$ ratio (right) with deposition time at growth temperatures of 350 °C and 500 °C.

Through a comprehensive analysis of deposition parameters, such as temperature, oxygen pressure and deposition rate, the study demonstrates that optimizing these conditions can mitigate Li loss, thereby enhancing the electrochemical stability and overall efficiency of the $LiCoO_2$ cathodes. This work underscores the importance of fine-tuning deposition techniques to achieve high-performance cathodes for energy storage applications.

References.

[1] M. J. Ramirez-Peral, J. Diaz-Sanchez, A. Galindo, M. A. Crespillo, C. Morant, C. Polop and E. Vasco. *Energy Storage Materials. 71, 103657 (2024)* DOI: 10.1016/j.ensm.2024.103658

Electrochemistry of physical vapor deposited LFP/LCO blending cathodes for "zero-strain" solid-state Li-ion batteries

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Solid-state lithium-ion batteries (SSLIBs) are presented as one of the main energy storage systems to be able to compensate for seasonality, intermittency, and low mobility of renewable sources. However, there are some technological limitations that need to be solved in order to embrace this green energy revolution. Enhancing the mechanical, chemical and thermodynamic stability of the interfaces between components would be the key to prevent degradation and loss of contact during battery cycling [1]. We focus on the preparation of $LiCoO_2$ (LCO)-based blending cathodes, as this cathode material is the only one whose volume shrinks upon lithiation. This allows the development of "zero-strain" blending cathodes by mixing materials with opposite chemical expansion coefficients in ad hoc geometries in order to minimize the volume changes of battery components during operation [2]. The thus-designed cathodes are presented as a solution to prevent interface instabilities and thus enhance the transition of SSLIBs from their current uses, mainly in mini-batteries for low-power devices, to energy-intensive applications. Moreover, these blends would present new electrochemical behaviors enhancing the properties of both materials, hence leading to the preparation of cathodes with both high energy density (like LCO) and good rate capability (like $LiFePO_4$, LFP) [3]. Here, we present the preparation of LFP-LCO blending cathodes by Pulsed Laser Deposition in different configurations, and their characterization in terms of microstructure (by Field Emission Scanning Electron Microscopy and X-ray Diffraction), composition (Rutherford Backscattering Spectrometry and Raman spectroscopy) and electrochemistry (Cyclic Voltammetry and Electrochemical Impedance Spectroscopy).

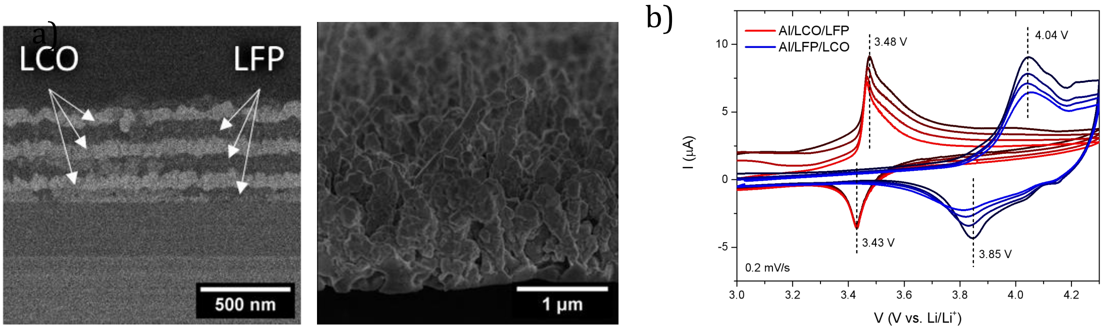

Figure. (a) SEM images of $(LFP/LCO)_3$ multilayer (left) and LCO-decorated LFP nanorods (right) blending cathodes. (b) Evolution of the Cyclic Voltammetry curves of bilayer samples with cycles (from black to color).

References:

[1] *Koerver, R. et al*, Energy Environ. Sci. **11** (2018) 2142, DOI: 10.1039/C8EE00907D.
[2] *Chikkannanavar, S.B. et al*, J. Power Sources **248** (2014) 91-100, DOI: 10.1016/j.jpowsour.2013.09.052.
[3] *Heubner, C. et al*, Journal of Power Sources **363** (2017) 311-316, DOI: 10.1016/j.jpowsour.2017.07.108.

Zn-air batteries based on hemoproteins

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In recent years, the demand for energy has increased, making it necessary to urgently search for energy conversion and storage devices. One very interesting option is zinc-air batteries (ZABs), mainly due to their high specific capacity, low cost and stable performance. The development of ZABs requires the use of electrocatalysts for the oxygen reduction reaction (ORR), which takes place at the cathode of this type of battery. Although most of the electrocatalysts proposed to date are based on inorganic or hybrid (organic and inorganic) nanomaterials, biological compounds have emerged as a promising alternative that could provide excellent ORR electrocatalytic performance, as previously reported with proteins containing heme groups, such as hemoglobin (Hb) and catalase (Cat).[1,2]

This work investigates the potential application of these two hemoproteins as electrocatalyst material in the cathode of primary ZABs, using a neutral electrolyte (PBS, pH 7.4). Analysis of the specific capacity of these types of batteries using different electrode modification strategies, as well as their reaction kinetics and the study of the cathode-electrolyte interface will be reported.

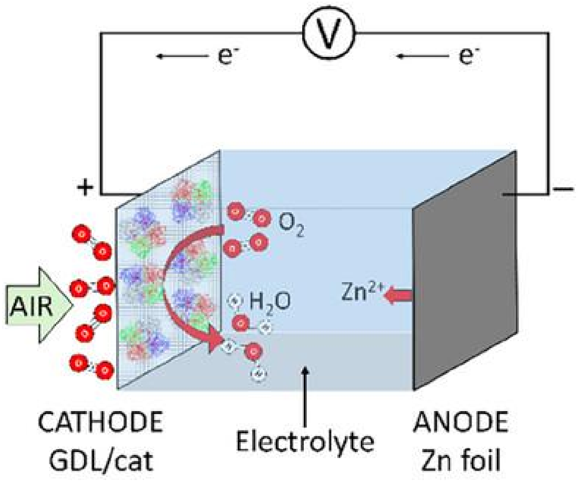

Figure. Scheme representation of the ZAB used for this work.

References.
[1] Energy & Fuels, 37 (2023) 23, DOI: 10.1021/acs.energyfuels.3c0251310
[2] ChemCatChem, (2024) e202401343, DOI: 10.1002/cctc.202401343

Connecting SEI Structure and Chemistry to Electron-Ion Transport Mechanisms and Rates Using Redox Probes

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The Solid Electrolyte Interphase (SEI) originates in the thermodynamic instability of electrolyte moieties on the negatively polarized anode surface. As a result, there is a (electro)chemical reduction of electrolyte moieties, which may react with Li ions and form solid, insoluble products on the anode surface. This SEI limits both electron and solvent transport while permitting Li ion transport, kinetically stabilizing the interface. [1] Despite its importance, several questions regarding central processes related to the SEI remain unresolved, such as the precise SEI formation mechanisms as well as electron and ion transport through SEI. [2, 3]

The objective of our study is (1) to unravel the mechanisms and rates of electron and ion transport across the SEI and (2) to establish a correlation between these processes and the structural and chemical properties of the SEI. For this purpose, we use ferrocene redox probe molecules to quantify the rate and mechanism of electron transfer from electrodes to ferrocene using cyclic voltammetry (CV). Here, we focused on an SEI composed “exclusively” of LiF (denoted as “LiF-SEI”) on a Pt electrode. [4] We perform *in situ* redox probe experiments after SEI formation. In the initial stage of the ferrocene experiments, LiF-SEI is effective in passivating the electrode. Upon multiple scans and/or time passed, the passivation of LiF gradually diminishes. This implies a change in the electronic and/or physical structure of LiF-SEI.

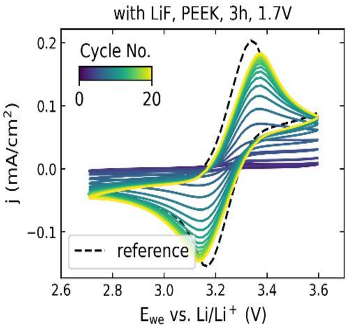

Figure 1 CV result at 20 mV/s on LiF-SEI@Pt.

To answer these questions, electrochemical impedance spectroscopy (EIS) and electrochemical quartz crystal microbalance (EQCM) experiments are carried out. Finally, we correlate these results to the SEI’s structure and chemistry at various stages as investigated via X-ray photoelectron spectroscopy (XPS). The mechanistic understanding gained at the atomic and continuum level will permit a direct rationalization of the observed nucleation, growth and evolution of SEI, and test whether electron tunneling plays a role in capacity fading. [5]

References.

[1] Wang, A., *et al., npj Comput Mater* 4 (2018) 15, DOI: 10.1038/s41524-018-0064-0
[2] Xu, K., *Journal of Power Sources* 559 (2023) 232652, DOI: 10.1016/j.jpowsour.2023.232652
[3] Horstmann, B., *et al., Current Opinion in Electrochemistry* 13 (2019) 61, DOI: 10.1016/j.coelec.2018.10.013
[4] Strmcnik, D., et al., *Nat Catal* 1 (2018) 255, DOI: 10.1038/s41929-018-0047-z
[5] Li, D., et al., *J. Electrochem. Soc.* 162 (2015) A858, DOI: 10.1149/2.0161506jes

Operando SHINERS - Dynamics of Interfacial Composition in Operating Li-Ion Battery

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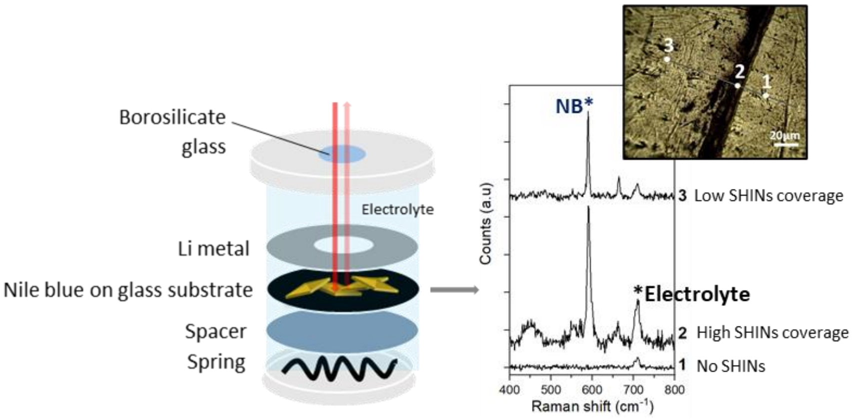
Our work aims to follow the dynamic formation and composition of interfacial layers (the so-called SEI/CEI) during Li-ion battery (LIB) operation by developing µRaman spectroscopy in combination with signal enhancement technique (SHINERS: Shell-Isolated Nanoparticle Enhanced Raman Spectroscopy). Introduced in 2010[1], SHINERS uses core-shell nanoparticles (SHINs: Au@SiO_2) as signal nano-amplifiers (near-field signal of compounds in the close vicinity of the SHINs: ≈ 10 nm). SHINERS, has seldom been applied to the energy storage field because its implementation to extract the signature of thin and buried SEI/CEI layers (i.e. in the electrode assembly, in the electrode porosity) is a major challenge.

