Surface characterisation of Ni-rich positive electrode material for Li-ion batteries

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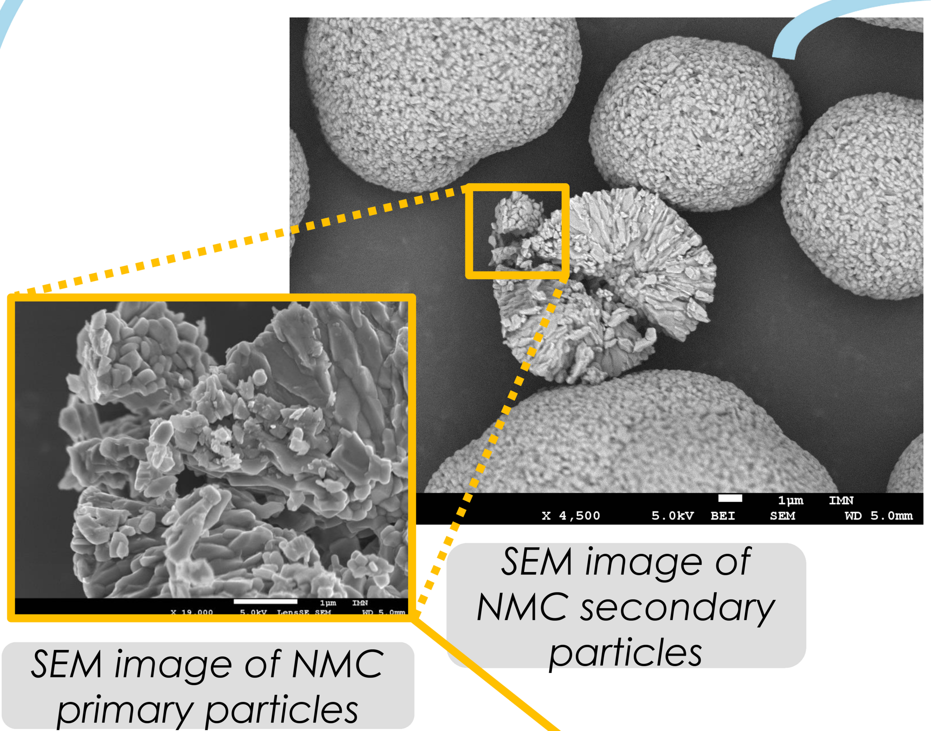
The electrification of vehicles presently relies on lithium ion batteries using layered oxides of nickel, manganese and cobalt (NMC) as positive electrode materials. High-nickel content NMCs allow to obtain higher energy densities, but they suffer from severe instabilities issue during all the manufacturing steps (synthesis, handling, electrode preparation) and gassing issues decreasing the cycle life and causing safety problems. In this context, we report a systematic study of the pristine material surface using a multi-analytical approach in order to elucidate the origin of this gas generation; different characterisation techniques such as MAS-NMR, XPS and STEM-EELS are combined to give a complete description of the material before cycling.

Context

- Layered oxide structure: NMC811;
- High capacity due to the high Ni content;
- Gassing problems during electrochemical cycles;
- Instability issues during manufacturing steps;

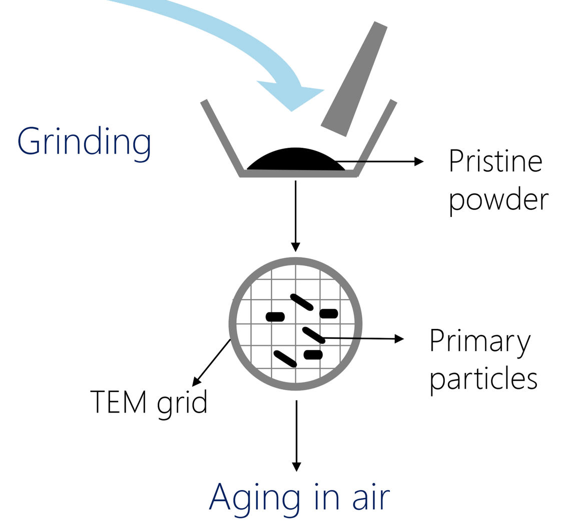
Systematic study and comprehension of the surface phenomena before cycling

