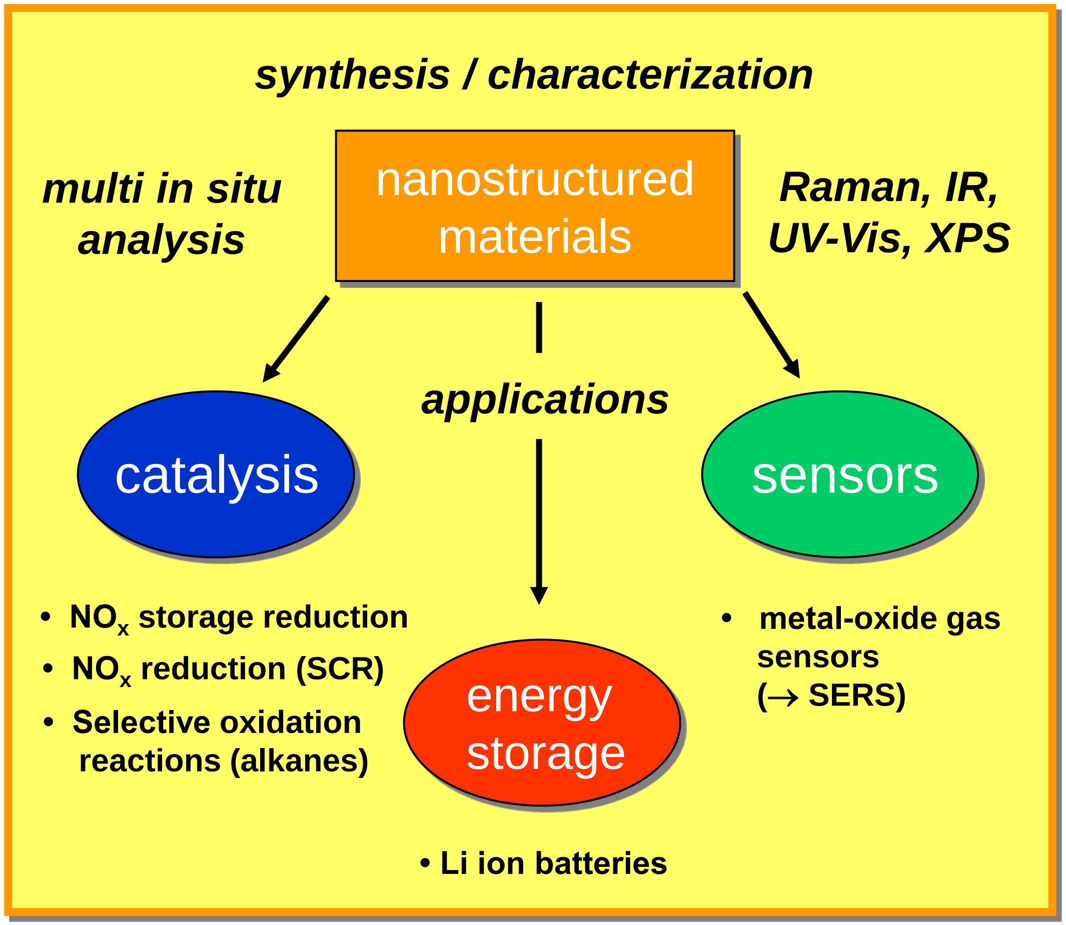
In situ Raman diagnostics of intercalation batteries

Christian Hess

Eduard-Zintl-Institut für Anorganische und Physikalische Chemie
Technical University Darmstadt
Germany

Current research activities



Outline

- Research strategy
- Intro to Raman spectroscopy
- Raman diagnostics of $LiCoO_2$ materials
- Spatially-resolved Raman analysis
- Summary

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Research Strategy

Vision

Knowledge-based design of functional materials

→ catalysts, batteries, gas sensors

Strategy

Establish structure-activity relations

Structural characterization under working conditions

→ *In situ/operando spectroscopy*

Li ion batteries

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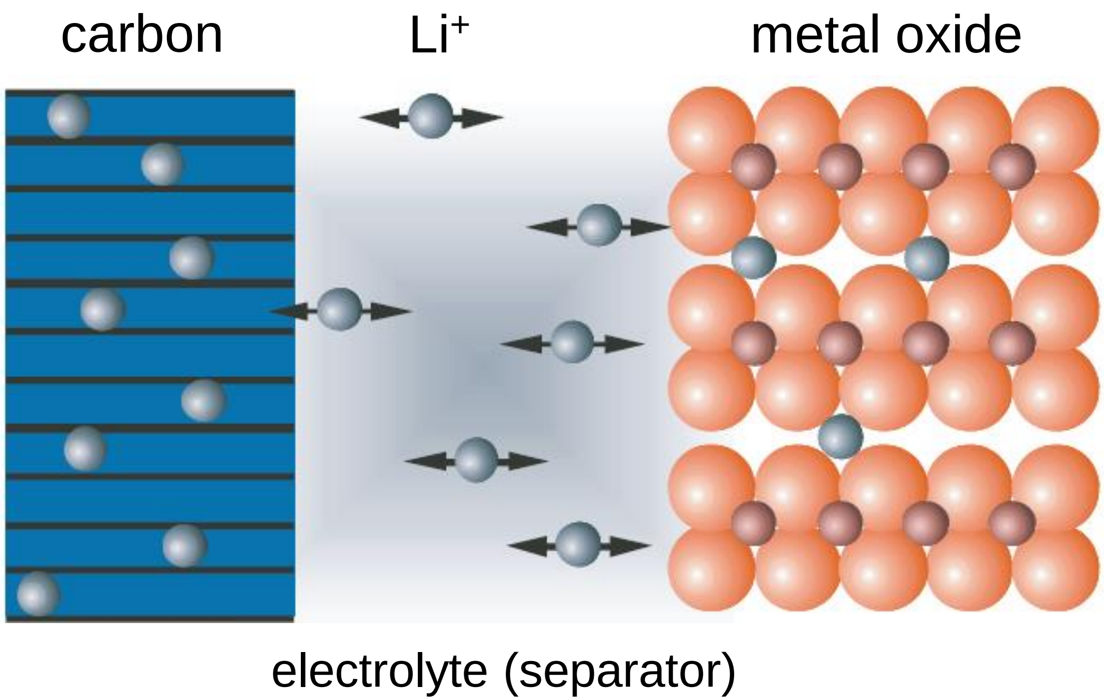

$$Li_xC_n \underset{C}{\overset{D}{\rightleftarrows}} C_n + xLi^+ + xe^-$$

$$Li_{1-x}MO_2 + xe^- + xLi^+ \underset{C}{\overset{D}{\rightleftarrows}} LiMO_2$$

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Why Raman spectroscopy?

- Infos on vibrational modes (phonons)

  → local structure information
- Usually small interference of electrolyte
- No specific conditioning of sample required
- Noninvasive and nondestructive analysis
- *In situ* spectra of batteries at work
- Spatially (1 μm^3) and time resolved information

