PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

Structural and chemical surface investigation of NCA electrodes during early stages of cycling using XPS and XPEEM spectroscopy

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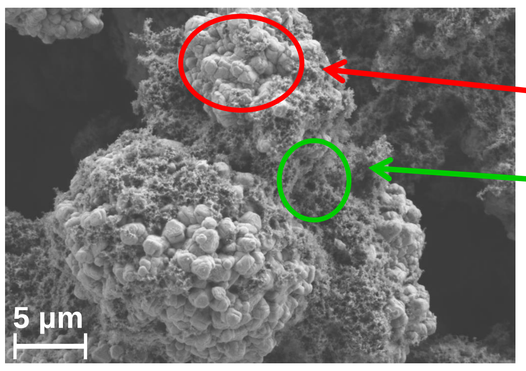
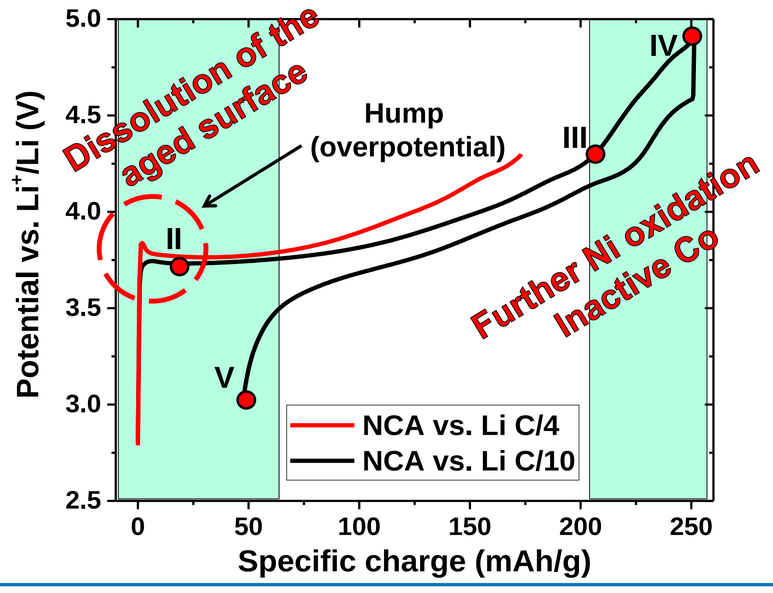
Motivation

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) vs. Li^+/Li

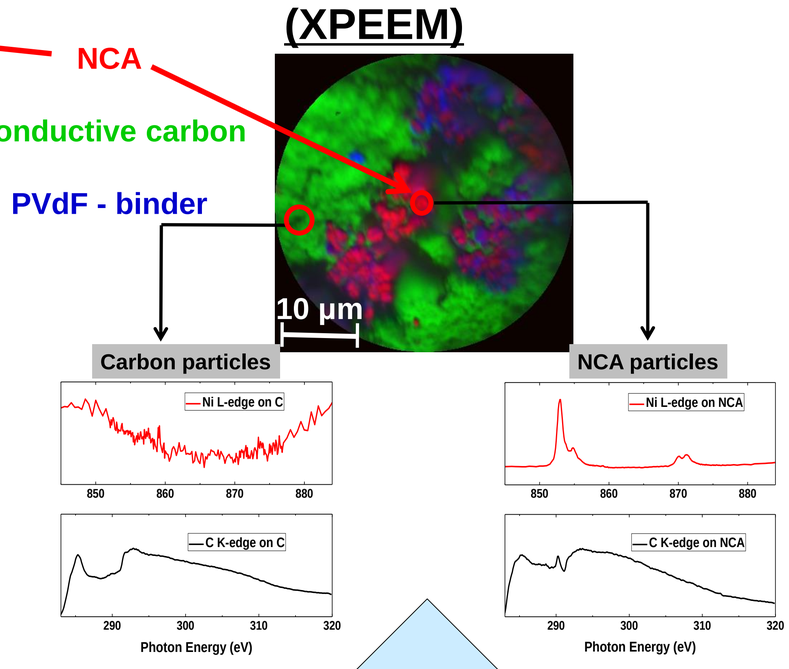
- **Elucidate electrolyte oxidation mechanism occurring at the surface of the different particles**
- **Determine origin of the irreversible overpotential at ≈ 3.7 V**
- **Determine oxidation state of transition metals at the NCA surface**
- **Detect possible formation of Li_2CO_3 during delithiation** [Robert *et al.*, Chem. Mater., 2015]
- **Study possible "cross-talk" between the cathode and the anode**

Need surface sensitive technique with good lateral resolution to monitor chemical evolution on single particles in complex commercial-like battery electrodes





