
Anton Paar
Anton Paar
Anton Paar
www.anton-paar.com

OPERANDO X-RAY DIFFRACTION ON $LiCoO_2$ BATTERIES UNDER NON-AMBIENT CONDITIONS

JULY 31ST , 2025

PRESENTER: ELAA BEN FREDJ

CANADIAN POWDER DIFFRACTION WORKSHOP 18 (CPDW18)

INTRODUCTION

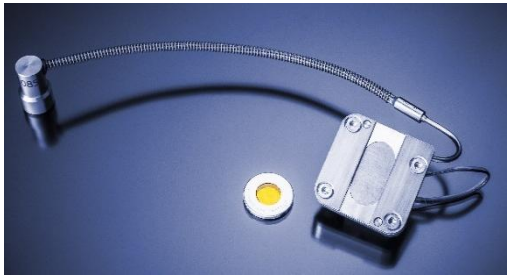
Why Study $LiCoO_2$ and Battery Structure Under Operation?

- $LiCoO_2$ (LCO): Common cathode in Li-ion batteries
- High energy density of LCO
- Structural instability at high voltages or at elevated and low temperatures
- Need to study structure under realistic operating conditions

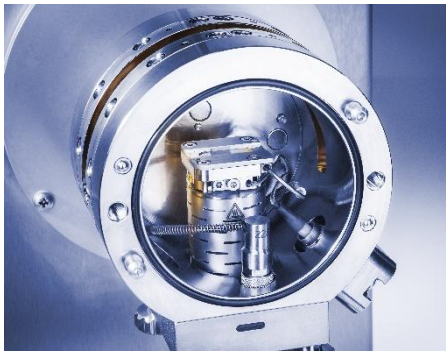
OPERANDO XRD SETUP UNDER NON-AMBIENT CONDITIONS

- $Li_{1-x}CoO_2$ (LCO) half-cell in coin cell format with Li metal anode
- Anton Paar XRDynamic 500
- Real-time cycling with potentiometer
  - Galvanostatic cycling
  - Charging rate: C/10
  - Full charge/discharge cycle from ~ 3.9 V up to 4.2 V and then down to 3.0 V.
- TTK 600 low-temperature chamber

XRDynamic 500 with TTK 600

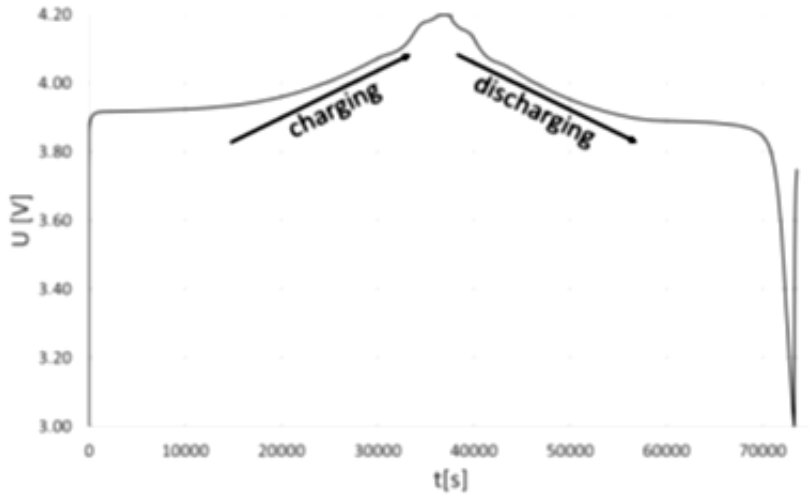


Battery sample holder TTK 600 (Reflection).

