In Situ Raman Diagnostics of Intercalation Batteries

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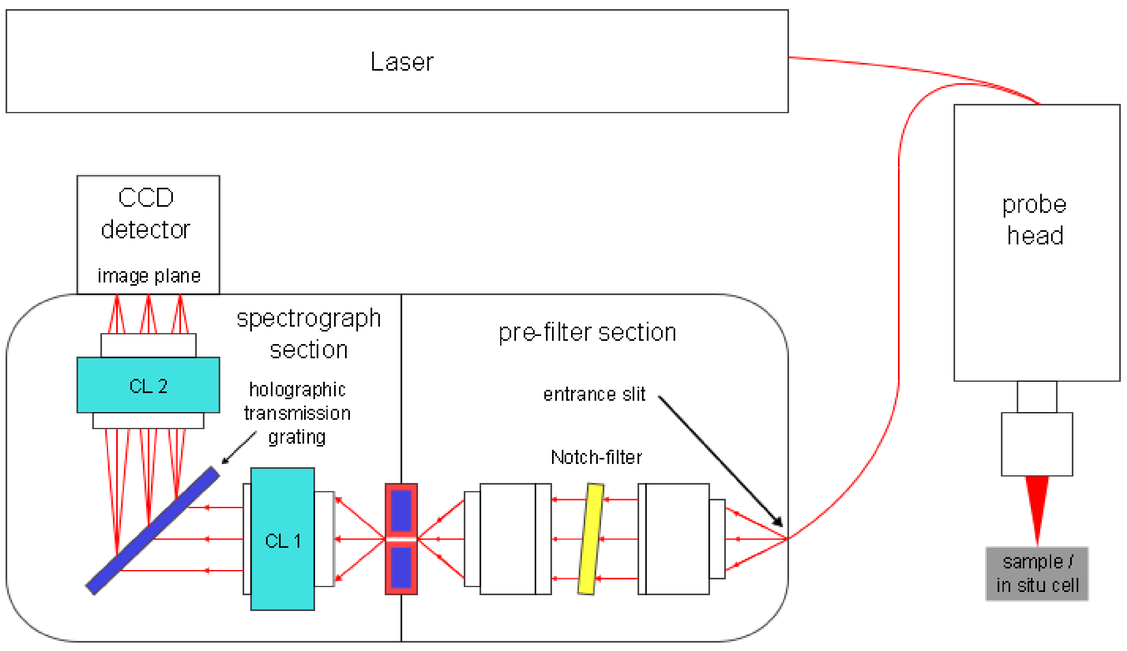
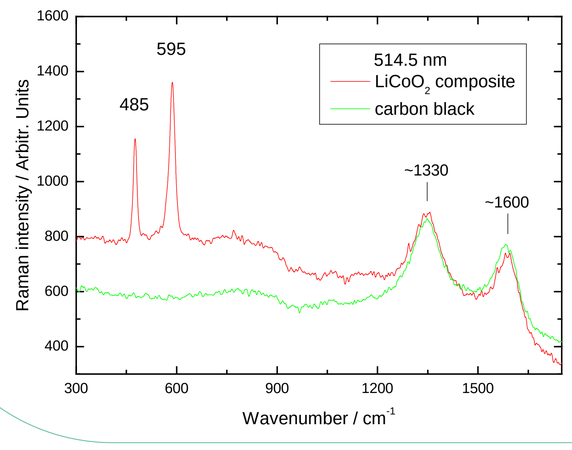
Motivation and experimental setup

In situ Raman experiments are performed in 180° backscattering geometry using a transmission spectrometer equipped with a CCD detector. The excitation laser (532 nm unless noted otherwise) is focused onto the sample through a confocal microscope coupled with a x-y-z-stage, allowing measurements with high lateral resolution (spot size is approximately 2,5 μm).



The $Li_{1-x}CoO_2$ composite cathode (84% active material, 8% PVDF, 8% carbon black) was used with commercial electrolyte (LP30, 1M $LiPF_6$ in EC:DMC 1:1 (wt), Merck) and metallic Li as counter-electrode.

