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Study of Specific Phase Degradation of Blended Cathodes by High Resolution in situ Synchrotron Diffraction

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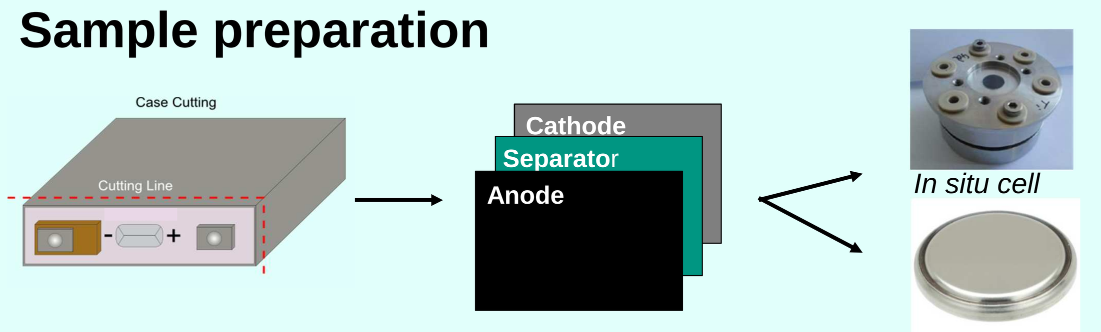
Recent development for Li ion battery commercialization is to use a blended system which consists of at least two types of cathode materials. Here we study a blended cathode system from a commercial cell consisting of a $LiNiCoMnO_2$ (NCM), $LiNiCoAlO_2$ (NCA) and $LiMn_2O_4$ (LMO) mixture. In situ XRD for fresh and fatigued cathodes have been measured to follow structural change during cycling. From in situ XRD pattern, we can determine : (1) weight fraction (2) selective activity and (3) lattice parameter of each phase during cycling. Based on the results, specific phase degradation in this cathode is discussed.

Sample Preparation, Fatigued Protocol and Morphology

Sample preparation



Cell opening

Washing, Cleaning, Stamping

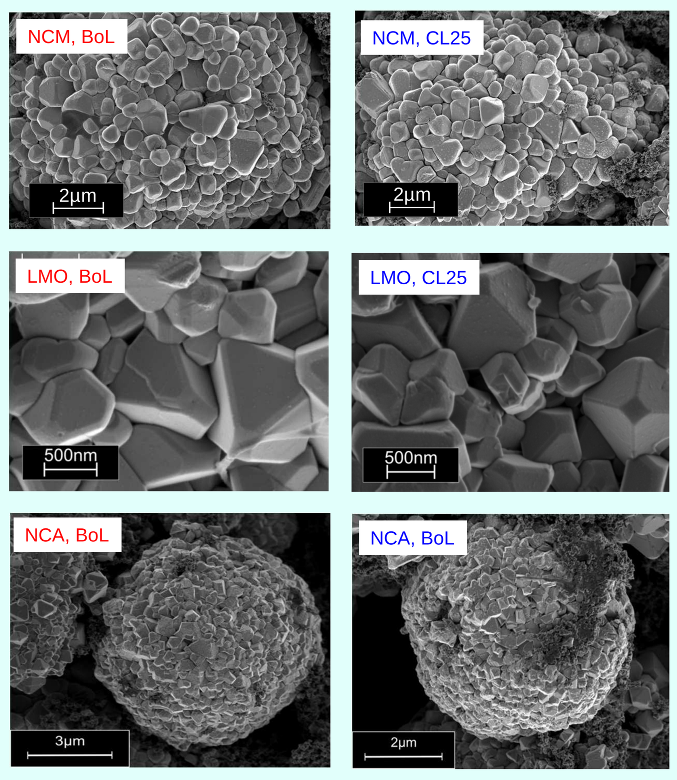
Cathode vs. Li

Fatigue protocol

Cathodes from fresh (BoL) and fatigued cells are studied

Cycling condition	BoL	CL25
Number of cycling	-	1600 cycles
Temperatur	25 ℃	25 ℃
Charge/Discharge Rate	-	1C/2C
Total Capacity Loss	-	13.5%

