In-situ X-ray diffraction: Time-resolved structure investigation of Li-transition metal-fluorides as cathode materials in Li-ion batteries

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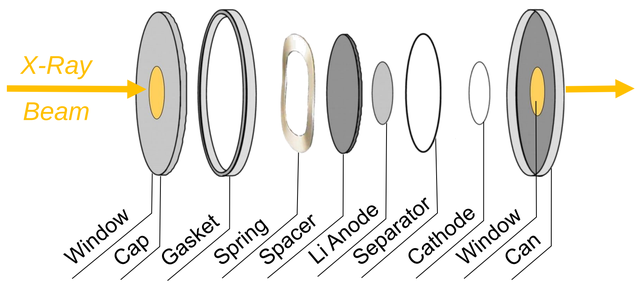
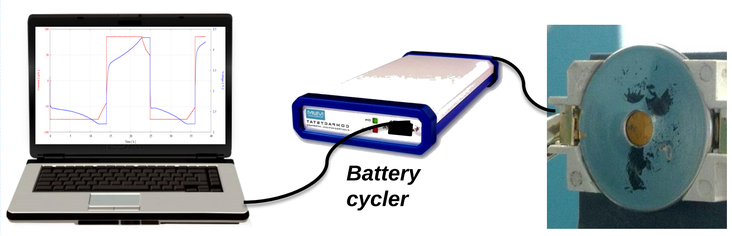
Motivation

Material transformation processes taking place within the electrode structure throughout charging and discharging of a Li-ion battery can pose high stresses on the atomic lattice of the active material. Volume changes during Li-intercalation, phase transitions, and chemical side reactions have implications on the cell properties including performance, capacity and lifetime. With the use of a sophisticated laboratory X-ray diffractometer, complemented by a microfocus rotating anode generator and a fast 2D detector, rapid collection of full powder-diffraction patterns and time-resolved recording of the structural changes during battery cycling can be established.

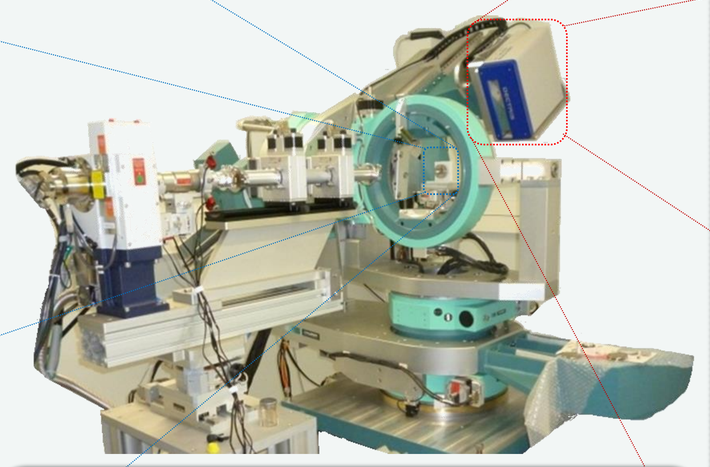
In-situ Coin Cell

- Electrochemical in-situ cell enables experimentation in Debye-Scherrer transmission mode
- Long-term stability over several cycles



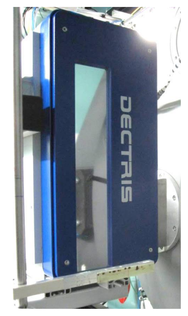


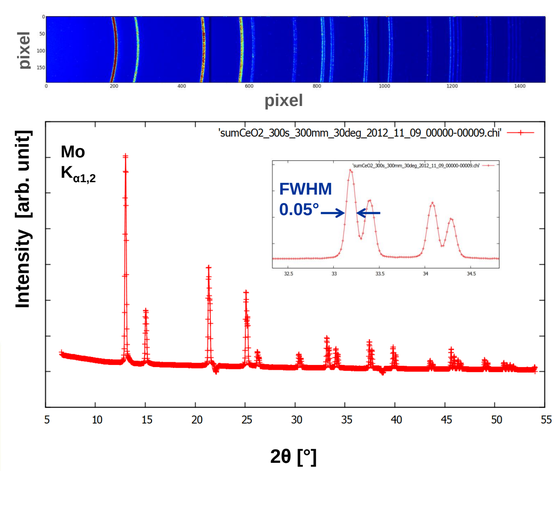
Huber 5 Circle Laboratory Diffractometer



