A Computational Phase-field Analysis of Dendrite Growth at the Li-LLZO Interface.

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All-solid-state lithium batteries (ASSLBs) offer the prospect of safer, higher-energy energy storage by replacing flammable liquid electrolytes with non-flammable solid electrolytes. However, their development is constrained by lithium-metal dendrites, which can nucleate at the lithium/solid-electrolyte interface, propagate through the electrolyte, and ultimately cause internal short circuits. While external stack pressure is commonly applied to improve interfacial contact and cell stability, the coupled roles of interfacial reaction kinetics, applied voltage, and pressure in controlling dendrite propagation remain incompletely understood.

Here, a computational phase-field framework is used to examine lithium dendrite growth at the lithium/garnet-type electrolyte interface, where the solid electrolyte is Li7La3Zr2O12 (LLZO). The model considers a polycrystalline LLZO electrolyte and assumes preferential lithium propagation along grain-boundary pathways, which are commonly more susceptible to lithium penetration than grain interiors. A systematic parameter study of 125 simulations was performed by varying the applied voltage, external stacking pressure, and interfacial electrochemical reaction rate. The resulting lithium morphology and propagation behaviour were evaluated using the evolving dendrite area ratio and the connectivity of lithium-filled grain-boundary pathways.

The simulations identify four distinct propagation stages governed by the combined electrochemical and mechanical driving forces. At low applied voltage, lithium advances primarily through a single grain-boundary channel, with limited lateral branching. At intermediate voltage, two pressure-responsive branching regimes emerge: an initial branching regime in which stack pressure can substantially constrain lithium expansion, followed by a more developed branching regime in which pressure still suppresses dendrite growth but with progressively reduced effectiveness. At high voltage, lithium forms a fully percolated network across the simulated electrolyte domain. In this regime, propagation is dominated by the electrical driving force, and increases in stack pressure provide little further suppression.

The voltage range over which pressure is effective is strongly dependent on the interfacial reaction rate. As the reaction rate increases, the pressure-responsive window shifts to lower applied voltages and becomes narrower, demonstrating that faster lithium-deposition kinetics promote branching and percolation under less severe electrical driving conditions. Conversely, lowering the interfacial reaction rate delays the onset of extensive dendrite propagation and preserves a wider operating range in which pressure can meaningfully regulate dendrite morphology. Across all 125 simulated conditions, reducing the interfacial reaction rate provides substantially greater suppression of lithium penetration than increasing external stacking pressure.

These results indicate that pressure management alone is unlikely to deliver robust dendrite resistance under high-voltage operation. Instead, stabilising the lithium/LLZO interface and moderating local charge-transfer kinetics should be treated as the principal design strategy, with stack pressure used as a complementary control variable. The framework provides experimentally testable predictions for coupled electrochemical–mechanical measurements and supports the rational design of interfacial coatings, engineered grain boundaries, and operating protocols for more reliable ASSLBs.

High-resolution chemical imaging of ion transport in hybrid polymer electrolytes: a FIB-SIMS workflow

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Hybrid polymer electrolytes composed of ceramic particles embedded in polymer matrix are promising as electrolytes for next-generation solid-state batteries as they combine the complementary advantages of both components [1]. By optimization of the design principles, they can achieve adequate Li^+ conductivity, high mechanical strength, a broad electrochemical stability window, good interfacial contact, and effective dendrite suppression. Such optimization requires detailed knowledge about the correlation between ion transport and parameters such as current density, temperature, and chemical composition. Breakthroughs in analytical techniques are needed to image sub-micron and nanoscale ion transport in operando conditions. Focused ion beam-secondary ion mass spectrometry (FIB-SIMS) is a valuable nanometrological technique for this purpose, as it enables the detection and high-resolution chemical imaging (sub 20nm spatial resolution) of light elements such as Li [2]. Furthermore, FIB-SIMS can distinguish isotopes of an element, making ^6Li isotope labelling a powerful approach for investigating ion transport and related bottlenecks in solid electrolytes [3]. Here, we present the steps toward the development of a workflow for real-time imaging of ion transport in hybrid polymer electrolytes across a broad temperature range. Building on our previously reported operando methodology [3], this workflow integrates controlled heating and cooling of solid-state battery samples between −20°C and +80°C with simultaneous electrochemical operation and FIB-SIMS analysis. This approach will enable a systematic investigation of how parameters such as analysis temperature, ceramic filler size, and filler loading influence ionic conductivity and ion-transport pathways in hybrid polymer electrolytes. The resulting insights will support the development of hybrid polymer electrolytes with enhanced electrochemical performance.