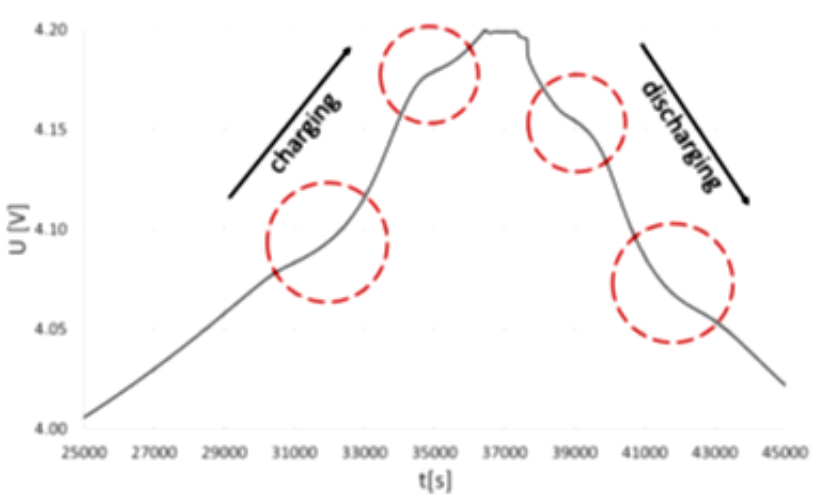


TTK 600 Low Temperature Chamber for in situ and in operando XRD studies with temperature range of -180 to +130 °C.

ELECTROCHEMICAL OBSERVATIONS DURING LCO CYCLING

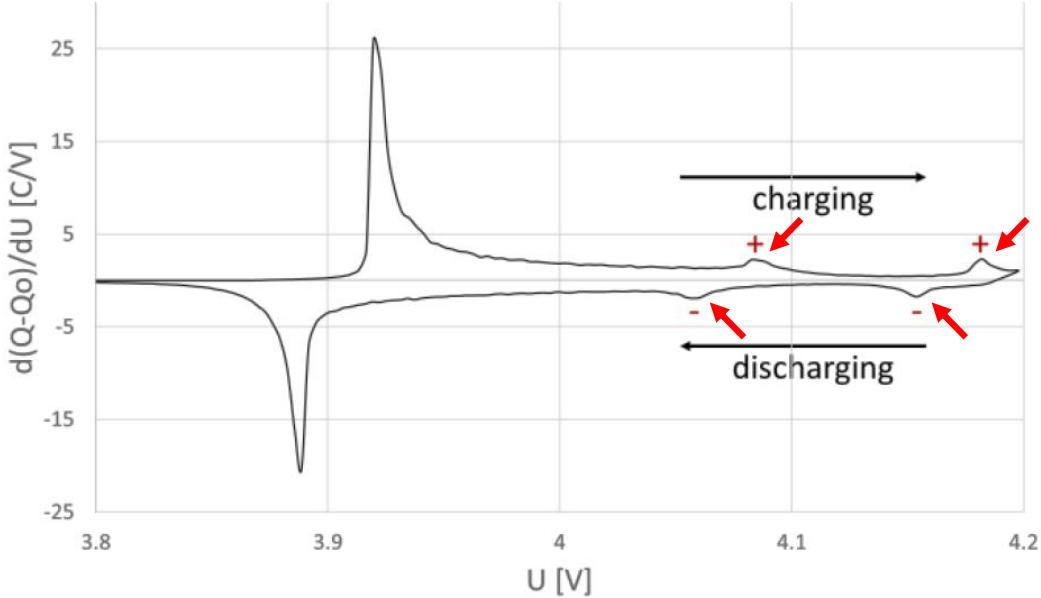


Charge curve for LCO coin cell at ambient conditions.



Close-up view of LCO charge curve. Slope changes are highlighted by red circles.

ELECTROCHEMICAL OBSERVATIONS DURING LCO CYCLING

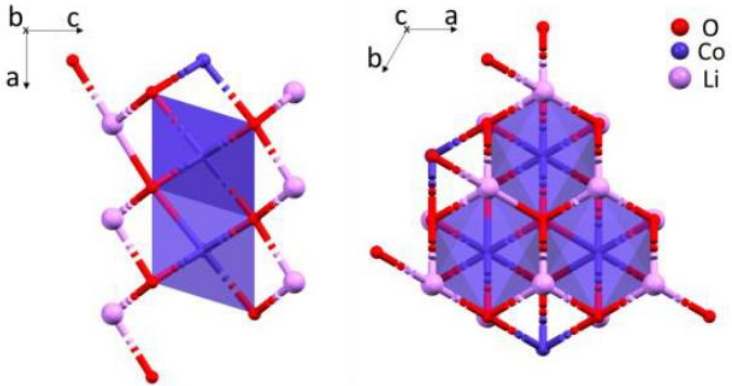


Capacity change derivative plotted against voltage. Peaks indicating slope changes in charging curve are marked with + (for charging) or - (for discharging).

