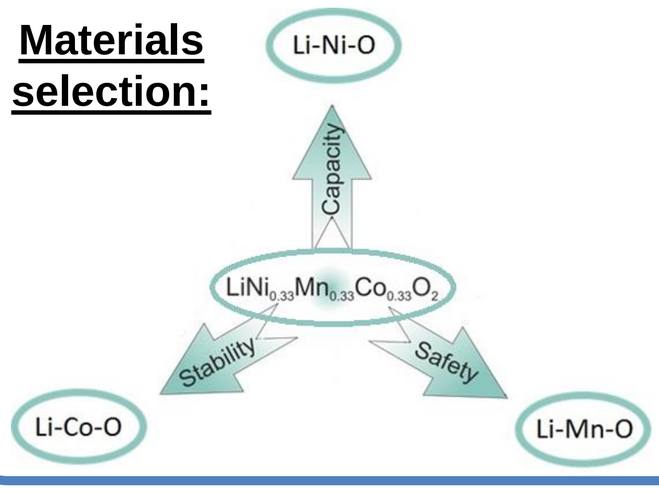
HELMHOLTZ Portfolio
Elektrochemische Speicher im System Zuverlässigkeit und Integration

AP 2.1
Structuring and processing of electrodes

Constitution and microstructure of Li-Ni-Mn-Co-O thin film cathodes

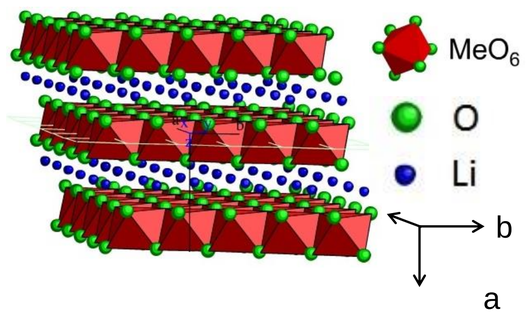
1.5 µm thick Li-Ni-Mn-Co-O cathodes have been deposited by r.f. magnetron sputtering from $Li_{1.25}(Ni_{0.42}Mn_{0.21}Co_{0.37})O_2$ target. The elemental composition varies with argon working gas pressure (0.2 Pa to 20 Pa) and was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in combination with carrier gas hot extraction. The microstructure of the films was characterized by X-ray diffraction (XRD) and by micro-Raman spectroscopy at room temperature. The as-deposited films are nanocrystalline and show their highest grade of crystallinity in the range between 0.2 Pa to 0.5 Pa and at 7 Pa. Correlations between process parameter, constitution and microstructure are discussed in detail.

Materials selection:



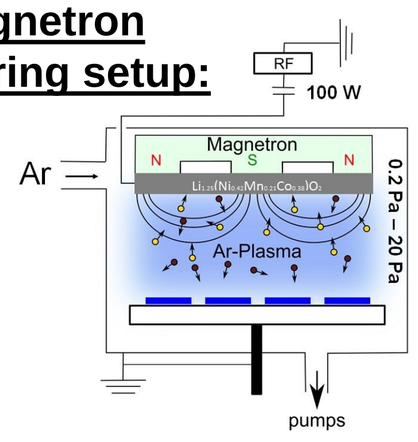
Properties and structure of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$:

- **Theoretical capacity:** 290 mAh/g
- **Practical capacity:** 160-180 mAh/g
- **Voltage vs. Li:** 2.5 V - 4.6 V
- **Space group:** R3m
  hexagonal lattice
  a = b = 2.867Å c = 14.246 Å
  α = β = 90° γ = 120°
- **Color:** black-grey



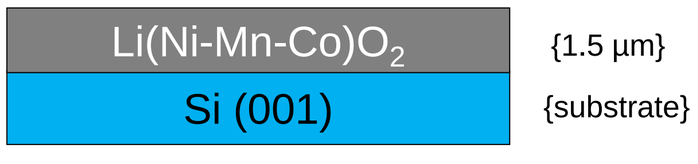
Prof. Dr. B. Scrosati, online lecture, Helmholtz Institute Ulm, 2013

Magnetron sputtering setup:



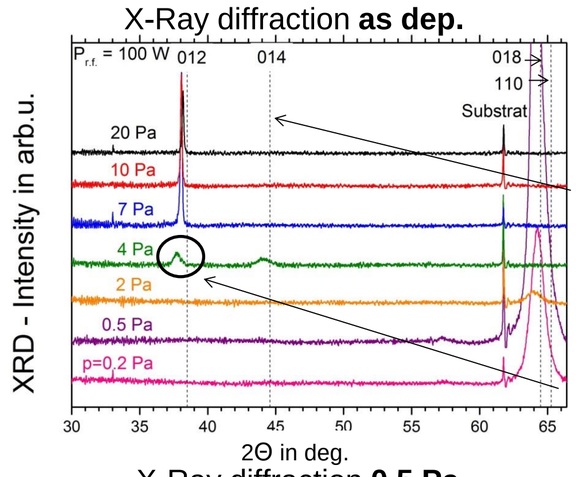
Deposition parameters: Argon working gas pressure: 0.2 Pa to 20 Pa / target power: 100 W
film thickness: ~1.5 µm

Annealing parameters: 300 °C / 600 °C, 1 hour, 10 Pa Ar/O_2 (80:20)-atmosphere



Results:

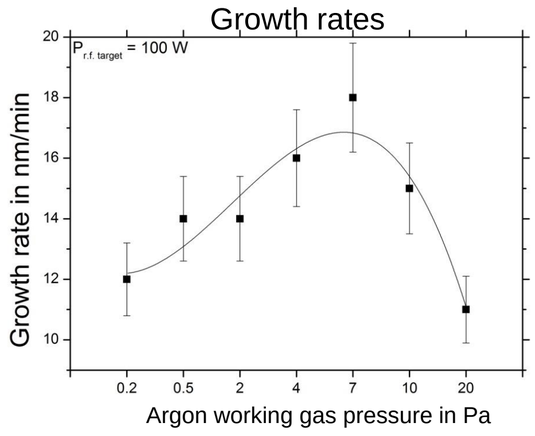
X-Ray diffraction **as dep.**



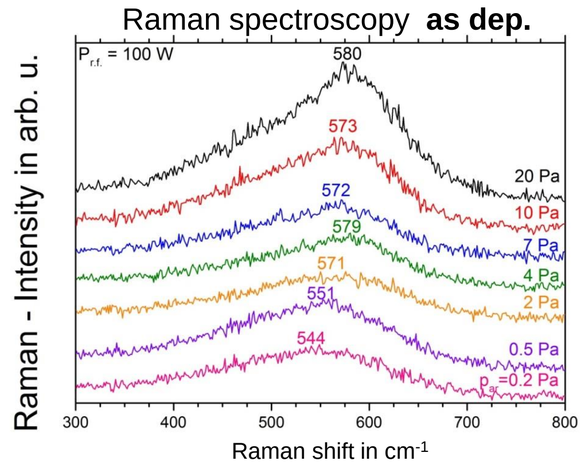
Dashed lines show reflection position reported in literature

