Phase Engineering Improves the Electrochemical Stability of Lithium-rich Cobalt-free Layered Oxides for Lithium-ion Batteries

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Introduction

The problem

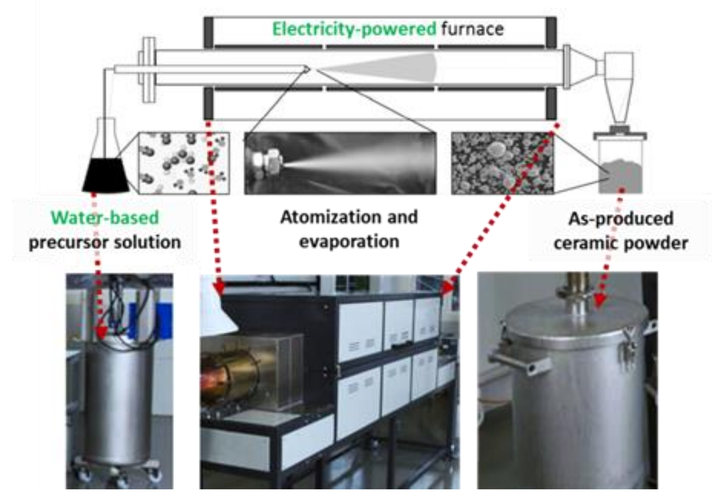
- The electric vehicle market relies on cobalt-rich materials.
- Cobalt has a vulnerable supply chain and is toxic.

The challenge

- Developing cobalt-free and performant materials.
- Li-rich Co-free layered oxides have high capacities but low stabilities.
- Can phase engineering help to mitigate capacity and voltage fade?

