PAUL SCHERRER INSTITUT

ELECTROCHEMISTRY LABORATORY

BATTERIES

Nanoscale **PEEM** Spectroscopy Combined with **XPS** to Elucidate the Surface Reaction Mechanism of Cycled Li-Ion Battery Electrodes

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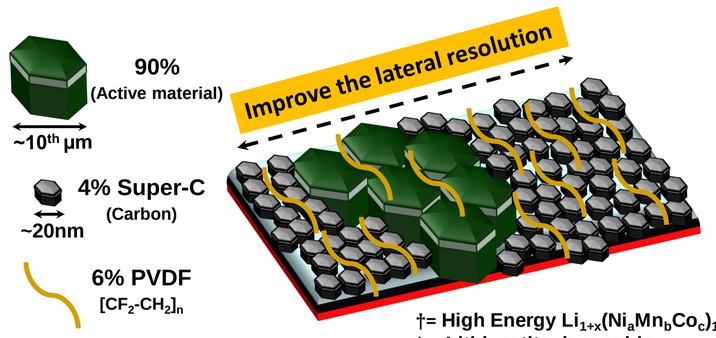
Goal

For the first time, X-Ray Photoemission Electron Microscopy (PEEM) is used, as a complementary technique to the conventional X-Ray Photoelectron Spectroscopy (XPS), to investigate commercial-like Li^+ battery electrodes and study separately, at the nanoscale level, the surface layer chemistry evolution on the conductive carbon and on the active material of positive (HE-NMC†) and negative (LTO*) electrodes cycled in carbonate-based electrolytes.

Motivation

PEEM on commercial-like Li^+ electrode

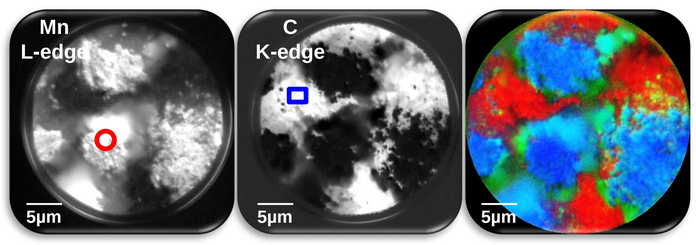
- PEEM elemental contrast images enable us to distinguish separately areas related to active materials, conductive carbon and binder.
- Local XAS on C and O K-edges together with transition metal (TM) L-edges allows us to study simultaneously the SEI** and TM oxidation states at the nanoscale level within the depth analysis of ~ 3 nm.
- Overcome XPS limitations associated with the poor lateral resolution, weak and complex signals of the TMs and local charging effect of non-conductive species.

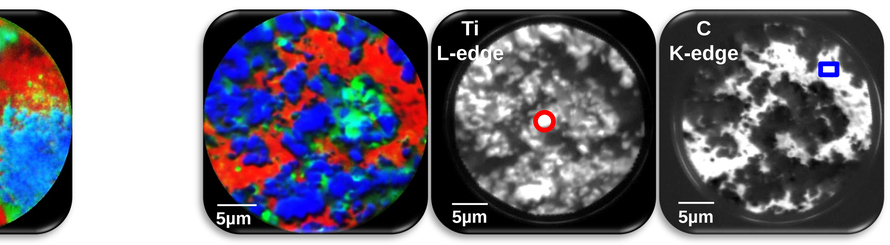


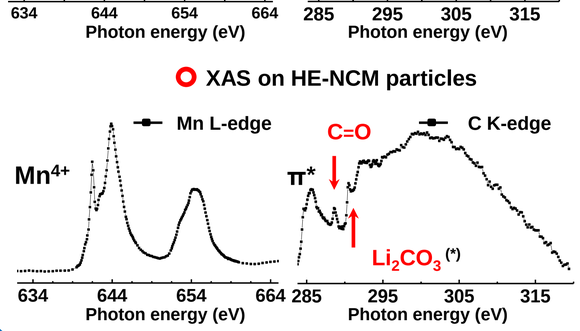
†= High Energy $Li_{1+x}(Ni_aMn_bCo_c)_{1-x}O_2$
* = Lithium titanium oxide
** SEI = Solid Electrolyte Interface
*** LC30 = 1M $LiClO_4$ in 1:1, DMC:EC