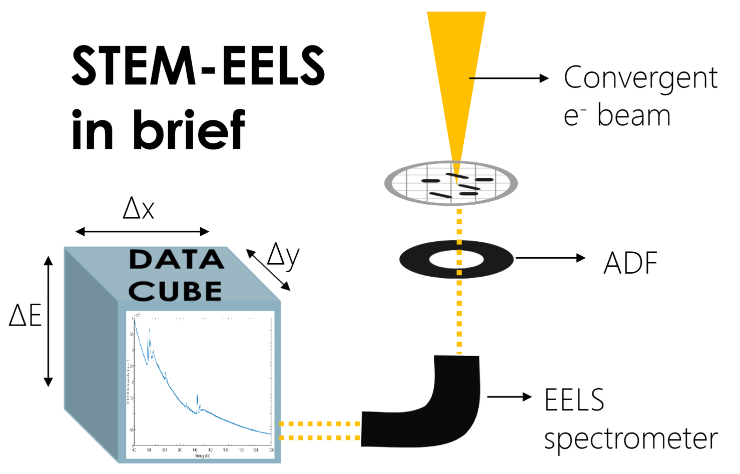
Contact with air: storage in ambient atmosphere for 5 days



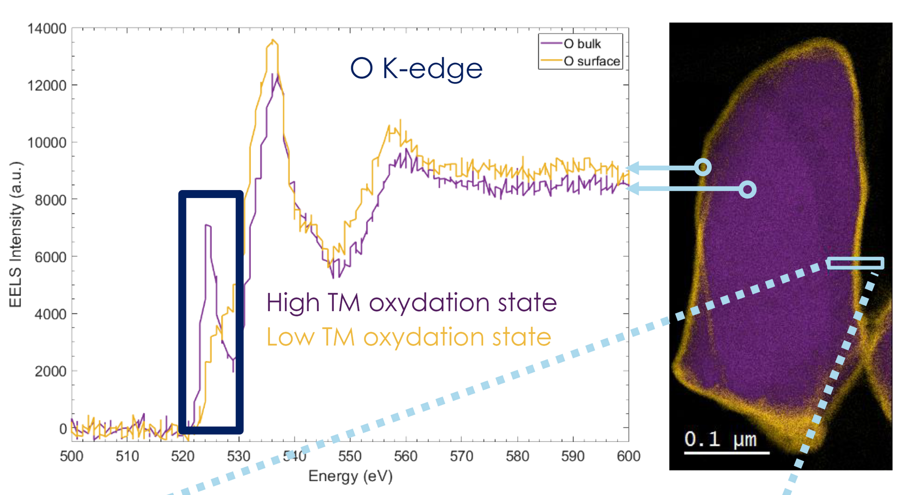
SEM image of NMC primary particles

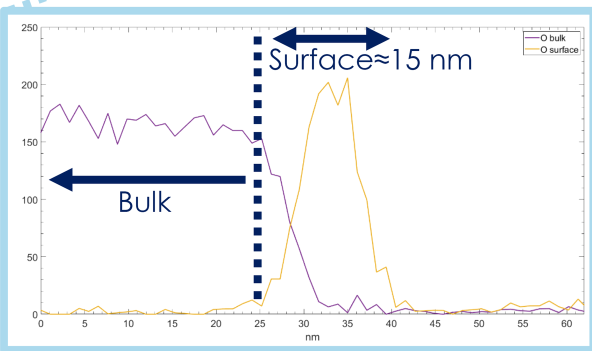
SEM image of NMC secondary particles





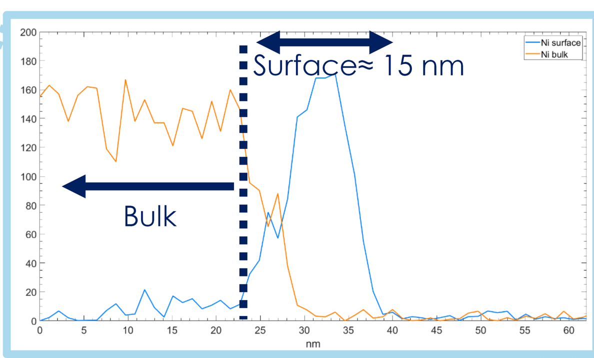
- Spatial resolution;
- Oxidation number;
- Coordination;
- Composition and quantification.