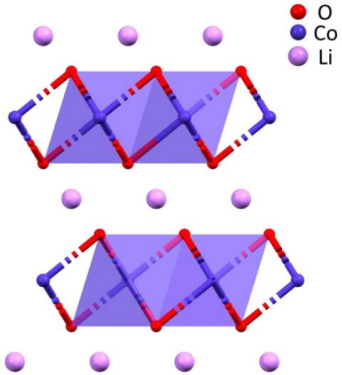
STRUCTURAL CHANGES DURING BATTERY CYCLING

LAYER STRUCTURE OF LITHIUM COBALT OXIDE

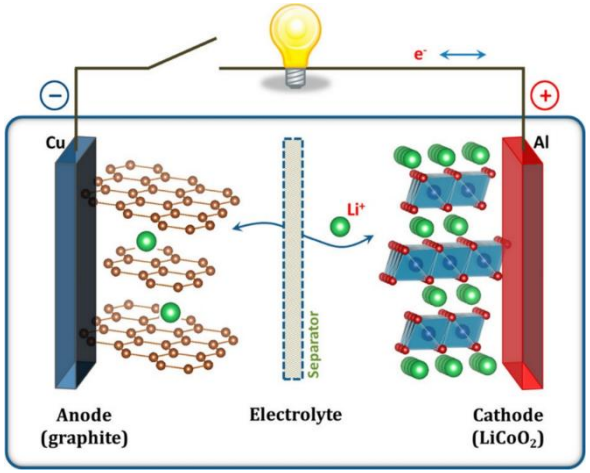
- $LiCoO_2$ crystallizes in the rhombohedral space group $R\bar{3}^*m$.
- $LiCoO_2$ forms a layered structure composed of edge-sharing, slightly distorted CoO_6 octahedra.



Co octahedrons of the $LiCoO_2$ structure observed along the crystallographic b- (left) and c-axis (right).



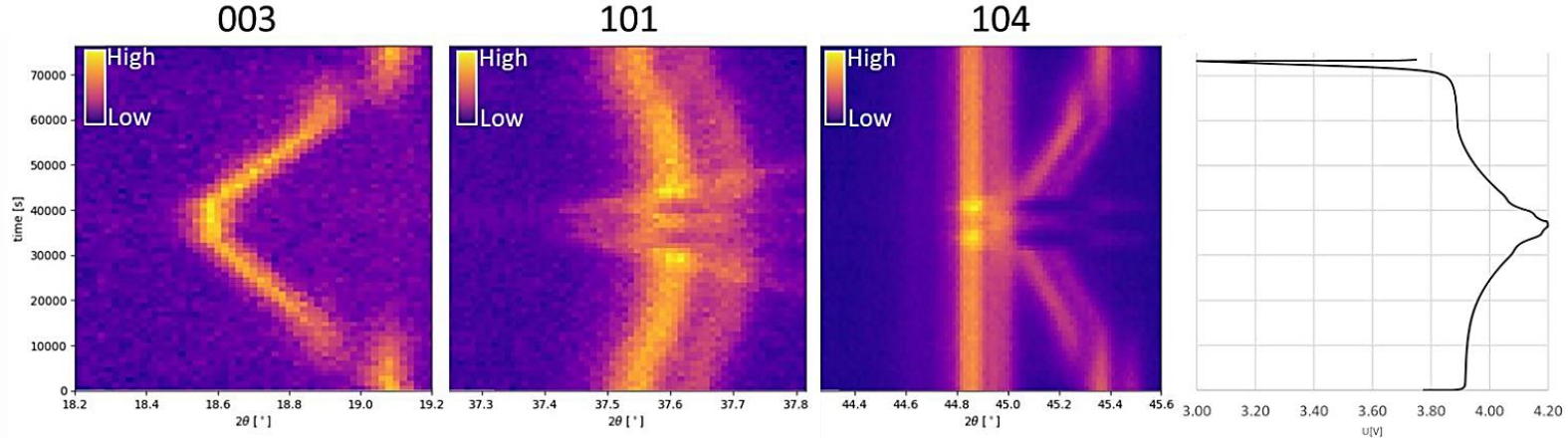
Layered CoO_2 structure with Li located between the layers.



