7-th Symposium on Vacuum based Science and Technology in conjunction with the 12-th Annual Meeting of the German Vacuum Society - DVG

Karlsruhe Institute of Technology

Institute for Applied Materials

Constitution and microstructure of magnetron sputtered Li-Ni-Mn-Co-O thin film cathodes for lithium-ion batteries as a function of working gas pressure

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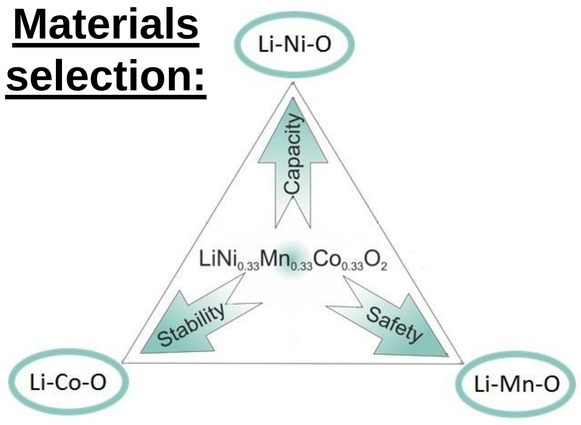
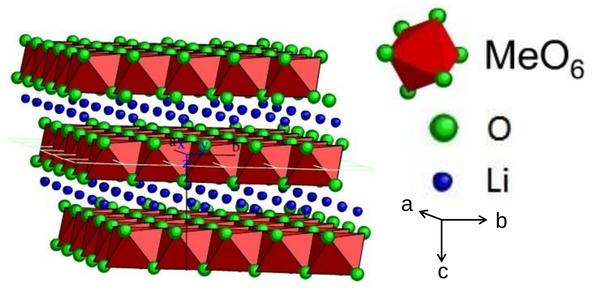
Li-Ni-Mn-Co-O thin film cathodes have been deposited onto Si substrates by non-reactive r.f. magnetron sputtering from a ceramic $Li_{1.25}(Ni_{0.42}Mn_{0.21}Co_{0.37})O_2$ target at various argon working gas pressures from 0.2 Pa to 20 Pa. Coating thickness is about 1.5 µm. Composition and microstructure were investigated comprehensively. The elemental composition varies with argon working gas pressure and was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in combination with carrier gas hot extraction (CGHE). The microstructure of the films was characterized by X-ray diffraction (XRD) and by unpolarized 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:



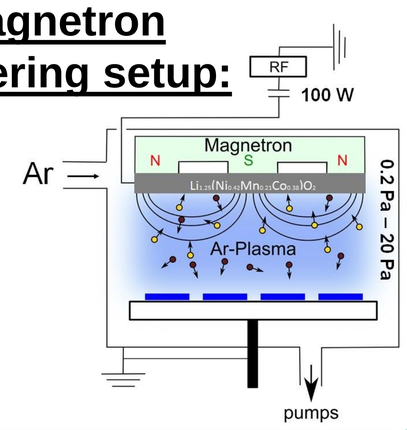
Properties and structure of $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$:

- **Theoretical capacity:** 290 mAh/g
- **Practical capacity:** 160-180 mAh/g
- **Voltage vs. Li:** 2.5 V - 4.6 V
- **Space group:** $R\bar{3}m$
  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:

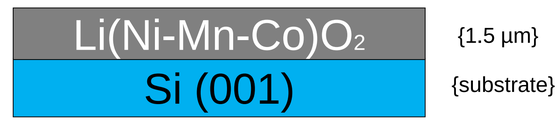


Deposition parameters:

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

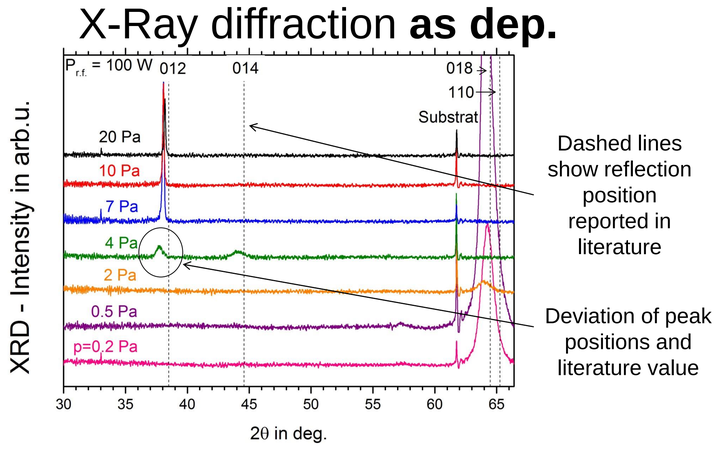
Annealing parameters:

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

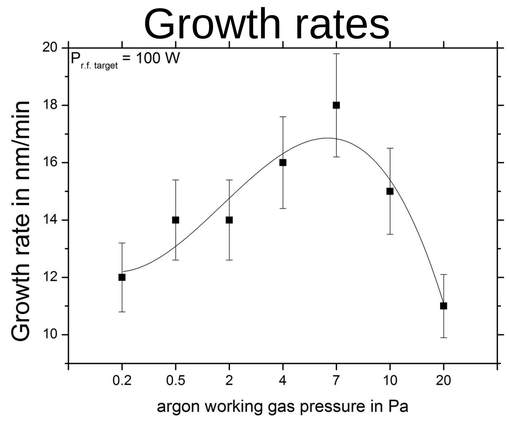


Results:

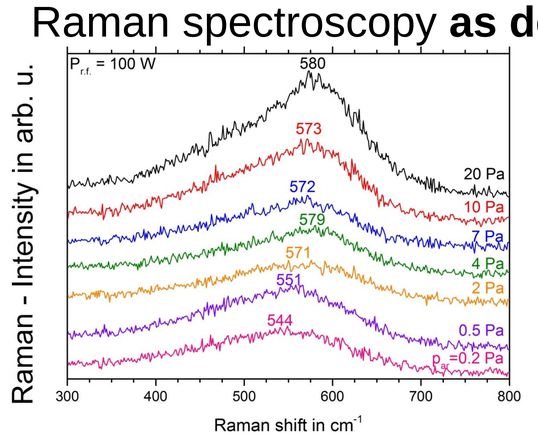
X-Ray diffraction as dep.



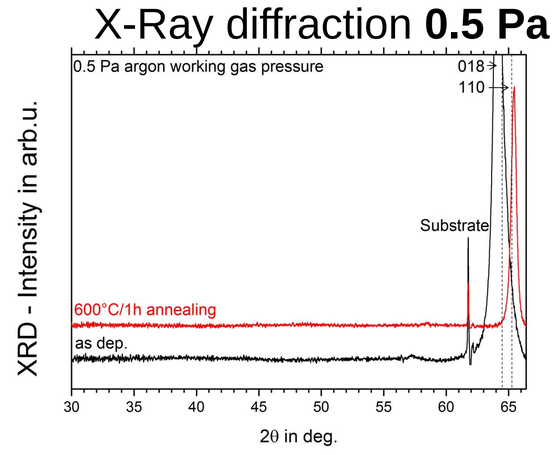
Growth rates



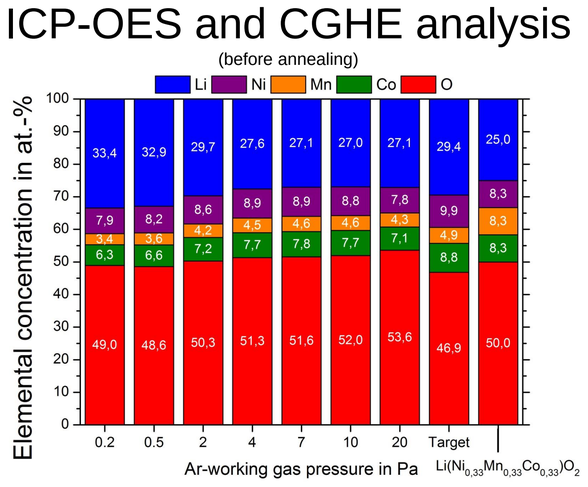
Raman spectroscopy as dep.



