

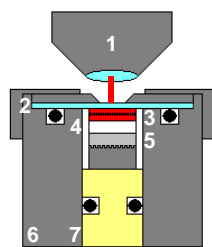
Investigation of Electrode Materials for Lithium-Ion Cells by Combined In Situ Raman and IR Microscopy

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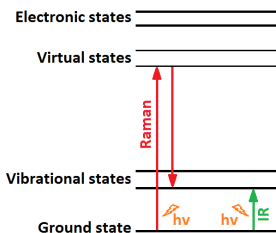
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In situ cell / Principle / Approach



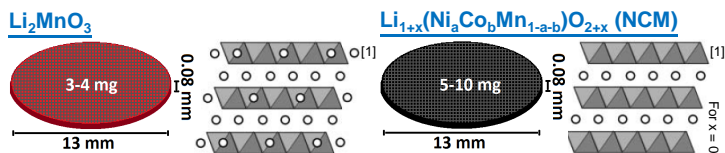
- Objective (Raman or IR)
- Window (CaF₂)
- Working electrode (stainless steel mesh)
- Separator (glass fibre)
- Counter/reference electrode (Li)
- Cell body (stainless steel)
- Current collector (Ti in PEEK) (PEEK = polyether ether ketone)



Combined in situ microscopic approach

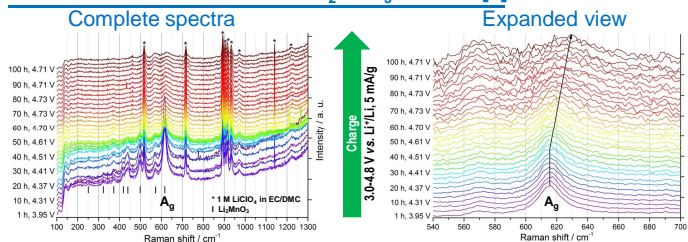
- **Raman:** Particularly sensitive to structural changes in the electrode material
- **IR:** Particularly sensitive to the interface with the organic electrolyte
- **In situ:** Avoids relaxation & determines the exact potential of electrochemical processes
- **Microscopy:** Allows lateral resolution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

Positive electrodes (Raman microscopy)



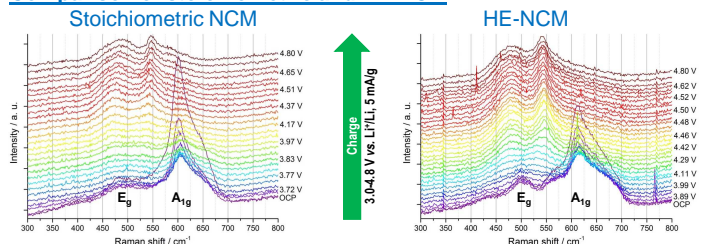
- Component of HE-NCM (domains)
- Activated during initial charging
- Promising electrode material
- Also called HE-NCM for $x > 0$

Electrochemical activation of Li₂MnO₃ at 50 °C [3]



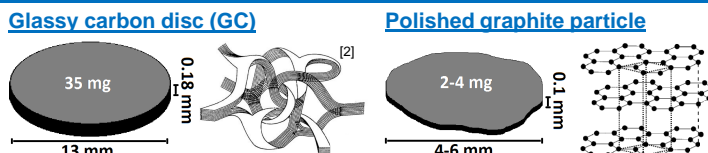
- **Observation:** Shift of A_g to higher wavenumbers starting at 4.4 V
- **Electrochemical activation of Li₂MnO₃ above 4.4 V**
- **In agreement with the potential plateau observed in HE-NCM**

Comparison of stoichiometric and HE-NCM



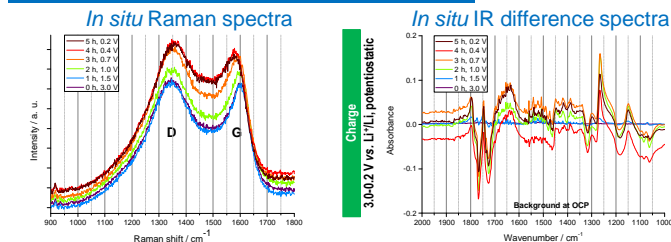
- **Observation 1:** Disappearance of A_{1g} (reversible, due to intercalation)
- **Observation 2:** New band at 545 cm⁻¹ (more pronounced in HE-NCM)
- **New band at 545 cm⁻¹ possibly due to activation products (e.g. Li₂O) of Li₂MnO₃ integrated in the NCM structure** (Small amounts of Li₂MnO₃ may be present in stoichiometric NCM)

Negative electrodes (Combined microscopy)



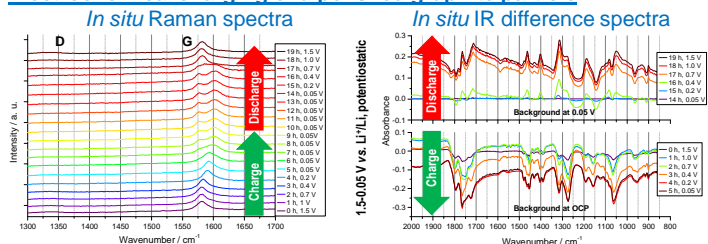
- Model system with high reflectivity
- No Li-intercalation
- Better reflectivity than powders
- Li-intercalation possible

Electrochemical charging of glassy carbon [4]



- **Raman:** No significant D and G shifts/splitting
- **No significant lithium intercalation**
- **IR:** Bipolar bands (separated by a few cm⁻¹) & positive band at 1650 cm⁻¹
- **Increase in free and decrease in coord. EC/DMC & SEI formation**

Electrochemical charging of a polished graphite particle



- **Raman:** G shifts/splitting (due to staging)
- **Reversible Li-intercalation**
- **IR 1:** Decrease/increase in free and coord. EC/DMC on charge/discharge
- **IR 2:** Pronounced jump in absorbance at the transition 0.4 V / 0.7 V
- **Potential-dependent solvation effects & Li-intercalation**

Free = not coordinated to Li⁺, coord. = coordinated to Li⁺

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).

Acknowledgements

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References

- [1] M.M. Thackeray et al., J. Mater. Chem., 2007, 17, 3115
- [2] G.M. Jenkins, K. Kawamura, Nature, 1971, 231, 175
- [3] P. Lanz et al., Electrochim. Acta, 2013, 109, 426-432
- [4] S. Perez-Villar et al., Electrochim. Acta, 2013, 106, 506-515

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