Schematic illustration of the first Li-ion battery ($LiCoO_2$/Li^+ electrolyte/graphite).
Yuanyuan, Bao et al., (2025). Journal of Solid State Electrochemistry. 1-25.

STRUCTURAL CHANGES DURING BATTERY CYCLING

PEAK SHIFTS AND UNDERLYING STRUCTURAL CHANGES



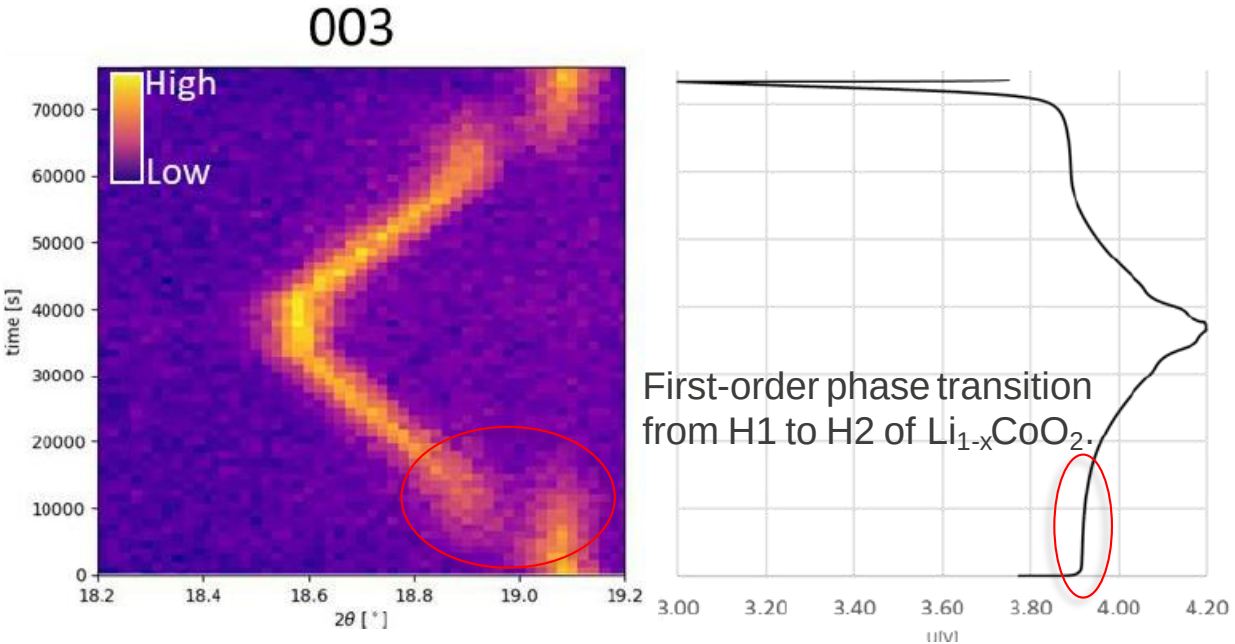
Heat maps of XRD scans for 003, 101, and 104 reflection of LCO during battery cycling (left), and charging/discharging curve (right).

In situ XRD monitor the structural changes in real time:

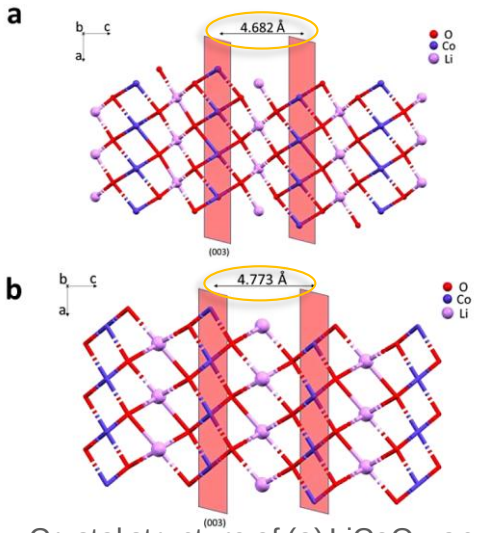
- Peak shifts
- Lattice parameter changes
- Phase transitions

