Karlsruhe Institute of Technology

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IAM Institute for Applied Materials

Constitution and microstructure correlations of magnetron sputtered Li-Ni-Mn-Co-O thin film cathodes for lithium-ion batteries

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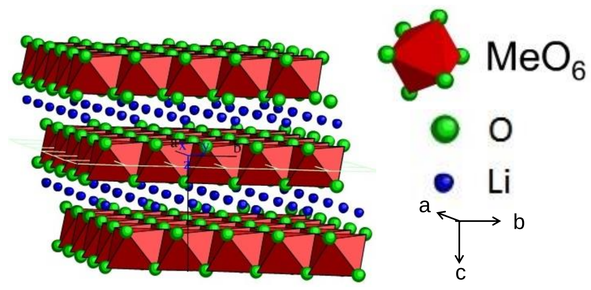
Li-Ni-Mn-Co-O thin film cathodes have been deposited onto Si and stainless steel substrates by r.f. magnetron sputtering from a lithium rich Li-Ni-Mn-Co-O target at various argon working gas pressures with a target power of 100 W. The elemental composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in combination with carrier gas hot extraction (CGHE). It was found that the elemental composition varies with argon working gas pressure. The microstructure of the films varies with argon working gas pressure and was characterized by X-ray diffraction (XRD) and by unpolarized micro-Raman spectroscopy at room temperature. Layered structured Li-rich thin film Li-Ni-Mn-Co-O –cathodes were successfully synthesized. Correlations between process parameters, constitution and microstructure are discussed in detail. These films are promising candidates for manufacturing of high capacity all solid state thin film batteries.

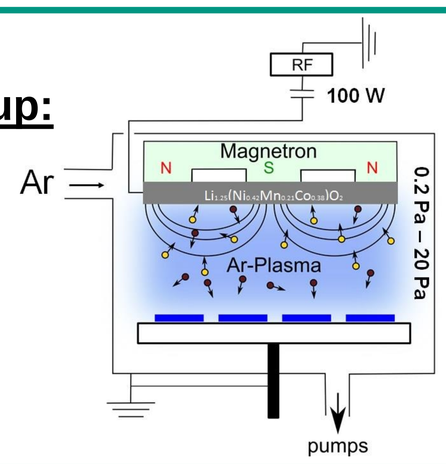
Properties and structure of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$:

- **Theoretical capacity:** 290 mAh/g
- **Practical capacity:** 160-180 mAh/g
- **Voltage vs. Li:** 2.5 V - 4.6 V
- **Space group:** R$\bar{3}$m
  hexagonal lattice
  a = b = 0.2867nm c = 1.4246 nm
  α = β = 90° γ = 120°
- **Color:** black-grey



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

Magnetron sputtering setup:

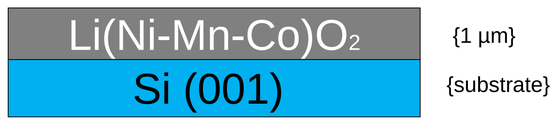


Deposition parameters:

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

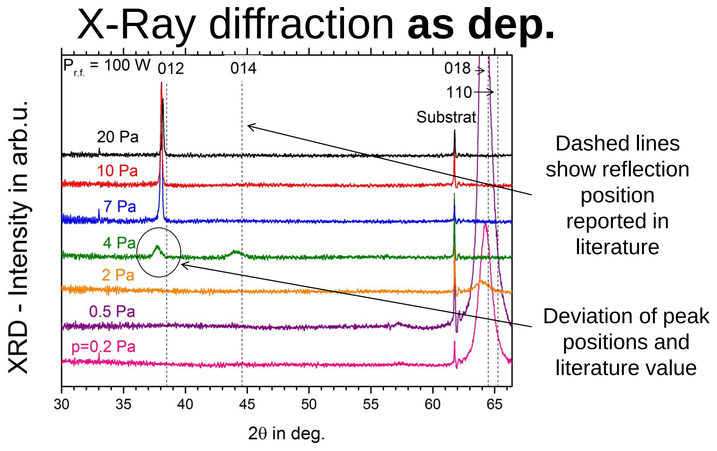
Annealing parameters:

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

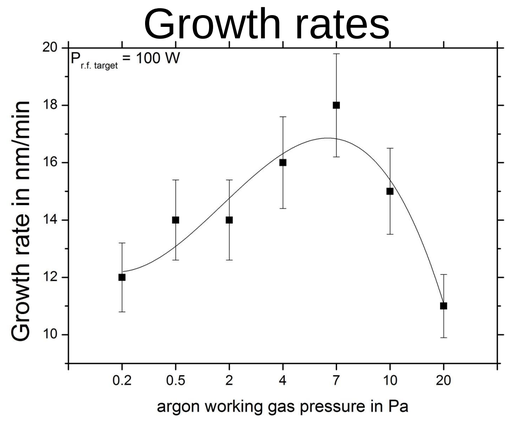


Results:

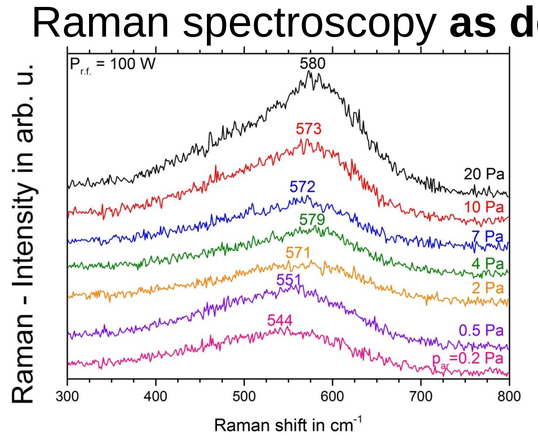
X-Ray diffraction **as dep.**



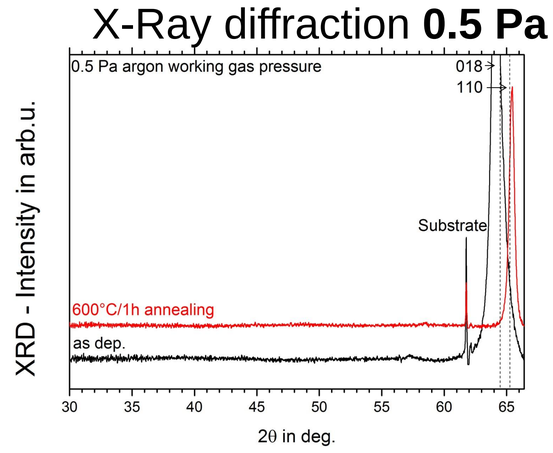
Growth rates



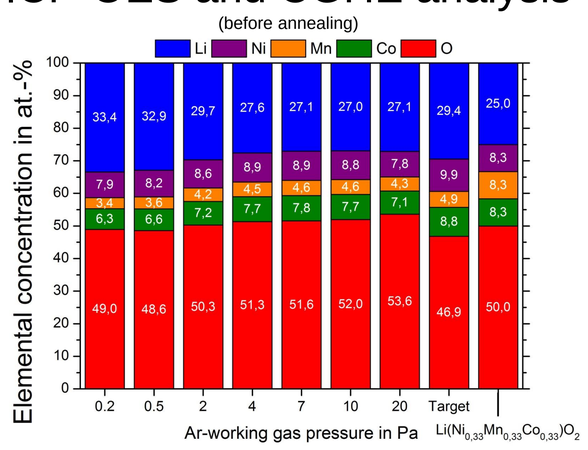
Raman spectroscopy **as dep.**



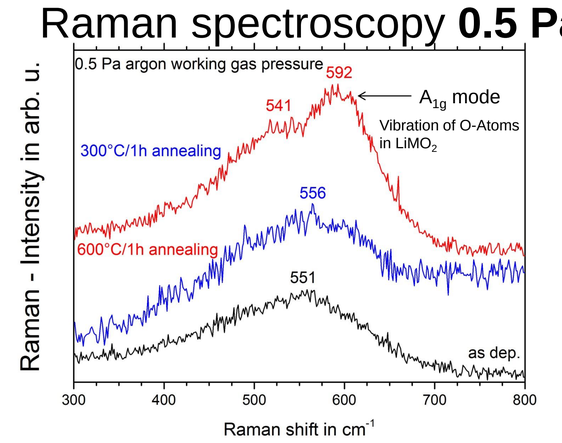
X-Ray diffraction **0.5 Pa**



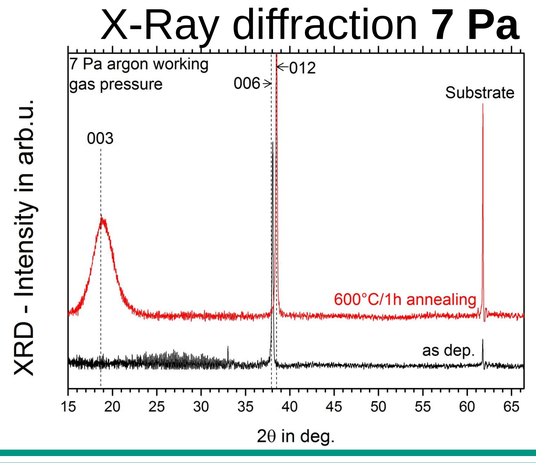
ICP-OES and CGHE analysis



Raman spectroscopy **0.5 Pa**

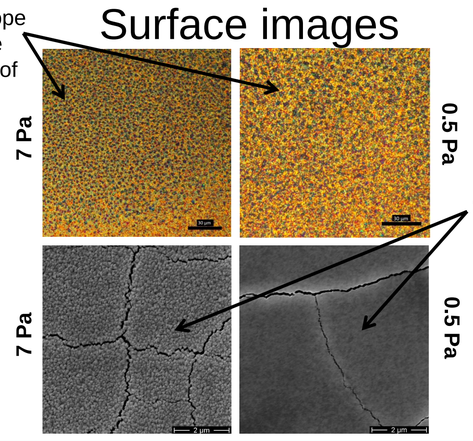


X-Ray diffraction **7 Pa**



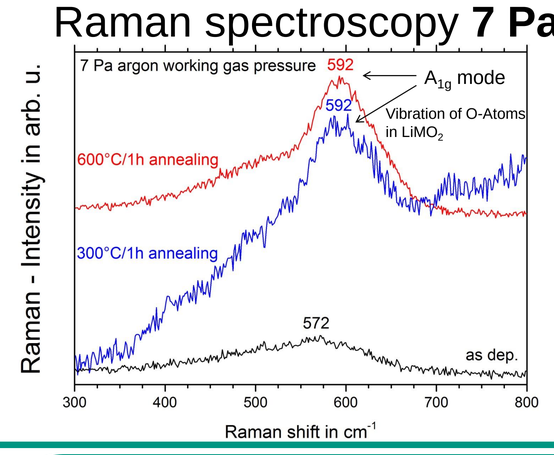
Surface images

Optical microscope images before annealing, free of cracks



SEM images after annealing at 600 °C, with cracks

Raman spectroscopy **7 Pa**



Conclusions and Outlook:

- Li-Ni-Mn-Co-O thin films were synthesis 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.
- After annealing at 600 °C the film deposited at 7 Pa shows less cracks than at 0.5 Pa.
  Also at 7 Pa the film shows a rougher surface than at 0.5 Pa.
- Next steps will be annealing in different atmospheres, surface modifications and investigations of the electrochemical behavior.

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