Our group has developed SHINs with plasmonic resonance in the near-IR excitation (anisotropic bipyramid NPs)[2], which allows to enhance the interfacial signal while minimizing that of the electrode material and of the electrolyte ("bulk" Raman and autofluorescence signals). Proof of concept was established on a sample with no µRaman, i.e. far-field, signal (Nile Blue molecular layer on glass substrate[3]) in contact with thick LIB electrolyte layers. Our efforts have been focused on (i) developing a spectro-electrochemical cell with a design as close as possible to the real system (electrode size and positioning, low flooding factor) and (ii) on sensitivity optimization, including interface signal excitation (SHIN surface density) and collection improvement (collection angle, confocality) to extract the interface signature on a non-metallic negative electrode materials such as silicon.



SHINERS proof of concept. Model sample assembled (Nile Blue dye molecular layer on glass decorated with SHINs and covered with LIB electrolyte), in a modified coin cell mimicking battery conditions (i.e. low Raman scattering cross section components as found in interfacial layers). The surface density of SHINs on the sample (NPs drop-cast on the electrode) directly affects the recovered NB signal intensity.

References.
[1] Nature 464 (2010) 392–395 https://doi.org/10.1038/nature08907
[2] ACS Energy Lett. 44 (2021) 994–998, https://doi.org/10.1002/jrs.4317
[3] Nano Lett. 15 (2015) 7956–7962. DOI: https://doi.org/10.1021/acs.nanolett.5b04177

Nucleation and early stage growth of Li and Na anodes in ZESSBs at the nanoscale: dose, energy and current effects and AFM characterization

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Zero-Excess Solid-State Batteries (ZESSBs), where the anode is formed during the charge cycle, are a promising alternative to today Li-ion batteries, as they offer a higher energy density, improve safety and cut on anode production. Further advances are done in substituting Li-based electrolytes to Na-based, as it is not a critical material. Deeper knowledge is needed in the early stages of anode nucleation [1,2] to bring this technology into daily use.

We investigated the initial stages of Li and Na anode formation in zero-excess solid-state batteries by mimicking the current collector with a virtual electrode approach (fig. a). Combining Atomic Force Microscopy (AFM) at UAM and Photoemission Electron Microscopy (PEEM) at the CIRCE beamline of ALBA synchrotron, we have been able to study the growth kinetics, morphology and chemical state of the grown anodes with nanoscale resolution. Anode plating was studied varying the electron dose (fig. b to j), current and energy, and with/without the presence of a Li foil as cation reservoir. Studying the growths differences we aim to unveil the mechanisms behind anode growth in ZESSBs.

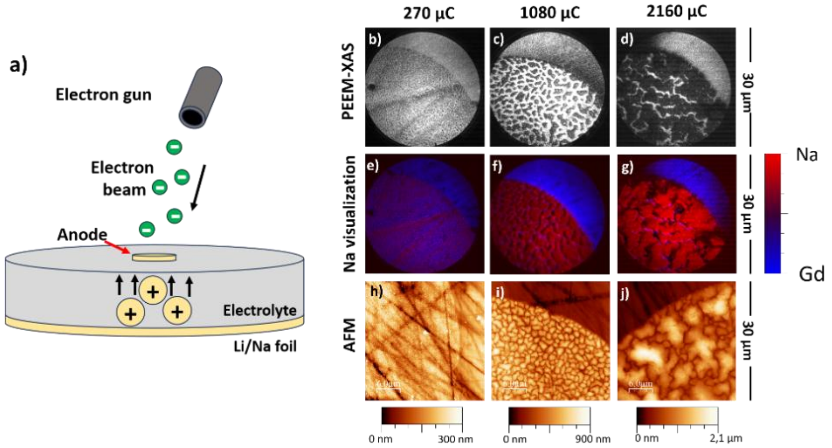

Figure. a) virtual electrode approach plating setup scheme. b) to j) growth of Na anode while plating. b) to d) PEEM-XAS measures for chemical composition information. e) to g) visualization of surface chemical composition. h) to j) anodes topographies.

References.

[1] *Nano Energy* 63 (2019) 103895, DOI: 10.1016/j.nanoen.2019.103895
[2] *Nature Materials 23* (2024) 1678-1685, DOI: 10.1038/s41563-024-02006-8

Li Plating on Flat Interfaces via Confocal Raman Spectroscopy

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The Li nucleation density and plating are controlled by two key factors. The first is the surface energy and chemical reactivity (alloying) of the tested layer with lithium. The second is the surface morphology, which also influences the nucleation density. To decouple these two effects, our main goal is to minimize the effect of surface roughness on Li nucleation and deposition.

Confocal studies on the nucleation and growth of Li at the SSE|CC interface at micrometer scale were carried out using CRM in a top-view geometry approach[1] developed by our team. First, we show the development of the Raman compatible battery cell, in terms of optimizing the cell assembly process, optimizing the deposition parameters of different current collectors, finding the optimal measurement conditions for CRM both in imaging mode and in single point measurement mode. Secondly, by integrating CRM with battery cycling, with particular attention to the first plating, the formation of the Li anode on the SSE|CC is described. Lastly, by analyzing the CRM data we determined the stages of Li anode formation and we support these by operando galvanostatic EIS (GEIS). The results are shown on Cu and ITO CC[2].

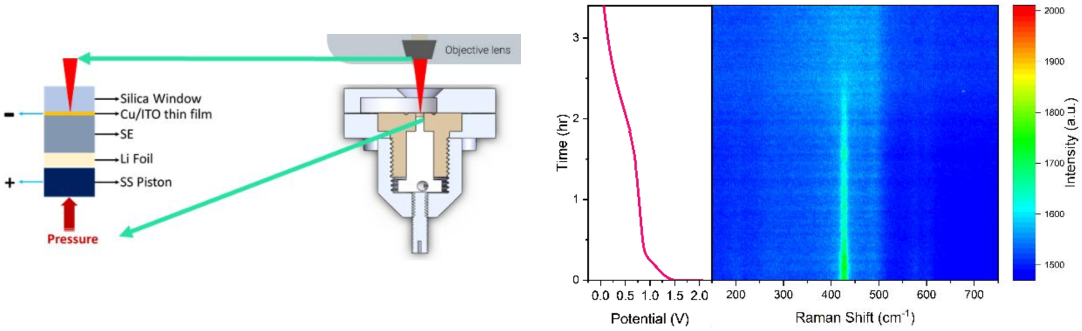

Figure. Scheme of the experimental setup (left). Potential and Raman spectra for Li-plating on Cu (right).

References.

[1] E. Kazyak, Matter 5 (2020) 3912, doi: 10.1016/j.matt.2022.07.020
[2] A. Raza, 2025 [manuscript in submission]

Investigation of Volatile Electrolyte Decomposition Products with Operando GCMS for Lithium-Ion Batteries

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For decades, great efforts have been devoted to developing Lithium-Ion Batteries (LIBs) with the goal to improve performance and further strengthen their market position in mobile and grid energy storage applications. Furthermore, post-lithium chemistries such as those based on magnesium are also promising for future applications. In both systems, the liquid electrolyte, which is a key component of the battery, undergoes decomposition during cell operation to form a protective layer, mainly on the anode. This solid electrolyte interphase (SEI) layer prevents further electrolyte reduction and is crucial for enhancing cell lifetime and safety. The most common strategy to form a stable passivation layer is to use SEI forming additives which are prone to polymerize in a rapid and controlled manner. [1]

In this work, we present the evolution of volatile components during the first formation cycle in a LIB and a magnesium metal battery (MMB). Commercially available carbonate-based electrolytes with different electrolyte formulations containing the SEI-forming additives and HF scavengers were investigated. Pouch cells (LIB) and laboratory-scale coin cells (LIB and MMB) were subjected to operando GC/MS experiments and evolved gas species measured in conjunction with the cell potential.

The study revealed that, in addition to major gaseous components such as CO, CO_2, methane, ethane, and ethene, a variety of C_3 to C_6 hydrocarbons, ethers, and carbonyls were observed. In the LIB systems under investigation, particular attention was given to decomposition products derived from carbonate-based electrolytes and processes related to the degradation the additive Tris(trimethylsilyl)phosphite (TMSP) and $LiPF_6$. Results from gas analysis were compared with XPS data of extracted electrodes and correlated with decomposition pathways of the electrolytes.

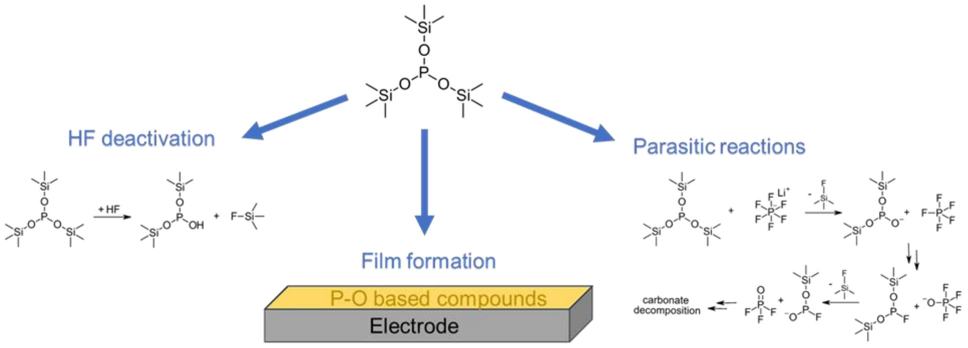

Figure. The two main functions of the additive are the formation of a film on the electrode surface and the deactivation of HF.

Acknowledgements: Co-Funded by the European Union under Grant Agreement No. 101135486 . Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them.

References.

[1] Qian, Y. et al. Investigations on the electrochemical decomposition of the electrolyte additive vinylene carbonate in Li metal half cells and lithium ion full cells. J. Power Sources 332, 60–71 (2016).