STRUCTURAL CHANGES DURING BATTERY CYCLING

PHASE TRANSITIONS



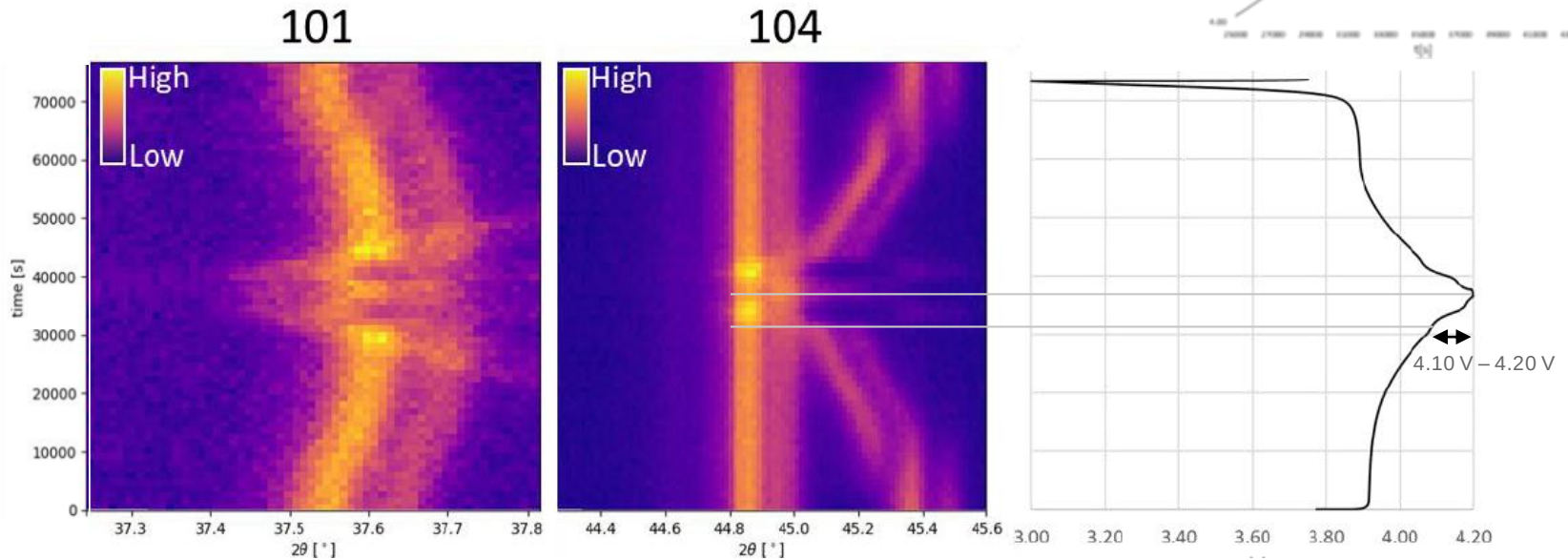
First-order phase transition from H1 to H2 of $Li_{1-x}CoO_2$.



Crystal structure of (a) $LiCoO_2$, and (b) $Li_{0.6}CoO_2$. Two planes of the (003) family. The distance between the Co layers increases.

Heat map of XRD scans for **003** reflection of LCO during battery cycling (left), and charging/discharging curve (right).