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High throughput EIS processing via online machine learning

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Electrochemical impedance spectroscopy (EIS) is one of the most information-rich non-destructive diagnostics for batteries, yet its use at scale is limited by slow, expert-dependent analysis. Equivalent circuit model (ECM) fitting is sensitive to model choice and initial guesses, distribution of relaxation times (DRT) inversion depends on regularization choices, and machine-learning (ML) models trained offline degrade when chemistry, cell format, or operating conditions drift. Here we present NEVORA, an end-to-end platform that ingests impedance spectra from multichannel potentiostats and processes them automatically through three coupled layers. First, every spectrum is screened by Kramers–Kronig validation to reject non-stationary or noise-corrupted data. Second, a physics-based layer performs automated ECM selection and fitting in parallel with regularized DRT deconvolution, extracting interpretable parameters (ohmic, interphase, charge-transfer, and diffusion contributions) and their characteristic time constants; cross-checking ECM parameters against DRT peak assignments provides an internal consistency test that reduces the ambiguity inherent to either method alone. Third, validated spectra and extracted features, including polar representations (|Z|, φ) that we previously showed outperform Cartesian inputs for ML, stream into a live-training pipeline that incrementally updates state-of-charge (SOC) and state-of-health (SOH) models as new data arrive and reports an uncertainty estimate with every prediction. We demonstrate the platform on thousands of spectra spectra from sulfide chemistries and model chemistries cycled under various conditions. Live-trained models reached SOH and SOC errors of < 1% MAE on held-out cells. By converting raw impedance into validated, physically interpretable, and continuously improving diagnostics, NEVORA lowers the barrier to deploying EIS in cell development, quality control, and battery-management applications.

Raman Spectroscopy for Ferroelastic and Polymorphic Transitions study in ferroelectric ceramics

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In the present work, Raman spectroscopy was used to study ferroelastic and polymorphic phase transitions in the compositions $Pb(Zr_{0.53}Ti_{0.47})O_3$:Gd (PZT53/47:Gd) and $K_{0.44}Na_{0.52}Li_{0.04})_{0.97}La_{0.01}Nb_{0.9}Ta_{0.1}O_3$ ($KNNLiTaLa_{0.01}$), respectively. Raman spectra of both samples were measured as a function of temperature, and the spectra were subsequently analyzed both qualitatively and quantitatively. The exact temperature of the ferroelastic transition in PZT53/47:Gd was determined, the vibrational mode associated with the ferroelastic phase transition was identified, and it was confirmed that the presence of Gd^{3+} in the structure induces the occurrence of this transition. It was also determined that the ferroelastic phase transition is of the pseudoproper type and, by applying the hard-mode spectroscopy approach, it was classified as a second-order transition. For the $KNNLiTaLa_{0.01}$ composition, the temperature interval in which the phase transition occurs was accurately determined. Furthermore, the transition was classified as a second-order phase transition using hard-mode spectroscopy.

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Operando ion beam analysis characterization of LLZTO-based solid-state batteries

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Solid-state batteries (SSBs) offer transformative potential with their higher energy density, enhanced safety, and extended longevity. However, their performance is often limited by interfacial challenges, including degradation, mechanical failure, and lithium transport issues at critical interfaces with a solid electrolyte such as LLZTO (Lithium Lanthanum Zirconium Tantalum Oxide). These interfacial processes, such as lithium accumulation or depletion, contact loss, and dendrite formation, directly influence ionic transport, interfacial resistance, and cycling stability, ultimately determining the battery's overall performance and lifespan.

