Karlsruhe Institute of Technology

LiBD-7 2015 – "Electrode materials"

IAM Institute for Applied Materials

Microstructural and electrochemical comparison of as deposited and heat treated Li-Ni-Mn-Co-O thin film cathodes for Lithium-ion batteries

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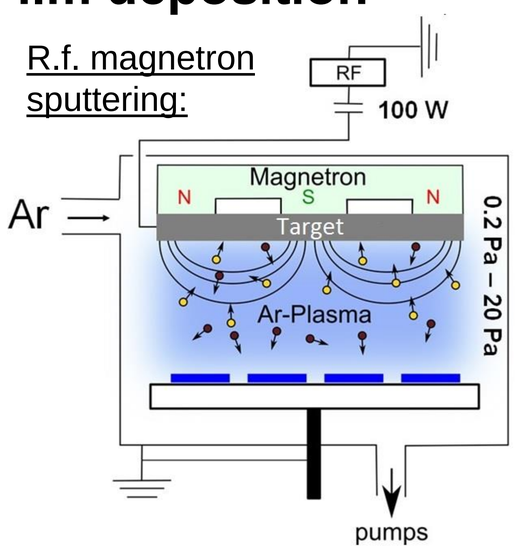
Li-Ni-Mn-Co-O thin film cathodes have been deposited onto stainless steel substrates by a non-reactive r.f. magnetron sputtering process from a Lithium-rich $Li_{1.11}(Ni_{0.37}Mn_{0.19}Co_{0.33})O_{1.77}$ target in a pure Argon atmosphere. The target power was 100 W and the deposition pressure 7 Pa. Coating thickness was about 1 µm. In order to induce a transition of the crystalline films from a disordered to an ordered layered structure the films were post heat treated between 300 °C and 700 °C for one hour at 10 mPa in Argon / Oxygen (80 : 20).