Li and Na anode growth in ZESSBs at the nanoscale by synchrotron-based PEEM: thin films, Mg interlayers and temperature effect

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In this work we present the LEEM/PEEM chemical and morphological nanoscale characterization of the alkali Li (or Na) anodes in Zero-Excess Solid-State Batteries (ZESSBs) during in-situ nucleation and growth. The virtual electrode method enables anode plating (corresponding to battery charging) on a solid-state electrolyte by irradiating an area of its surface with the electron beam using the LEEM electron gun. The provided negative charge promotes the cation migration and the formation of metallic Li/Na clusters on the electrolyte surface. This technique combined with the PEEM spectro-microscopy offers insight into the early-stage nucleation, revealing the influence of the various experimental parameters impacting the anode morphology and growth efficiency [1,2].

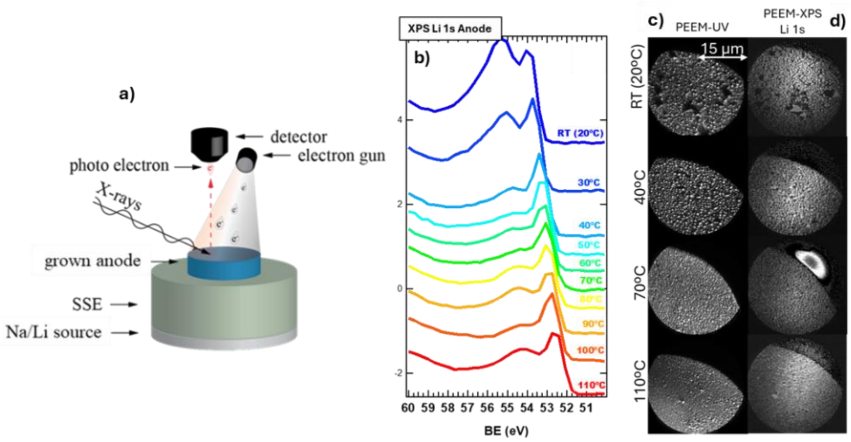

Figure. a) LEEM/PEEM operando experiment in a ZESSB with a "virtual electrode", b-d) influence of temperature on the growth of the Li anode on LLZTO: b) evolution of the Li 1s spectra c) PEEM-UV and d) PEEM-XPS for metallic Li 1s (53.4 eV BE) images showing growth at increasing T.

Three different electrolytes for ZESSBs were studied: NaGdSiO and LiLaZrTaO (LLZTO) bulk electrolytes (with and without Mg in-situ evaporated Mg interlayers as growth promoting surfactant) and LLZTO thin films. Temperature dependent experiments on bulk LLZTO/Li showed decreasing anode thickness and cluster lateral sizes as *T* increased from 20 to 110°C, counterintuitive to expected ion mobility trends. In the case of thin film LLZTO samples grown onto LCO/Al foil, after initial cycling of the stack, the experiments (plating/stripping) were successfully reproduced.

References.

[1] *Eur. J. Mineral.* 16 (2004) 809, DOI: 10.1127/0935-1221/2004/0016-0809
[2] *Nat. Mater.* 23 (2024) 1678, DOI: 10.1038/s41563-024-02006-8

On the use of XPS spectroscopy to unveil the protective film in coated cathodes for sodium-ion batteries

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X-ray photoelectron spectroscopy (XPS) is a powerful analytical technique that has become indispensable for studying the electrode-electrolyte interfaces in various energy storage and conversion systems, including batteries, supercapacitors, and fuel cells [1]. This technique provides critical insights into the chemical and electronic structures of materials, enabling a deeper understanding of interfacial phenomena that are crucial for optimizing device performance and longevity.

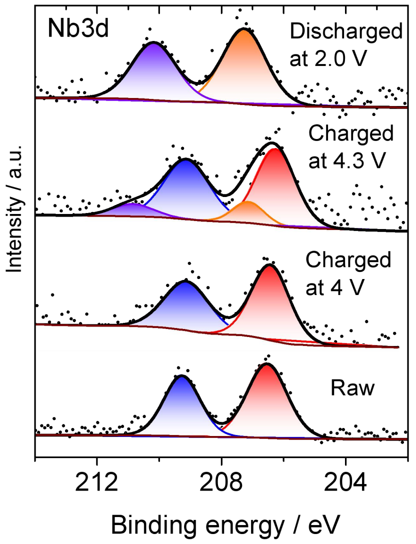

Figure 1. XPS spectra at the Nb 3d, core level recorded for raw NMO@Nb3 and selected charged and discharged electrodes.

Initial concerns about the commercialization of sodium-ion batteries (SIB) as competitors to lithium-ion batteries (LIB) are gradually fading [2]. The inherently less negative reduction potential and larger size of sodium compared to lithium were initially seen as significant limitations for achieving high-performance batteries. However, research on new electrode materials has led to significant breakthroughs. Notably, NASICON-type phosphates, and layered metal oxides have shown that their open frameworks are well-suited for fast ion diffusion at high working voltages, making them suitable as cathodes. Among other strategies to improve their electrochemical performance, chemical coating forms a protective layer between the cathode and electrolyte, effectively preserving the stability of the electrode/electrolyte interface and reducing metal dissolution while maintaining the bulk structure.

We have studied different metal oxides as coating agents for both layered oxides and NASICON type phosphates. For instance, figure 1 shows the XPS spectra at the Nb3d core level for a raw electrode and partially charged and discharged electrodes. On charging the cell, a new Nb 3d band shifted to higher binding energy appears, becoming predominant after full discharge. This phenomenon cannot be attributed to niobium oxidation. Instead, a change in ionicity may explain this observation. The harmful presence of HF traces in the electrolyte can be effectively scavenged according to the next equation:

$$NaNbO_3 + 6\ HF \rightarrow NaF + NbF_5 + 3\ H_2O$$

This transformation into metal fluorides significantly reduces the electrolyte's acidity, thereby delaying the onset of cathode corrosion during cycling [3].

The authors acknowledge financial support from research project PCI2023-143355 founded by MCIN /AEI and European Union (/10.13039/501100011033 / UE).

References.

[1] *Anal. Bioanal.* 400 (2011) 691–696. DOI: 10.1007/s00216-010-4646-z.
[2] *J. Alloys Compd.* 958 (2023) 170486. DOI: 10.1016/j.jallcom.2023.170486.
[3] *ACS Appl. Mater. Interfaces* 16 (2024) 56975–56986. DOI: 10.1021/acsami.4c09706.

Understanding the Impact of Structural Vacancies on Cation Intercalation in Prussian Blue Analogs

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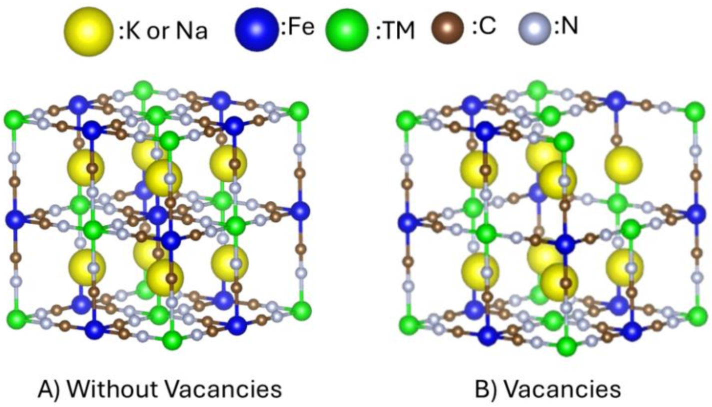
The increasing global demand for sustainable energy storage, driven by urbanization, industrial growth, and the rise of electric vehicles, calls for the development of advanced battery technologies. While lithium-ion batteries currently dominate the market, diversifying storage solutions is critical to reduce dependence on scarce materials and address the economic, environmental, and performance needs of various applications. Among alternative systems, those utilizing cations such as Mg^{2+}, K^+, Na^+, Ca^{2+}, Zn^{2+}, and Al^{3+} offer promising advantages, including improved safety, lower costs, and higher energy density [1].

Prussian Blue Analogs (PBAs), with their cubic perovskite-like structure (Fm-3m)(Fig.1), have shown excellent electrochemical performance in potassium- and sodium-ion batteries and are considered strong candidates for multivalent-ion systems [2]. Structural defects, particularly vacancies, are known to significantly influence electrochemical behavior, as observed in sodium-ion technologies, where minimizing vacancies improves performance.

In this study, we investigate the effect of structural vacancies on the intercalation behavior of various cations in PBAs. Electrochemical performance was assessed through galvanostatic measurements, focusing on specific capacity and cycling stability. Our results highlight the pivotal role of vacancies in modulating cation intercalation, affecting both capacity and reversibility. These findings provide critical insights into the relationship between structural features and electrochemical performance, contributing to the optimization of PBAs as next-generation energy storage materials.



A) Without Vacancies

B) Vacancies

Figure 1. Structure of Prussian Blue Analogs a) without and b) with vacancies.

Acknowledgement.
This work was funded by the Ministerio de Ciencia e Innovación (MCIN/AEI/10.13039/501100011033 / Project PID2022-142391OA-I00 and TED2021-129314A-100), Junta de Andalucía (Project ProyExcel_00330), and the European Union through NextGenerationEU/PRTR. We also acknowledge the Ministerio de Universidades for the FPU predoctoral fellowship (FPU23/01119).

References.

[1] *ChemSusChem*, (2023) e202301224, DOI: 10.1002/cssc.202301224
[2] Advanced Energy Materials (2018), 8, 1702619, DOI: 10.1002/aenm.201702619

Funded by the European Union

A new operando device for advanced X-ray diffraction stress and phase mappings at high-spatial resolution

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Solid-state batteries are expected to be one of the next generations of electrochemical energy storage systems. They exhibit high thermal stability and a high energy density, they are compatible with the “holy grail” metallic lithium anode and they are safer than classical Li-ion batteries [1] [2]. Nonetheless, their performances can be reduced because of mechanical stresses occurring during lithiation/delithiation leading to cracks or dendrite formations [1] [2] [3].

To date, the reasons for spatio-temporal heterogeneous distributions of stresses are still little understood in SSBs [1] [3]. That is why we want to probe precisely mechanical stresses in operando conditions with X-ray diffraction while applying a necessary stack pressure. To do so, we have built a new device (Fig.1). We will achieve a high-spatial resolution by using the X-ray nano-beam (50-100 nm) of ID13 at the ESRF.

In this poster we present the constraints imposed on the device by this experiment: air tightness, X-ray transparency, device mass, controlled pressure, set-up geometry. Then, we explain how to extract the stress from the X-ray diffraction data and illustrate the method’s capabilities with the first results we obtained.