To address the lack of direct insight into these dynamic interfacial phenomena, this study employs operando Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) with 3 MeV protons to visualize and quantify lithium distribution and depth profile in real time during battery cycling. Furthermore, we present the first operando NRA/RBS characterization results, enabling real-time tracking of lithium migration.

This work underscores the critical role of operando IBA techniques in advancing the understanding of interfacial processes in SSBs, paving the way for optimized designs and improved performance.

Development of an in-house operando XRD technique for the observation of lithium-ion diffusion in NMC-based SSB

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Study and observation of the lithium-ion diffusion is essential for a deeper understanding and the development of high-loading solid-state batteries. The time-dependent lithium-ion diffusion was observed using advanced, high-power X-ray sources such as synchrotrons, thereby tracking structural changes in the cathode mixture [1]. We have developed an in house operando XRD technique using a state-of-the-art high-brilliance laboratory microfocus X-ray source (Ag Kα radiation) and a highly sensitive CdTe 2D X-ray detector operating in transmission mode. Lithium diffusion in cathode active material was observed using an operando setup that utilised wide-angle X-ray scattering (WAXS) for real-time analysis of the structural changes due to redox reactions during battery cycling under laboratory conditions. Two SSB batteries were prepared with carbon black (CB) as the X-ray window on the current collector side, NMC811 cathode with two different catholytes, Li6PS5Cl (slow) and Li5.5PS4.5Cl1.5 (fast), Li6PS5Cl (LPSCl) as electrolyte and Li-In as anode, were built. The lithium-ion diffusion was observed at the two cathode interfaces (CB-NMC & NMC-LPSCl), during cycling at different C-rates. The XRD data, combined with electrochemical data, revealed the homogeneous reaction in the cathode mixture for the fast LPSCl and delayed lithium-ion diffusion between the two probed interfaces for slow LPSCl.

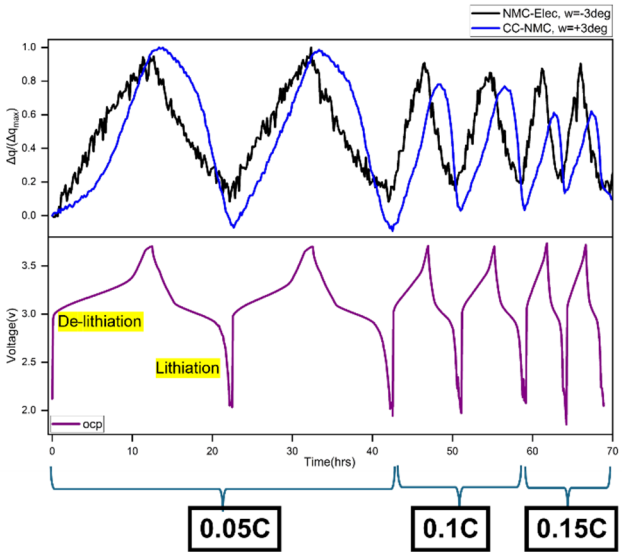

Figure 1. *Evolution of normalized NMC 101 diffraction peak position for the NMC/solid electrolyte interface (black curve) and the CC/NMC interface (blue curve) vs. battery cell potential during de-lithiation and lithiation for slow LPSCl.*

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Evolution of Fabrication-Induced Residual Stresses in Solid-State Batteries