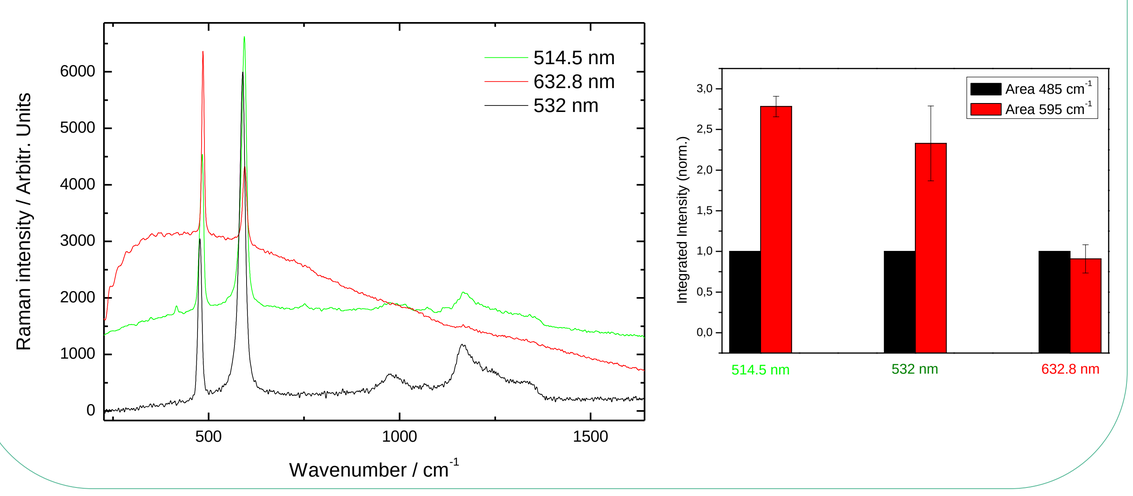


Observable Raman signals in $LiCoO_2$ electrode:

E_g (O-Co-O bending)	→ 485 cm^{-1}
A_{1g} (Co-O stretching)	→ 595 cm^{-1}
D band	→ 1330 cm^{-1}
G band (C-C stretching)	→ 1600 cm^{-1}

Resonant enhancement

Resonant enhancement of $LiCoO_2$ A_{1g} mode when exciting the sample with 514.5 or 532 nm in contrast to non-resonant excitation with 632.8 nm (below).



Publications last funding period

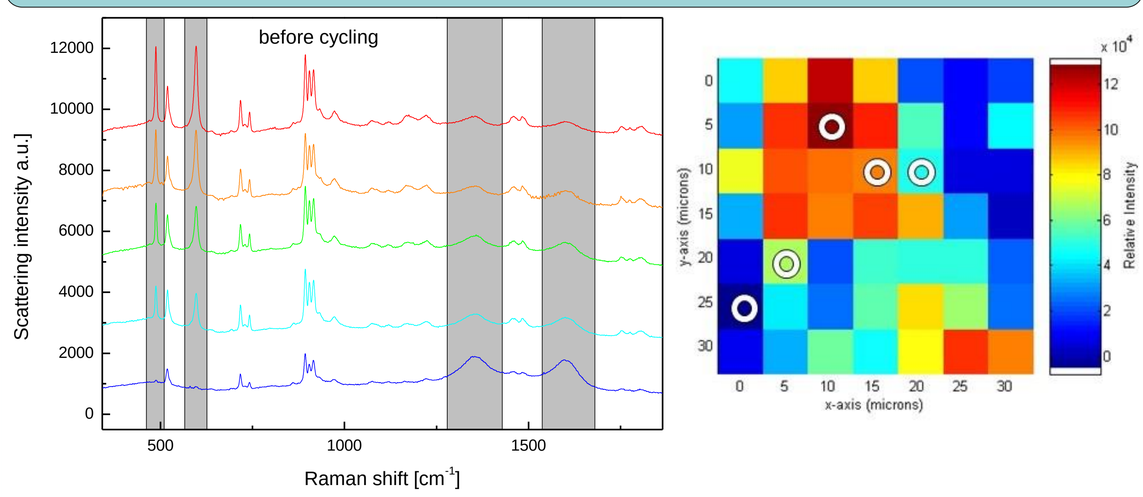
1) T. Gross, L. Giebeler, C. Hess, *Novel in situ cell for Raman diagnostics of lithium-ion batteries,* Rev. Sci. Instrum. **84**, (2013), 073109

2) T. Gross, C. Hess, *Raman diagnostics of $LiCoO_2$ electrodes for lithium-ion batteries,* J. Power Sources **256**, (2014), 220