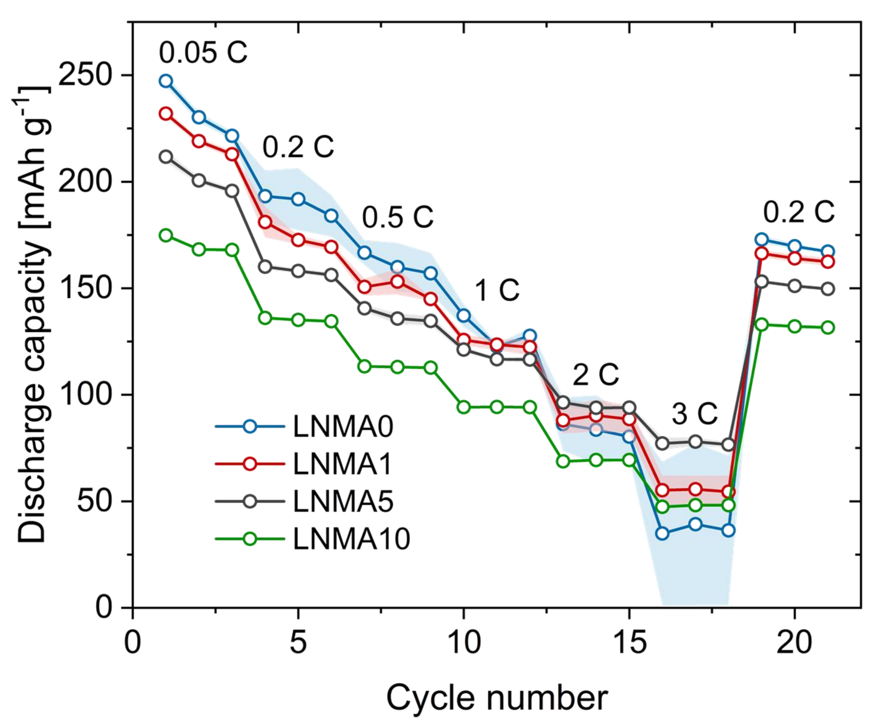
The solution

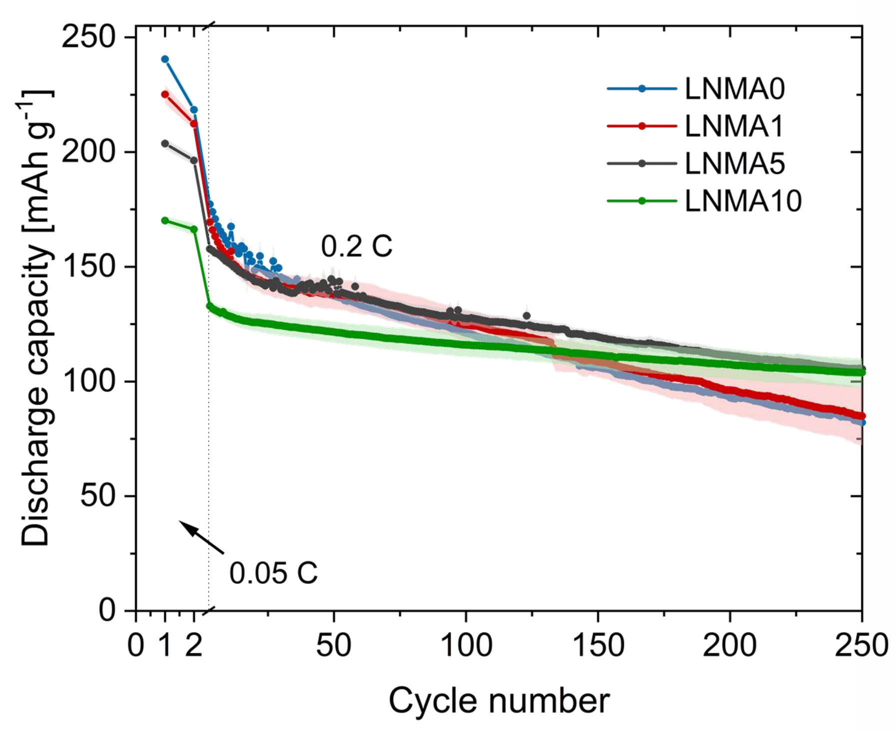
- Spray pyrolysis was used to synthesize a series of samples ($Li_{1.26}Ni_{0.15}Mn_{0.61-x}Al_xO_2$) with increasing amount of Al doping.
- With increasing Al amount, the samples are termed LNMA0, LNMA1, LNMA5, and LNMA10.
- The powders were investigated in terms of their electrochemical performance, and structural properties before and after galvanostatic cycling (100 cycles, 0.2 C, 2 – 4.7 V vs Li^+/Li).

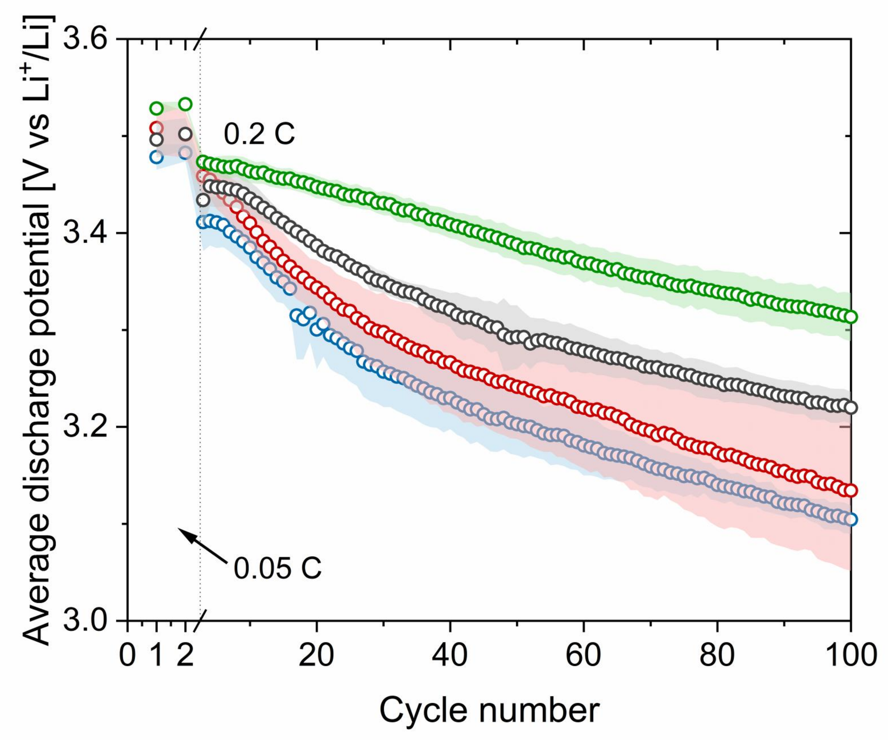


Electrochemical characterization

- Al doping increases the rate performance from 36 mAh g^{-1} to 77 mAh g^{-1} at 3 C, even though the initial discharge capacity decreases with doping.
- The capacity retention is improved from 46% for LNMA0 to 67% for LNMA5 (250 cycles, 0.2 C).
- Voltage fade is significantly suppressed.