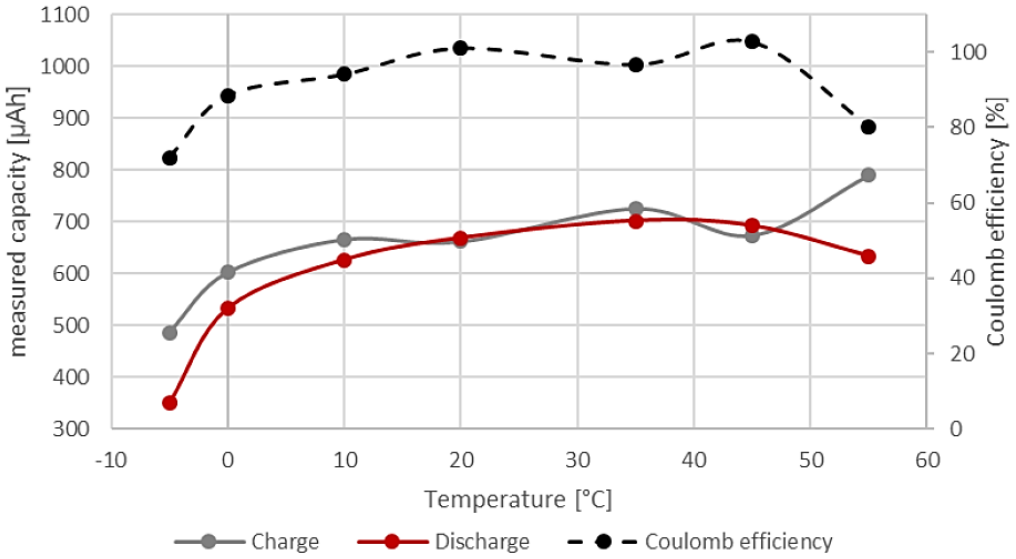
STRUCTURAL CHANGES DURING BATTERY CYCLING
PHASE TRANSITIONS



Heat maps of XRD scans for 101, and 104 reflection of LCO during battery cycling (left), and charging/discharging curve (right).

NON-AMBIENT CYCLING OF LCO

- Capacity decreases at low temperatures
- Capacity is relatively stable between 10 °C and 45 °C
- At higher temperatures:
  - capacity measured during discharge drops
  - capacity obtained during charging seems to increase.



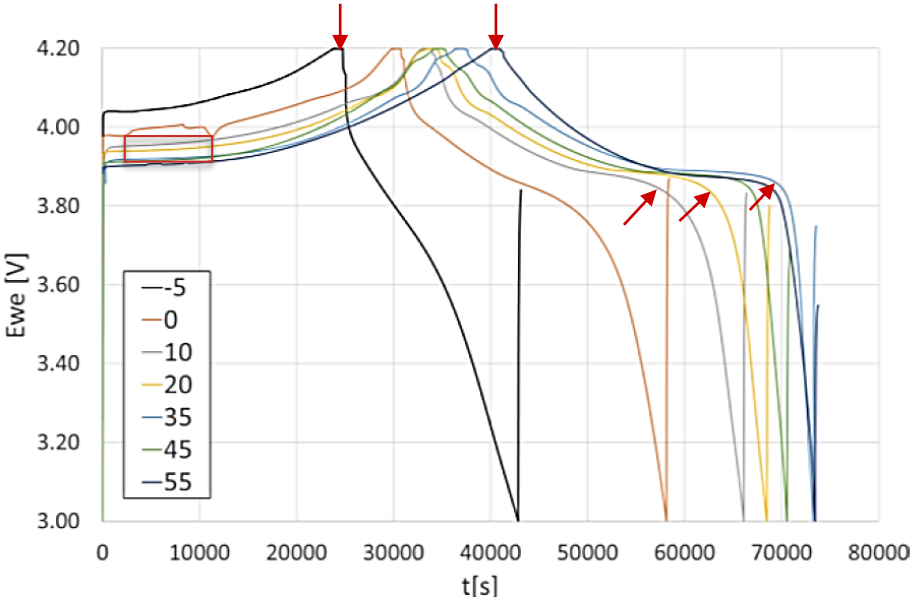
Capacity and Coulomb efficiency of LCO coin cell at different temperatures.