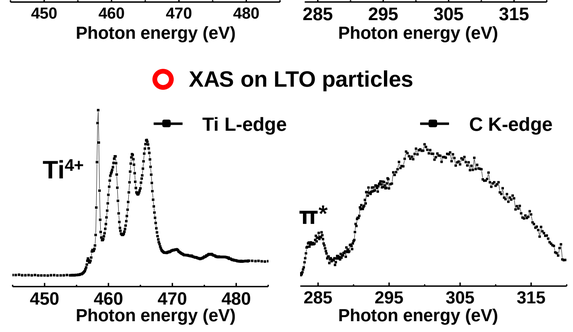
PEEM on pristine electrodes

HE-NMC electrodes







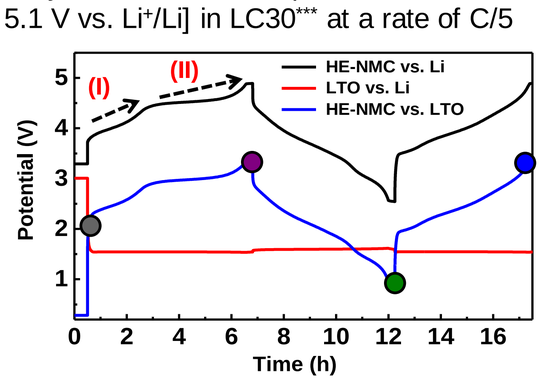


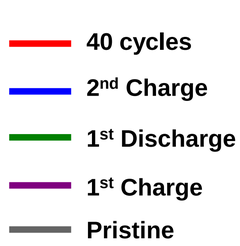
(*) $Li(Ni,Mn,Co)O_2 + x/2\ CO_2 + x/4\ O_2 \rightarrow Li_{1-x}(Ni,Mn,Co)O_2 + x/2\ Li_2CO_3$

TM oxidation states evolution upon cycling

Galvanostatic cycling

- HE-NCM cycled vs. the LTO plateau within the cutoff limits [2.4 V – 5.1 V vs. Li^+/Li] in LC30*** at a rate of C/5



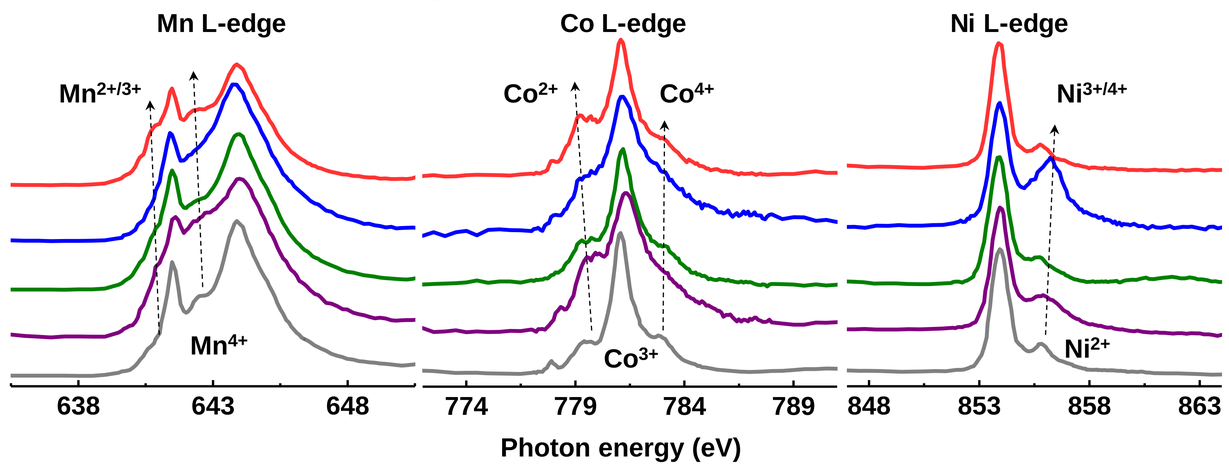


Mechanism of the TM oxidation states in the bulk of HE-NCM

(I) $Li[Ni^{(II)},Co^{(III)},Mn^{(IV)}]O_2 \longrightarrow Li_{1-x}[Ni^{(IV)},Co^{(IV)},Mn^{(IV)}]O_2 + xLi^+ - xe^-$