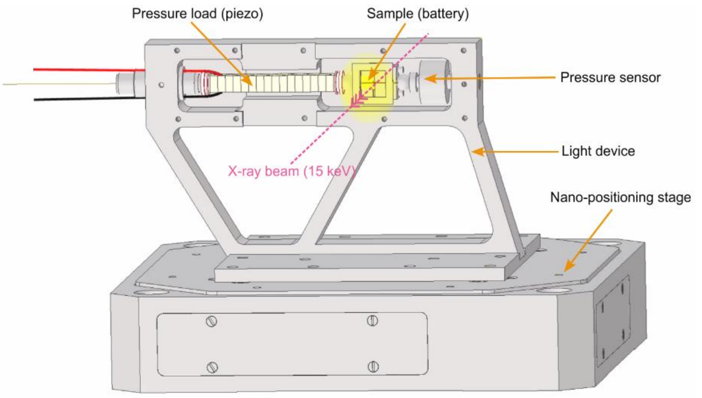

Figure 1. Scheme of the device allowing operando measurement on the electro-chemistry cell and

References.

[1] Operando Spatial and Temporal Tracking of Axial Stresses and Interfaces in Solid-state Batteries. *S. Mičky, E. Šimon, J. Todt et al.* Small 2024.

[2] Accelerating the Development of LLZO in Solid-State Batteries Toward Commercialization: A Comprehensive Review. *Y. Wang, Z. Chen, K. Jiang, Z. Shen, S. Passerini, M. Chen*. *Small* 2024.

[3] Silicon as Emergin Anode in Solid-State Batteries. *H. Huo and J. Janek.* ACS Energy Letters 2022.

[4] Effect of pulse-current-based protocols on the lithium dendrite formation and evolution in all-solid-state batteries. *Reisecker, V., Flatscher, F., Porz, L. et al.* Nat Commun 2023.

Influence of Aging Time on the Synthesis of Prussian Blue Analogue

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The present energy demand and the prediction of its future growth have driven the exploration of advanced materials to develop new energy storage systems, specifically for applications in battery technology. In recent years, Prussian Blue Analogues (PBAs) have attracted significant attention because of their potential for intercalating various cations (Na^+, K^+, Mg^2, etc.) in their open framework (Figure 1A). This suggests that PBAs could be promising candidates as a cathode material for the next generation of batteries [1]. It has been demonstrated that PBAs' synthesis parameters significantly impact their structure and electrochemical performance, such as the nature of precursors, different concentrations, and the drip rate in coprecipitation [2]. This communication examines the influence of a synthesis parameter called “Aging”. This parameter is frequently omitted in other synthesis studies. The crystallinity and morphology of the samples have been analyzed by X-ray diffraction and scanning electron microscopy respectively. The influence of the PBAs (Nickel hexacyanoferrate) on the electrochemical performance of sodium batteries (aqueous and non-aqueous) was analyzed (Figure 1B), demonstrating a significant impact on the material’s capacity to reversibly (de-)intercalate sodium into and from its open framework structure.

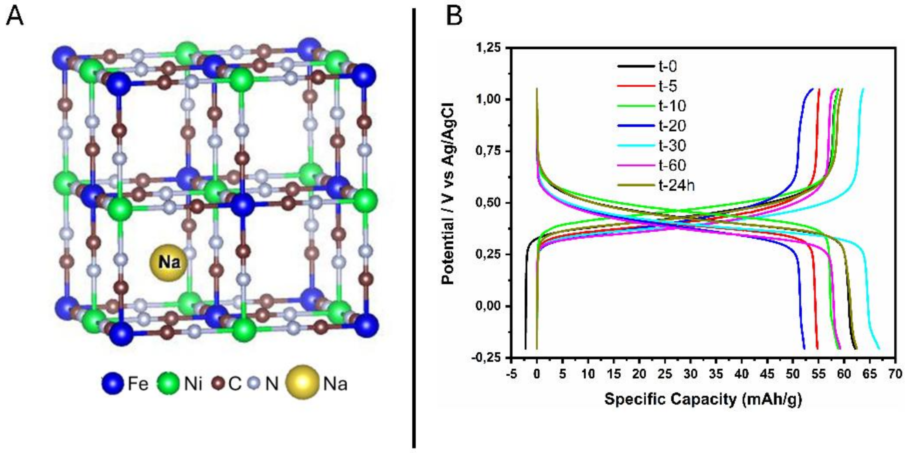

Figure. 1 Cubic structure of Prussian Blue Analogue (A) and galvanostatic measurements at different aging times (B)

Acknowledgements.

This work has been support of the Junta de Andalucia through funding the projects “Program EMERGIA Emergía_0153“ and “Project Excel_00330”, as well as to the Ministry of Science, Innovation, and Universities through the projects “TED20213129314 A-100“ and PID2022-142391OA-100, and the grant RYC2022-037564 founded by the MCI/AEI// 10.13039/501100011033 and European Union NextGenerationEU/ PRTR, FEDER a way of making Europe and the 287 FSE invest in your future.

References.

[1] *L. Ma, et al. 81 (2021) 2211-2855, DOI: 10.1016/j.nanoen.2020.105632*
[2] *B. Xie, et al. 460 (2022) 0010-8545, DOI: 10.1016/j.ccr.2022.214478*

Probing SEI Formation and Dynamics in Silicon/Graphite Anodes Using Ex Situ and In Situ Solid-State NMR Spectroscopy

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Silicon (Si) is a highly promising anode material due to its exceptional theoretical capacity (~3,580 mAh g^{-1}), significantly surpassing that of graphite (~372 mAh g^{-1}). However, the substantial volumetric expansion (~300%) of Si during lithiation generates mechanical stress, leading to particle fracturing and repeated exposure of fresh surfaces to the electrolyte. This triggers continuous SEI growth, consuming lithium and electrolyte, and accelerating capacity degradation. To mitigate these challenges, combining Si with graphite (Gr) composites and optimizing electrolyte formulations have emerged as effective strategies to enhance the stability and performance of Si-based anodes. In this study, we employed both in situ and ex situ solid-state NMR spectroscopy to investigate Si/Gr anodes in two systematically selected electrolytes: one EC-based (producing organic-rich SEI) and one FEC-based (yielding inorganic-rich SEI). NMR spectroscopy, with its element-specific sensitivity and ability to probe local chemical environments, is uniquely suited to investigate both surface and bulk properties of battery materials. In situ NMR experiments allowed real-time monitoring of lithiation mechanisms and SEI evolution during cycling, while ex situ 1D ^{7}Li, ^{19}F, and ^{1}H NMR experiments provided detailed identification of SEI decomposition products in fully discharged states after the first and extended cycles. Additionally, cross polarization (CP) and 2D exchange spectroscopy (EXSY) NMR experiments offered insights into the spatial distribution and dynamics of SEI species interacting with lithiated Si and Gr. These NMR findings were correlated with the electrochemical performance of Si/Gr anodes in the two electrolytes, providing a comprehensive understanding of their stability and behavior.

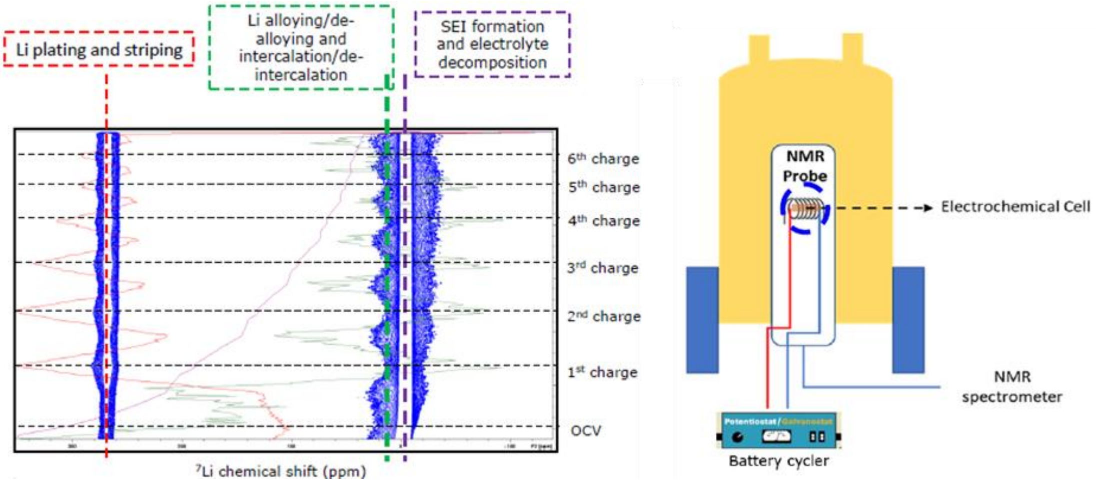

Figure. In-situ NMR monitoring of silicon/graphite anodes

Understanding the Silicon Voltage Hysteresis and Relaxation: A Chemo-Mechanical Core-Shell Model

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Silicon anodes are a promising successor to graphite anodes with an increased capacity. One major challenge for their implementation is the understanding and treatment of the silicon voltage hysteresis, observed even during slow cycling and open-circuit storage. This contribution explains the silicon voltage hysteresis and relaxation with a chemo-mechanical core-shell model.

Our study considers the chemo-mechanical interaction between an active silicon core and an inactive shell. The shell can represent the solid-electrolyte interphase (SEI), inactive silicon, or a silicon oxide layer. During cycling, the volume of the silicon anode changes substantially due to (de)lithiation. At the same time, the shell has to accommodate the anode volume changes with purely mechanical deformations. The occurring stresses inside the shell can cause pronounced capacity loss [1]. Moreover, the shell generates stresses acting on the silicon particle and the respective chemo-mechanical potential. Accounting for a visco-elastoplastic shell behavior, our simulation elucidates the observed silicon voltage hysteresis during cycling and open-circuit storage [2]. Furthermore, a recent advancement of our model captures the logarithmic voltage relaxation over weeks [3]. Focusing on the interaction at the core-shell interface, we derived a simple hysteresis model preserving physical information for easy voltage predictions during cycling and open-circuit relaxation.

To conclude, our chemo-mechanical core-shell model explains the silicon voltage hysteresis and long-term relaxation behavior. Thus, our study highlights the impact of interfaces and interphases for silicon anodes, whose understanding is crucial for applying pure silicon anodes.