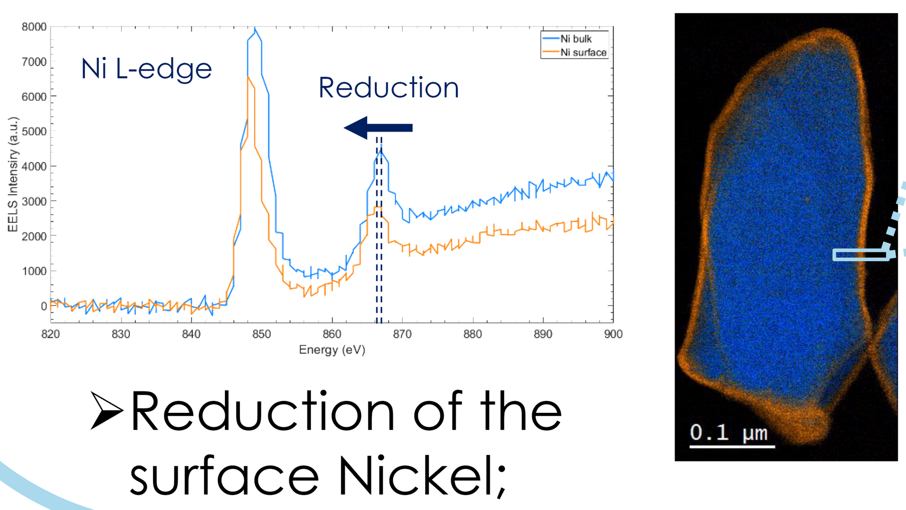


Concentration profile of the contribution of the bulk/surface environments

- Change in the Oxygen coordination sphere at the surface;



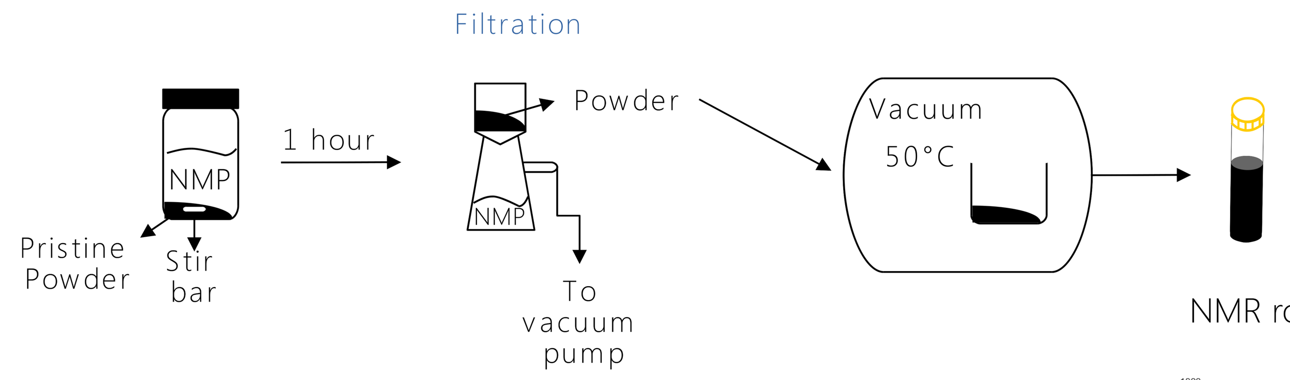
Concentration profile of the contribution of the bulk/surface environments

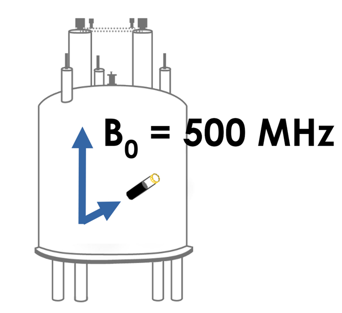


- Reduction of the surface Nickel;

- The aging in air changes the electronic structure at the surface of the primary particles.