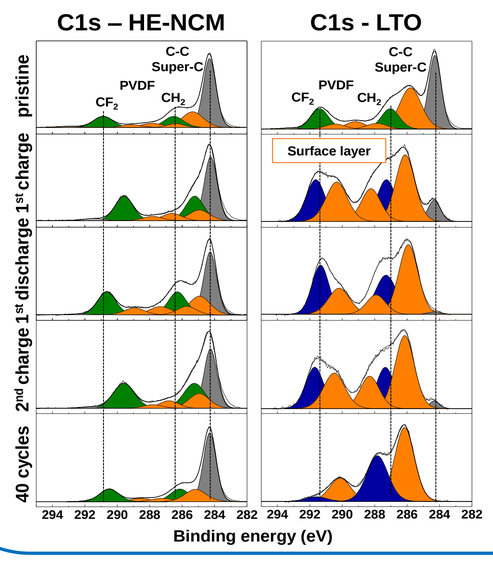
(II) $Li_2Mn^{(IV)}O_3 \longrightarrow Mn^{(IV)}O_2 + 2Li^+ + O + 2e^-$ (O_2 release)

Local L-edges XAS on HE-NMC particles



TM oxidation states evolution at surface differs from bulk counterpart

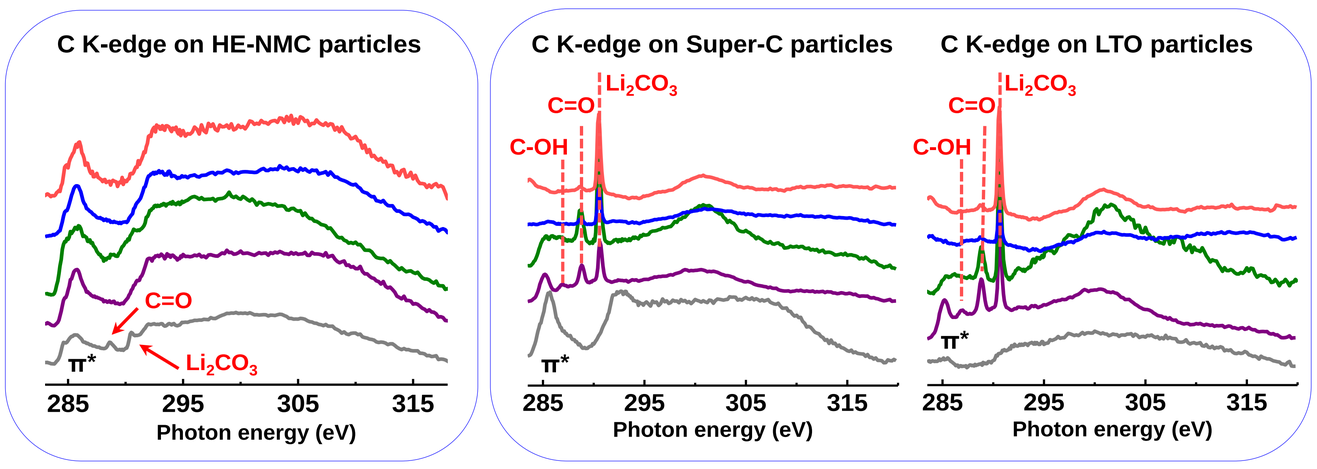
Surface layer evolution upon cycling



XPS characterization

- Surface layer evolution monitored by XPS C1s core level performed on HE-NMC and LTO upon cycling.
- Negligible surface layer observed on HE-NCM.
- Thicker surface layer (~8 nm) detected on LTO.

Local C K-edge XAS on HE-NMC and LTO electrodes



Conclusion

- PEEM has been performed successfully on commercial-like electrodes to monitor simultaneously the evolution of SEI and TM oxidation states at the nanoscale.
- Local XAS at the C K-edge evidences the presence of C-OH, C=O and Li_2CO_3 species at the surface of HE-NMC particles originating from the Li^+ reaction with air.
- The evolution of the Mn, Co and Ni oxidation states reveals a different redox mechanism on the surface of HE-NMC, compared to the bulk.
- C K-edge spectra show presence of an homogeneous surface layer on LTO, but absence on HE-NCM, in agreement with XPS C1s.

Acknowledgement

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