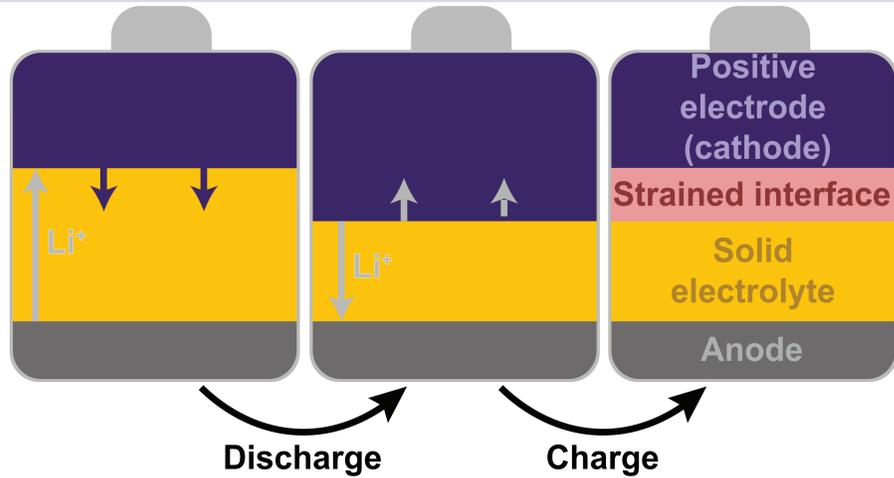


# The SOLIMEC consortium: cathode-electrolyte interfaces in ASSBs

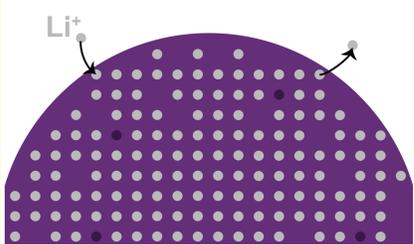
I. Cuevas<sup>a\*</sup>, J. Keckes<sup>b</sup>, Peter Siffalovic<sup>c</sup>, Bernhard Brunsteiner<sup>d</sup>, E. Vasco<sup>e</sup>, D. Rettenwander<sup>af</sup>, and C. Polop<sup>gh</sup>

The climate conference in Glasgow 2021 emphasized the importance of reducing CO<sub>2</sub> emissions. This endeavor requires a more significant step towards sustainable energy sources and storage. The rationale for this project is to improve the next generation of emerging solid-state Li batteries (SSLBs), which can eliminate hazards and energy density issues associated with conventional liquid electrolyte-based Li-ion batteries (LIBs). To achieve this goal, five leading research groups and a large technological company in the EU have developed the following strategy to face the current challenges of SSLBs. We rely on multicomponent engineering of cathode material and its interface with the solid-state electrolyte to prevent stress-induced loss of contact during charge/discharge, which degrades electron/ion transfer, and thus improving the SSLB performance and longevity. Potential benefits are seen in the application of SSLB as true alternative to LIB to replace fossil fuels in the car industry. The poster presents the ongoing efforts in the consortium to further the understanding of cathode materials and mitigate strain upon cycling. Both synthesis methods and advanced characterisations are placed in the spotlight. Scan the QR codes to access our already published articles!



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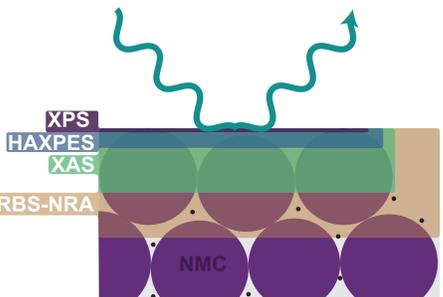
## Cathode characterisation



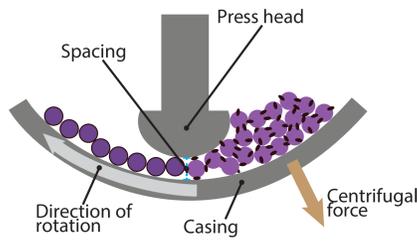
In cathode materials such as LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>O<sub>2</sub> (NMC), the effective insertion and extraction of lithium is ruled by the available sites and the oxidation states of the redox centers.

Nickel-rich NMC materials are promising cathode materials for the next-generation batteries, owing to their low cost and their associated high energy density. The high Ni content leads, however, to poor cyclability due to structural deterioration, oxygen evolution and electrolyte oxidation among other reasons.

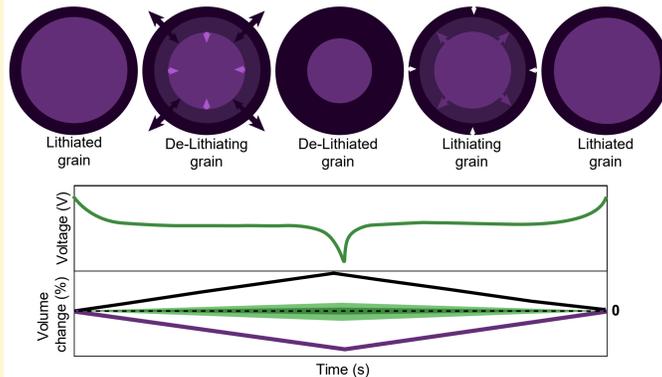
In the present work, the lithium concentration in NMC811 is analysed in multiple depths, as well as interpreted in accordance to the Ni oxidation states. To map it, multiscale material characterisation is established.