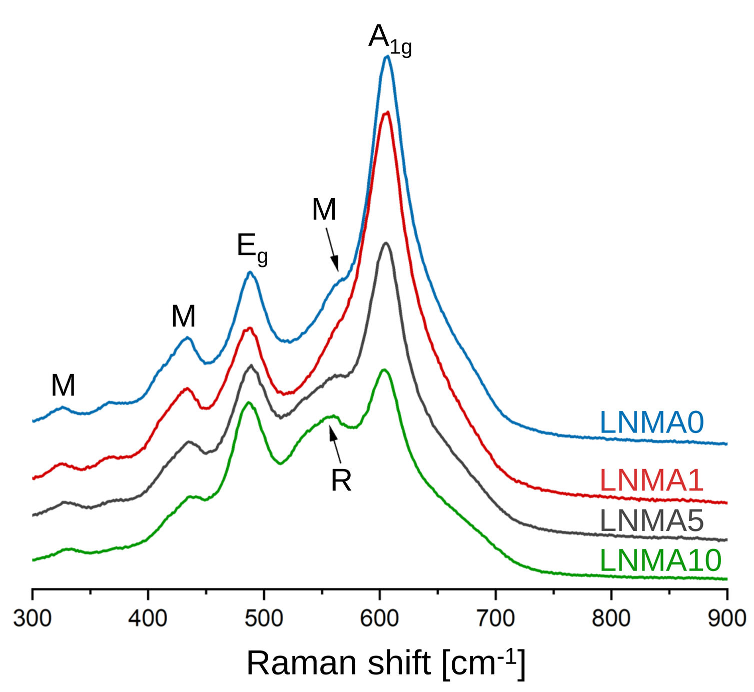




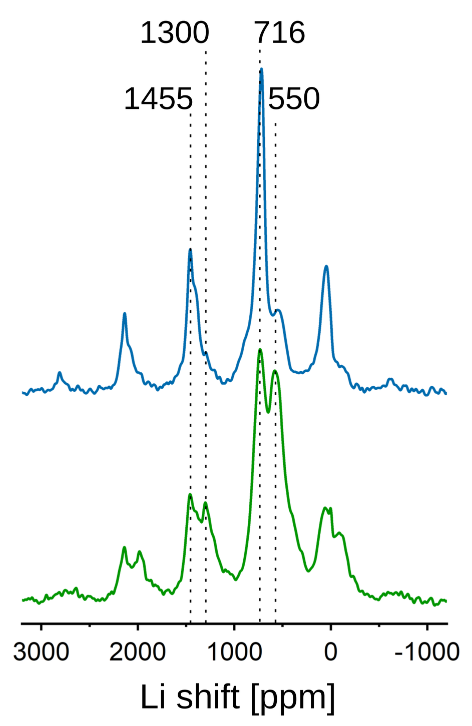
Structural characterization

Powders

Raman spectroscopy



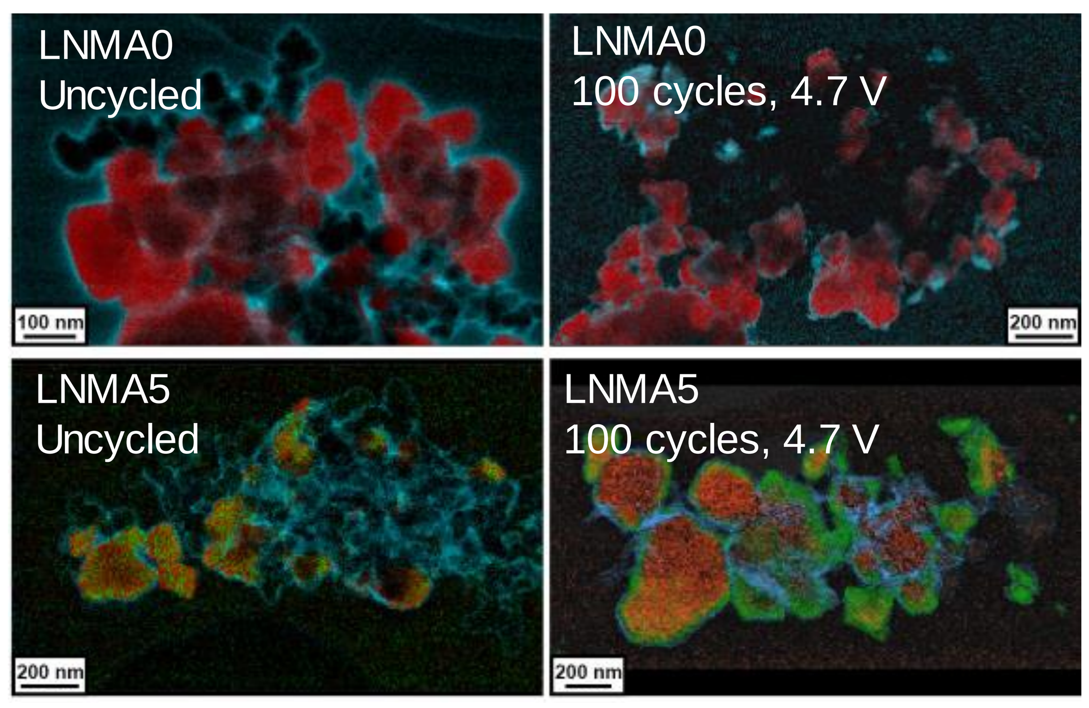
⁶Li NMR spectroscopy