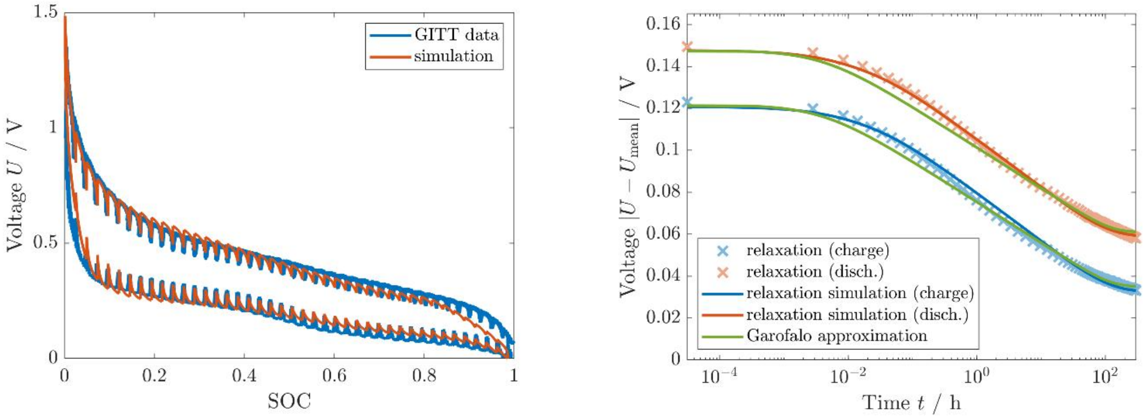

Figure. Simulation of the silicon voltage hysteresis and long-term voltage relaxation.

References.

[1] *Batter. Supercaps* 5 (2022), 2, e202100216, DOI: 10.1002/batt.202100216.
[2] *Adv. Funct. Mater.* 34 (2024), 7, 2308818, DOI: 10.1002/adfm.202308818.
[3] *ACS Appl. Mater. Interfaces* 16 (2024), 49, 67609-67619, DOI: 10.1021/acsami.4c12976.

Optimization of NCO synthesis by physical vapor deposition for Na-ion batteries (NIB)

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While Li reserves are insufficient to meet global demand on the secondary battery market, Na is much more abundant and environmentally friendly. However, Na ions are larger, slower and more reactive, which limits the electrochemical performance of the NIB components in terms of capacity, power delivery, rate properties and cycling lifespan. In this context, the research on thin-film NIBs seeks to overcome the kinetic limitations to the Na-ion transport.

Using commercial Na_xCoO_2 (NCO) targets, we deposited thin-films by pulsed laser deposition (PLD) over different substrates (Al foil, SiO_2/Si) under the same growth conditions during 200 minutes. Substrate temperature was kept at 500 °C, oxygen pressure was fixed at 0.05 mbar and the same laser fluency ($1.8\,J/cm^2$) and pulse rate were used for the preparation of the two samples shown in the figure below. As it can be seen from the XRD analysis, the film grown on $SiO_2/Si(100)$ is mostly Co_3O_4, while that deposited on Al appears to be a Na_xCoO_2 and Co_3O_4 mixture. While many causes can in principle be associated to Na deficiency in a PLD process, we suspect Na diffusion inside the Si substrate to play a key role in the formation of Co_3O_4. We confirmed by cross-sectional EDX the presence of Na inside the SiO_2 layer. Bulk diffusion does not take place at a noticeable level in the Al substrate possibly due to the low reciprocal solubility of the two elements.

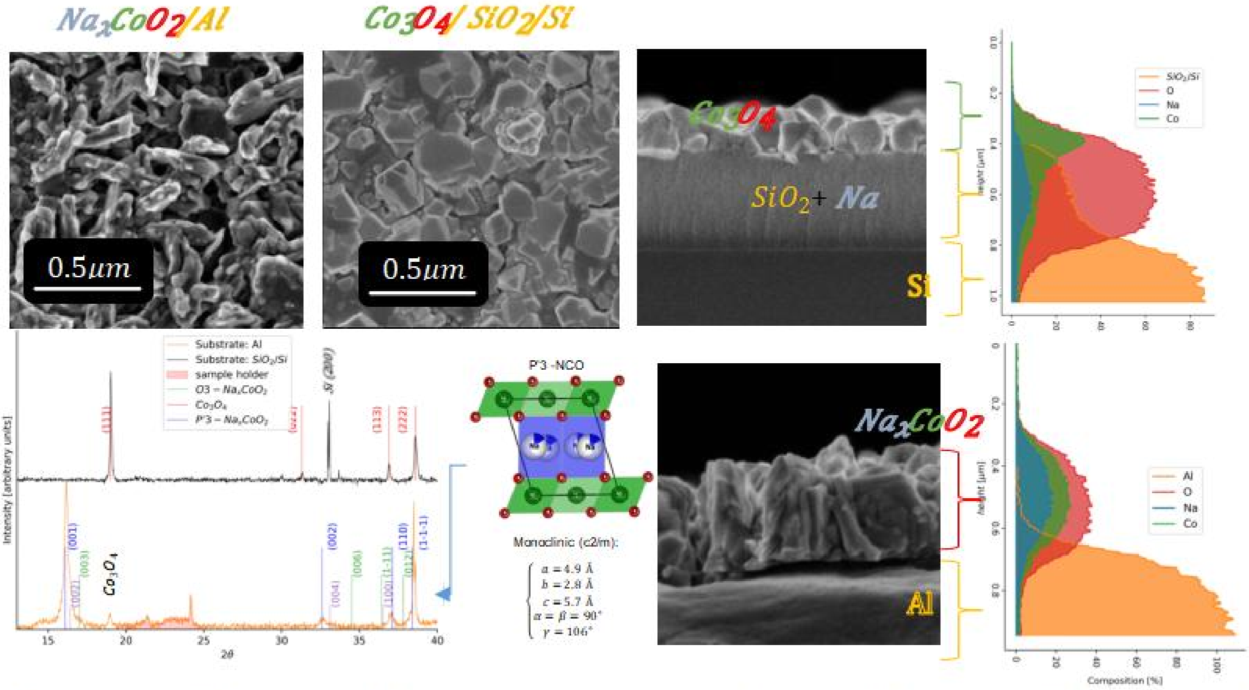

Figure. (Top left) Top view SEM images of samples grown on SiO2/Si and Al substrates. (Bottom left) XRD spectra of the two samples. (Right) Cross-section SEM images with composition depth profiles by EDX for the SiO2/Si (top) and Al (bottom) substrates.

Study on polysulfides adsorption enhancement in Metal-Sulfur batteries with *Alpeorujo*-derived activated carbons

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The olive oil industry faces challenges in sustainably managing *alpeorujo* (A), a phenolic-rich by-product with significant environmental and economic impacts [1]. Nowadays, there is also a global need for more efficient energy systems, where carbon-based materials are key [2]. In response to these issues, this study explores the potential use of *alpeorujo*-derived activated carbons (ACs) as cathodes in lithium-sulfur (Li-S) batteries to improve sustainable energy storage systems. Using three different activating agents [KOH (K), $ZnCl_2$ (Z) & H_3PO_4 (H)] in a 2:1 ratio, followed by thermochemical treatment at 900 °C and chemical purification, AK, AZ and AH carbons were prepared, respectively. These ACs exhibited suitable structural and textural properties for incorporating 70% sulfur, leading to promising electrochemical performance.

One key challenge in Li-S batteries is the shuttle effects of soluble lithium polysulfides (LiPSs) which leads to rapid capacity decay and short cycling lifespan [3]. To address this, we investigated the Li polysulfides adsorption capacity of the ACs through continuous monitoring of absorbance changes in a Li_2S_6 solution. Figure (A) shows the evolution of the adsorption time by monitoring Li_2S_6 absorbances and (B) the specific capacities of the ACs at 0.5C. The results reveal that the AC with H_3PO_4 (AH) had superior LiPS adsorption capacity, correlating with enhanced electrochemical performance (1100 mAh/g over 300 cycles). These findings highlight the importance of LiPSs retention in optimizing Li-S battery performance and represent a major technological advancement.

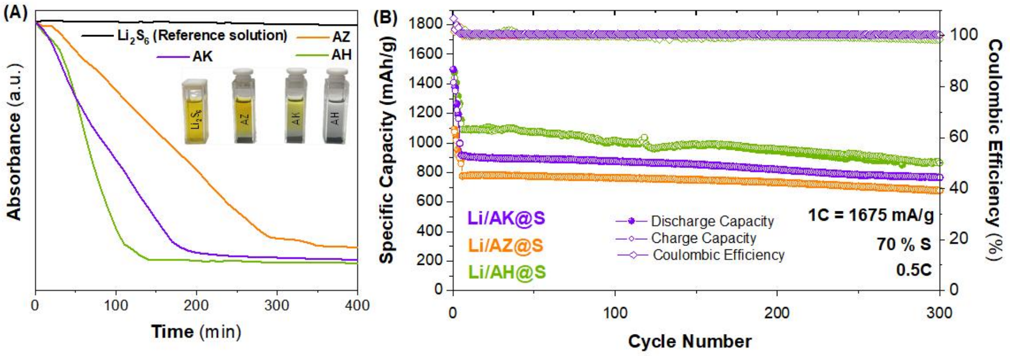

Figure (A) Li polysulfide adsorption tests and **(B)** Electrochemical performance of the Li-S batteries for *alpeorujo*-derived ACs (AK, AZ and AH).

Acknowledgements.
This research was funded by the Ministry of Science and Innovation (PID2020-117438RB-I00, PID2020-113931RB-I00, and PID2023-147080OB-I00), Regional Government of Andalusia (GOPO-CO-23-0006, Operational Groups of the European Innovation Partnership), and University of Córdoba (UCOLIDERA 2023).

References.

[1] *Crit. Rev. Food Sci. Nutr.* 61 (2020) 920–945, DOI:10.1080/10408398.2020.1748563
[2] *J. Environ. Chem. Eng.* 10 (2022) 107260, DOI: 10.1016/j.jece.2022.107260
[3] *Adv. Sci.* 9 (2022) 2106004, DOI: 10.1002/advs.202106004

Numerical Foot-print Correction Methodology for X-ray Reflectivity

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X-ray reflectivity (XRR) is a powerful method that employs model electrodes, such as mm-sized single crystals or thin films, to measure the structural properties of the solid-liquid interfaces and interphases in lithium-ion batteries (LIBs) [1,2,3]. Our overall objective is the development of high-throughput *operando* XRR to measure 20 electrochemical cells per day instead of a single cell. Here, we identified the so-called "foot-print effect" – i.e., µm-sized beam overspill at small angles – as a potential bottleneck for the accuracy and precision of XRR.