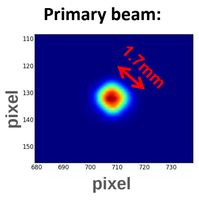
- ⇨ *Rigaku MM007 Mo microfocus rotating anode generator*
- ⇨ *2D collimating multilayer optics*
  - 0.5 mrad divergence
  - flux of 10^8 photons/sec

Pilatus 300 K-W Area Detector



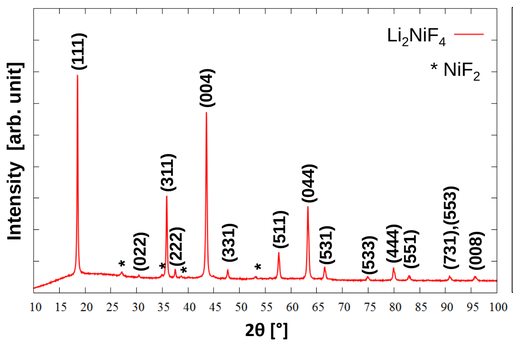


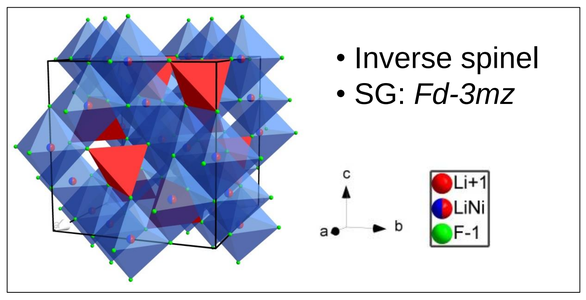
Primary beam:



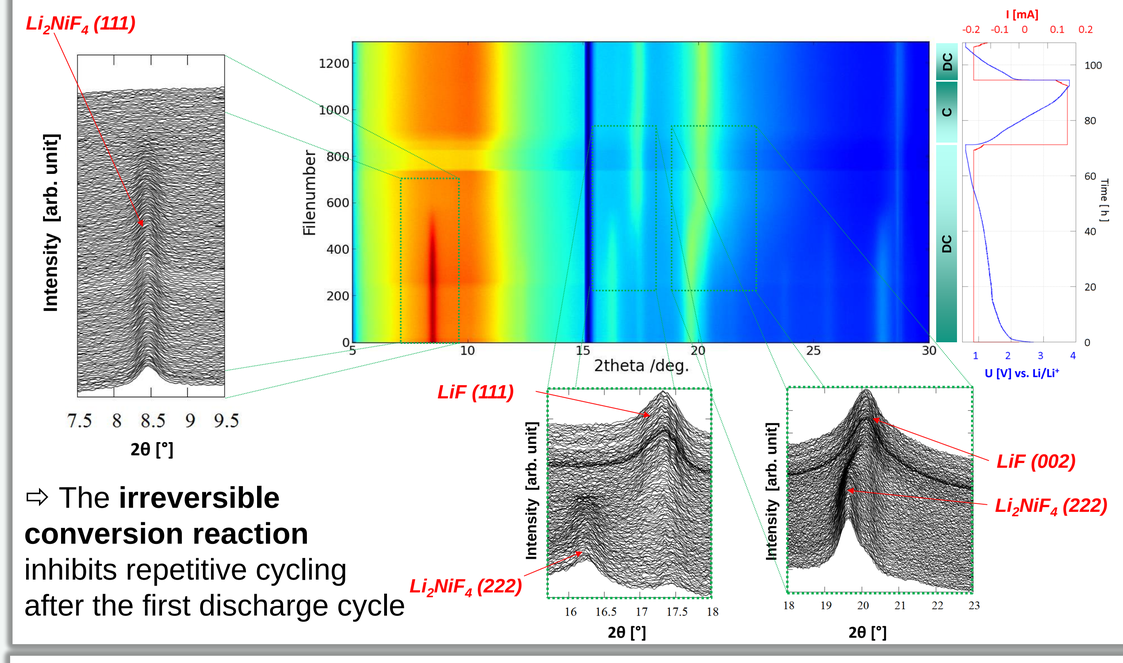
- Time resolved structural information
- Variable sample- detector-distance
- High counting efficiency and good averaging by integration along Debye-Scherrer rings

