PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

Operando neutron powder diffraction of $LiNi_{0.5}Mn_{1.5}O_4$ vs. graphite performed in a cylindrical cell

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New optimized cylindrical cell for neutron powder diffraction (NPD)

Goal:

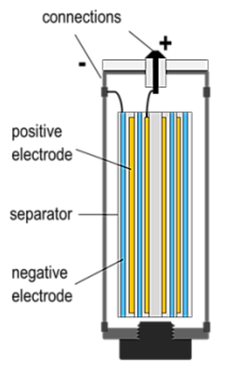
Follow during cycling the structural changes and the lithium content of $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) and graphite

Challenges:

☹ Weak neutron/matter interaction
→ Large amount of material
→ Good electrochemistry?

☹ Incoherent neutron scattering of H
→ Deuterated electrolyte ($$)

Cell design:



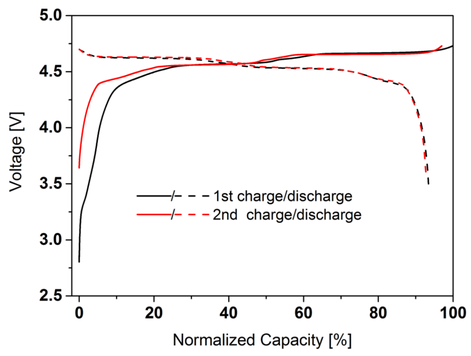
✓ Choice of:
- active materials
- electrolyte

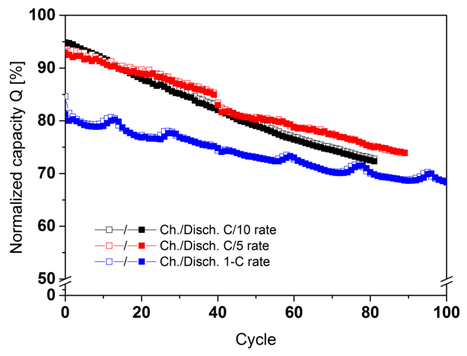
✓ Thin polymeric separator

✓ Large area to scan

✓ Ideal shape for diffraction

Electrochemical performance:



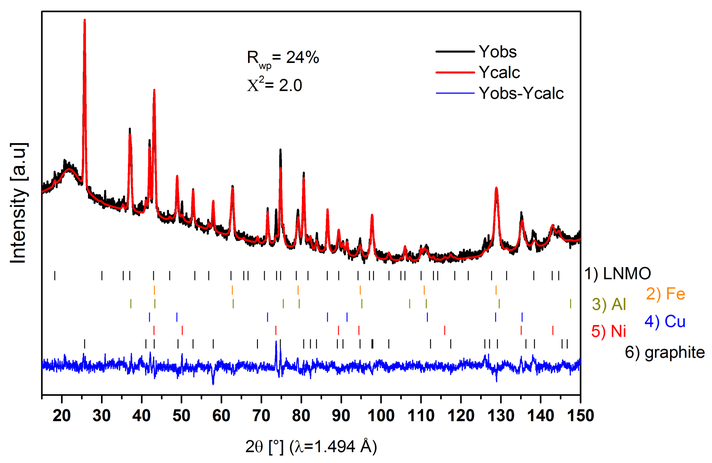


➢ Electrochemistry of LNMO vs. graphite system similar to standard cells

➢ Cycling at fast and slow rates possible

Neutron powder diffraction of the cylindrical cell

OCV state

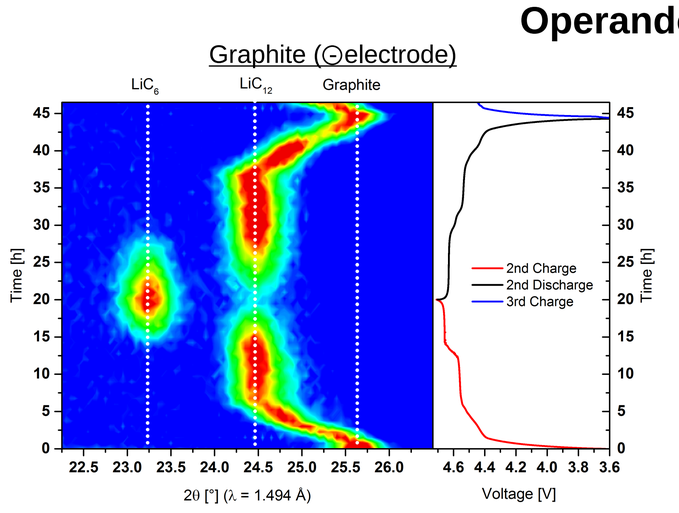


➢ Rietveld refinement possible

➢ Reasonable background

Operando measurement

Graphite (⊖electrode)