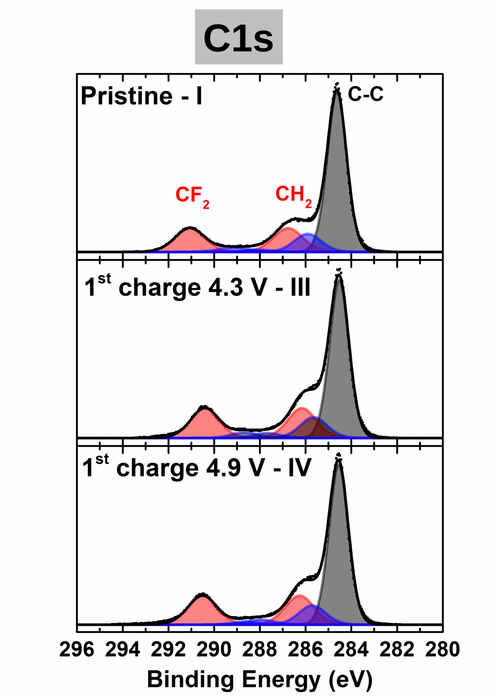
X-ray photoemission electron microscopy (XPEEM)



XPEEM: unique technique that provides local surface XAS measurements on single particles without change of the working environment

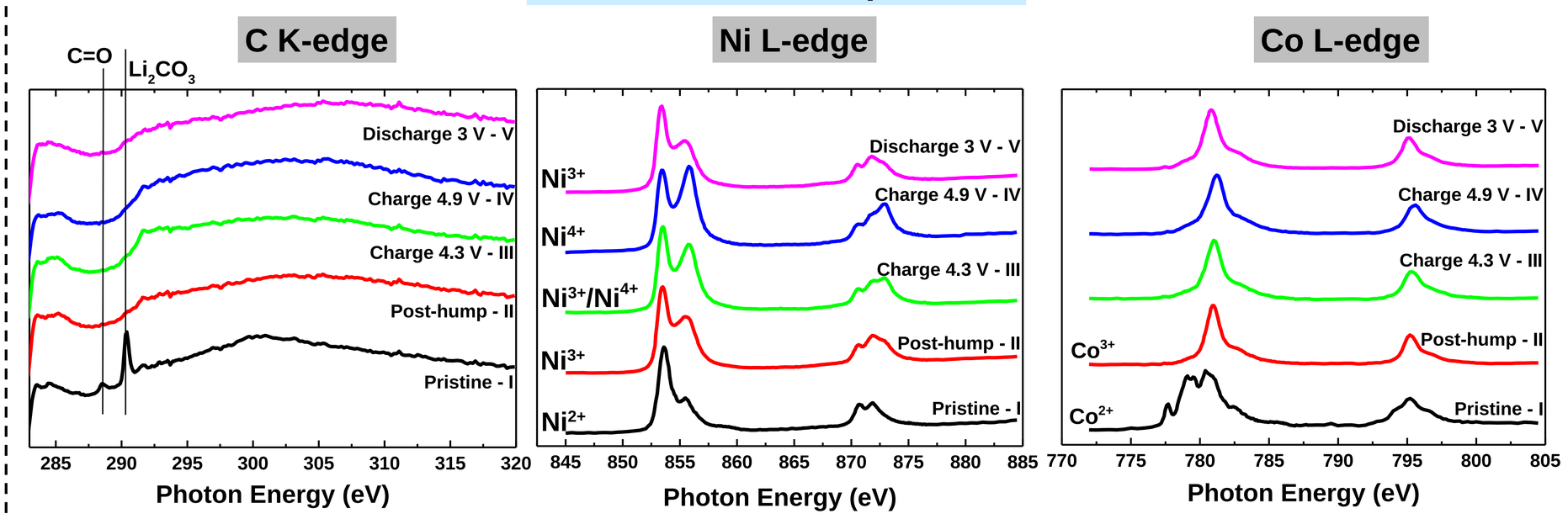
Surface evolution of NCA particles during first cycle

XPS on NCA electrodes

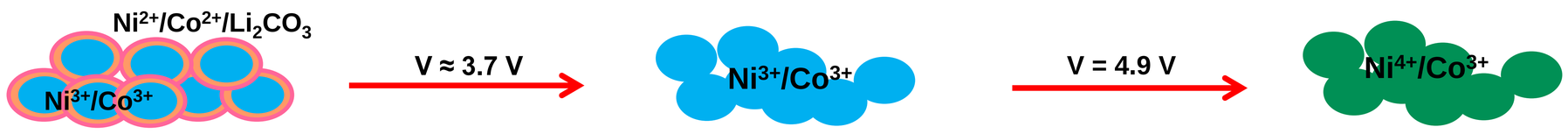


- **No obvious surface modification is observed on C 1s, Ni 2p and Co 2p**

Local XAS on NCA particles



- **Carbonate layer is detected on pristine electrode, which dissolves completely at 3.7 V**
- **No further organic/inorganic species are detected during lithiation and delithiation**
- **Ni^{2+} and Co^{2+} species are detected on the pristine electrode, then completely dissolved at 3.7 V**
- **Between 4.3 V and 4.9 V Ni is further oxidized to +4, however Co remains in +3 state**



Conclusions

- **Limitation in XPS detection of C 1s, Ni 2p and Co 2p core level can be overcome by XPEEM**
- **Aging the surface of the NCA particles leads to irreversible overpotential at 3.7 V during the 1st delithiation**
- **Organic/inorganic species are not detected either above 3.7 V or during NCA lithiation**
- **Between 4.3 V and 4.9 V only Ni is involved in the redox process while Co remains inactive**

Acknowledgement

Financial support from a CROSS grant (PSI) is gratefully acknowledged