## Core-shell structures

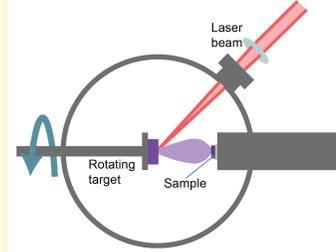


Mechanofusion enables the creation of particles with a different composition at the core and the outer part. The synergy between those structures can be used to tackle dimensional changes.

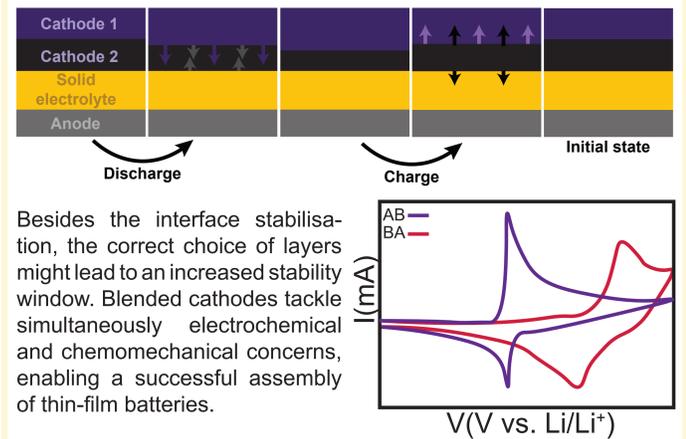


Cathodes and catholytes produced from non-expanding engineered grains will show reduced volume changes upon cycling.

## PLD heterostructures



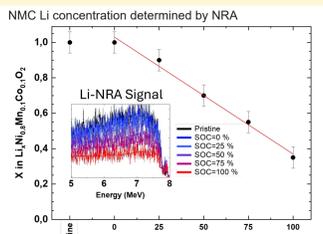
Pulsed Laser Deposition (PLD) enables the synthesis of blended cathode layers. Highly crystalline layers can be subsequently deposited, using the previous layer as a substrate. The blended structures feature excellent contact in between the layers and adjustable dimensions.



Besides the interface stabilisation, the correct choice of layers might lead to an increased stability window. Blended cathodes tackle simultaneously electrochemical and chemomechanical concerns, enabling a successful assembly of thin-film batteries.

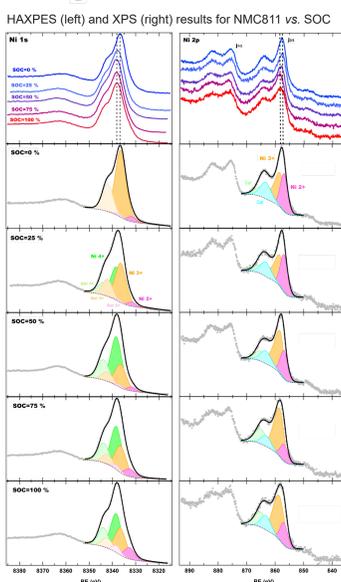
## The bulk

Nuclear Reaction Analysis (NRA) results demonstrate the successful extraction of lithium on the battery charging process. Lithium concentration linearly decreases from 100% to 35% in a full charge cycle.



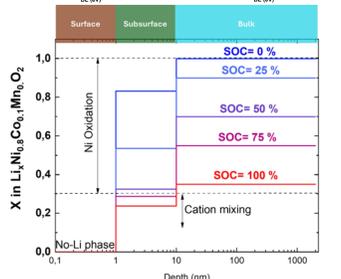
## The subsurface layer

Below the outermost surface, HAXPES shows the transition of Ni<sup>3+</sup> to Ni<sup>4+</sup> as the Li ions gradually leave the lattice, matching the XANES results. At later charge stages, the Ni<sup>2+</sup> content increases again. Such increase is attributed to Ni/Li cation mixing.