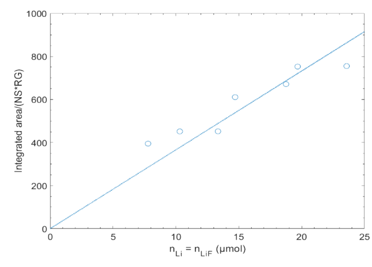
Electrode preparation: contact with NMP



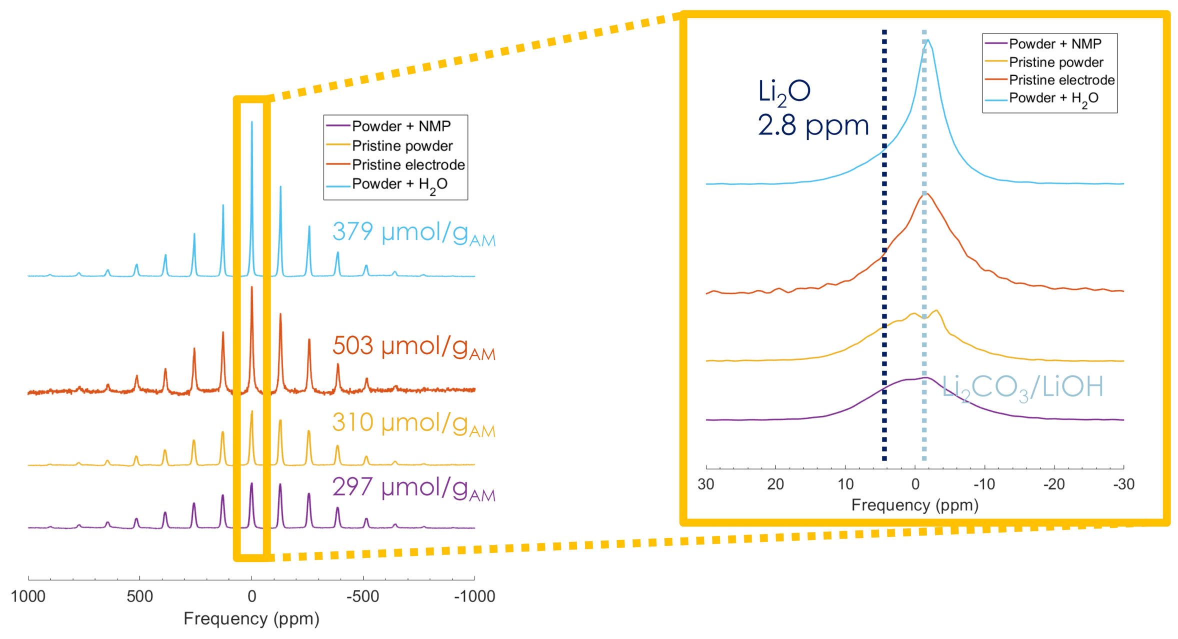


Magic Angle Spinning = 54.7°

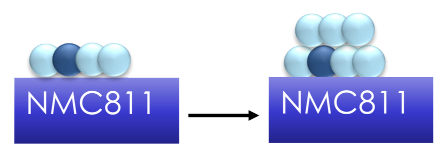
- High magnetic field → signal of the paramagnetic bulk is hidden → investigation of the diamagnetic surface;
- Surface Li amount => lithium impurities at the surface;



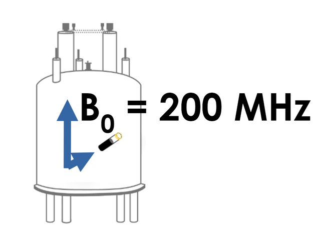
Used as quantification technique;



- $LiOH/Li_2CO_3$ increase

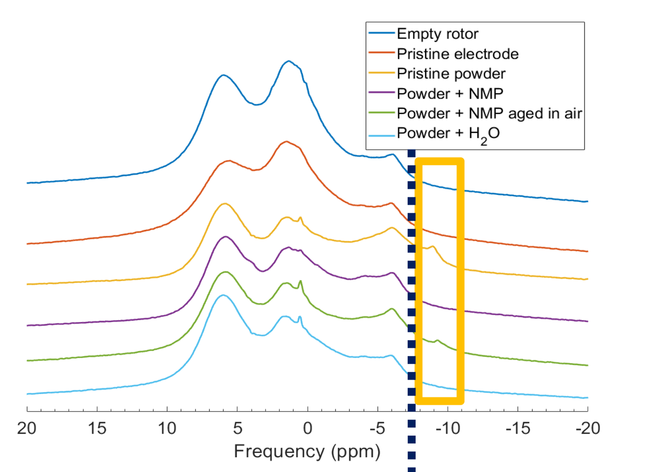


- Important increase of surface Li from pristine powder to electrode formulation → Li extraction from bulk;
- Modification of the surface before cycling → Impact on gassing?



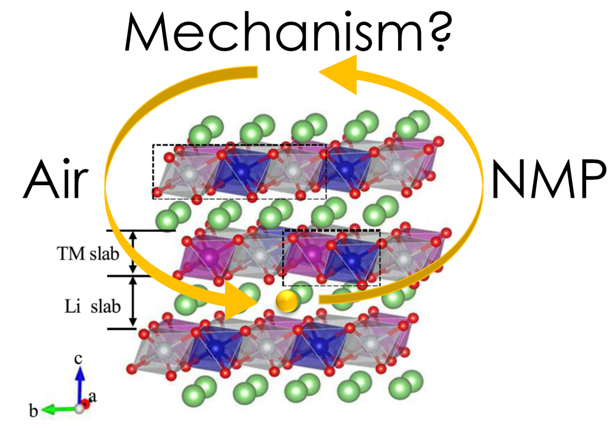
Magic Angle Spinning = 54.7°

- Low magnetic field → investigation of the paramagnetic bulk;



Surface proton Bulk proton [1]

Mechanism?



(1) Ménétrier, M.; Vaysse, C.; Croguennec, L.; Delmas, C.; Jordy, C.; Bonhomme, F.; Biensan, *Electrochemical and Solid-State Letters* 2004, *7* (6), A140.

- Proton environment in the bulk of the pristine powder;
- Proton reversibly removed after the contact with NMP;
- Modification of the bulk before cycling → effect on gassing?

- The electrode formulation has an effect on the impurities quantity as well as on the surface and bulk composition;
- Bulk proton is probably exchanged with surface Li after contact with air, but not with NMP → two different mechanisms?

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