NON-AMBIENT CYCLING OF LCO

- Similar charging curves **from 10 °C to 35 °C**
- At temperatures **above 35 °C**, the charging is significantly prolonged

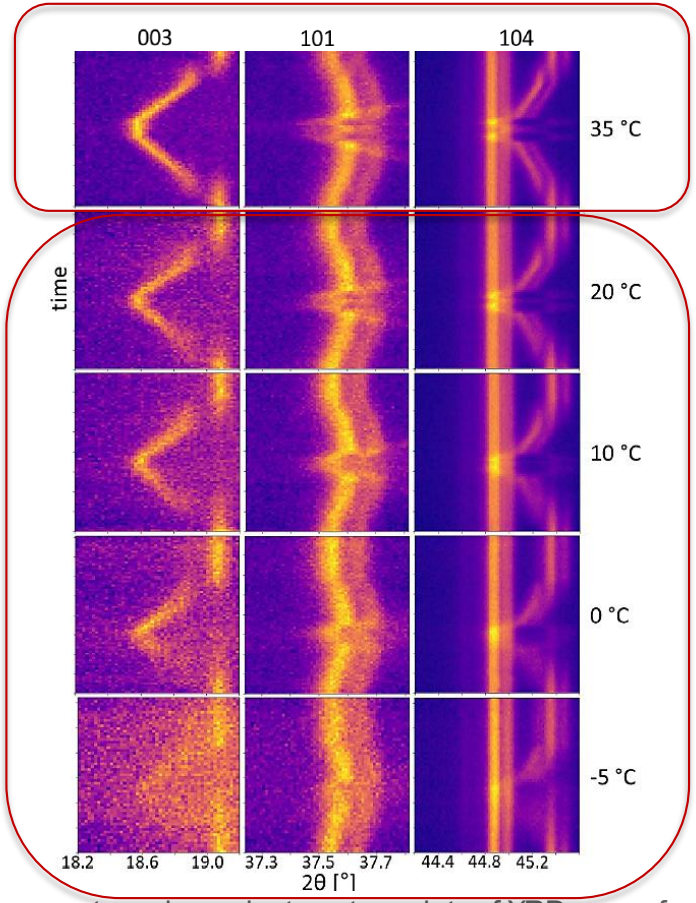
  → irreversible side reactions, facilitated at higher temperatures.
- **Below 10 °C,** the charging voltage increases significantly, the discharge happens much faster

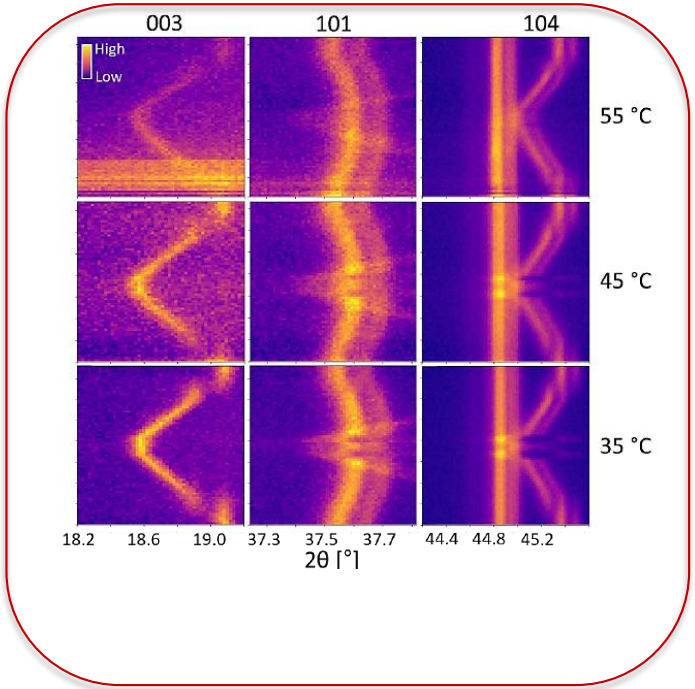
  → increased internal resistance in the battery



Temperature-dependent charging and discharging curves of LCO coin cell.

NON-AMBIENT CYCLING OF LCO





Temperature-dependent contour plots of XRD scans for 003, 101 and 104 reflection of LCO during battery cycling.

CONCLUSION

- Operando XRD is a powerful tool for real-time structural insights
- Non-ambient studies uncover thermal/chemical instability
- Helps design more robust and safer Li-ion batteries

Q&A