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A gradual uniaxial compression procedure fabricates solid-state batteries (SSBs) by applying fabrication pressures, concluding with the stack pressure. The primary goal of the fabrication pressures is to reduce the porosity in the anode, solid electrolyte (SE), and cathode powders. In contrast, the stack pressure ensures optimal contact at the interfaces, which facilitates the proper transport of Li ions through these interfaces and preserves high ionic conductivity in the battery stack. Here, we report residual stress measurements using $\sin^2\psi$ method in a solid-state battery containing LPSCl. [1] The LPSCl SE was compressed up to 400 MPa. However, the evaluated axial compressive stress was only 200 MPa. This difference is due to LPSCl being confined within the PEEK and steel parts of the battery cell. Therefore, the LPSCl pressing follows a triaxial stress state consisting of the axial stress (σ_x) and the constrained radial stresses (σ_r=σ_ϑ). Using the $\sin^2\psi$ method, the difference between the axial and radial stresses is measured in the solid-state battery. After reaching an external pressure of 400 MPa, the LPSCl was released and exhibited significant tensile strain due to the spring-back effect induced by the expansion of Ar gas in the compressed pores of the SE powder. Additionally, the study indicates that applying a stack pressure of 50 MPa, commonly used in the literature, does not induce axial compressive strain in the battery stack; instead, it returns it to its initial zero MPa state.

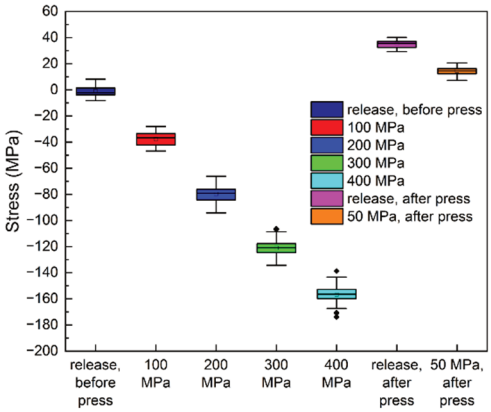

Figure 1. *The figure shows the evolution of difference between axial and radial stress, calculated from elastic strain, during the step-by-step fabrication of the LPSCl layer.*

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Electrochemical cycling and multitechnique characterization of $NaCoO_2$ cathodes grown by pulsed laser deposition

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$NaCoO_2$ (NCO) has emerged as a promising sodium-based battery electrode and a potential alternative to the widely used $LiCoO_2$ (LCO) [1]. In this work [2], NCO films were synthesized using pulsed laser deposition (PLD), and the assembled cells were electrochemically cycled to different states of charge (SOCs). Afterwards, a multi-technique characterization combining scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy was performed to study the phase composition, morphology and conducting properties of the cathodes. Electrochemical measurements revealed reversible charge/discharge behavior with an average Coulombic efficiency of ~94 % and volumetric charge capacities up to ~740 mAh/cm^3. Microscopy analyses showed a more homogeneous morphology after cycling, while AFM measurements indicated enhanced conductivity in the desodiated state. Raman spectroscopy identified characteristic peaks associated with O3- and P3-type NCO phases, confirming structural changes induced by sodium extraction and insertion. These results contribute to the development of sodium-ion battery technologies.

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Operando Synchrotron FTIR at the MIRAS Beamline Reveals Structural-Water Dynamics in Prussian Blue Analogues

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Prussian Blue Analogues (PBAs) have attracted considerable interest as cathode materials for next-generation sodium-ion and multivalent batteries due to their open framework, rapid ion diffusion, structural versatility, and low cost synthesis. However, the role of structural water and its influence on electrochemical performance remains incompletely understood. Here, we combine *operando* Fourier-transform infrared (FTIR) spectroscopy at ALBA's MIRAS beamline[1] with *operando* X-ray diffraction (XRD) to elucidate reaction mechanisms, structural evolution, and water dynamics in PBAs. Continuous monitoring of the cyanide (CN^-) and water (OH^-) stretching vibrations reveals distinct redox mechanisms across different hydrated PBA compositions. In Berlin Green (FeFe-PBA), the reversible shift of the CN^- stretching band from 2113 to 2102 cm^{-1} directly tracks Fe redox activity and spin-state transitions during Na^+ and Ca^{2+} intercalation.[2] Structural water also exhibits composition-dependent behavior. Commercial MnFe-Prussian White undergoes progressive, irreversible water release coupled to structural phase transitions, whereas FeFe-Prussian Blue and Berlin Green seem to exhibit some reversible water dynamics that closely follow the Fe^{2+}/Fe^{3+} redox process and associated lattice-volume changes.[3] These findings showcase *operando* synchrotron FTIR as a unique tool to complement to XRD and XAS and reveal structural-water dynamics largely hidden from conventional *operando* techniques.