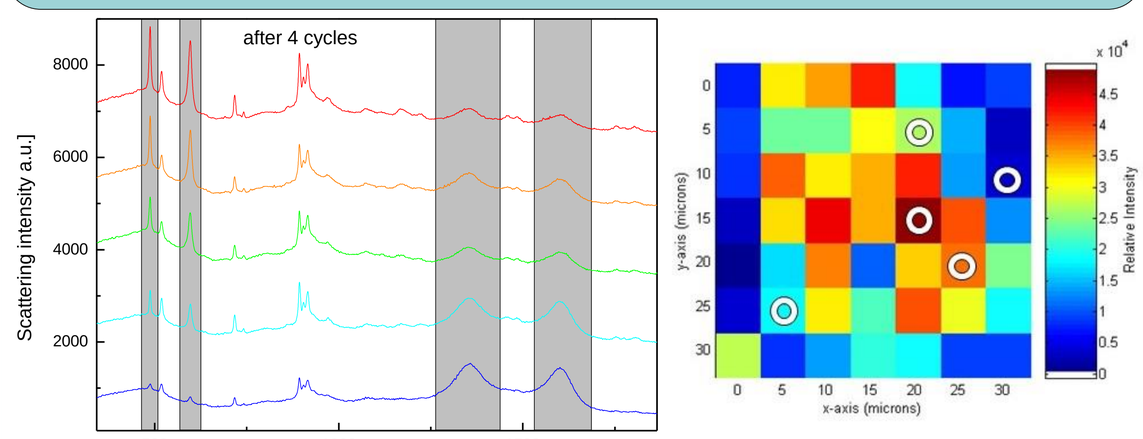
3) T. Gross, C. Hess, *Spatially-resolved in situ Raman analysis of $LiCoO_2$ electrodes.,* ECS Transactions (2014)

Spatially-resolved Raman analysis

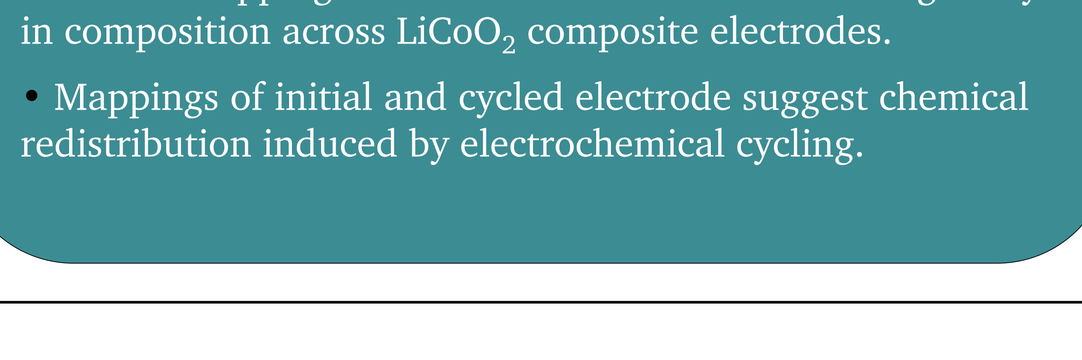
Raman mapping of a $LiCoO_2$ composite electrode. Individual Raman spectra show the heterogeniety of chemical composition across the surface [3] (below).



In situ Raman data for a $LiCoO_2$ composite electrode immersed into electrolyte before (above) and after cycling (below). Spectra were taken at 532 nm excitation. Signals correspond to integrated areas of the 595 cm^{-1} $LiCoO_2$ band after background subtraction. The individual spectra were taken at the indicated positions. Spectra were offset for clarity.



Raman mapping of a $LiCoO_2$ composite electrode. Shown is the integrated Raman signal of the $LiCoO_2$ A_{1g} phonon band before cycling (top) and after five cycles (bottom).



Summary:

- Raman spectrocopy enables *in situ* studies on positive and negative electrodes with lateral resolution (~2,5 μm).
- Wavelength-dependent studies elucidate the presence of a Resonance Raman enhancement for $LiCoO_2$ materials.
- Raman mapping demonstrates the chemical heterogeneity in composition across $LiCoO_2$ composite electrodes.
- Mappings of initial and cycled electrode suggest chemical redistribution induced by electrochemical cycling.