Vibrational Raman scattering

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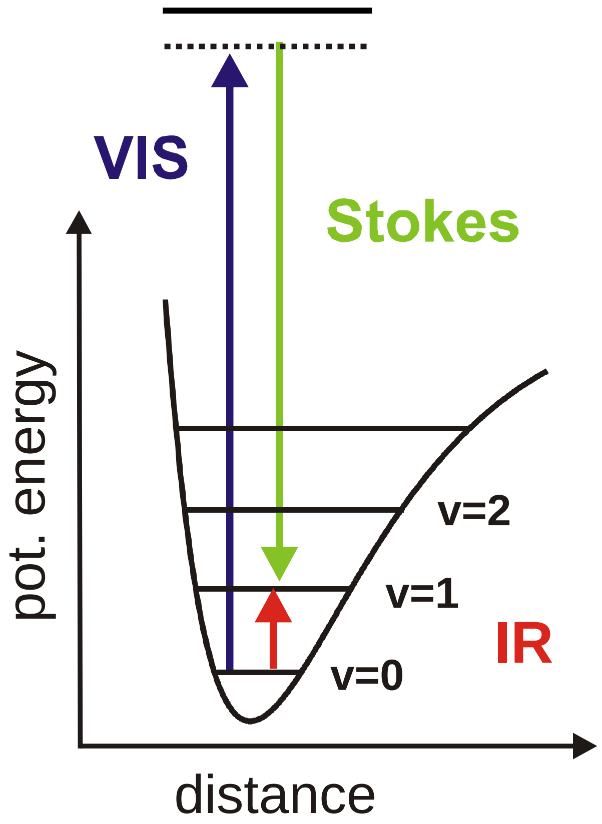
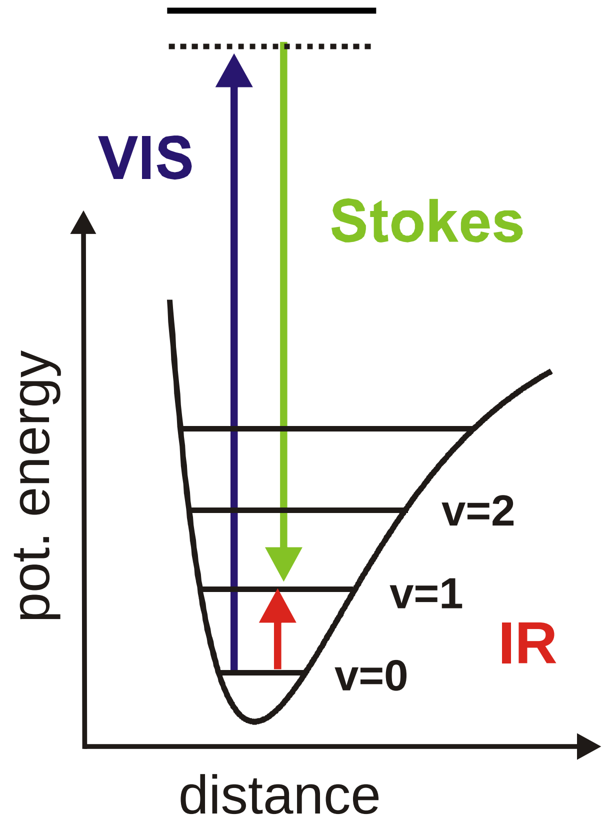
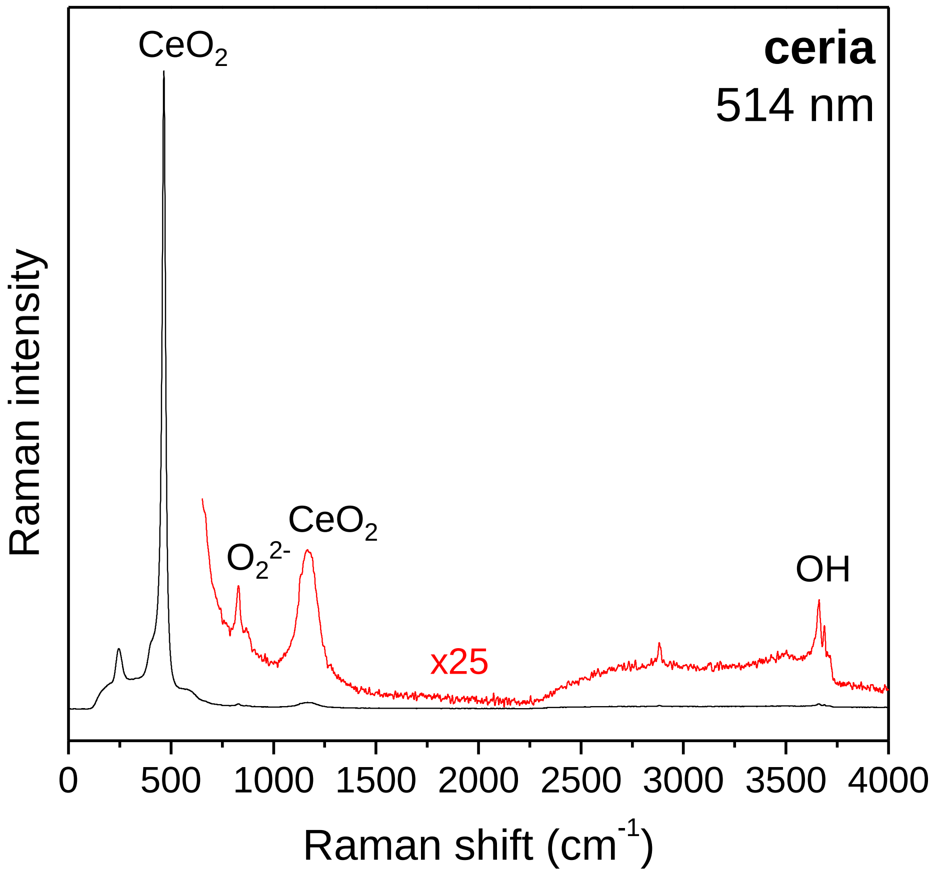


v(Raman shift) = v(VIS) – v(Stokes)

Vibrational Raman scattering



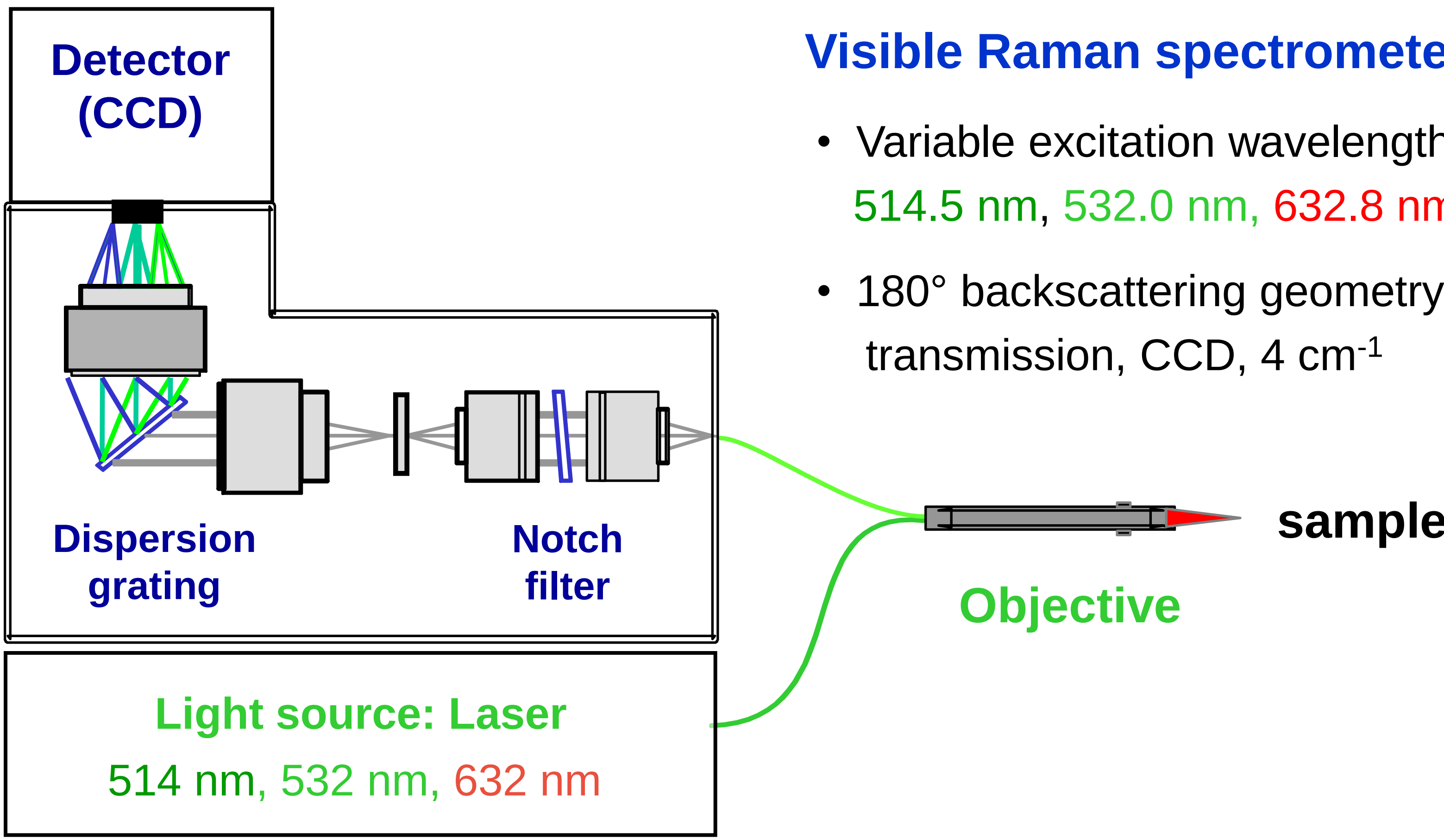


v(Raman shift) = v(VIS) – v(Stokes)

Raman setup - single stage

Visible Raman spectrometer

- Variable excitation wavelength
  514.5 nm, 532.0 nm, 632.8 nm
- 180° backscattering geometry, transmission, CCD, 4 cm^{-1}



Potential of Raman diagnostics

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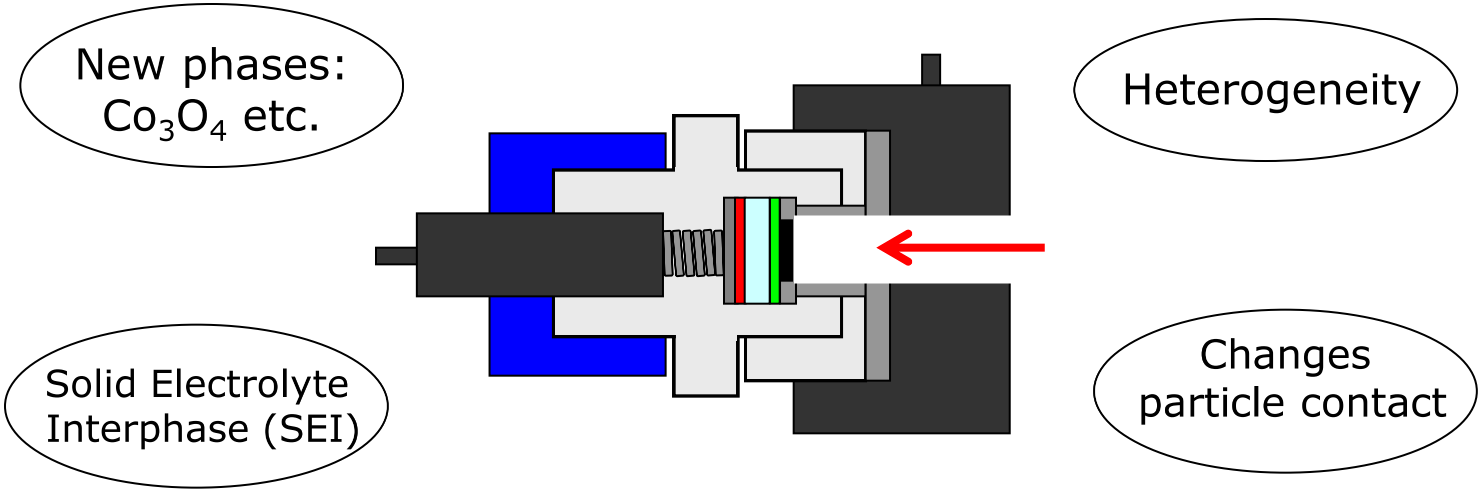
→ Origin of fatigue