Cathode morphology by SEM

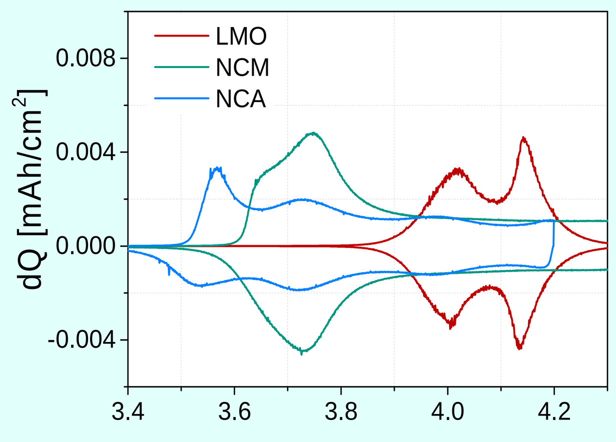


No significant morphology change of CL25 cathode compared to BoL cathode

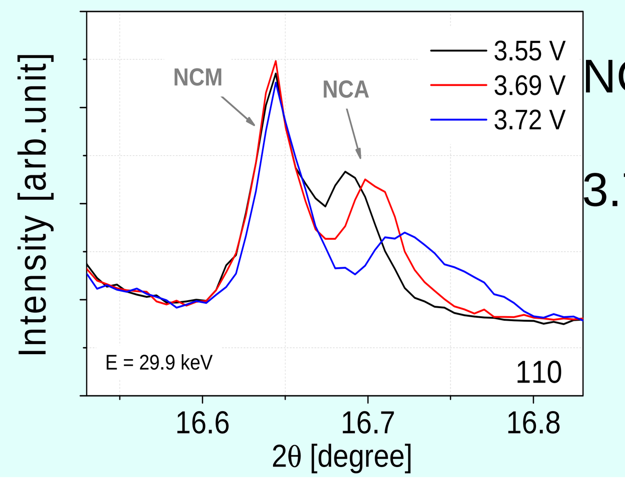
Primary particle ~100-500 nm

Secondary particle ~ µm range

NCM and NCA identification



dQ vs E of individual component of composite cathode

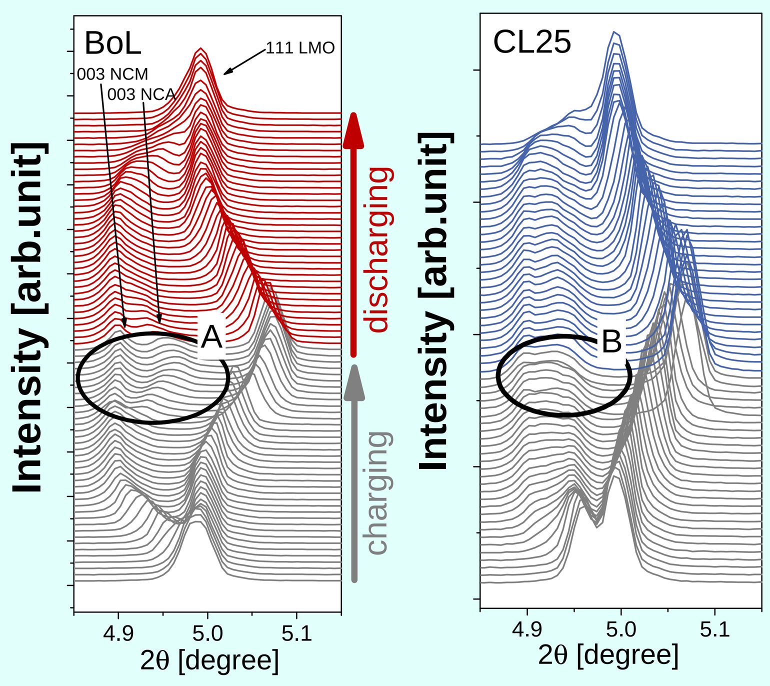


NCM and NCA can be distinguished from their different electrochemical ativity: NCA actives below 3.72 V, NCM does not.