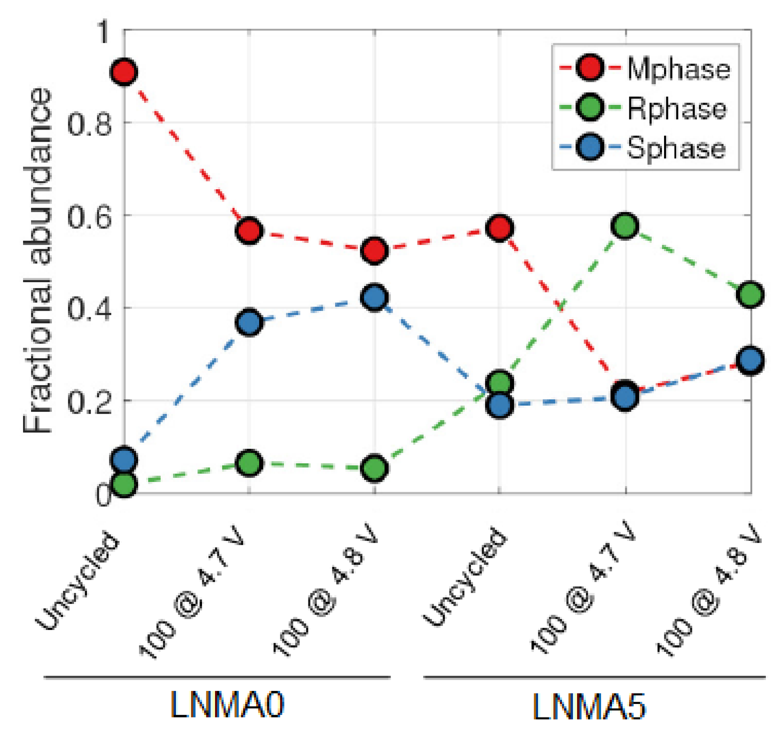
- The materials' average crystal structure can be described using a monoclinic structure, but Al doping increases the rhombohedral character of the materials.