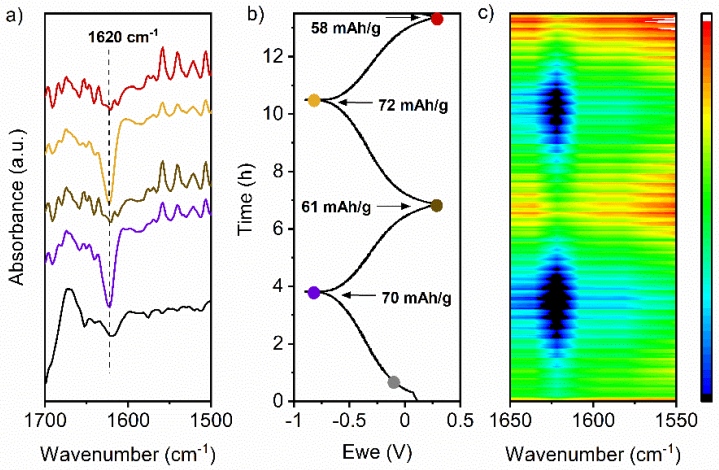

Figure 1. *a) OH^- stretching band (1620 cm^{-1}), b) Electrochemical cycling profile at C/5 and c) contour plot tracking the OH^- band evolution during operando FTIR at ALBA MIRAS beamline on a cell using $Fe[Fe(CN)6]\cdot nH_2O$ as active material in the working electrode, 1M $NaPF_6$ in diglyme electrolyte and activated carbon cloth as counter electrode.*

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Thin-film components and interfacial studies for sodium solid-state batteries

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Solid-state batteries (SSBs) are attractive energy-storage systems due to their improved safety and thermal stability compared to conventional liquid-electrolyte batteries. While considerable progress has been achieved for lithium-based SSBs, the development of solid-state sodium-ion batteries (SSNIBs) remains at an early stage despite the abundance and wider availability of sodium compared with lithium. To contribute to this field, we are developing thin-film SSNIB components, including $NaCoO_2$ (NCO) cathodes, NASICON solid electrolytes deposited by Pulsed Laser Deposition (PLD) and metallic anodes fabricated by thermal evaporation. The electrochemical performance of NCO was initially evaluated using a liquid electrolyte (LE), followed by the fabrication and testing of NCO/NASICON bilayers. Although initial cycling attempts were dominated by non-faradaic currents, the system exhibited improved stability after passivation in the presence of species originating from the LE, highlighting the importance of interface engineering in Na-SSBs. As part of the development of metallic anodes for sodium batteries, Sn, Ag and Cu were investigated as model systems during sodiation and desodiation. While the fabrication of thermally evaporated Sn thin-film anodes is already underway, similar studies on Ag and Cu are planned for future work. Hard X-ray Photoelectron Spectroscopy (HAXPES) was employed to investigate the interfacial chemistry associated with sodiation and desodiation processes. HAXPES measurements can provide insight into the evolution of the chemical species formed during cycling and the influence of the metallic substrate on interfacial reactions.

