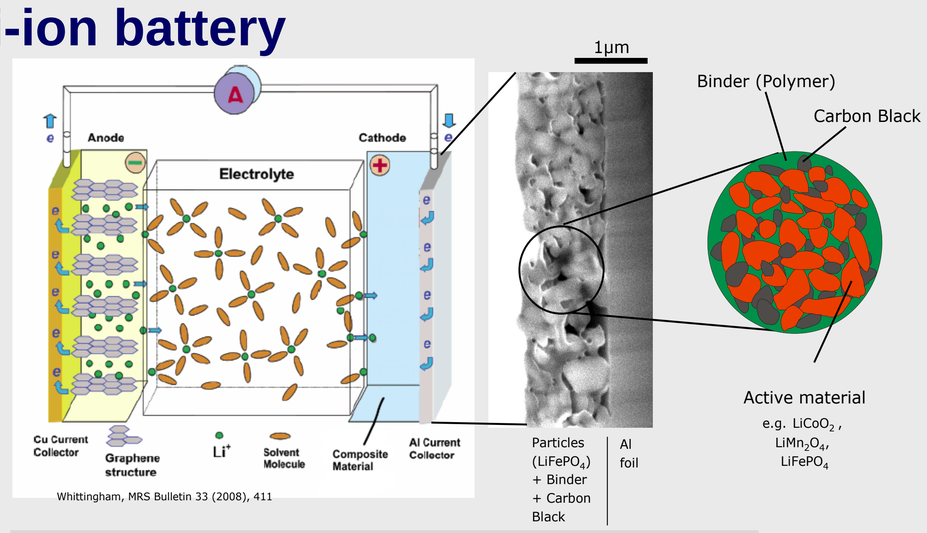
Karlsruhe Institute of Technology

Institute for Applied Materials

In situ X-ray diffraction studies of Fe/F co-doped $LiNi_{0.5}Mn_{1.5}O_4$ spinel cathodes

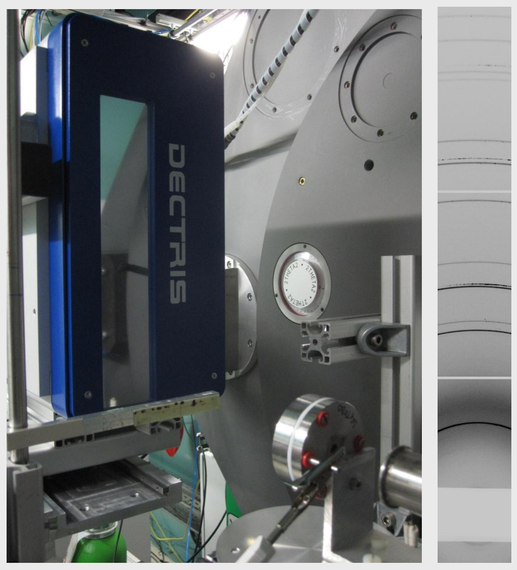
H. Geßwein, S. Glatthaar, R. Moenig. S. Doyle, J. R. Binder

Li-ion battery

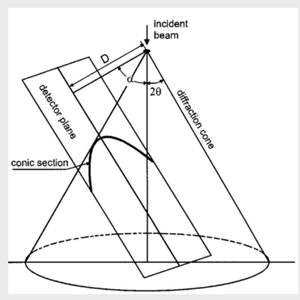


Cell reaction: $Li_{1-x}MO_2 + Li_xC_n \underset{C}{\overset{D}{\rightleftarrows}} LiMO_2 + C_n$

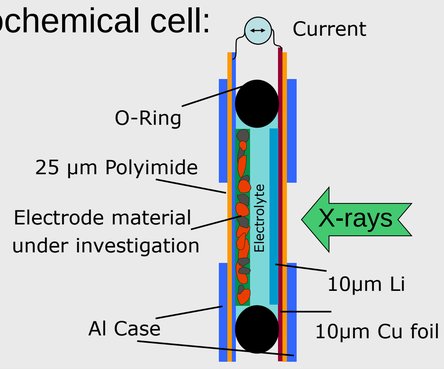
In situ SXRD @ ANKA PDIFF



- X-ray beam size 500x250 µm², λ = 0.8853 Å
- Data collection time 30 s per diffraction pattern
- Sample-detector-distance: 23 cm
- Pilatus 300K-W detector



Electrochemical cell:



Results

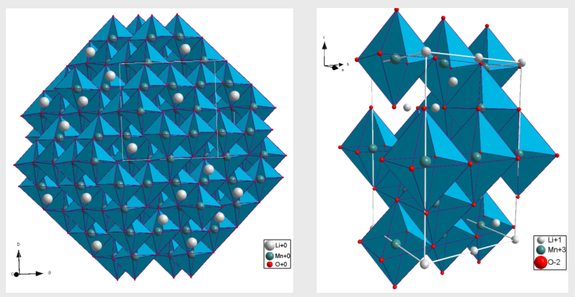
▪ Structural changes during discharge/charge processes

