In situ Raman diagnostics of intercalation batteries

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Current research activities

- Selective oxidation reactions (alkanes)
- \( \text{NO}_x \) storage reduction
- \( \text{NO}_x \) reduction (SCR)
- Selective oxidation reactions (alkanes)
- Li ion batteries
- \( \text{NO}_x \) storage reduction (SCR)
- \( \text{NO}_x \) reduction (SCS)
- Selective oxidation reactions (alkanes)

**Applications**

- **Catalysis**
  - \( \text{NO}_x \) storage reduction
  - \( \text{NO}_x \) reduction (SCR)
  - Selective oxidation reactions (alkanes)

- **Sensors**
  - Metal-oxide gas sensors (SERS)

**Synthesis / Characterization**

- Multi in situ analysis
- Raman, IR, UV-Vis, XPS

**Nanostructured Materials**
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

\[ \text{Li}_x\text{C}_n \xrightarrow{D} \text{C}_n + x\text{Li}^+ + x\text{e}^- \quad \text{Li}_{1-x}\text{MO}_2 + x\text{e}^- + x\text{Li}^+ \xrightarrow{D} \text{LiMO}_2 \]
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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 μm³) and time resolved information
Vibrational Raman scattering

\[ \nu(\text{Raman shift}) = \nu(\text{VIS}) - \nu(\text{Stokes}) \]
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

Light source: Laser 514 nm, 532 nm, 632 nm
Potential of Raman diagnostics

→ Origin of fatigue

New phases: Co$_3$O$_4$ etc.

Solid Electrolyte Interphase (SEI)

Heterogeneity

Changes particle contact
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Active cathode materials $\text{LiM}O_2$

$\text{M} = \text{Co, Ni or mixtures}$

**Hexagonal LiCoO$_2$**

$A_{2u}$  $E_u$  $A_{1g}$  $E_g$

IR active  Raman active
Active cathode materials LiMO$_2$

M = Co, Ni or mixtures

Hexagonal LiCoO$_2$

IR active

Raman active

514.5 nm LiCoO$_2$ as prepared
Raman spectra of LiCoO$_2$ cathode mix

84% LiCoO$_2$, 8% carbon black, 8% PVDF

**In situ** Raman cell for battery research

In situ Raman: Li$_{1-x}$CoO$_2$ deintercalation

85% LiCoO$_2$, 10% PVDF, 5% Carbon black
1M LiClO$_4$ (PC); Rate: C/4, Δx = 0.1

→ Raman of working battery
In situ vs ex situ Raman spectroscopy

Importance of studying Li ion batteries at work!

Resonance Raman effect – LiCoO$_2$

Excitation wavelength dependence

→ Intensity changes / overtone bands reveal resonance effect

Resonance Raman effect – *in situ*
Raman scattering

non-resonant Raman

resonant Raman

\[
\text{Vis} \quad \text{Stokes} \quad g_1 \quad g_0
\]

\[
\text{resonance} \quad \text{virtual level}
\]

\[
\{ \text{ev} \}
\]
Raman scattering

\[
\left( \alpha_{\rho\sigma} \right)_{GF} = k \sum_{i} \left( \frac{\langle F | r_{\rho} | I \rangle \langle I | r_{\sigma} | G \rangle}{\omega_{GI} - \omega_{L} - i\Gamma_{I}} + \frac{\langle I | r_{\rho} | G \rangle \langle F | r_{\sigma} | I \rangle}{\omega_{IF} + \omega_{L} - i\Gamma_{I}} \right)
\]
Advanced Raman setup

triple spectrometer & CCD

wavelength tunable excitation laser

D. Nitsche, C. Hess, J. Raman Spectrosc. 44, 1733 (2013)
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Raman mapping - LiCoO$_2$ cathode mix

→ Chemical heterogeneity across surface of cathode material
Raman mapping - LiCoO$_2$ cathode mix

In situ Raman mapping

LiCoO$_2$ mapping

Electrolyt present
No electrochemistry

→ Chemical heterogeneity across surface of cathode material

**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

- **Raman spectroscopy**: New insights during battery operation
- **Resonance Raman**: Sensitivity, probing electronic structure
- **Raman Microscopy**: Spatially-resolved chemical analysis
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**LiCoO₂ materials**

- New phases: Co₃O₄ etc.
- Heterogeneity
- Solid Electrolyte Interphase (SEI)
- Changes particle contact
Summary and Outlook

- **Raman spectroscopy**: New insights during battery operation
- **Resonance Raman**: Sensitivity, probing electronic structure
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*LiCoO$_2$ materials*

- New phases: $\text{Co}_3\text{O}_4$ etc.
- Heterogeneity
- Changes particle contact
- Solid Electrolyte Interphase (SEI)
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Project B4: LiCoO$_2$ samples

Thank you for your attention