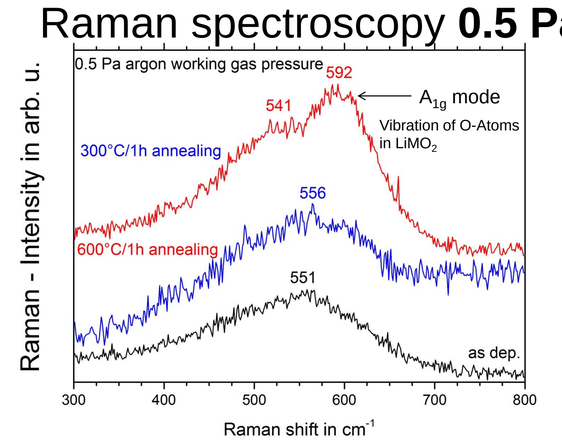
X-Ray diffraction 0.5 Pa



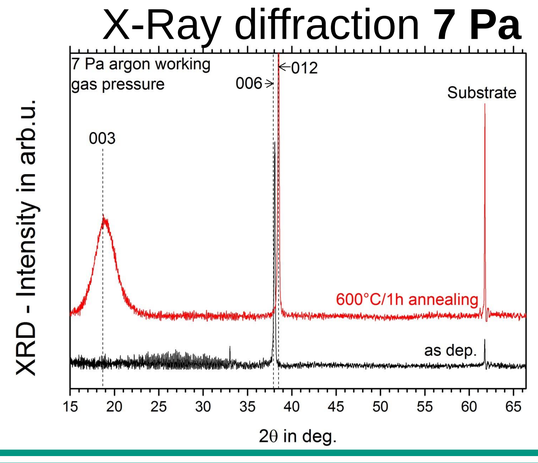
ICP-OES and CGHE analysis



Raman spectroscopy 0.5 Pa

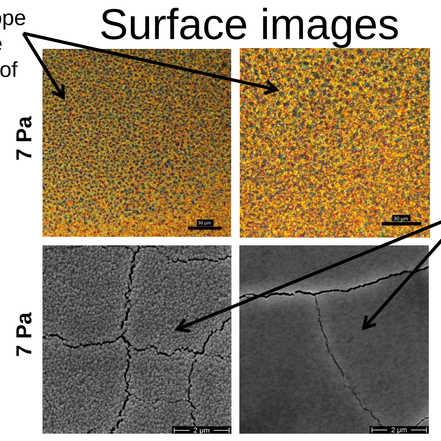


X-Ray diffraction 7 Pa



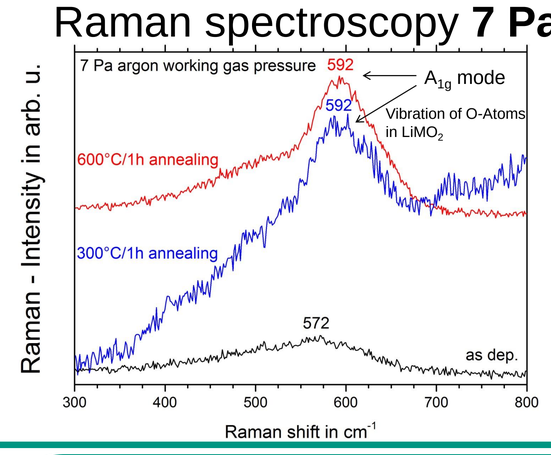
Surface images

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.

Acknowledgment:

The authors gratefully acknowledge the financial support by the Helmholtz-Portfolio-project “Elektrochemische Speicher im System - Zuverlässigkeit und Integration“