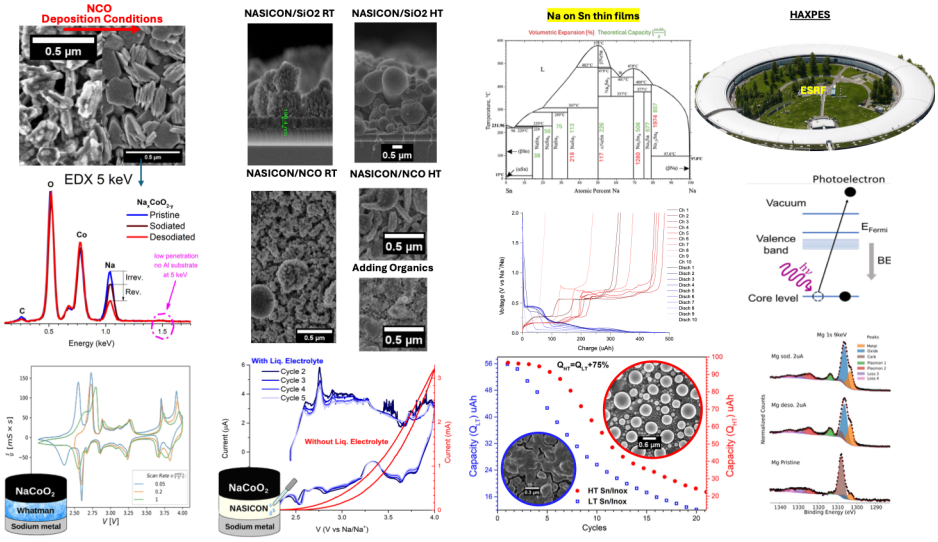

Figure 1. ***Left (top to bottom):*** *Morphological changes in NCO films grown on aluminum resulting from optimizing the PLD conditions; post-mortem energy-dispersive X-ray spectroscopy (EDS) analysis demonstrating the sensitivity of the technique to changes in the state of charge after electrochemical cycling; cyclic voltammetry confirming the O3 crystallographic phase of the sample.* ***Center left:*** *SEM micrographs illustrating the effect of deposition conditions on NASICON deposition on SiO_2 and NCO substrates, and the corresponding surface modifications after exposure to the organic species present in the liquid electrolyte, which contribute to the formation of a passivating solid-electrolyte interface observed during cyclic voltammetry.* ***Center right:*** *Na-Sn phase diagram, charge-discharge profile of a representative Sn thin-film electrode, and the influence of temperature-induced morphological changes on coulombic efficiency.* ***Right:*** *The European Synchrotron Radiation Facility (ESRF), schematic representation of core-level excitation in HAXPES, and deconvolution of the Mg 1s core level for three different samples.*

Determination of the local chemical strain on single crystal LCO by c-AFM

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Li_xCoO_2 (LCO) is one of the most widely used cathode materials in lithium-ion batteries due to its high energy density and technological maturity. Unlike most Li-based cathodes, LCO exhibits a negative chemical expansion coefficient in the compositional range 0.6 < x < 1 and undergoes a transition between two main hexagonal phases: HEX-I, a semiconducting phase at high Li content, and HEX-II, a highly conductive phase at intermediate lithiation levels. These unique structural and electrochemical properties, together with its manufacturability, underpin the widespread success of LCO in commercial batteries [1,2].

In this work, 50 nm-thick epitaxial LCO films were deposited by Pulsed Laser Deposition (PLD) on $SrTiO_3$ (STO) (100) and STO (111) substrates buffered with a 20 nm-thick conductive $SrRuO_3$ (SRO) layer. Galvanostatic cycling was used to reach selected lithiation states (x = 0.6, 0.8, and 1). The epitaxial quality of the films and grain orientation were confirmed by SEM and XRD analyses.

Conductive Atomic Force Microscopy (c-AFM) has emerged as a powerful technique for probing local electrical and mechanical properties of battery materials with nanometer-scale resolution [4]. Here, current mapping and local I-V spectroscopy measurements performed under different normal loading forces are combined to investigate the relationship between local conductivity, lithiation state, and chemically induced strain in epitaxial LCO grains. By exploiting the strong coupling between electronic transport and lattice expansion in LCO, c-AFM provides a route to quantify local chemical strain at the nanoscale.