Conventionally, the foot-print is corrected analytically, including the estimation or fitting of the beam shape with a given functional form [4]. In reality, however, the beam shape often significantly deviates from these assumptions, limiting the accuracy and precision of the foot-print correction. High accuracy and precision of the foot-print correction is particularly relevant at high X-ray energies – where the reflection angles are particularly small – and for small samples, which is often the case for electrochemical interfaces relevant to LIBs. Moreover, high quality XRR data are imperative for employing machine learning-based analysis [5] and to quantify the effect of the X-ray absorption in the material. Finally, for large beam sizes – e.g., at laboratory sources for increased flux – the foot-print correction plays a significant role.

Towards this end, we developed a numerical methodology for foot-print correction, which will be introduced in this contribution. Here, the angle dependent sample size projection is computed and used to extract the relative portion of the incident beam that contributes to the XRR signal. This methodology is highly precise and accurate and independent of beam shape (assumptions). We will present the concept and workflow and show initial results (see example in Figure 1). Moreover, we will show a comparison between the numerical and analytical correction methods for different beam shapes and sizes.

In conclusion, our numerical methodology for footprint correction offers a more accurate, precise, and effective solution to this challenge, irrespective of the beam shape/size.

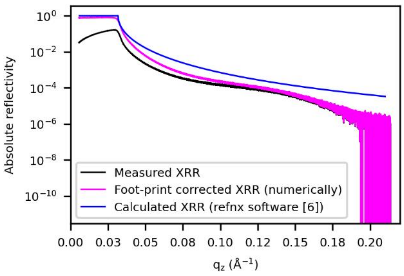

Figure 1: Numerical foot-print correction applied to XRR measurement of 4.5 mm long Si wafer and a nominal 0.1 mm beam size.

References.

[1] Fister, T. T. et al. *Chem. Mater.* 28 (2016) 47-54, DOI: 10.1021/acs.chemmater.5b01809
[2] Cao, C. et al. *Nano Lett.* 16 (2016) 7394-7401, DOI: 10.1021/acs.nanolett.6b02926
[3] Cao, C. et al. *Encycl. Solid-Liquid Interfaces* (2024) 391-416, DOI: 10.1016/B978-0-323-85669-0.00105-7
[4] Gibaud, A. et al. *Acta Crystallogr. A* 49 (1993) 642-648, DOI: 10.1107/S0108767392013126
[5] Greco, A. et al. *J. Appl. Crystallogr.* 55 (2022) 362-369, DOI: 10.1107/S1600576722002230
[6] Nelson, A. R. et al. *J. Appl. Crystallogr.* 52 (2019) 193-200, DOI: 10.1107/S1600576718017296

Towards FIB-SEM/SIMS low-dose high-speed acquisition using alternative scanning methodologies

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Focused Ion Beam - Scanning Electron Microscopy (FIB-SEM) and Secondary Ion Mass Spectrometry (SIMS) are techniques used to characterize structural and chemical properties of samples, valuable in many scientific fields [1].

Two factors that influence the resolution in FIB-SEM-SIMS analysis are beam damage and shot noise. Beam damage causes structural modifications, while shot noise affects the signal-to-noise ratio (SNR), leading to image distortion [2]. To mitigate these defects, different scan methodologies are being explored.

One method that stands out is the Adaptive Sampling. This technique consists in performing a fast scan to get a low-resolution image, followed by a second scan but only in significant pixels of the image to get features of interest with a better resolution. An algorithm makes the decision of the pixels of interest by using the first scan information. This method helps reduce the acquisition time and dose without losing resolution [3]. To avoid too many samples being close to each other leaving other areas of the image sparsely sampled, a stratified random sampling was implemented for the second scan. This is done by recursively dividing the image into blocks or stratas and introducing a condition that each strata has a fixed number of samples.

This work presents the implementation of this novel scanning method on a high-vacuum FIB-SEM platform (Scios from Thermo Fisher Scientific) equipped with a SEM column, Ga-FIB column, and a SIMS system [1]. We tested this approach using a custom-built acquisition system controlled by a USB-6351 acquisition card from National Instruments. The system manages scan control and data acquisition, with a LabVIEW program overseeing operations.

These improvements in raster schemes are expected to enhance materials research by facilitating high-resolution imaging of transient processes and radiation-sensitive samples.

The authors acknowledge funding from the European Union’s Horizon Europe research and innovation program under Grant Agreement No. 101104032 (OPINCHARGE).

References.

[1] O. De Castro et al., Analytical Chemistry, 94 (2022), DOI: 10.1021/acs.analchem.2c01410
[2] D. Nicholls et al., Ultramicroscopy, 233 (2022), DOI : 10.1016/j.ultramic.2021.113451
[3] Dahmen, T., & Trampert, P. Microscopy and Microanalysis, 25 (2019), DOI:10.1017/S1431927619000035

Alternative scan pattern mitigates radiation damage in beam sensitive battery material LiF

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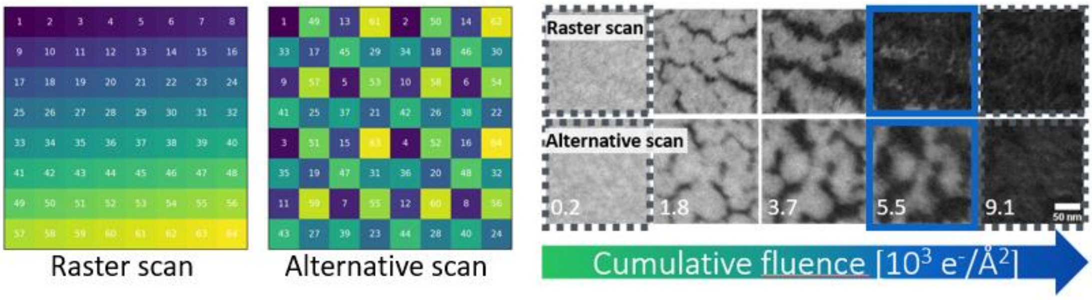
Electron-beam sensitivity of battery materials hinders the full potential of high-resolution STEM-EELS insights on battery failure mechanisms. It is therefore important to understand how electron beam induced alterations can be minimized. Beam damage in STEM can be mitigated by adjusting electron probe properties such as beam size, current, and acceleration voltage, as well as by modifying dwell time [1] or the scan pattern [2], [3]. Velazco et al. [2] demonstrated a promising approach by increasing the spacing between successive probe positions while maintaining the same overall pixel distribution per frame as a raster scan. Their alternative scan reduced damage compared to conventional raster scanning for the beam sensitive sample zeolite [2]. Since beam damage is a process that is highly dependent on the type of material being irradiated damage mitigation techniques require material-specific investigations to ensure effective adaption of the scanning parameters. Here we are interested in reducing radiation damage in the beam sensitive battery material LiF and we therefore compare radiation damage by conventional raster scanning to our different "alternative" scanning (see Fig. 1). From the electron beam induced alterations in image intensity the imposed damage could be quantified. We found that our alternative scan pattern successfully mitigates radiation damage in the beam sensitive battery material LiF. Optimized scanning parameters enable higher imaging flexibility and could provide new insights into battery failure mechanisms.[4]



1	2	3	4	5	6	7	8
9	10	11	12	13	14	15	16
17	18	19	20	21	22	23	24
25	26	27	28	29	30	31	32
33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48
49	50	51	52	53	54	55	56
57	58	59	60	61	62	63	64

Raster scan

1	49	13	61	2	50	14	62
33	17	45	29	34	18	46	30
9	57	5	53	10	58	6	54
41	25	37	21	42	26	38	22
3	51	15	63	4	52	16	64
35	19	47	31	36	20	48	32
11	59	7	55	12	60	8	56
43	27	39	23	44	28	40	24

Alternative scan

Figure 1. HAADF intensity decay for increasing cumulative fluence for conventional raster scan compared to alternative scan on a LiF thin film sample.

References.

[1] *Micron*, vol. 119, pp. 72–87, Apr. 2019, doi: 10.1016/j.micron.2019.01.005.
[2] *Ultramicroscopy*, vol. 232, p. 113398, Jan. 2022, doi: 10.1016/j.ultramic.2021.113398.
[3] *Nanoscale*, vol. 12, no. 41, pp. 21248–21254, 2020, doi: 10.1039/d0nr04589f.
[4] Acknowledgements: The authors thank the OPINCHARGE project, which received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101104032. We acknowledge Battery2030+ for their support to the OPINCHARGE project. Measurements were performed using the IMN's characterization platform, PLASSMAT, Nantes, France.

Development of correlative approaches for battery investigation

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Synchrotron facilities, with their unparalleled capabilities in spectroscopies, X-ray scattering, and X-ray imaging, offer key insights into battery materials properties and their dynamics. Several challenges are identified for the development of more performing and sustainable batteries. From one side, it is needed a multi-modal approach, where only a combination of techniques is able to provide a comprehensive answer to the scientific question. On the other hand, massive data production due to the multi-modal approach and by the operando or imaging capabilities imply challenges in the data analysis. Moreover, the current development of the artificial intelligence provides unprecedented opportunities for an efficient and exhaustive data analysis, including automated identifications of correlations.

In particular, XAS provides full chemical information, electronic structure, and/or local geometry of materials, with surface or bulk sensitivity depending on the measurement approach. The two regions of a XAS spectrum, the x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) provide complementary information which are typically under exploited. The approach needed for analyzing big multi-edge XAS operando datasets enabling automated correlative investigations will be discussed, exploiting the example of Li-rich NMC cathodes studies [1].

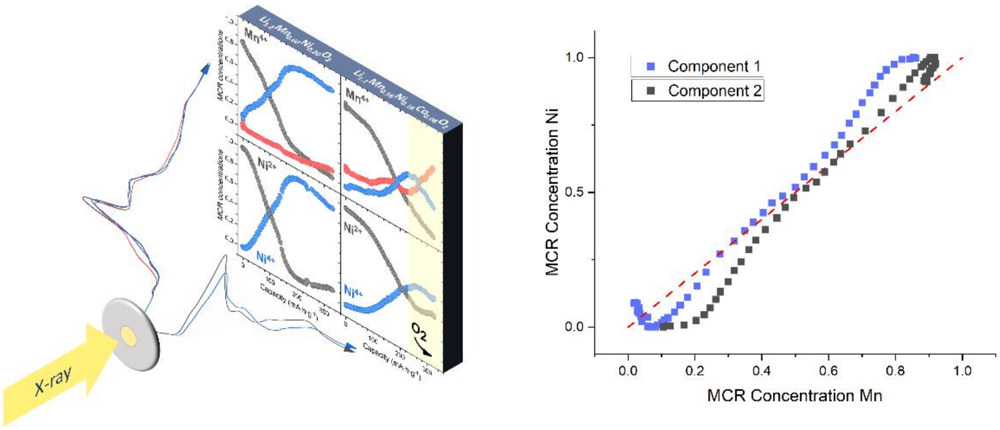

Figure 1. Diagram of the MCR data obtention workflow derived from XAS spectra of Mn K edge and Ni K edge in a cobalt-free NMC Li-ion cathode (left), and linearity between corresponding MCR components for both edges (right).

