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

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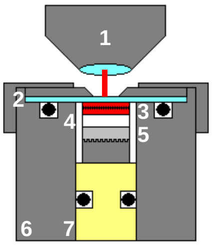
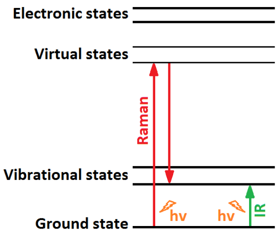
In situ cell / Principle / Approach



1 Objective (Raman or IR)
2 Window (CaF_2)
3 Working electrode (stainless steel mesh)
4 Separator (glass fibre)
5 Counter/reference electrode (Li)
6 Cell body (stainless steel)
7 Current collector (Ti in PEEK)
(PEEK = polyether ether ketone)

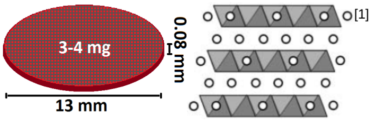


Combined *in situ* microscopic approach

- **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

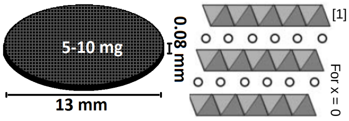
Positive electrodes (Raman microscopy)

Li_2MnO_3



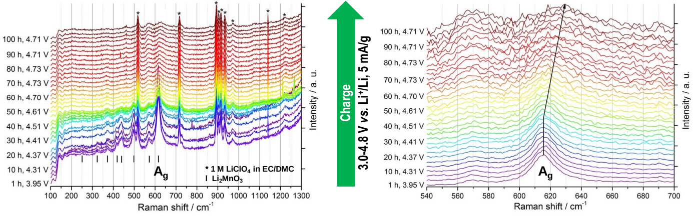
- Component of HE-NCM (domains)
- Activated during initial charging

$Li_{1+x}(Ni_aCo_bMn_{1-a-b})O_{2+x}$ (NCM)



- Promising electrode material
- Also called HE-NCM for x > 0

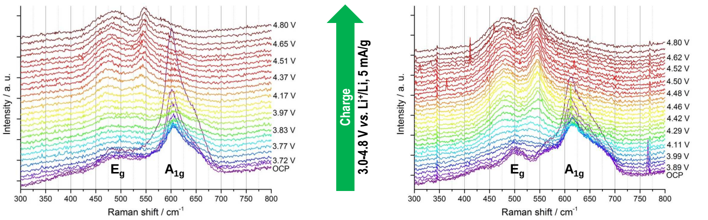
Electrochemical activation of Li_2MnO_3 at 50 °C [3]


Complete spectra
Expanded view

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

☞ **Electrochemical activation of Li_2MnO_3 above 4.4 V**
In agreement with the potential plateau observed in HE-NCM

Comparison of stoichiometric and HE-NCM

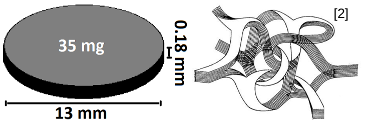

Stoichiometric NCM
HE-NCM

- **Observation 1:** Disappearance of 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.* Li_2O) of Li_2MnO_3 integrated in the NCM structure**
(Small amounts of Li_2MnO_3 may be present in stoichiometric NCM)

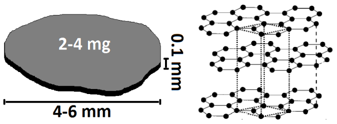
Negative electrodes (Combined microscopy)

Glassy carbon disc (GC)



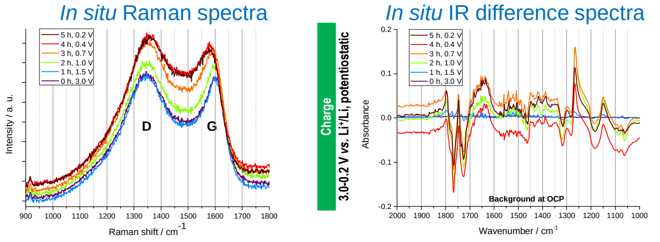
- Model system with high reflectivity
- No Li-intercalation

Polished graphite particle



- Better reflectivity than powders
- Li-intercalation possible

Electrochemical charging of glassy carbon [4]


In situ Raman spectra
In situ IR difference spectra

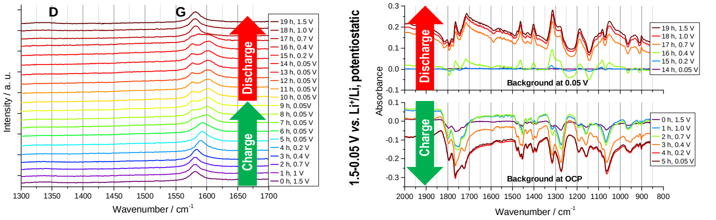
- **Raman:** No significant D and G shifts/splitting

☞ **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


In situ Raman spectra
In situ IR difference spectra

- **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

- Li_2MnO_3 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

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