Specific Phase Degradation at Room Temperature by in situ XRD

1. Specific Phase Activity by In situ XRD

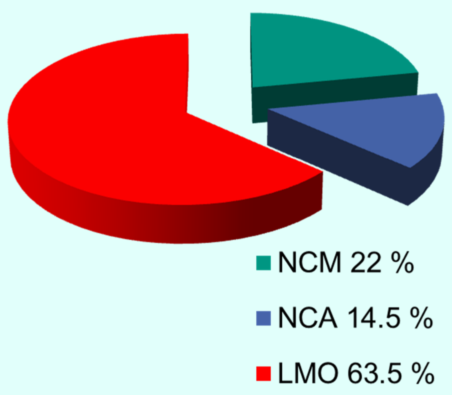
- At ALBA
- E = 29.9 keV
- 2.8 – 4.2 V
- Cathode vs. Li
- C/3 rate



Specific activity of each phase at BoL during charging:

- NCM : active below 3.72 V
- NCA : active above 3.55 V
- LMO : active above 3.97 V

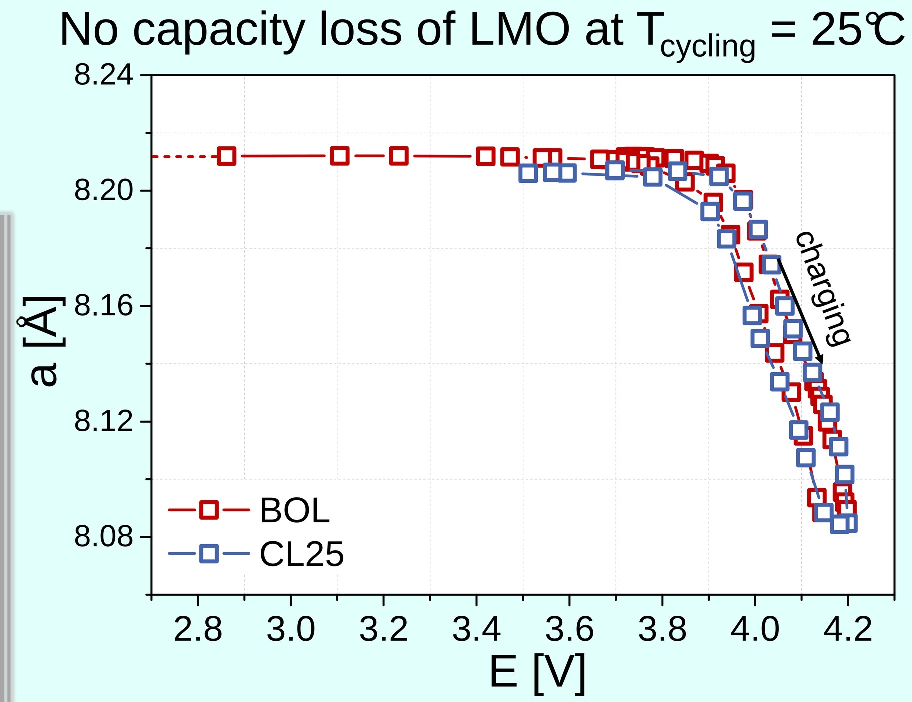
2. Phase Fraction of BoL cathode (XRD)



Phase	Space Group	Lattice parameter [Å]
$LiNiCoMnO_2$	R -3 m	a = 2.86094(3) c = 14.29877(17)
$LiNiCoAlO_2$	R -3 m	a = 2.85447(3) c = 14.2408(32
$LiMn_2O_4$	F d -3 m	a = 8.21015 (6)