Li_2NiF_4



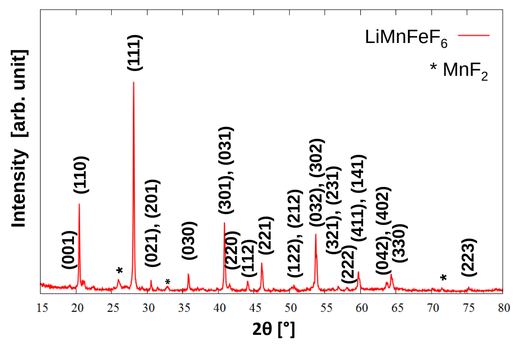


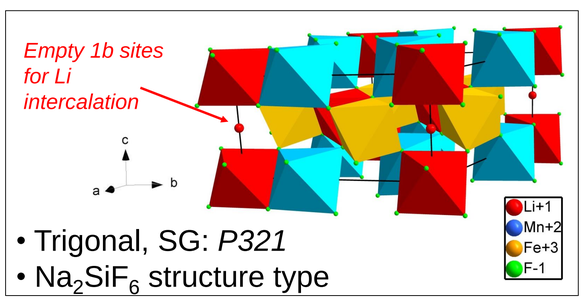
Cell reaction: $Li_2NiF_4 + 2Li^+ + 2e^- \underset{DC}{\overset{C}{\rightleftharpoons}} 4LiF + Ni^0$



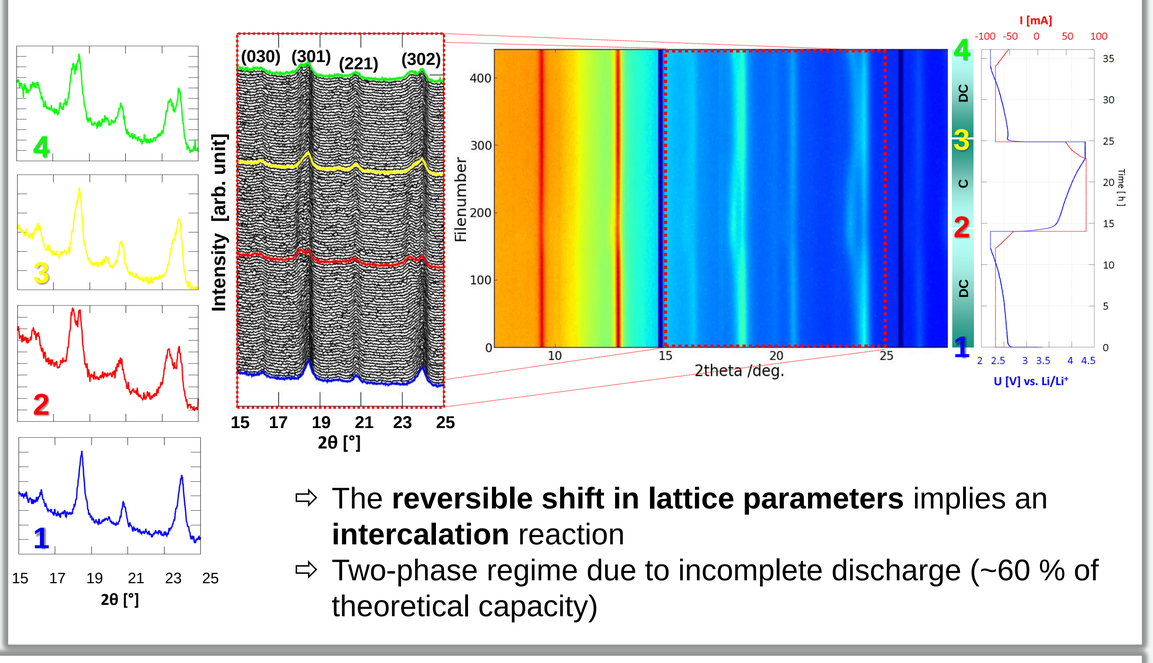
⇨ The **irreversible conversion reaction** inhibits repetitive cycling after the first discharge cycle

$LiMnFeF_6$





Cell reaction: $LiMnFeF_6 + Li^+ + e^- \underset{DC}{\overset{C}{\rightleftharpoons}} Li_2MnFeF_6$



⇨ The **reversible shift in lattice parameters** implies an **intercalation** reaction

⇨ Two-phase regime due to incomplete discharge (~60 % of theoretical capacity)

Conclusion and Outlook

- ⇨ The different lithium insertion mechanisms e.g. conversion and intercalation reactions can be detected
- ⇨ The electrochemical and structural state of the electrode material can be directly correlated
- ⇨ Long-term studies (> 20 cycles) and heating experiments will provide further insights into present electrode degradation mechanisms
- ⇨ Further in situ XRD measurements of promising electrode materials will be performed (e.g. Li-silicates, high-voltage spinels, Li-titanates)