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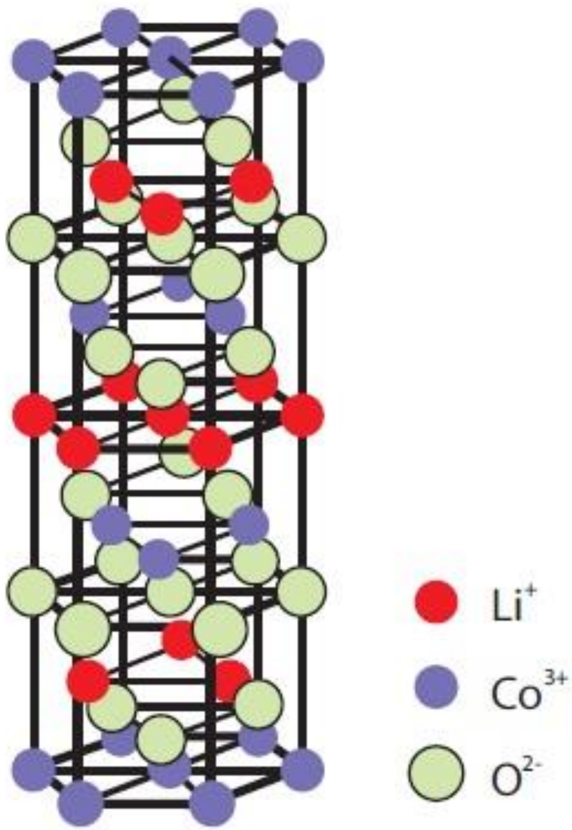
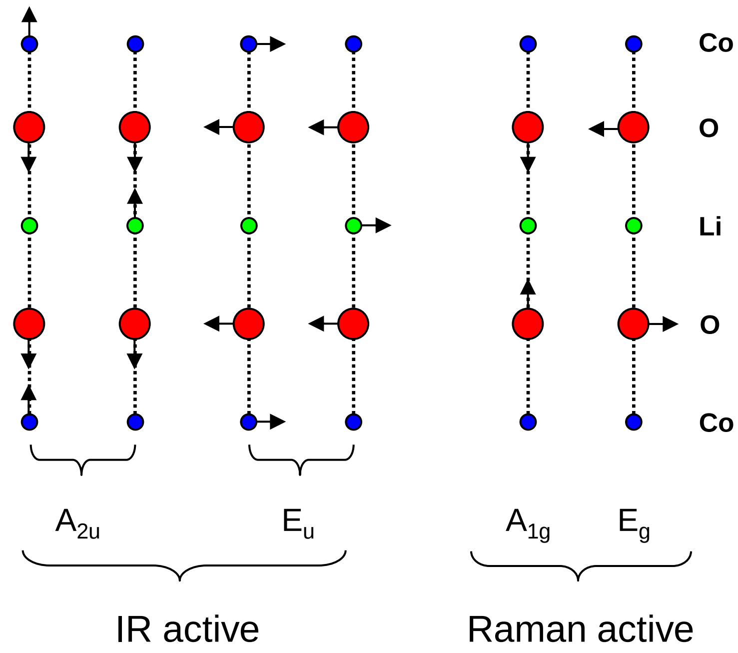
Active cathode materials $LiMO_2$



M = Co, Ni or mixtures

Hexagonal $LiCoO_2$



Active cathode materials $LiMO_2$

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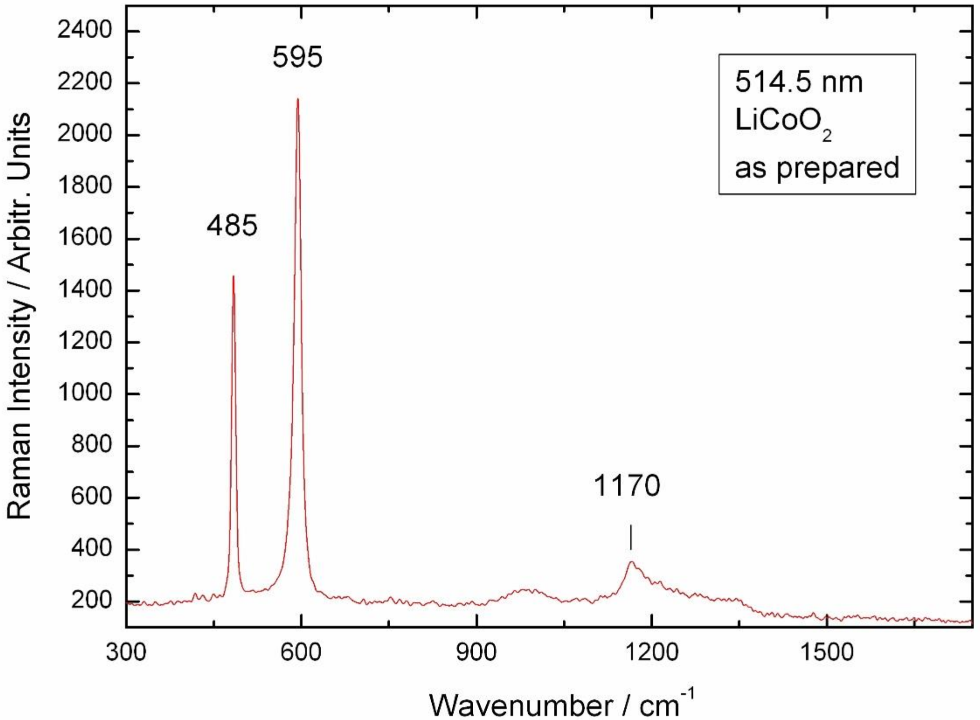
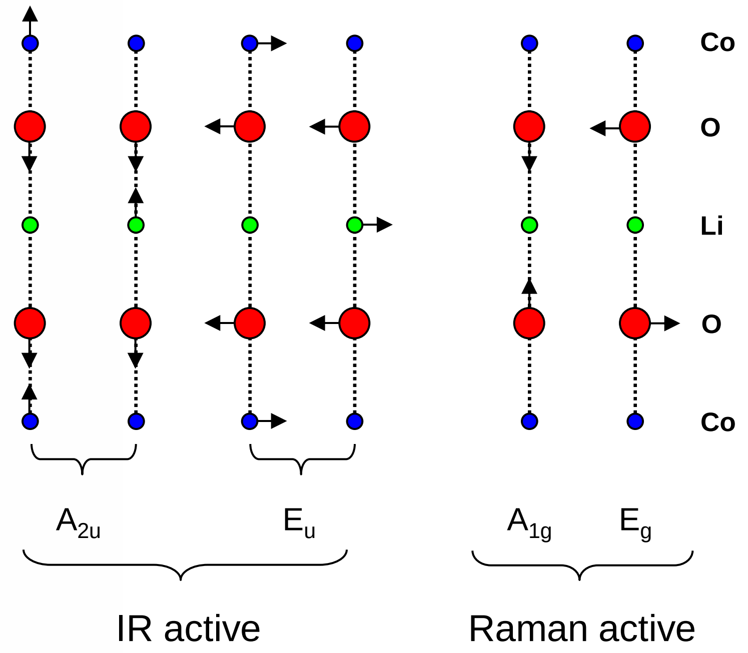
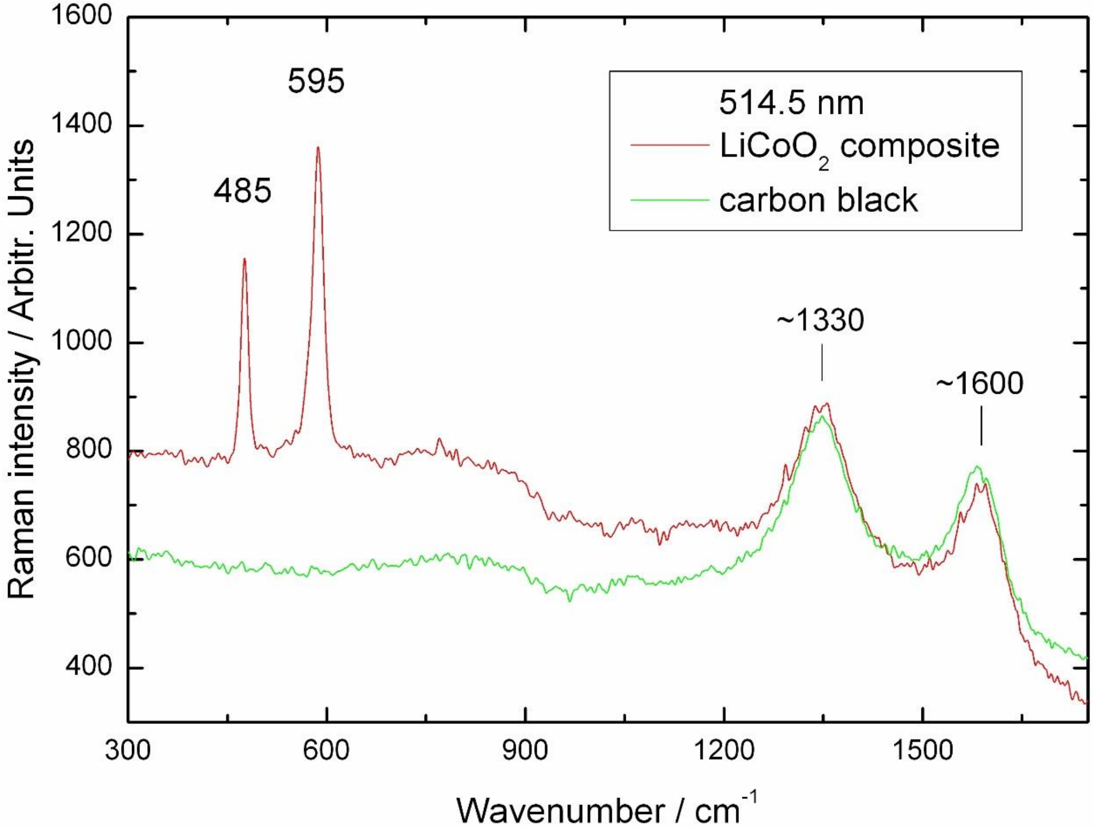