Electrochemical Li (de)intercalation reaction:

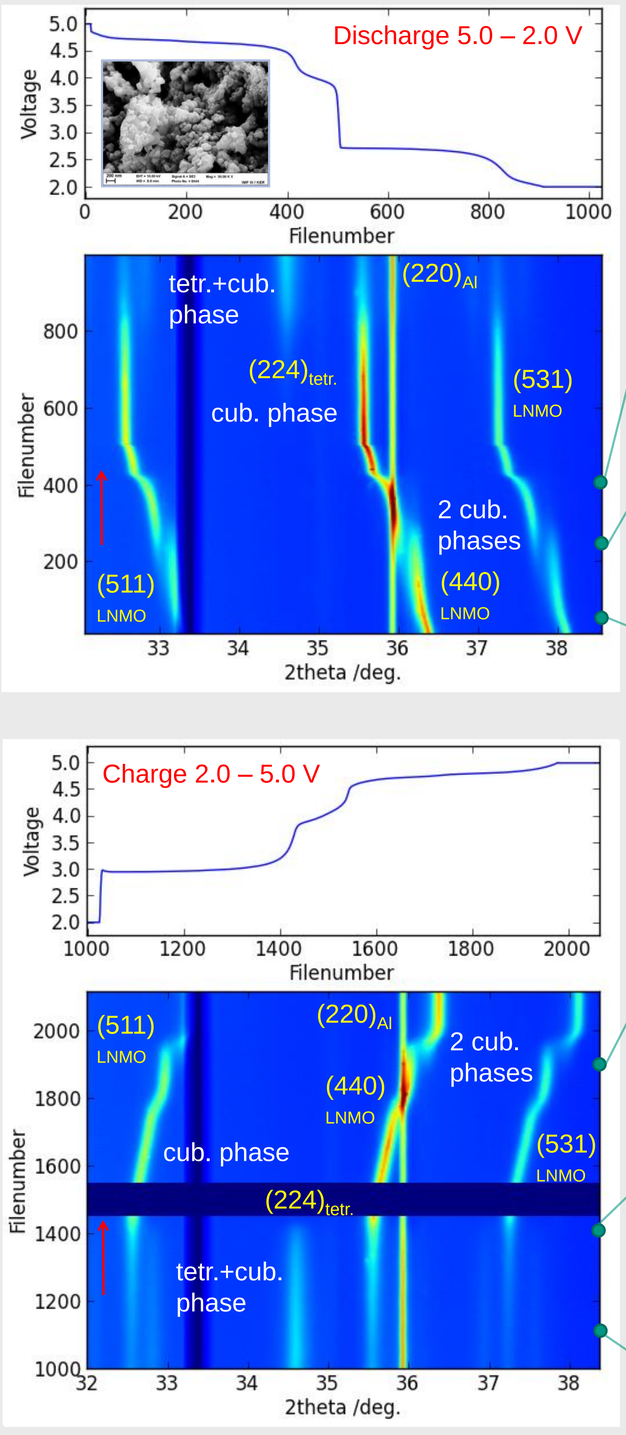
$$Li^+_1[\,Ni^{2+}_{0.5}Mn^{4+}_{1.5}]O_4 \underset{D}{\overset{C}{\rightleftarrows}} Li^+_{1-2x}[\,Ni^{2+}_{0.5-x}Ni^{4+}_{x}Mn^{4+}_{1.5}]O_4 + 2xLi^+ + 2xe^-$$