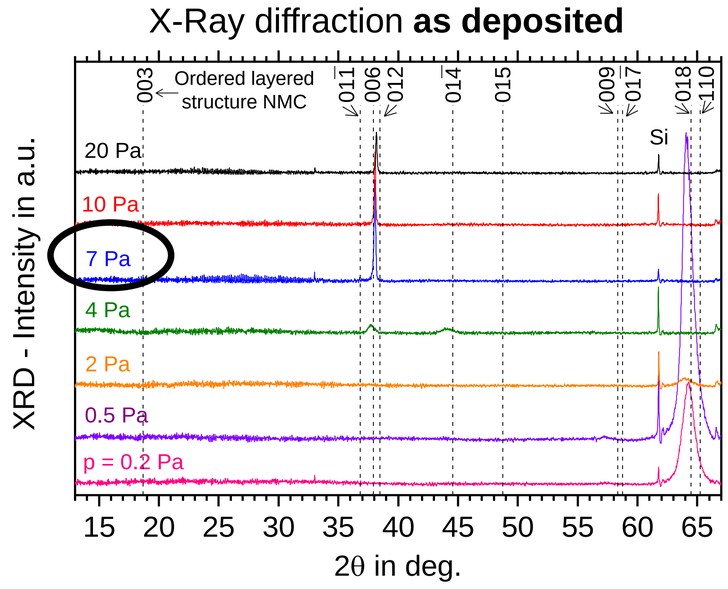
Film deposition

<u>R.f. magnetron sputtering:</u>



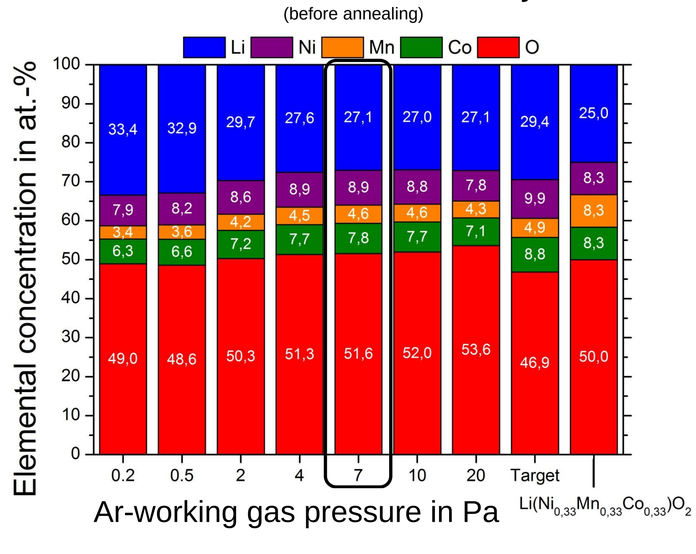
Pressure variation

X-Ray diffraction **as deposited**



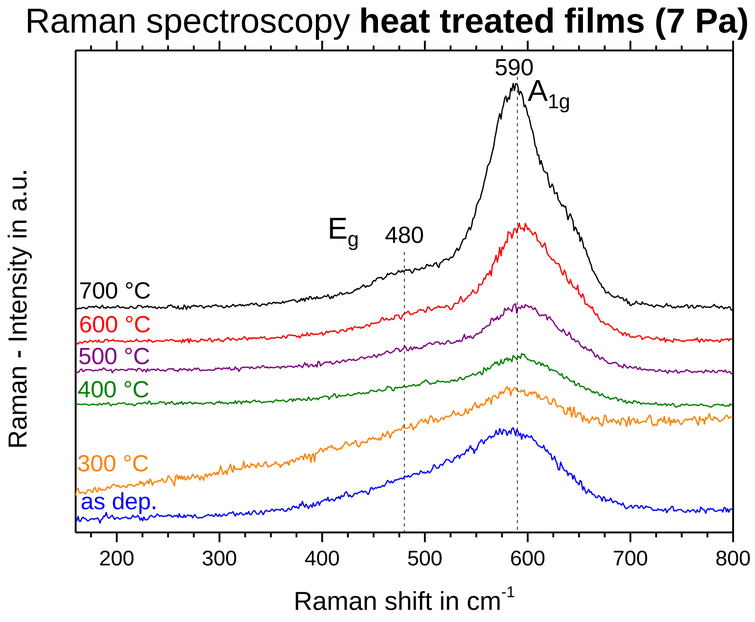
ICP-OES and CGHE analysis

(before annealing)

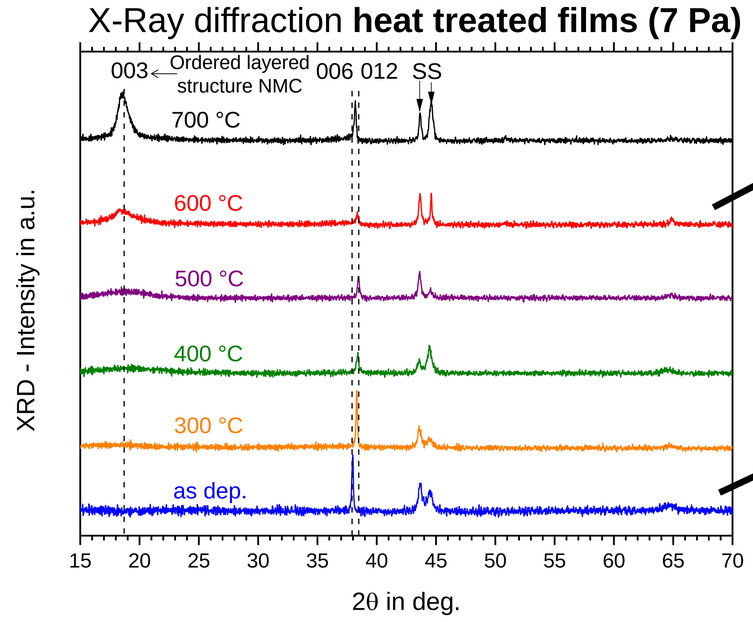


Heat treatment of selected film (7 Pa)

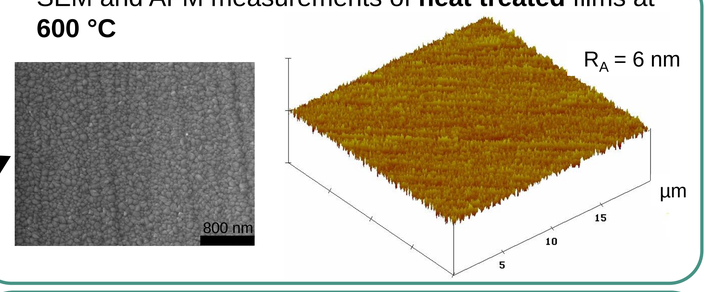
Raman spectroscopy **heat treated films (7 Pa)**



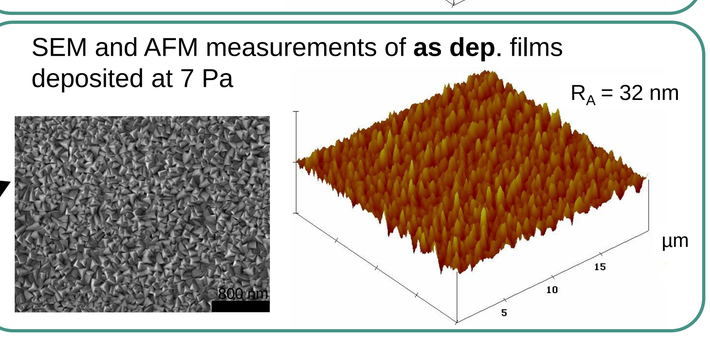
X-Ray diffraction **heat treated films (7 Pa)**



SEM and AFM measurements of **heat treated** films at **600 °C**



SEM and AFM measurements of **as dep.** films deposited at 7 Pa



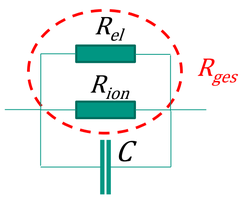
AC-impedance spectroscopy of heat treated film at 600 °C