Hexagonal $LiCoO_2$



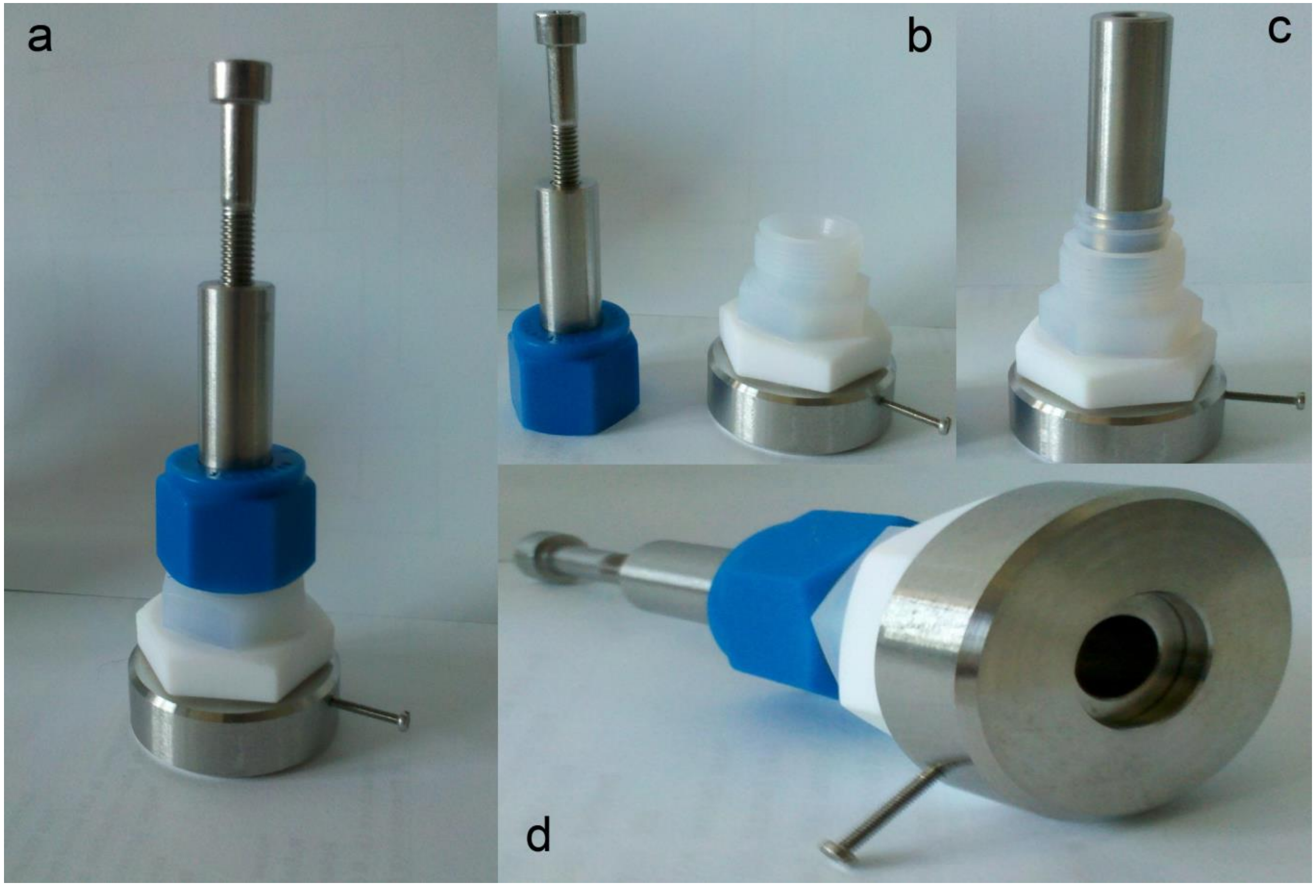
Raman spectra of $LiCoO_2$ cathode mix

84% $LiCoO_2$, 8% carbon black, 8% PVDF



T. Gross, C. Hess, J. Power Sources **256**, 220 (2014)

In situ Raman cell for battery research



T. Gross, L. Giebeler, C. Hess, Rev. Sci. Instr. **84**, 73109 (2013)

In situ Raman: $Li_{1-x}CoO_2$ deintercalation

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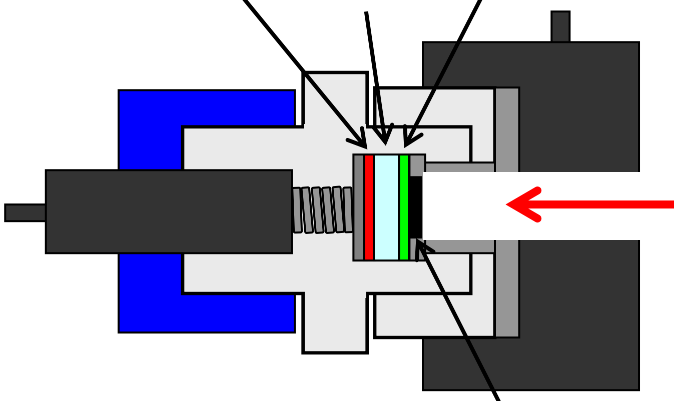
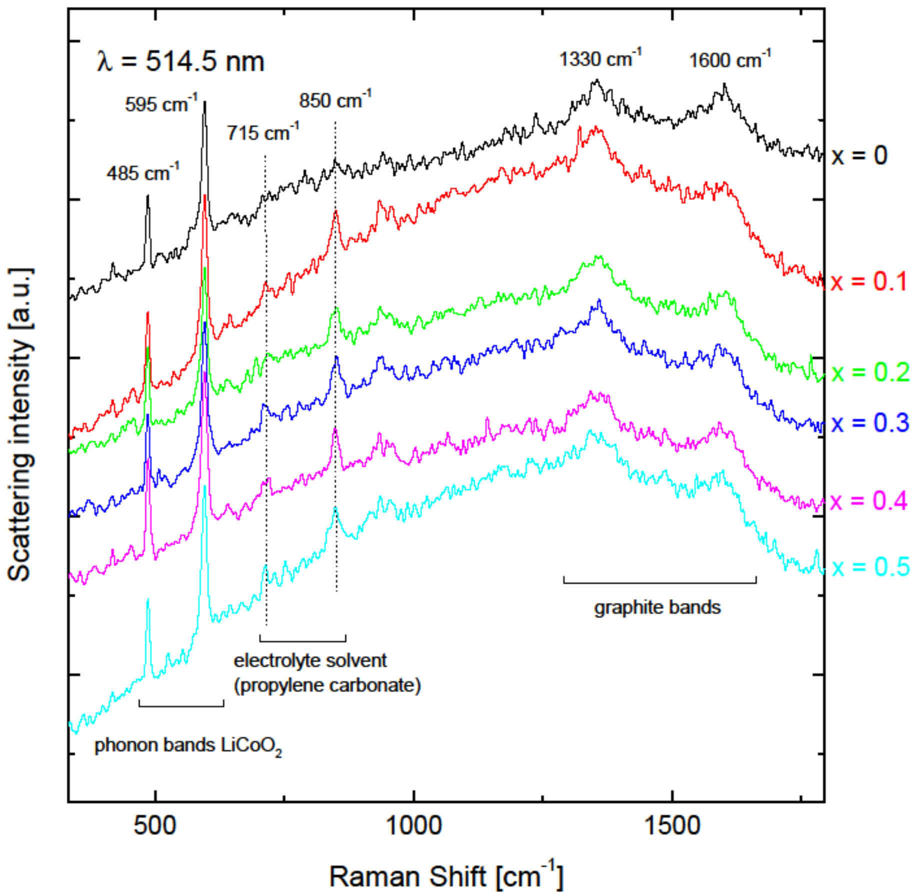
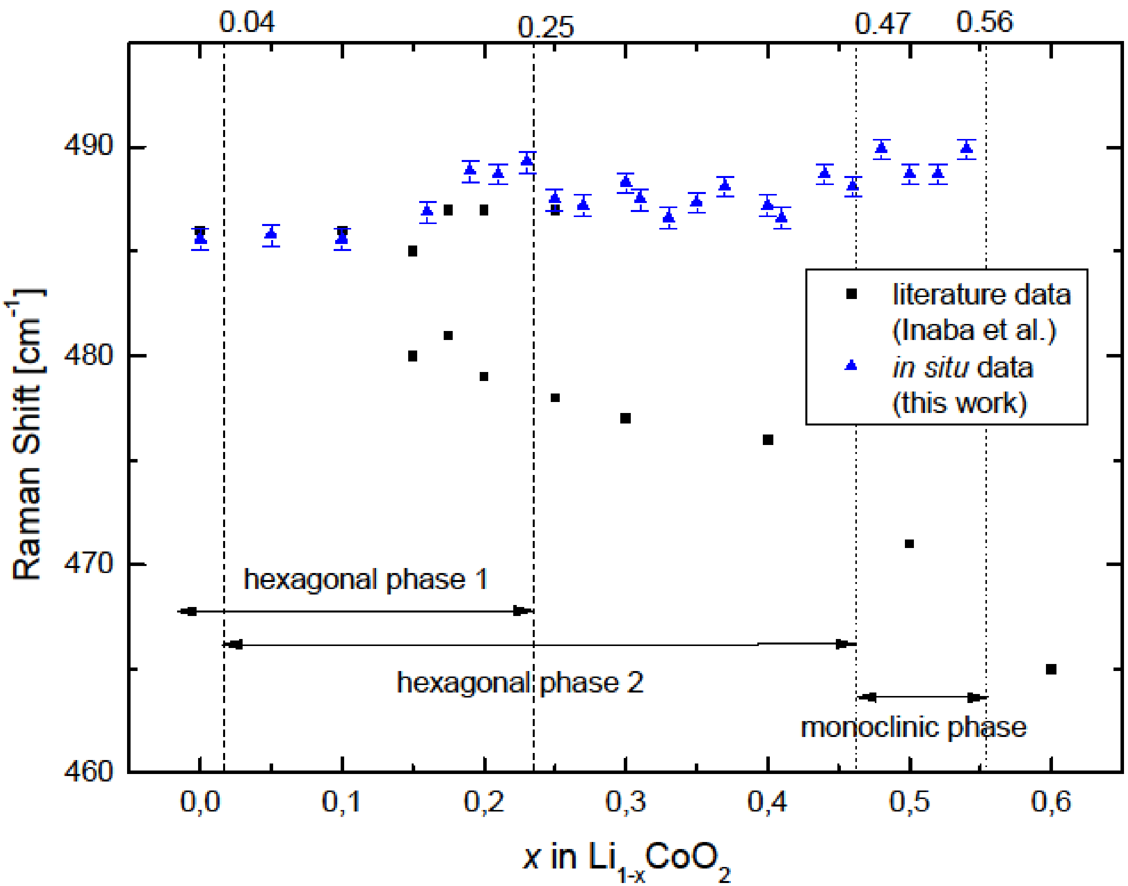