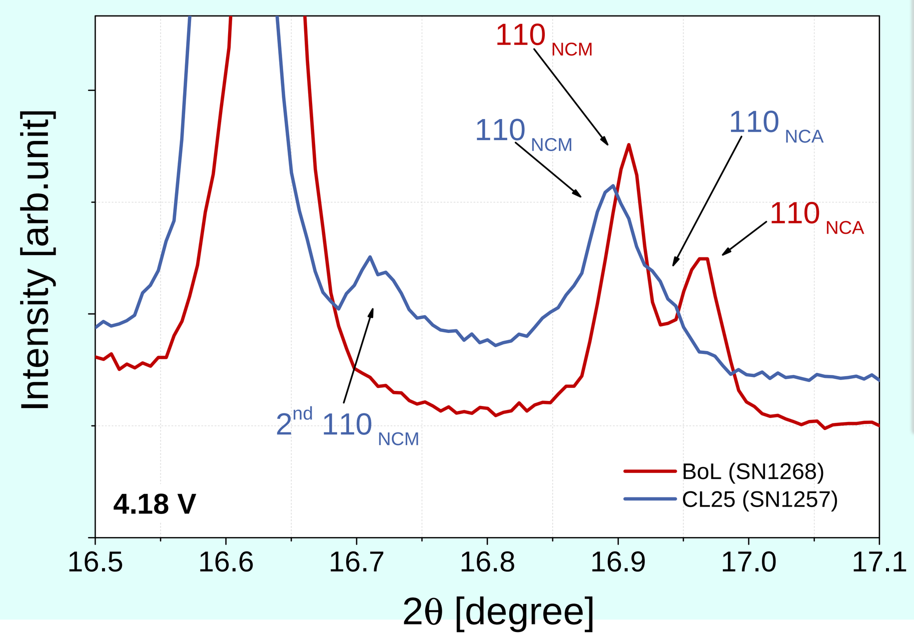
3. Degradation of LMO

No capacity loss of LMO at $T_{cycling}$ = 25℃

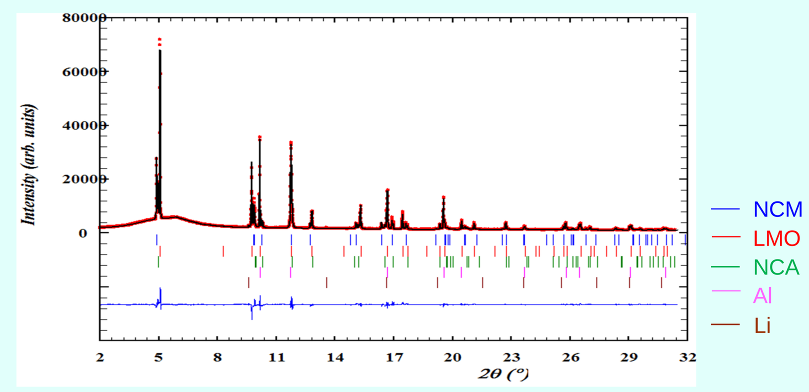


4. Degradation of NCM

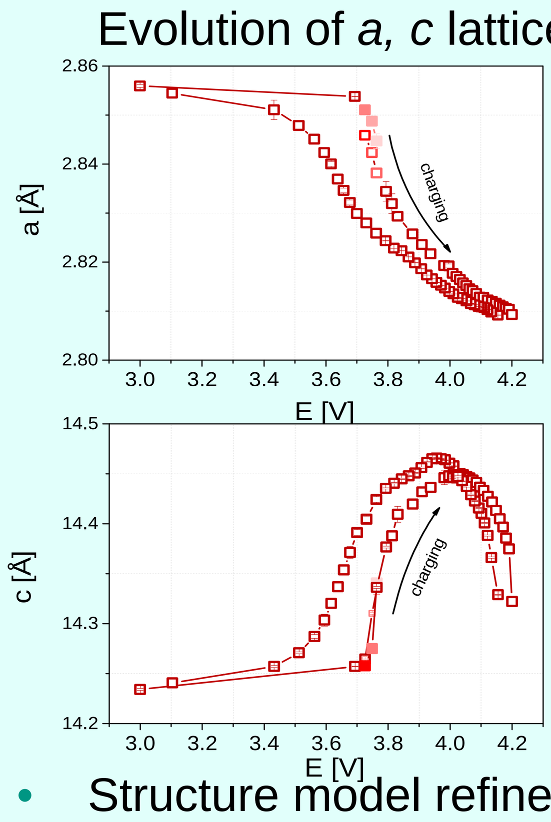
Inactive phase of NCM in partialy lithiated state is observed at CL25 cathode (~ 7% capacity loss of cathode).



5. Degradation of NCA



Evolution of *a*, *c* lattice parameter of BoL



In the range of 3.72 - 3.76 V during charging, NCA shows two layered phases. This might be due to Li gradient in the NCA particle during charging, creating two phases.

- Structure model refinement from in situ XRD for CL25 sample is in progress.
- 003 reflection of NCA above 4.09 V (region A and B in in situ XRD pattern):
  - BoL : shift to lower angle significantly
  - CL25: slight shift → NCA of CL 25 is less active

Summary and Outlook

At room temperature cycling, degradation of our composite cathode is related to NCM and NCA phases. For NCM, origin of capacity loss is due to inactive phase at partially lithiated state (~ 30% NCM is inactive). No inactive NCA phase is found, however it is observed from XRD pattern that NCA of fatigued cathode is less active than fresh cathode. Lattice parameter evolution of fresh and fatigued battery reveals that LMO phase is not degraded. To get more understanding of degradation mechanism, surface sensitive analysis will be performed. ESR experiment wil also be performed to investigate the reason for decreasing lattice parameter *c* of NCA at higher potential which might be related to capacity loss of NCA.