Deviation of peak positions and literature value

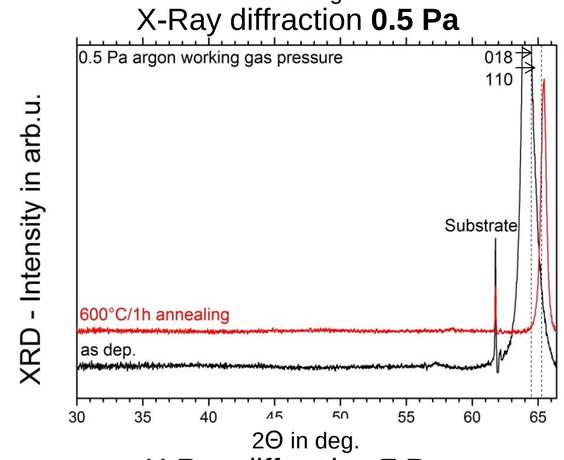
Growth rates



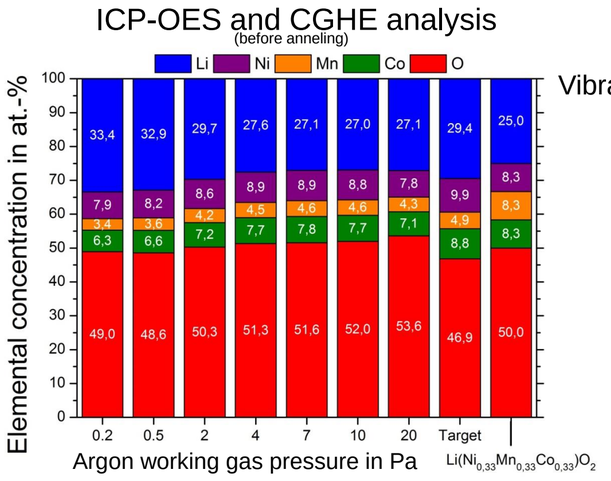
Raman spectroscopy **as dep.**



X-Ray diffraction **0.5 Pa**

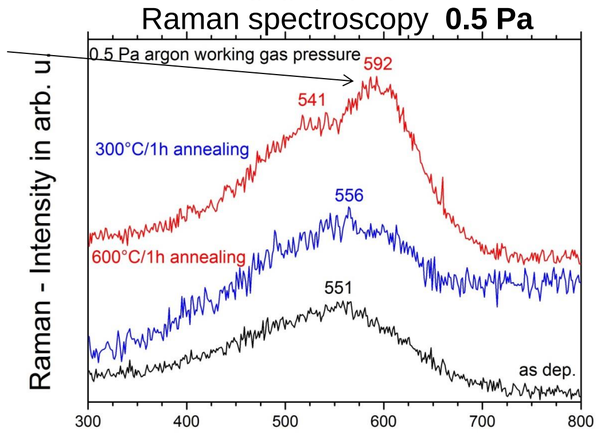


ICP-OES and CGHE analysis
(before anneling)

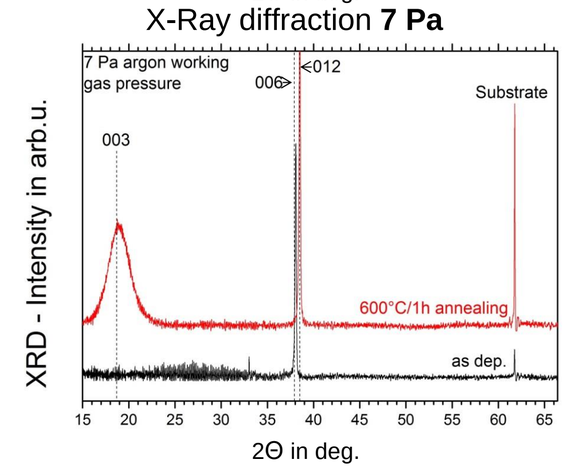


A_{1g} mode
Vibration of O Atoms in $LiMO_2$

Raman spectroscopy **0.5 Pa**



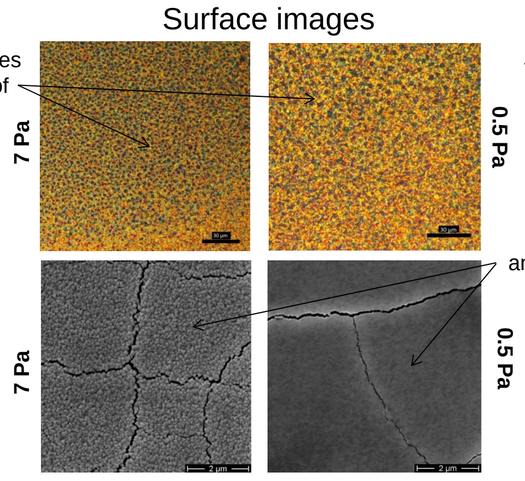
X-Ray diffraction **7 Pa**



Surface images

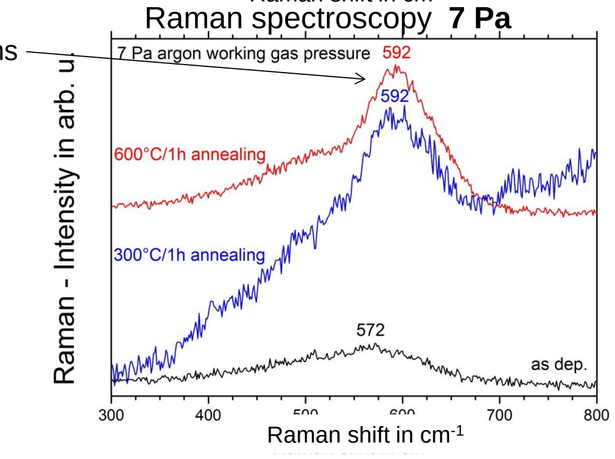
Optical microscope images before annealing, free of cracks

SEM images after annealing at 600 °C, with cracks



A_{1g} mode
Vibration of O Atoms in $LiMO_2$

Raman spectroscopy **7 Pa**



Conclusions and Outlook:

- Li-Ni-Mn-Co-O thin films were synthesised with different microstructures and elemental compositions.
- The X-Ray reflections deviate from positions reported in literature.
  The difference is probably caused by residual stresses or different elemental composition.
- At 0.5 Pa and 7 Pa the as deposited films show the highest grade of crystallinity.
- Next steps will be annealing in different atmospheres, investigations of the electrochemical behavior, surface modifications with laser and plasma technology, development of an artificial SEI.

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