85% $LiCoO_2$, 10% PVDF, 5% Carbon black
1M $LiClO_4$ (PC); Rate: C/4, $\Delta x = 0.1$

→ Raman of working battery

In situ vs ex situ Raman spectroscopy



Importance of studying Li ion batteries at work!

T. Gross, L. Giebeler, C. Hess, Rev. Sci. Instr. **84**, 73109 (2013)

Resonance Raman effect – $LiCoO_2$

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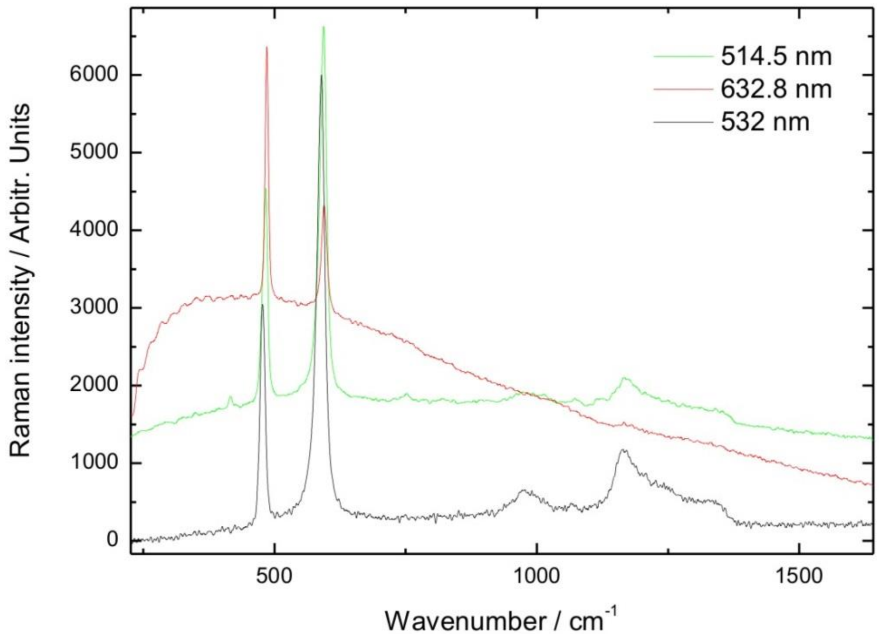
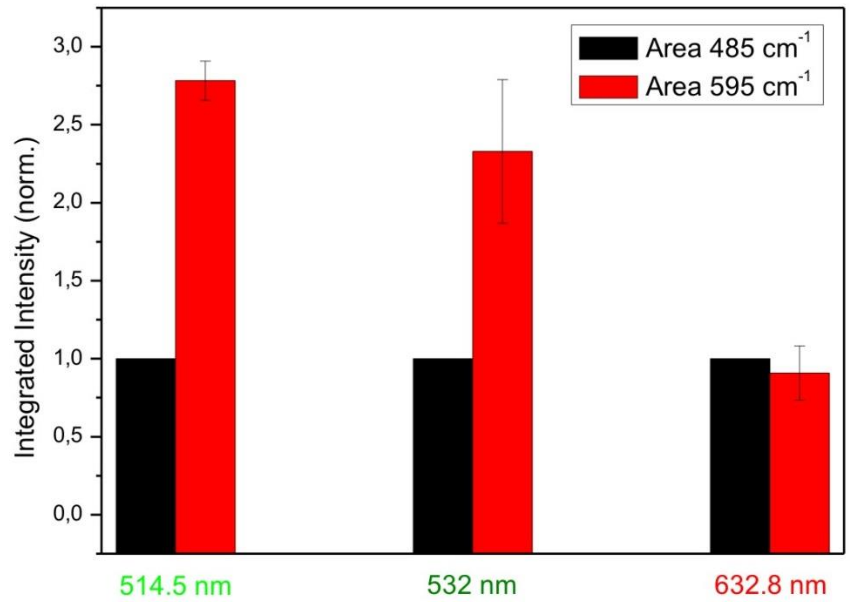
Excitation wavelength dependence





→ Intensity changes / overtone bands reveal resonance effect

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Resonance Raman effect – *in situ*

