

On the $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ system upon (de)lithiation: surface and bulk characterizations during the first three cycles

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Introduction

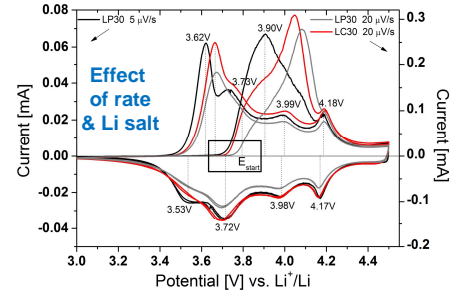
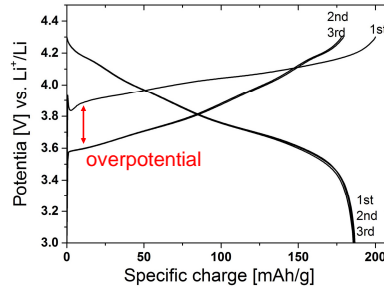
$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)

- Promising 4 V electrode material
- High practical specific charge, ~200 mAh/g
- Co doping: maintains the layered structure
- Al doping: improves thermal stability

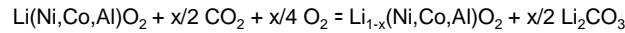
Motivation:

Detailed understanding of:

- Activation mechanism
- (de)lithiation reaction mechanism for first three cycles



Surface reaction characterization: XRD, DEMS & EIS

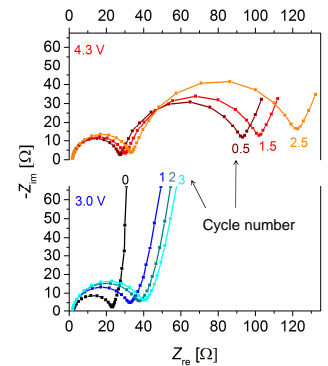


- Decomposition of the Li_2CO_3 film during oxidation $\rightarrow \text{CO}_2$ evolution
- Li_2CO_3 phase re-formed during reduction \rightarrow consumption of CO_2

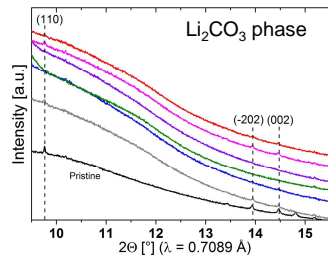
EIS

After 1st cycle: resistance decreases during delithiation (4.3V) and increases upon lithiation (3.0V) \rightarrow dissolution and re-formation of the insulating Li_2CO_3 surface film

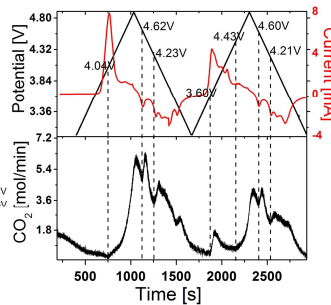
Kinetic limitations due to resistance to Li^+ ion transfer through the surface films \rightarrow CV peaks shift in the order of tens of mV



XRD

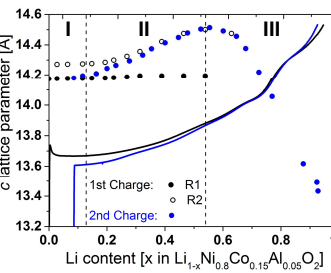
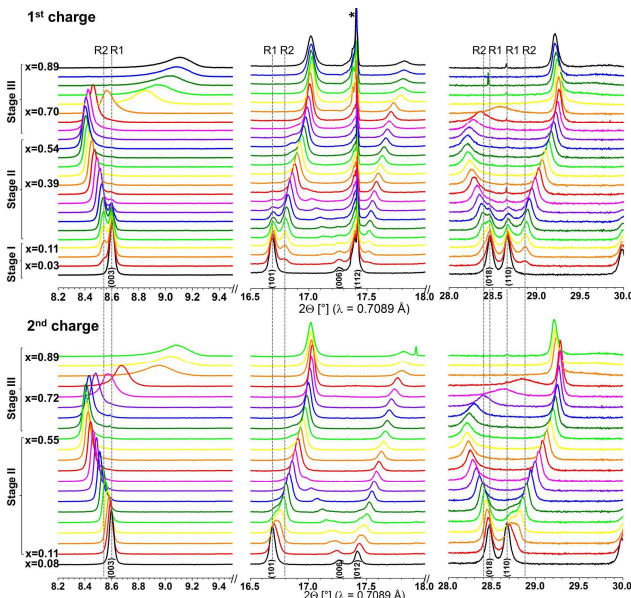


DEMS



Bulk characterization: reaction mechanism by *in situ* XRD & electrochemical exp.

Operando synchrotron XRD



1st charge:

- Stage I-II: two-phase/solid solution



- Stage III: R2 solid solution (contraction of the c axis)

2nd & 3rd charges:

- Mainly solid solution

Shift of E_{start} to lower potentials in CV: composition & reaction mechanism changes

Electrochemical experiments

