Combined IR and Raman *In Situ* Microscopy on Single Particles – A New Tool for Interface Studies

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### **In situ** cell / Principle / Approach

- **Objective** (Raman or IR)
- **Window** (CaF₂)
- **Working electrode** (stainless steel mesh)
- **Separator** (glass fibre)
- **Counter/reference electrode** (Li)
- **Cell body** (stainless steel)
- **Current collector** (Ti in PEEK) (PEEK = polyether ether ketone)

**Electronic states**

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Raman</th>
<th>IR</th>
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<td>-0.2</td>
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<td>-0.1</td>
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**Virtual states**

- **Vibrational states**
- **Ground state**

**Combined in situ** microscopic approach

- **Raman:** Particularly sensitive to structural changes in the electrode material
- **IR:** Particularly sensitive to the interface with the organic electrolyte
- **In situ:** Avids relaxation & determines the exact potential of electrochemical processes
- **Microscopy:** Allows lateral resolution
- **Automation:** Switches between Raman & IR

### **Positive electrodes (Raman microscopy)**

- **Li₂MnO₃**
  - Component of HE-NCM (domains)
  - Activated during initial charging

**Electrochemical activation of Li₂MnO₃ at 50 °C [3]**

**Observation:** Shift of A₂ to higher wavenumbers starting at 4.4 V

In agreement with the potential plateau observed in HE-NCM

**Comparison of stoichiometric and HE-NCM**

- **Stoichiometric NCM**
- **HE-NCM**

**Observation 1:** Disappearance of A₁₂ (reversible, due to intercalation)

**Observation 2:** New band at 545 cm⁻¹ (more pronounced in HE-NCM)

New band at 545 cm⁻¹ possibly due to activation products (e.g. Li₃O) of Li₂MnO₃ integrated in the NCM structure

(Small amounts of Li₂MnO₃ may be present in stoichiometric NCM)

### **Negative electrodes (Combined microscopy)**

- **Glassy carbon disc (GC)**
  - Model system with high reflectivity
  - No Li-intercalation

**Electrochemical charging of glassy carbon [4]**

**Observation:** No significant D and G shifts/splitting

**Raman:** Bipolar bands (separated by a few cm⁻¹) & positive band at 1650 cm⁻¹

**IR:** Increase in free and decrease in coord. EC/DMC & SEI formation

**In situ Raman spectra**

**In situ IR difference spectra**

### **Conclusions & Outlook**

- **Li₂MnO₃** is activated at 4.4 V vs. Li⁺/Li when charged at 50 °C. Charging of NCM leads to the evolution of a new band at 545 cm⁻¹ (stronger in HE-NCM).
- Unlike GC, graphite intercalates Li. Strong solvation effects in both carbons. SEI products were detected on GC (band at 1650 cm⁻¹ due to EC reduction).
- Further *in situ* IR experiments to identify SEI products on polished graphite particles are planned.
- Combined *in situ* Raman and IR microscopy is a powerful method for the characterization of Li-ion batteries (electrode materials and electrolyte).

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### **References**