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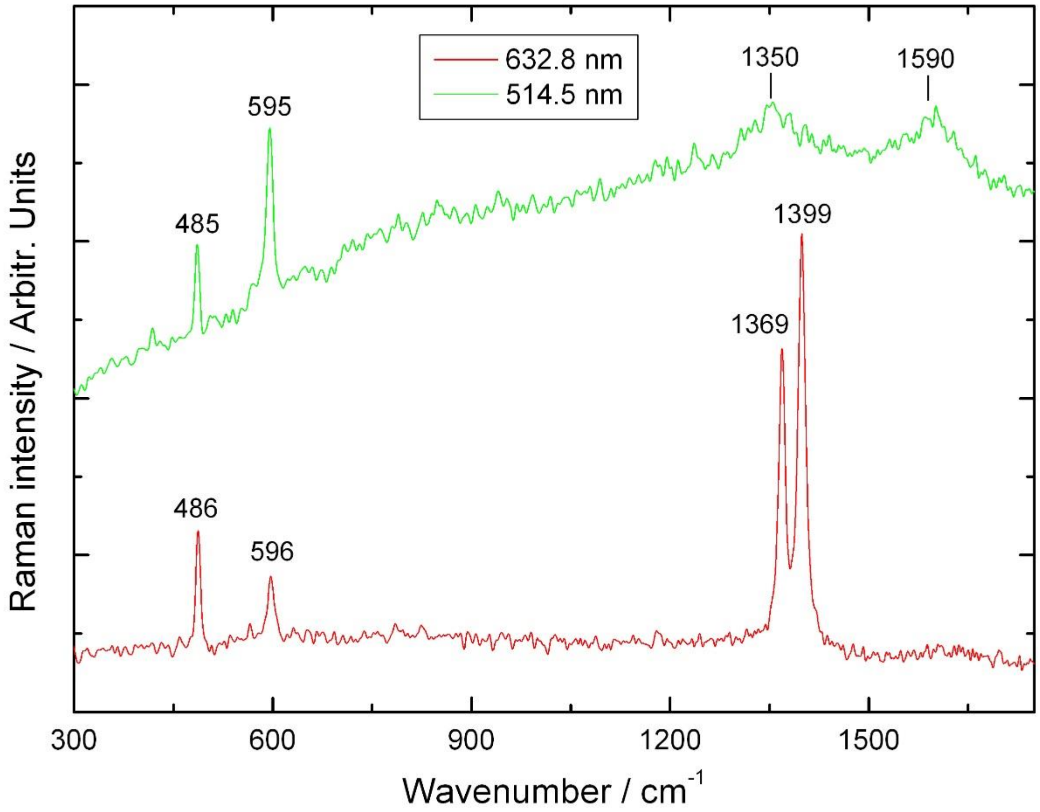
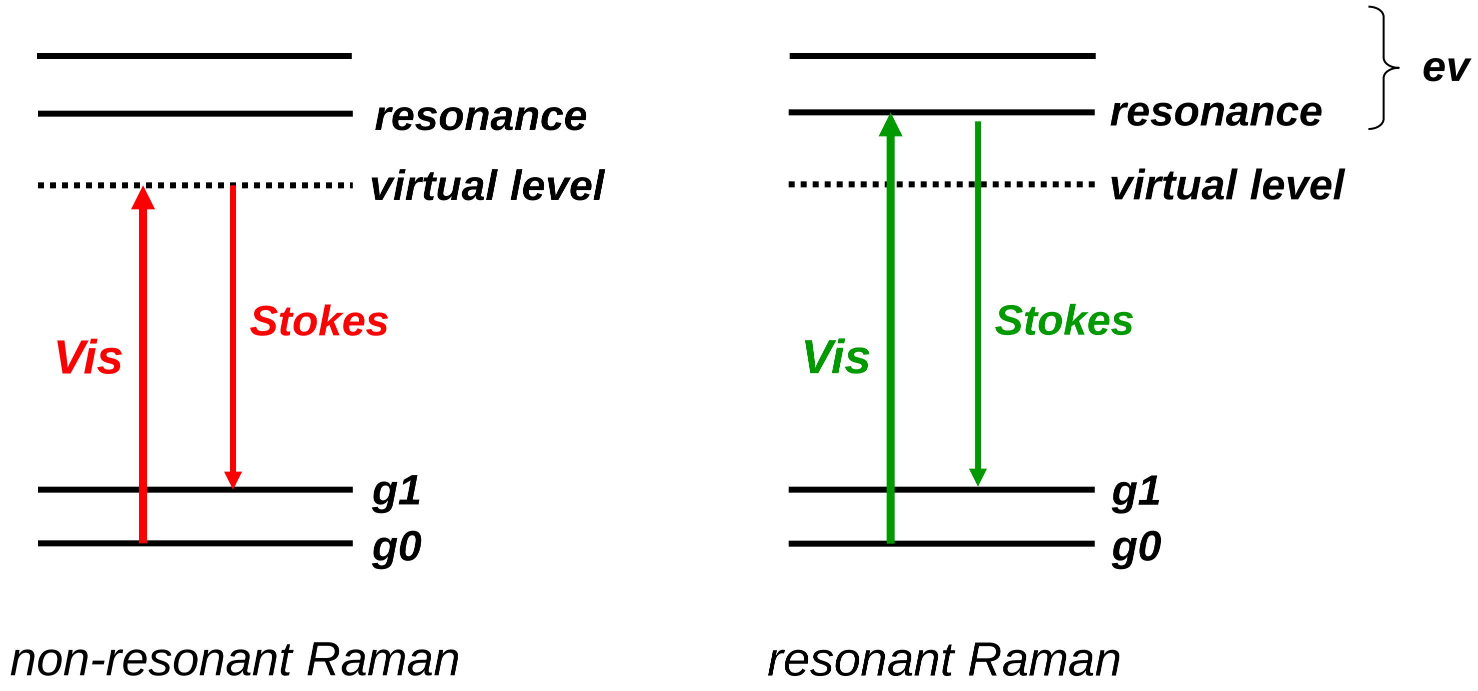


Raman scattering



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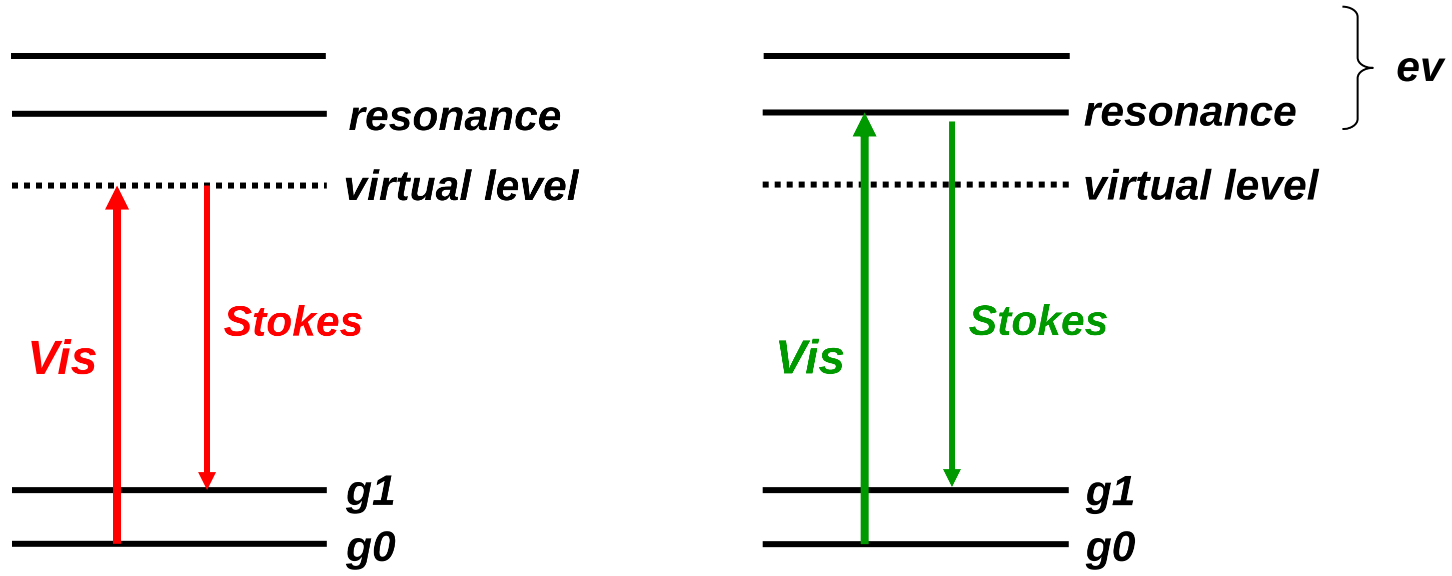
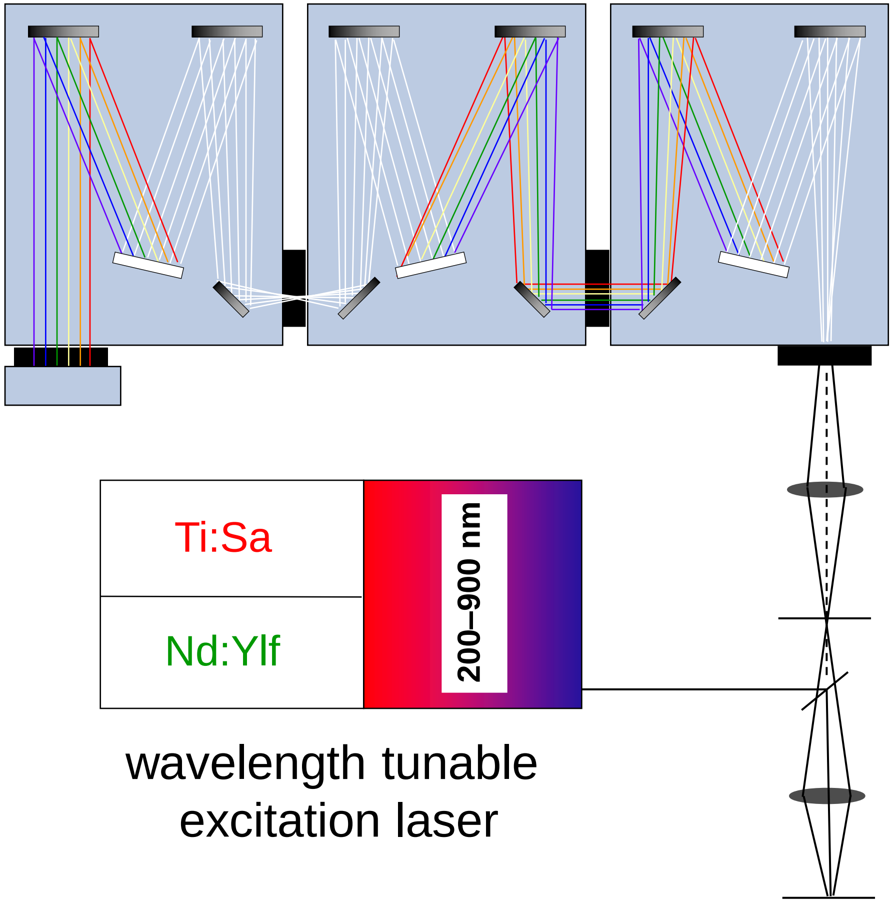


non-resonant Raman

resonant Raman

$$\left(\alpha_{\rho\sigma}\right)_{GF} = k\sum_{I}\left(\frac{\langle F|r_\rho|I\rangle\langle I|r_\sigma|G\rangle}{\omega_{GI}-\omega_L-i\Gamma_I}+\frac{\langle I|r_\rho|G\rangle\langle F|r_\sigma|I\rangle}{\omega_{IF}+\omega_L-i\Gamma_I}\right)$$