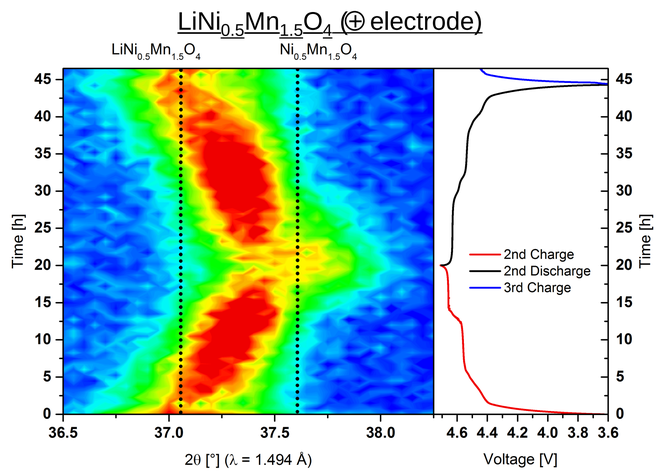


➢ $Li_0C \leftrightarrow LiC_{24} \leftrightarrow LiC_{12} \leftrightarrow LiC_6$

➢ Lattice expansion (~9%) during lithiation

➢ Solid-solution + two-phases reactions visible

$LiNi_{0.5}Mn_{1.5}O_4$ (⊕ electrode)



➢ 3 different cubic phases (Fd-3m)

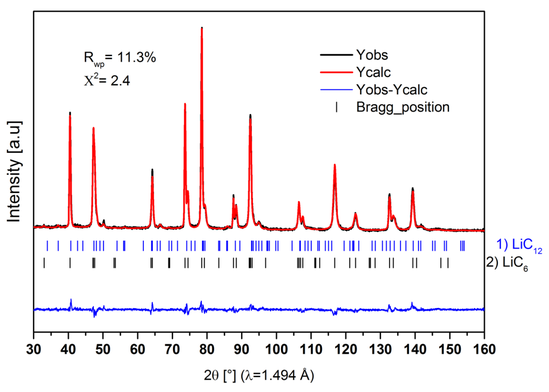
➢ LNMO ↔ $Li_{0.5}$NMO ↔ Li_εNMO

➢ Solid-solution + two-phases reactions during delithiation (~5.5% volume shrinkage)

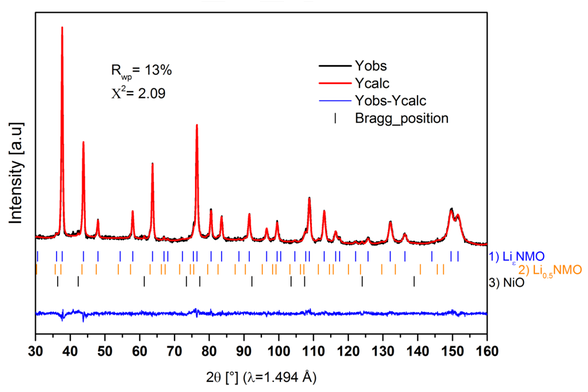
Ex situ NPD confirmation

Fully charged state (1st charge)

Graphite (⊖electrode)



$LiNi_{0.5}Mn_{1.5}O_4$ (⊕ electrode)



➢ $Li_{0.8}C_{12}$ (20%) and $Li_{0.9}C_6$ (80%)

➢ ~93% of the available Li inserted into graphite

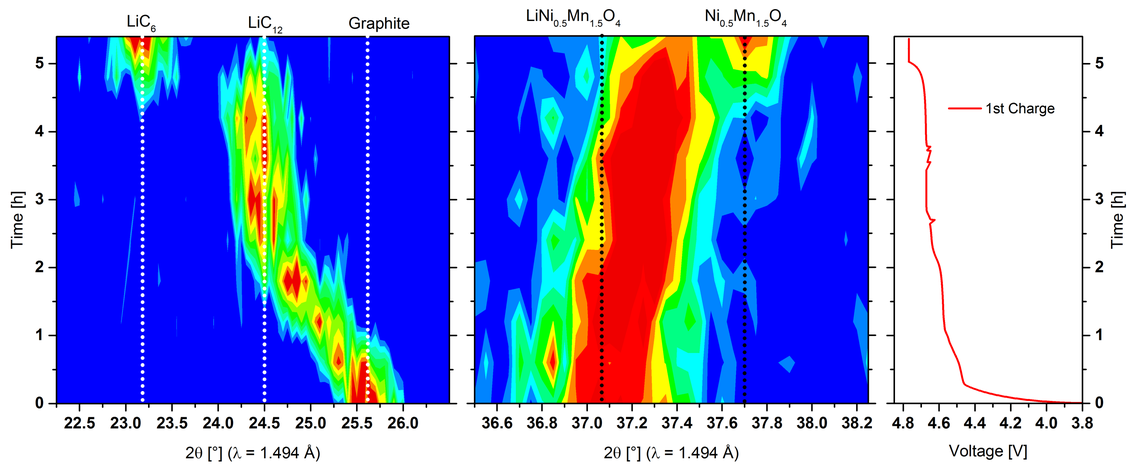
➢ $Li_{0.5}$NMO (6%) and Li_εNMO (94%)

➢ ~3% of LNMO not fully delithiated

→ ~7% of available Li from LNMO consumed in side-reactions (SEI, …)

After 50 cycles at 1-C rate

Operando measurement at C/5 rate



➢ Same shift evolutions as at slower rate
→ Possible to follow the evolution of lattice parameters

Conclusions

❖ **Validation of the cylindrical cell design**

❖ **Operando NPD measurement at fast and slow rate demonstrated**

Scan me !

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