Electrodes

Hypermodal data fusion: abundance maps



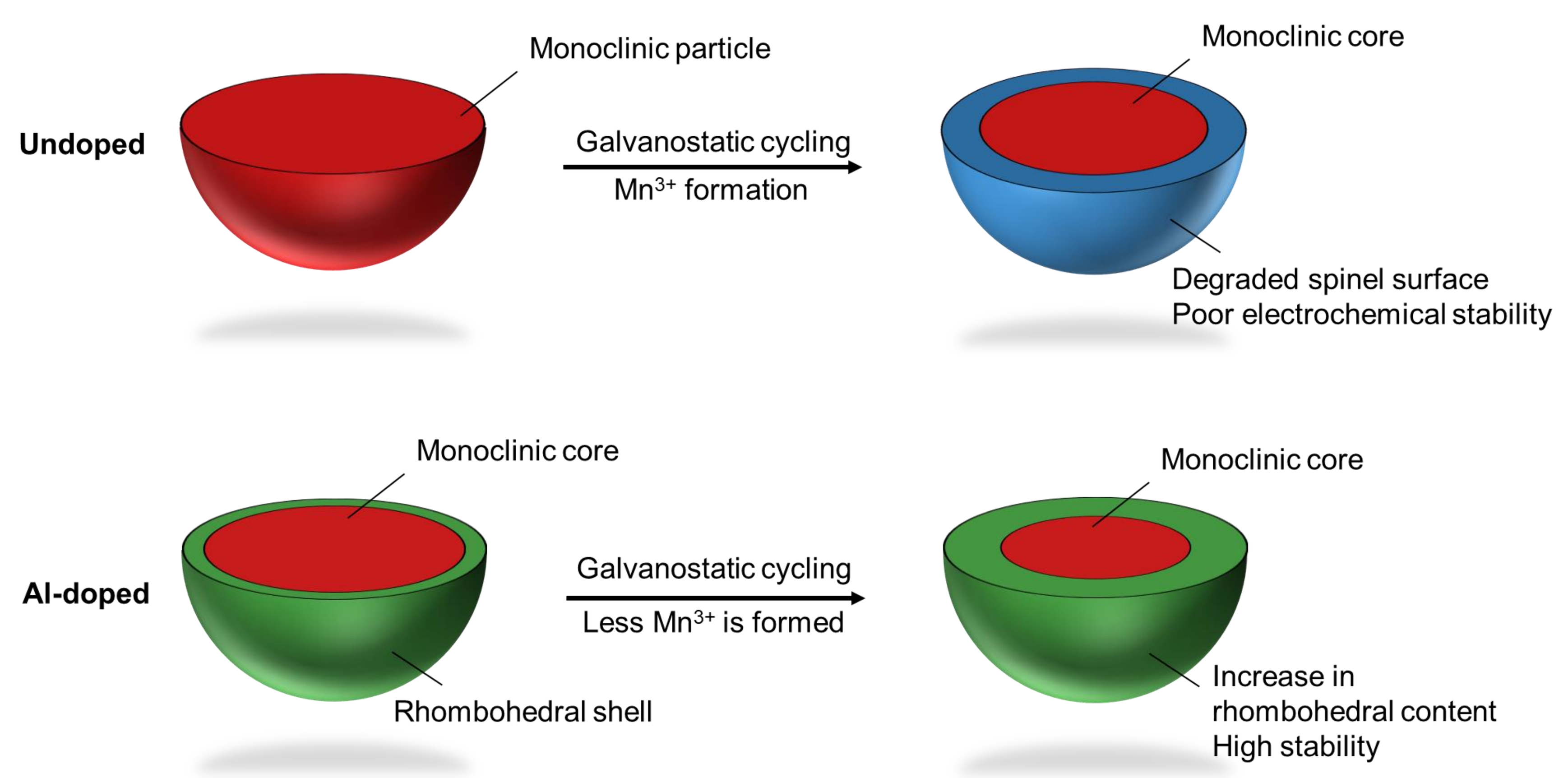
Fractional phase distribution



- HyDF is a statistical methodology which can jointly analyze spectroscopic information for correlations. The method extracts a monoclinic, a rhombohedral, and a disordered spinel phase from the spectroscopic information.
- The rhombohedral phase preferentially forms as an encapsulating shell surrounding a monoclinic phase core. In the doped samples, the amount of rhombohedral phase increases during cycling, thereby avoiding the formation of a disordered spinel and the related voltage fade.

Conclusion

- Al doping ($Li_{1.26}Ni_{0.15}Mn_{0.61-x}Al_xO_2$) induces the formation of a rhombohedral shell around a monoclinic core. The samples also contain a disordered spinel at the particle edges.
- Al doping improves the rate performance, suppresses voltage fade, and improves capacity retention.
- In the doped samples, the rhombohedral shell mitigates the formation of Mn^{3+} during electrochemical cycling, and thereby avoids the formation of a disordered spinel. Instead, the rhombohedral fraction of the doped material increases during galvanostatic cycling.
- The superior stability of the rhombohedral phase helps stabilize this system against decomposition into a disordered spinel during cycling.
- This study provides fundamental insight into the complex role that Al plays in phase engineering and in the improvement of the electrochemical stability in lithium-rich cobalt-free layered oxides.



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 875568.

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