Advanced Raman setup



D. Nitsche, C. Hess, J. Raman Spectrosc. **44**, 1733 (2013)

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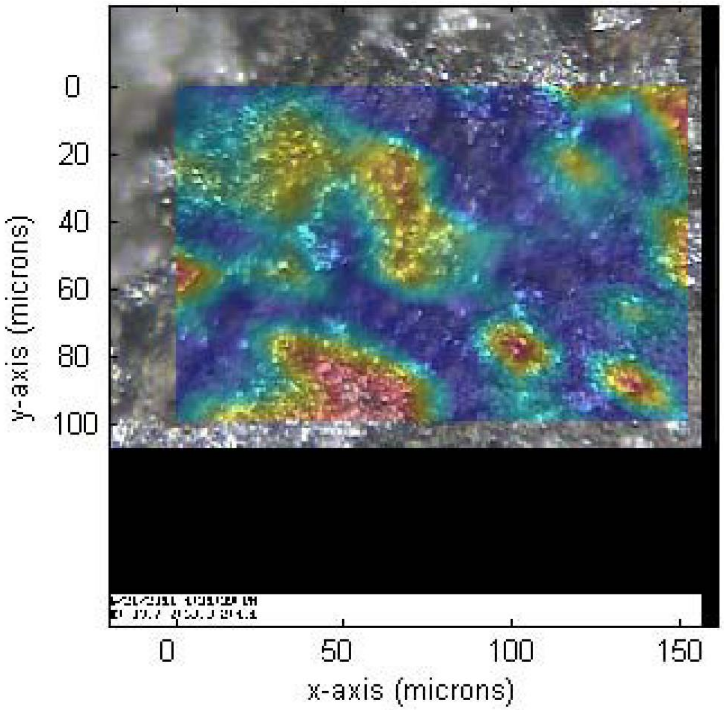
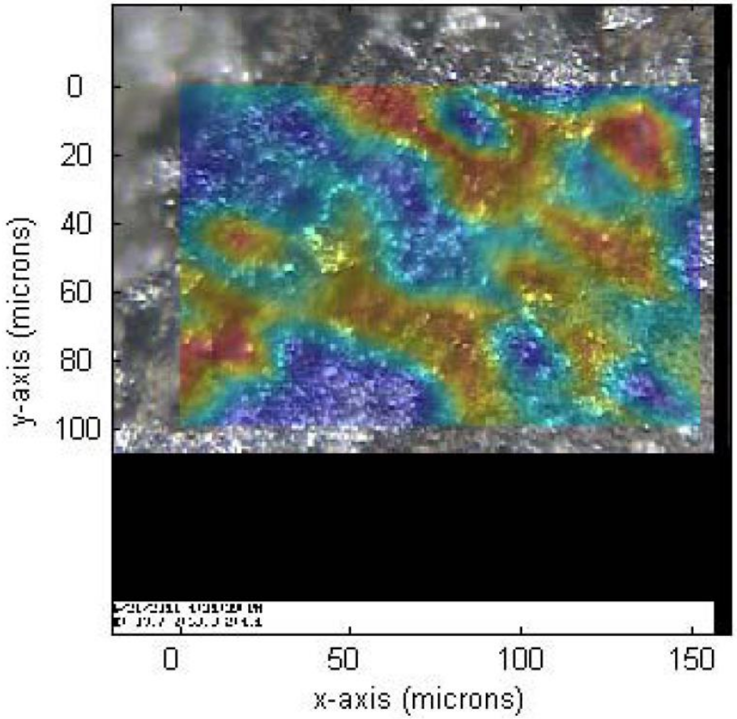
Raman mapping - $LiCoO_2$ cathode mix

$LiCoO_2$

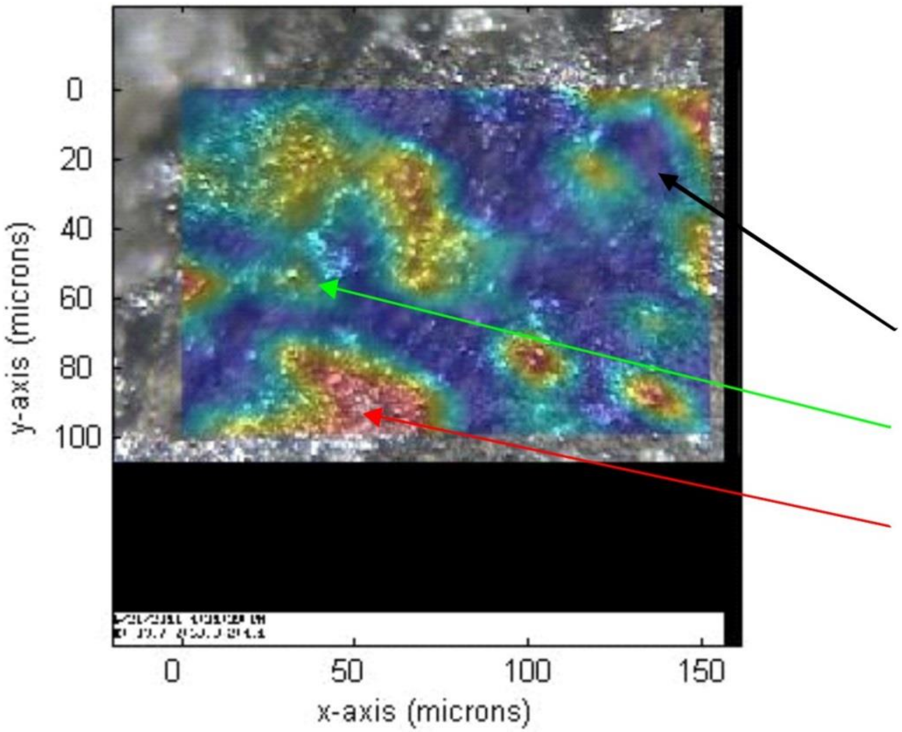


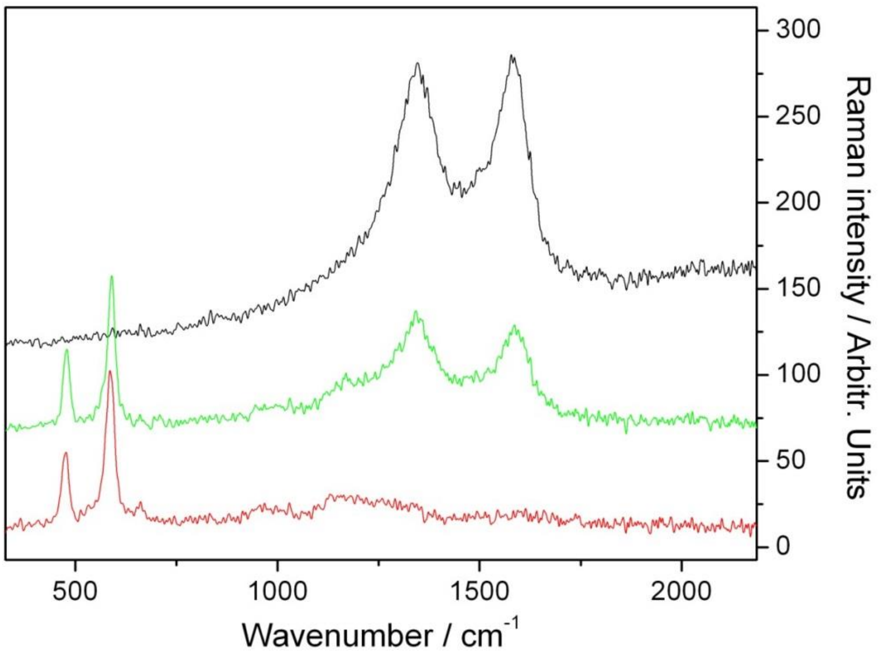
Carbon



→ Chemical heterogeneity across surface of cathode material

Raman mapping - $LiCoO_2$ cathode mix





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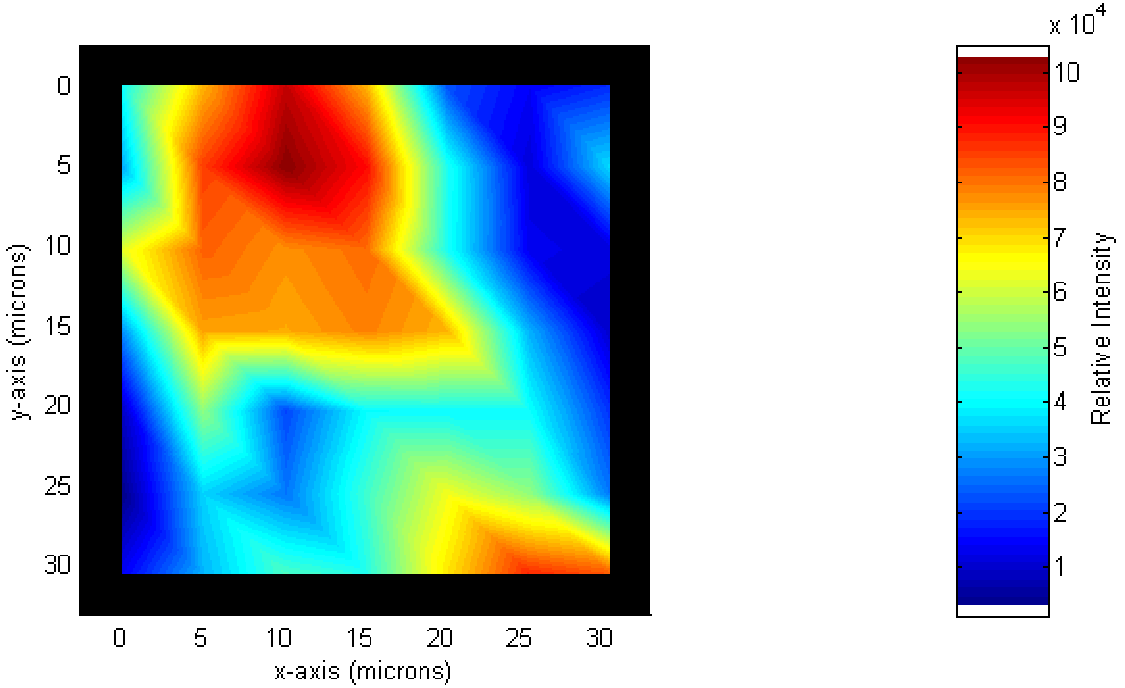
In situ Raman mapping