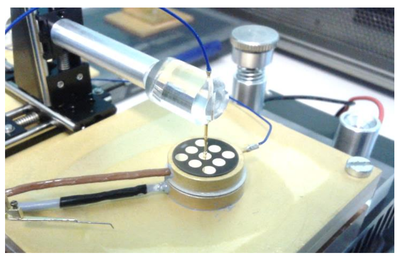
<u>Assumed Model:</u>

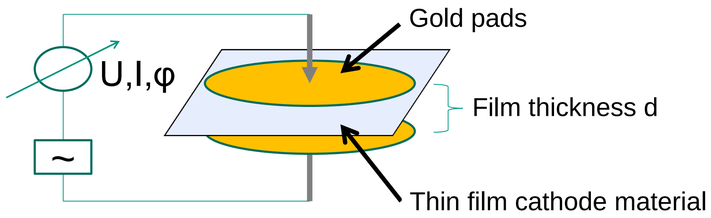
$$\frac{1}{Z} = \frac{1}{R_{ion}} + \frac{1}{R_{el}} + i\omega C$$

$$\sigma''(\omega) = \omega \cdot C \cdot \frac{d}{S}$$

$$\sigma'(\omega \approx 0) = \sigma_{dc} = \frac{d}{S} \cdot \frac{R_{el} + R_{ion}}{R_{el} R_{ion}} = \frac{d}{S} \cdot \frac{1}{R_{ges}}$$







<u>Nyquist plot:</u>

It is possible to calculate the specific conductivity of the thin film with the intersection of the semicircle at small frequencies (10 Hz) and the real part axis of the Nyquist-plot.

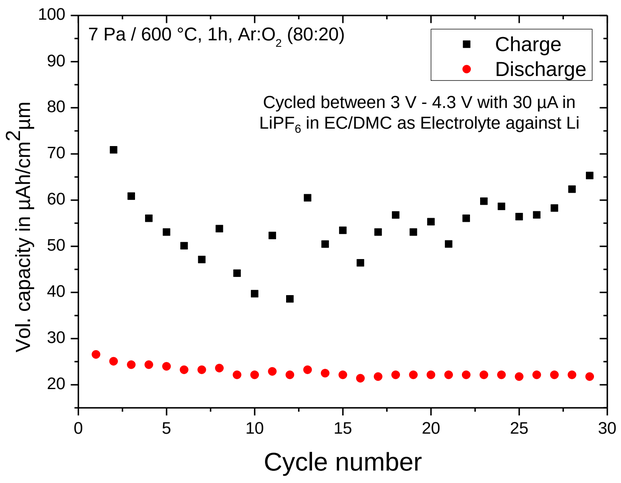
T [°C]	σ_{dc} [Scm^{-1}]
20	1,72*10^{-8}
30	2,39*10^{-8}
40	3,05*10^{-8}
50	3,82*10^{-8}
60	5,18*10^{-8}
70	6,30*10^{-8}

<u>Arrhenius-Plot:</u>

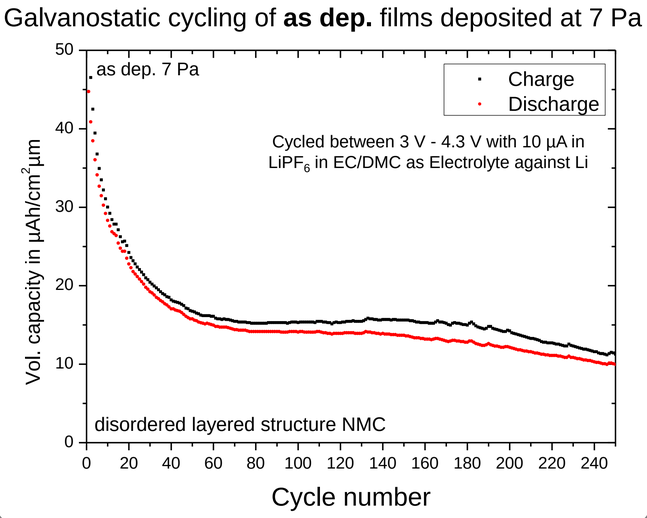
The measurements depending on the temperature allows the determination of the activation energy E_a of the ionic hopping mechanism.

Galvanostatic cycling

Galvanostatic cycling of **heat treated** films at **600 °C**



Galvanostatic cycling of **as dep.** films deposited at 7 Pa



Conclusions and Outlook:

- Li-Ni-Mn-Co-O thin films were successfully deposited on stainless steel with different compositions and microstructures.
- In crystalline as dep. films at 7 Pa a transition has been successfully induce of from a disordered to an ordered layered structure by post deposition heat treatment.
- As deposited and heat treated films at 600 °C are battery active.
- Heat treated thin film cathodes show a lower loss of discharge capacity at first cycles.

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