References.

[1] Oleg Usoltsev et al., Operando multi-edge XAS to reveal the effect of Co in Li- and Mn-rich NMC Li-ion cathodes, Materials Today Energy Volume 50, June 2025, 101853

Fluorine-doping of spinel-type $NiCo_2O_4$ for sodium-ion batteries

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Lithium-ion batteries are currently the most widely used energy storage systems. However, their limitations drive us to search for alternatives, such as sodium-ion batteries, which could have similar performance while being more sustainable. Thus, nickel and cobalt oxides are potential candidates for use as anodes in sodium-ion batteries, but firstly their behavior requires further optimization. The mechanism of the electrochemical reaction involves a conversion process, although it is not yet fully understood [1, 2]. Anion-doping can be a promising strategy to improve the electrochemical behavior of electrode materials for sodium-ion batteries [3].

In this work, we have studied the effect of fluorine doping on the spinel-type compound $NiCo_2O_4$. A series of $NiCo_2O_{4-z}F_z$ compounds was synthesized using a procedure based on the precursor method. The resulting secondary particles have a spherical morphology with diameter of several microns, and containing primary nanoparticles (Fig. 1). Chemical analysis using WDXRF confirms the presence of fluorine. The electrochemical performance of these new materials $NiCo_2O_{4-z}F_z$ has been evaluated in sodium half-cells. In addition, theoretical calculations based on DFT are performed to study the fluorine/oxygen substitution.

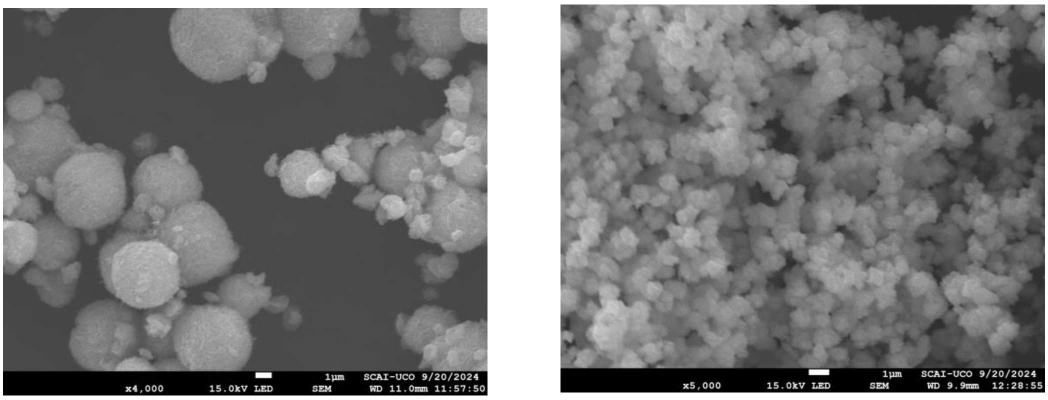

Figure 1. SEM micrographs of F-doped $NiCo_2O_4$.

Acknowledgments

This work was supported by Junta de Andalucía (research group PAIDI FQM288 and ProyExcel_0001020).

References.

[1] *Q.Wang, B. Liu, X. Wang, S. Ran L. Wang, D. Chen, G. Shen. J. Mater. Chem.* 22 (2012) 21647.
[2] R. Alcantara, M. Jaraba, P. Lavela, J. L. Tirado. *Chem. Mater.* 14 (2002), 2847.
[3] C. Pérez-Vicente, R. Alcántara. *Phys. Chem. Chem. Phys*. 25 (2023) 15600.

Studying Li Anode Formation via Solid-State Hull cell Architecture

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The formation of Li metal anodes during initial charging has attracted significant attention due to its potential to overcome production challenges, reduce manufacturing costs, enhance safety, increase energy density, and extend cycle life. However, the so-called zero-excess Li metal anode approach faces new obstacles related to non-uniform Li metal plating on the bare current collector, leading to substantial capacity loss and detrimental failure modes such as Li dendrite formation[1].

To address this, we have developed the first solid-state Hull cell with $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ as the solid electrolyte. The Hull cell configuration allows us to investigate the Li morphology over a range of current densities with applied stack pressure in a single galvanostatic experiment. A 5 µm copper layer is deposited via DC magnetron sputtering, and stack pressures of ~0, 5, and 10 MPa are applied to evaluate their impact on Li plating uniformity. Ex-situ PFIB-SEM characterization reveals that at 0 MPa, Li islands and extrusions form, causing current constrictions and heterogeneous interfaces[2]. In contrast, applying stack pressure during cycling promotes a more uniform Li layer. Additionally, the amount of uniformly plated Li varies significantly across the current gradient, demonstrating the feasibility of the Hull cell approach for studying Li plating kinetics in solid-state batteries.

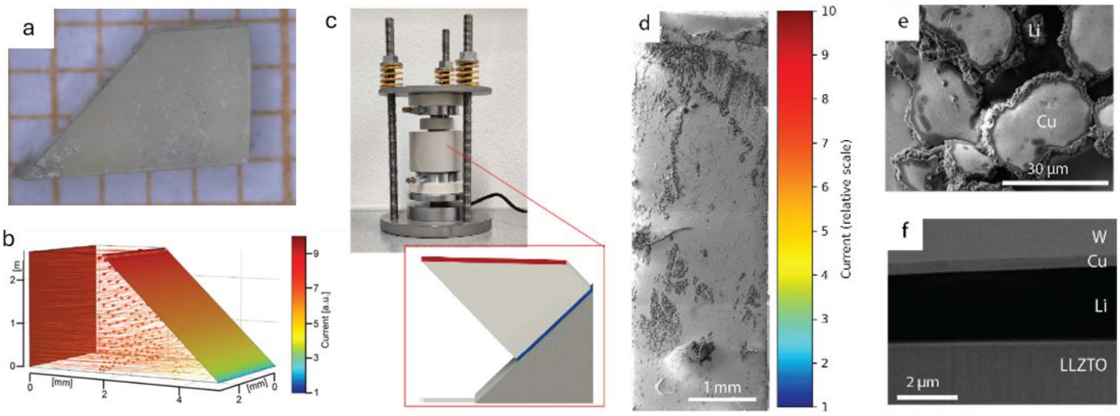

Figure 1. (a) Solid-state Hull cell. (b) Finite element analysis of the calculated distribution along the shaped surface. (c) Customized Hull cell testing setup used to maintain constant stack pressure during the experiment. (d) Top-view SEM image of the solid-state Hull cell after plating. (e) Magnified view of a selected area in (d). (f) FIB-SEM cross-section after plating experiment with the application of 5 MPa stack pressure.

References:

[1] Adv. Energy Mater. 2022, 12, 2201044, DOI: 10.1002/aenm.202201044

[2] Adv. Energy Mater. 2023, 13, 2203174, DOI: 10.1002/aenm.202203174

Real-Time Imaging of Li-ion Redistribution in Solid-State Batteries: An *Operando* FIB-SIMS Approach

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Solid-state Li-ion batteries have garnered a lot of interest in recent years due to their enhanced safety. But widespread commercialization of these batteries is impeded due to limitation in their overall electrochemical performance. So, efforts are now focused on enhancing their key electrochemical parameters, such as cycling life, capacity, and charge transport properties. Achieving these improvements requires a thorough understanding of the degradation mechanisms within these batteries, particularly at the electrode-electrolyte interface. This, in turn, demands high-resolution *operando* characterization techniques capable of correlating microstructural and chemical information. *Operando* electron microscopy techniques have gained a lot of popularity as they provide excellent spatial resolution for microstructural imaging. However, utilizing electron microscopy to simultaneously obtain microstructural and chemical information is challenging. Conventional chemical analysis methods in electron microscopes, such as energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), face limitations in detecting lithium. These challenges arise from lithium's low characteristic transition energy and low fluorescence yield in EDX and the stringent sample requirements for EELS. In this context, secondary ion mass spectrometry (SIMS) can be a great alternative as it is capable of detecting lithium even at very low concentration and can even distinguish between different isotope of an element. *Operando* approach based on focused ion beam (FIB)-SIMS instruments can provide a direct correlation between microstructure, chemical and electro-chemical information. In this contribution, we report on the development of an *operando* methodology for microstructural and chemical imaging of solid-state batteries with nano-scale spatial resolution using a prototype dual-beam FIB-SIMS platform developed at Luxembourg Institute of Science and Technology (LIST) [1]. Our approach addresses the limitation of previously reported *in-situ/operando* SIMS [2,3] methods by allowing SIMS analysis without interrupting the electrochemical operation of the cell. As a proof of concept, we image in real time the Li-ion redistribution in a solid electrolyte due to applied current using isotopically labelled lithium electrodes. From the results of the *operando* experiment we could detect formation of Li ion gradient in our cell during *operando* analysis, which would otherwise not be detectable from *ex-situ* or *in-situ* analysis as the cell would be going towards an equilibrium in the absence of any external stimulus (in this case the current applied by the potentiostat). This *operando* methodology paves the way for detailed investigation of the charge transport properties of different phases of composite electrode and electrolytes with high spatial resolution. The authors acknowledge funding from the European Union's Horizon Europe research and innovation program under Grant Agreement No. 101104032 (OPINCHARGE).

References.

[1] O. De Castro et al., Analytical Chemistry 94 (2022).
[2] H. Masuda et al., Journal of Power Sources 400 (2018).
[3] L. Cressa et al., Analytical Chemistry 95 (2023).

(No) Gas evolution in $LiMn_{0.6}Fe_{0.4}PO_4$ full cells – an Online Electrochemical Mass Spectrometry Study

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As the demand for low-budget electric vehicles with long cruising ranges is increasing, the energy density of the current state-of-the-art electrode material $LiFePO_4$ (LFP), advantageous from an environmental and economical point of view, no longer satisfies the needs.[1] An alternative olivine cathode material, $LiMnPO_4$ (LMP), shares the same theoretical capacity as LFP and comes with the benefit of a higher operational voltage of 4.1 V, resulting in a 21% increase in energy density.[2] However, due to the material's low conductivity and structural instability, $LiMnPO_4$ suffers from low capacity retention.[3] A combination of LFP and LMP, the solid solution $LiMn_xFe_{1-x}PO_4$ (LMFP), promises to overcome the beforementioned challenges by combining the higher energy density of LMP and excellent cycling stability of LFP and has therefore attracted global interest in the industry and in academia.