$LiCoO_2$ mapping

electrolyt present
no electrochemistry



→ Chemical heterogeneity across surface of cathode material

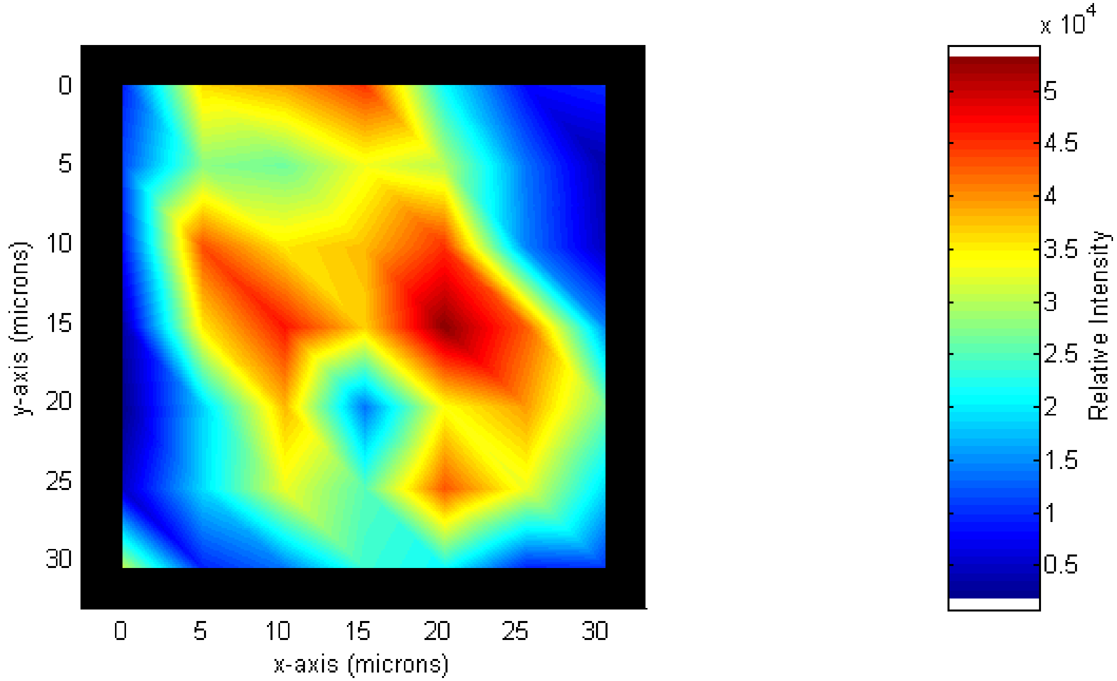
T. Gross, C. Hess, ECS Transactions (2014)

In situ Raman mapping

$LiCoO_2$ mapping

after 4 cycles

532 nm, Rate: C/12,
1M $LiPF_6$ (EC/DMC = 1:1)



→ Significant changes in composition during battery operation

Summary and Outlook

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- Raman spectrocopy: New insights during battery operation
- Resonance Raman: Sensitivity, probing electronic structure
- Raman Microscopy: Spatially-resolved chemical analysis

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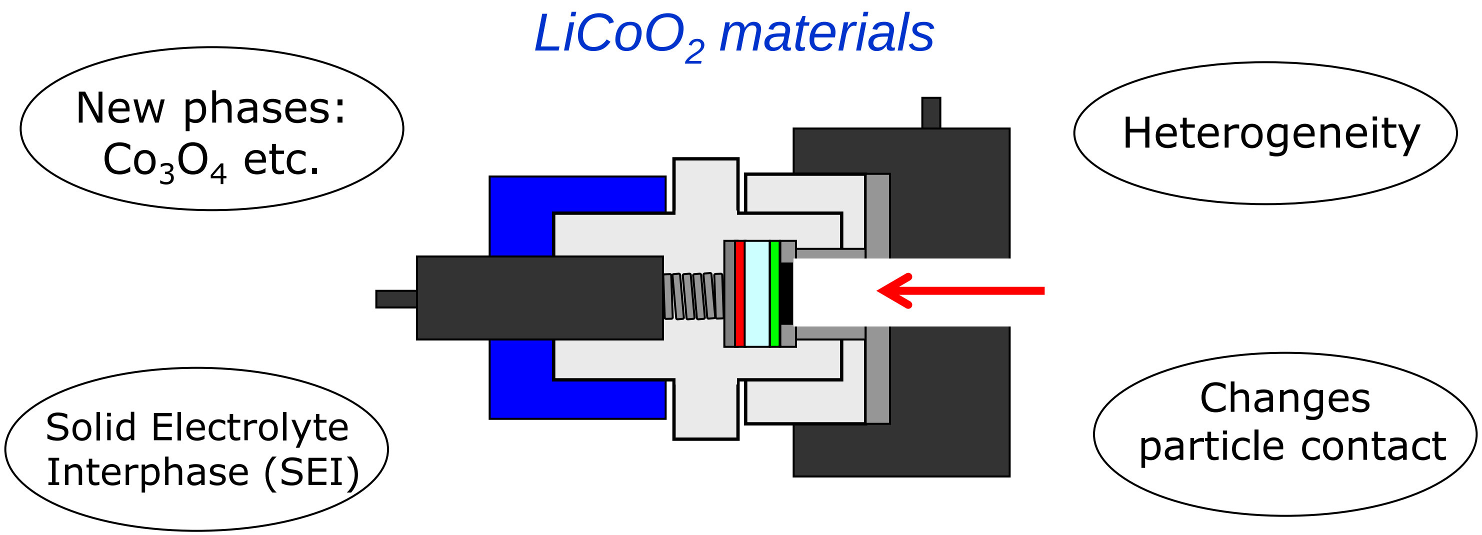

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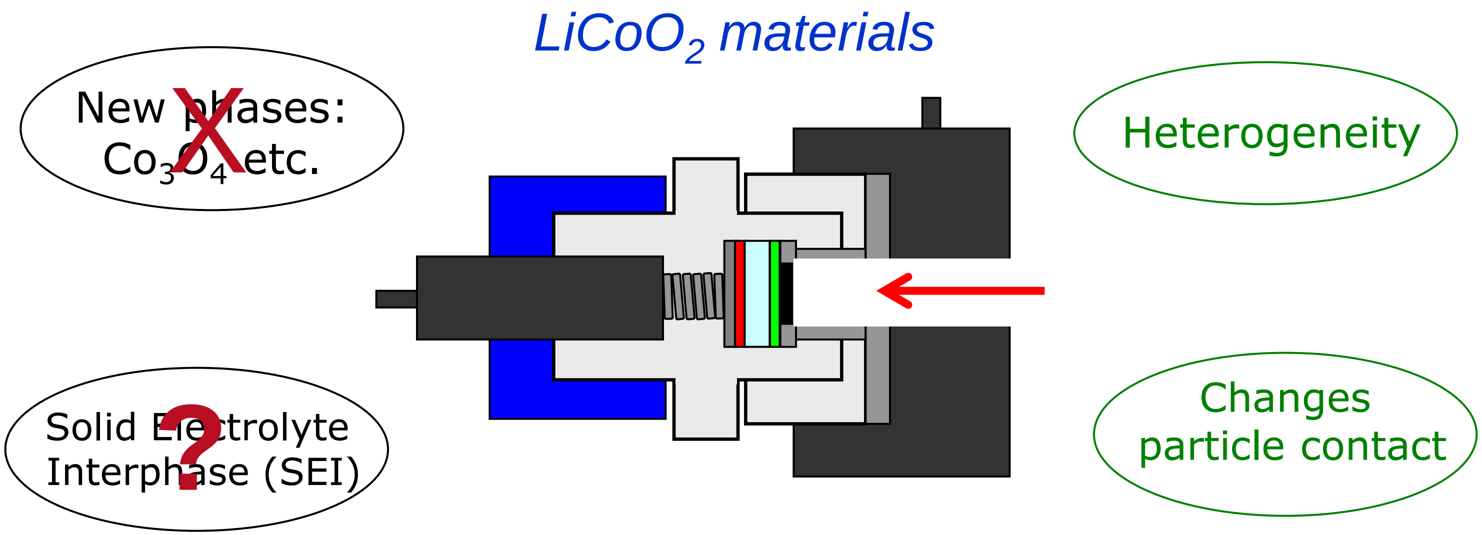

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Project B4:

$LiCoO_2$ samples

SFB 595

Synthese
Charakterisierung
Elektrische Ermüdung
Modellierung
Bauteil

Deutsche
Forschungsgemeinschaft

DFG