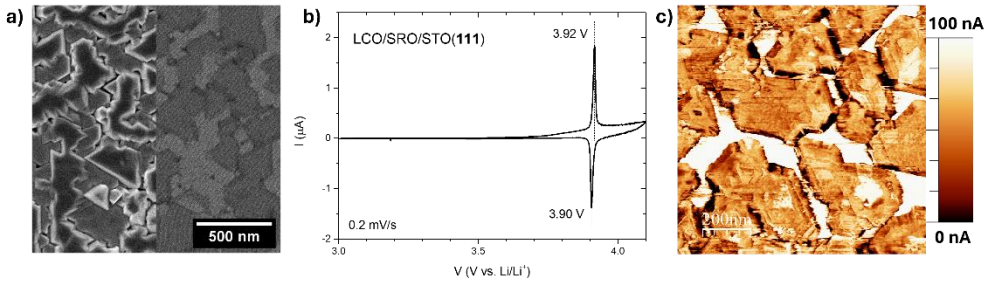

Figure 1. *a) SEM scans of the top view of epitaxially pulsed laser deposited LCO(111). b) Galvanostatic cycle of LCO(111). Oxidation and reduction peak at 3.92V and 3.90V respectively. c) c-AFM current map of LCO(111) scanned with a bias voltage of 1 V. Conductive layer of SRO is observed between the LCO grains*

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Low-energy electron microscopy study of the growth of M_2Mo3O8 (M = Mn, Fe) on Mo (110)

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The family of ternary molybdenum oxides, $M_2Mo_3O_8$, where M is a 3d transition metal (TM), has attracted attention as a model system for studying multiferroic properties. The compounds crystalize in a polar hexagonal ($P6_3mc$) structure, in which layers of octahedrally and tetrahedrally coordinated M^{2+} cations alternate with layers of Mo_3O_{13} trimers along the c-axis. At low temperatures, the crystal's intrinsic polarity is strongly coupled to the magnetic ordering of M^{2+} sublattice, resulting in a large and tunable magnetoelectric effect that is strongly dependent on the nature of the cation M. Furthermore, the compounds are associated with areas such as nonreciprocal optics and spin-caloritronics, and recently, have been identified as candidates for altermagnets.

In this work, we present a low electron microscopy study of the high-temperature, molecular-oxygen-assisted growth of two $M_2Mo_3O_8$ family members, $Mn_2Mo_3O_8$ and $Fe_2Mo_3O_8$. The compounds were synthesized by depositing the transition metal only, with the Mo (110) substrate acting as a source of Mo^{4+} cations. A similar phenomenon was previously observed for the heavier member of the 6th group – tungsten, leading to formation of $M^{II}WO_4$ tungstates when depositing a another element on a W (110) surface. However, to the best of our knowledge, such behaviour has never been reported for molybdenum.

A range of techniques were used to elucidate the structure and chemistry of the samples. *In-situ* low-energy electron diffraction (LEED) measurements indicate that the $Mn_2Mo_3O_8$ and $Fe_2Mo_3O_8$ structures - islands and wires – show preferential growth along the [100] and [111] directions of the Mo (110) surface, with the (001) face of the molybdate facing upwards in the case of the islands. Through the laterally-resolved X-ray photoelectron spectroscopy (XPS-PEEM), we confirm the presence of Mo^{4+} in the structures, while X-ray absorption spectroscopy (XAS-PEEM) measurements on the $L_{2,3}$ edges of the transition metals, and the O K edge give us insight into the details of Mo^{4+} and M^{2+} coordination and bonding. Via the use of polarized Raman spectroscopy, we confirm that the compounds crystalize with a $P6_3mc$ symmetry. Finally, we complement the low-electron microscopy study of the morphology with three-dimensional atomic force microscopy (AFM) images of the samples.

References

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