Within the wider framework of the OPINCHARGE project, we were aiming to shed light on the reactions happening at LMFP interfaces by gas evolution analysis. While the full-cells, comprising $LiMn_{0.8}Fe_{0.2}PO_4$ vs graphite as counter electrode, have recently been reported to exhibit gassing[4], this work explored full-cells of $LiMn_{0.6}Fe_{0.4}PO_4$ vs LFP (as a non-gassing counter electrode) with LP30 (1 M $LiPF_6$ in EC:DMC (50:50)) as an electrolyte. Evolved gasses were tracked using Online Electrochemical Mass Spectrometry (OEMS), and it will be shown that gas evolution due to the electrolyte decomposition is observed only at very high potentials, exceeding the standard LMFP working potential, and beyond the accepted LP30 electrolyte stability window.

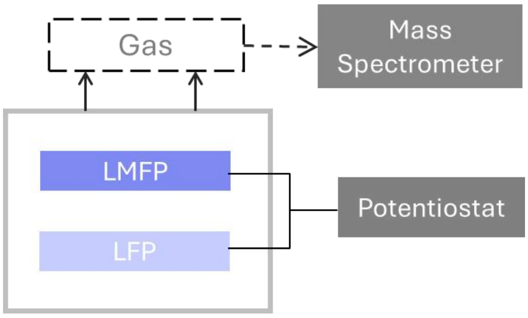

Figure 1. Schematic depiction of OEMS experimental setup for the gas evolution at LMFP interfaces.

References.

[1] *Nano Energy* 52 (2018) 510, DOI: 10.1016/j.nanoen.2018.08.007
[2] *Adv. Energy Mater.* 7 (2017) 1601958, DOI: 10.1002/aenm.201601958
[3] *J. Power Sources* 119-121 (2003) 232, DOI: 10.1016/S0378-7753(03)00239-8
[4] *J. Electrochem. Soc.* 171 (2024) 040520, DOI: 10.1149/1945-7111/ad3b77

The effect of halogens on the formation of PS_4^{3-} in Li_6PS_5Cl during liquid-phase synthesis

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Sulfide solid electrolytes (SSEs) are critical for next-generation solid-state batteries due to their high ionic conductivity, electrochemical stability, and superior mechanical properties. Among them, lithium argyrodite Li_6PS_5Cl has gained attention for its high ionic conductivity and favorable synthesis conditions. While solution-based synthesis offers a scalable route for fabricating Li_6PS_5Cl, the formation mechanism of the thiophosphate (PS_4^{3-}) units remains unclear, particularly compared to β-Li_3PS_4, which forms solvent/precursor complexes. Unlike β-Li_3PS_4, Li_6PS_5Cl crystallizes directly upon low-temperature annealing, suggesting a distinct formation pathway influenced by halogens.

This study investigates the formation mechanism of Li_6PS_5Cl during solution-based synthesis, focusing on the role of halogens and phase stabilization. Microwave-assisted synthesis and in situ Raman spectroscopy were used to monitor reaction kinetics and structural evolution in real-time. Microwave irradiation enabled uniform heating, enhancing precursor dissolution and influencing intermediate phase formation. Post-reaction X-ray diffraction, scanning electron microscopy, and AC impedance spectroscopy provided further insights into phase composition and solvent interactions.

Our findings indicate that halogens directly influence the nucleation and crystallization of Li_6PS_5Cl, differentiating its formation pathway from β-Li_3PS_4. The absence of solvent/precursor complexes suggests that halogens stabilize the structure, impacting the final electrolyte properties. These insights contribute to optimizing solution-processed sulfide solid electrolytes, facilitating their scalable production for high-performance solid-state battery applications.

Acknowledgment

This research was supported by the ELISA project (ref. CNS2023-145494), funded by MCIN/AEI/10.13039/501100011033 and «Next Generation EU»/PRTR

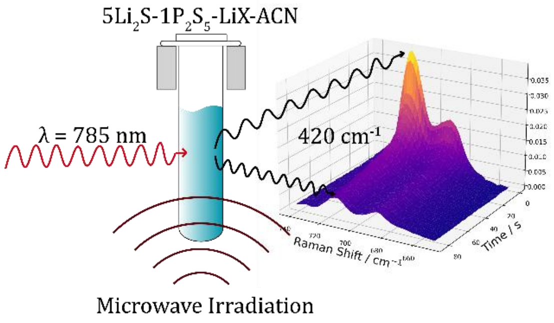

Figure. Time-resolved *in situ* Raman spectroscopy of the liquid-phase synthesis of the argyrodite-type sulfide solid electrolyte.

Thin film sample preparation for the OPINCHARGE project

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The *OPerando analyses and modelling of INterface dynamics and CHARGE transport in lithium-ion batteries* – OPINCHARGE – project is an EU-funded research initiative aimed at advancing the understanding and optimization of lithium-ion batteries (LIBs). Its primary objective is to develop a comprehensive understanding of LIB interfaces, encompassing atomic and nanoscale interactions as well as mesoscale transport phenomena. To achieve this, a combination of experimental characterization techniques and computational modeling approaches is employed to gain deeper insights into LIB interfaces. Each experimental technique, however, has specific requirements for samples, particularly to enable precise and accurate methodological development where high sample quality is essential. To tackle this challenge, we employ physical vapor deposition (PVD) to produce high-quality thin films. For this purpose, we utilize a sputtering system equipped with six sputter sources, a flash lamp annealing (FLA) chamber, and a plasma cleaning system (see Fig. 1). This system provides flexibility in adapting sample designs and stack configurations, ensuring their suitability for the diverse experimental techniques used in OPINCHARGE. Additionally, it enables the preparation of small sample quantities, which are often not commercially viable for large-scale manufacturers. The sample preparation with PVD is not limited to specific substrates or materials; any material available as a commercial sputtering target can be deposited. Within the scope of OPINCHARGE, we prioritize the deposition of amorphous silicon (Si, p-type), lithium fluoride (LiF), lithium iron phosphate ($LiFePO_4$, LFP), and lithium manganese iron phosphate ($LiMn_{0.4}Fe_{0.6}O_4$, LMFP) as active materials for *operando* experiments, with film thicknesses in the range from 50 nm to 600 nm. The coating of grids for transmission electron microscopy (TEM), wafers for surface sensitive X-ray measurements, and secondary ion mass spectrometry (SIMS), as well as copper sheets for Raman measurements within OPINCHARGE will be presented.

Fig. 1: Sputter-FLA system for thin film sample preparation for the OPINCHARGE project.

Electrochemical Performance and Stability of AlF_3-Containing Lithium Phosphate and Borate Glass Electrolytes: A Comparative Study on the Fluorine Effect

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This work investigates the influence of aluminum fluoride (AlF_3) incorporation on two distinct families of glassy solid electrolytes—lithium phosphate ($Li_2O–P_2O_5$) and lithium borate ($Li_2O-B_2O_3$). In the lithium phosphate system, glass was first prepared by melting $Li_2O–P_2O_5$ and subsequently remelting with stoichiometric AlF_3, yielding an optimized composition of 10 AlF_3·50 Li_2O·40 P_2O_5. Physicochemical characterization (including glass composition, NMR spectra, and glass transition temperature) and electrochemical measurements reveal that AlF_3 addition strengthens the interface stability against lithium metal at high current densities, without diminishing the ionic conductivity or altering the activation energy of the baseline $Li_2O–P_2O_5$ glass. By contrast, in lithium borate glasses using the composition 10 AlF_3·50 Li_2O·40 B_2O_3, AlF_3 incorporation is found to negatively impact long-term electrochemical stability. Although both borate glasses with and without AlF_3 maintain amorphous structures and demonstrate stable cycling at current densities from 0.01 to 1 mA cm^{-2} at 160 °C, the AlF_3-containing samples unexpectedly suffer from short-circuiting under 0.3 mA cm^{-2} in extended symmetrical cell tests. These divergent outcomes underscore the nuanced role of fluorine doping in different glassy matrices: while fluoride incorporation can bolster interfacial stability and cycling performance in certain compositions (e.g., phosphate-based glasses), it may degrade stability in others (e.g., borate-based glasses). The results presented here provide valuable insights for designing and optimizing glassy electrolytes for all-solid-state lithium batteries, highlighting the need to tailor fluoride doping strategies to the specific glass chemistry.

Acknowledgments
This work was supported by the ELISA project (Ref. CNS2023-145494), funded by MCIN/AEI/10.13039/501100011033 and Next Generation EU/PRTR.

References.

[1] Battery Energy (2025) 70007, DOI: 10.1002/bte2.70007
[2] *J. Power Sources 625 (2025) 235640, DOI: 10.1016/j.jpowsour.2024.235640*

High precision neutron imaging for lithium-ion batteries

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Neutron imaging lends itself as valuable tool to study lithium distribution and its evolution in Li-ion batteries, as neutrons interact strongly with some light elements such as lithium while being less sensitive to heavy elements. Local lithium thicknesses are indicated by attenuation of the neutron beam. However, even with ^{6}Li isotope-enriched samples, neutron radiography can hardly achieve a thickness precision smaller than 1µm which corresponds to an attenuation of merely 0.71%. In particular for operando studies the signal-to-noise ratio is not sufficient for such sensitivity.

To overcome this limitation, we developed a novel neutron imaging method which directly detects the neutron capture reactions instead of attenuation. We experimented with three different detector set-ups to test our methods and one reference system, namely (a) conventional neutron radiography set-up utilizing a state-of-the-art scintillator/camera set-up. For the novel neutron capture imaging (NCI) method we gradually improved the detection by initially utilizing (a) the same camera system (b) a novel TPXCAM and (c) an optimized TPXCAM with an improved optical setup. To test and qualify our novel method we conducted measurements on four electrochemically plated samples with average ^{6}Li thicknesses of 10µm, 1µm, 100nm and 10nm, and samples with well-defined uniform-thicknesses of 1µm and 100nm produced by thermal evaporation. Subsequently, in-situ and operando tests were performed, which we could calibrate with the measurement of the 1µm reference ^{6}Li sample measured in the same operando cell.

We found that while conventional imaging was limited to resolve the Li distribution of the 10µm and 1µm ^{6}Li samples, NCI with the same optical setup enabled to resolve features in the 100nm plated sample. Ultimately our optimized set-up enabled the resolution of features in the 10nm ^{6}Li plated sample and could be shown to provide a precision of 20nm for the 100nm uniform-thickness ^{6}Li reference sample. Finally, the calibrated results of operando measurements implied a steady trend in Li evolution which agreed well with the corresponding electrochemical data.

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