▪ Spinel crystal structures

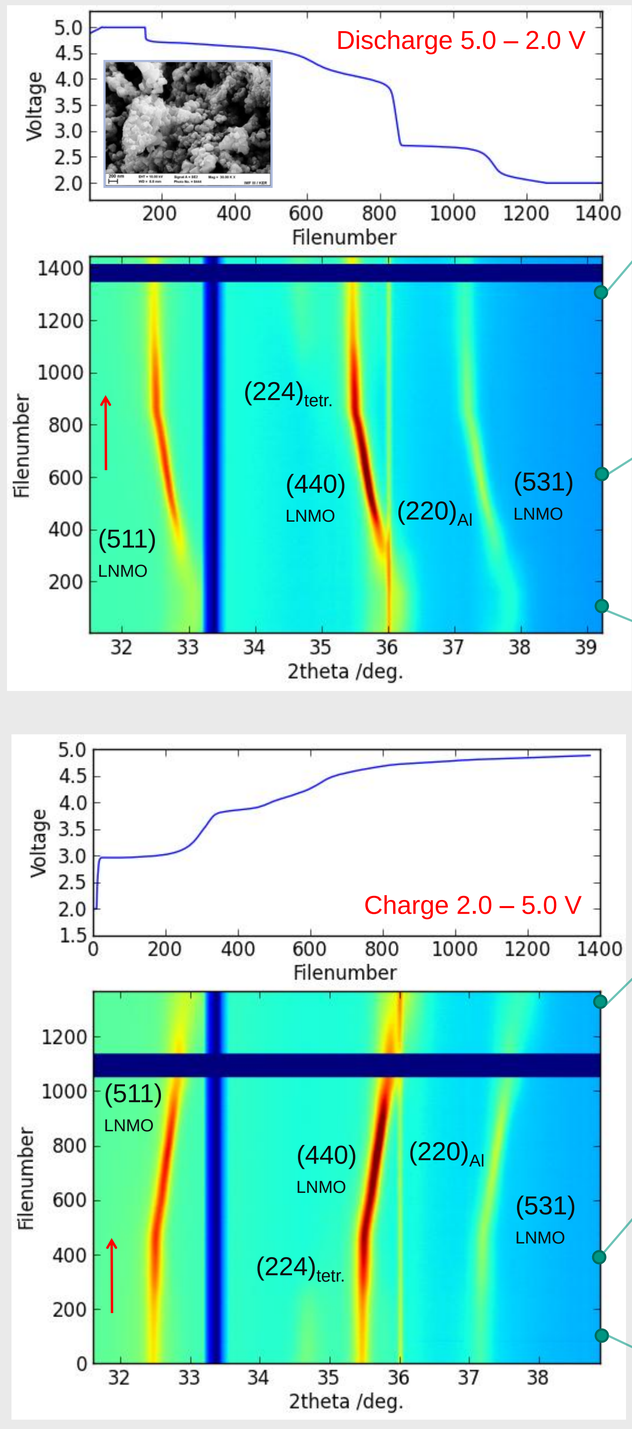
- $LiMn_2O_4$: SG *Fd-3m*
- $Li_2Mn_2O_4$: SG *I4₁/amd*
- γ-MnO_2 $\overset{4V}{\leftrightarrow}$ $LiMn_2O_4$ $\overset{3V}{\leftrightarrow}$ $Li_2Mn_2O_4$



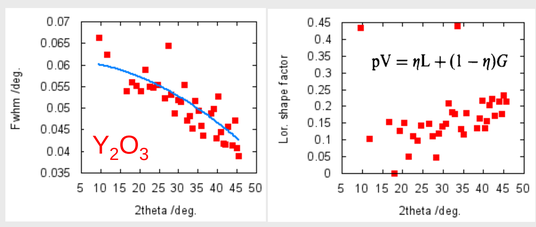
▪ $LiNi_{0.4}Mn_{1.5}Fe_{0.1}O_4$

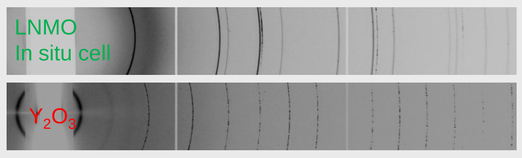


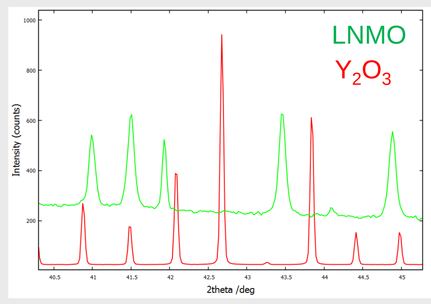
▪ $LiNi_{0.5}Mn_{1.4}Fe_{0.1}O_{3.8}F_{0.2}$



Instrumental resolution

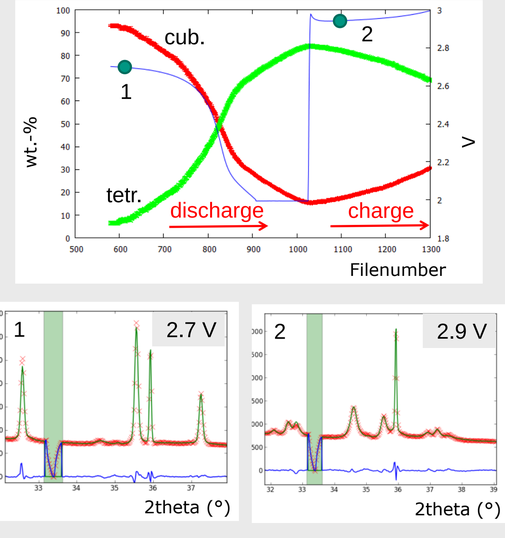






Quantitative phase analysis

- $LiNi_{0.4}Mn_{1.5}Fe_{0.1}O_4$



Conclusions

- SXRD is a powerful tool for *in situ* studies of Li ion batteries. XRD can monitor phase evolution, change of lattice parameters, microstructure and long range order.
- Cation and/or anion substitution in lithium manganese oxide based spinel materials greatly affects the electrochemistry and cycle behaviour of the cathode. Fluoride substitution changes phase behaviour in the 4 – 5 V region.
- Fluoride substitution induces partial supression of the tetragonal Jahn-Teller distortion and a reduction of strain in the structure (<c/a).

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