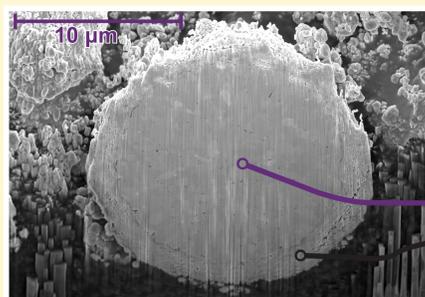


## The surface

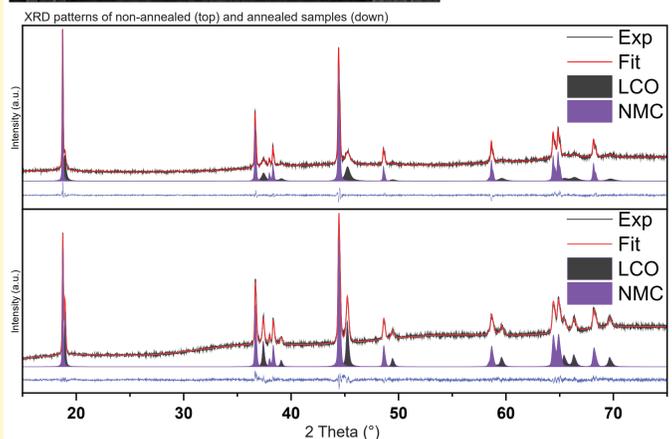
Surface sensitive XPS reveals a sharp contrast in between the surface composition and the bulk. The prevalence of Ni<sup>2+</sup> on surface indicates the irreversible degradation of the surface, due to the formation of species such as NiO and Ni<sub>3</sub>O<sub>4</sub>. The surface is, therefore, Lithium depleted.



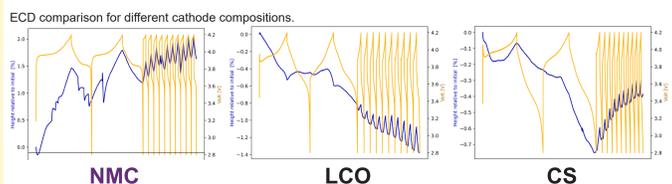
Li content and oxidation states can be coupled via multi-scale characterisation. Three regions are defined: a delithiated surface, a bulk governed by the Ni oxidation, and an intermediate layer where a partial Li depletion triggers Ni/Li cation mixing at higher SOC.



Quasi-spherical particles with adequate coatings are obtained after mechanofusion and dedicated annealing.

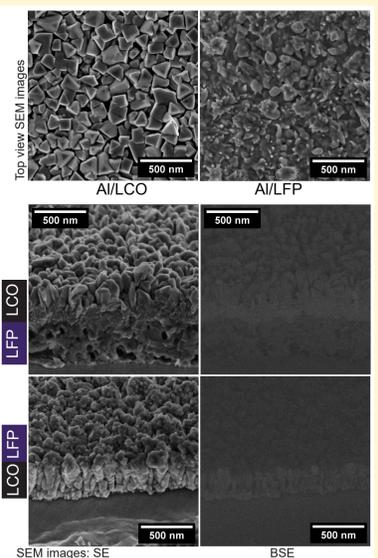


Both phases appear to be crystalline, with enhanced crystallinity at optimised annealing temperatures. Excessive annealing leads to TM cross-diffusion and phase mixing.



Preliminary dilatometric results hint to a lower cathode strain for the mechanofused cathode particles. Such behavior appears to be due to a combination in between both electrode materials.

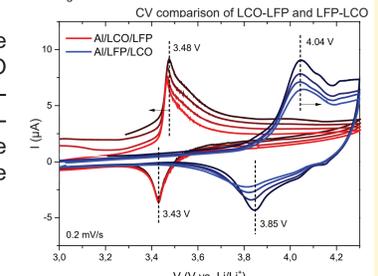
Both LiCoO<sub>2</sub> (LCO) and LiFePO<sub>4</sub> (LFP) compositions show adequate adherence to the aluminium substrate, with LCO grains appearing to be highly crystalline.



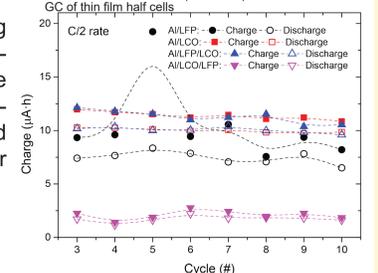
Layered blended cathodes are elaborated by successive deposition of LCO and LFP in an aluminium collector substrate.

LCO shows excellent adherence to previously deposited LFP, forming an attractive bilayer structure. LFP shows lower adherence on LCO as substrate.

Blended cathodes where the outer layer is based on LCO show reactions at higher voltages (circa 4.05V). The outermost layer can be used to tune the material ESW, and might be key to higher energy densities.



Thin film galvanostatic cycling data reveals an improved performance of the cells where LCO is deposited over LFP. Opposite behaviour is observed when LCO is the substrate for LFP.



## Conclusions:

- The implementation of ASSBs strongly relies on cathode optimisation, and addressing the dimensional changes upon cycling. Improved understanding of the cathode materials, from both chemical and mechanical perspectives acquires capital importance.
- Optimised CAM powders are a promising method to address the chemo-mechanical challenges of ASSBs at an industrial scale. Mechanofusion is a reliable method that might provide such optimisation.
- PLD offers promising results into blending cathode materials to mitigate dimensional challenges for thin film batteries. Optimisation of CAMs through PLD could as well improve ASSB performance.
- Electrochemical Dilatometry is a promising operando tool for the assessment of viability of ASSBs.

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