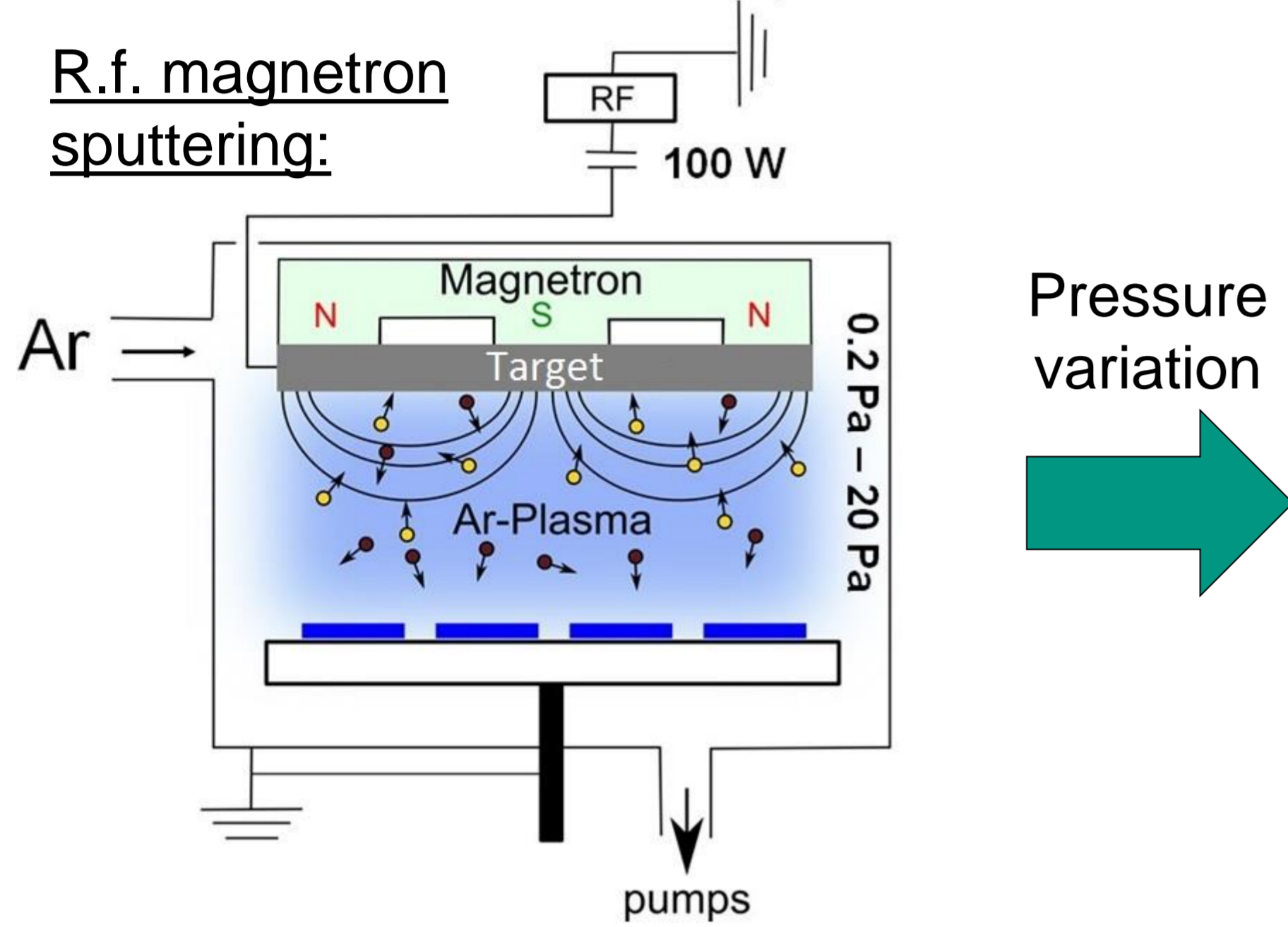


Microstructural and electrochemical comparison of as deposited and heat treated Li-Ni-Mn-Co-O thin film cathodes for Lithium-ion batteries

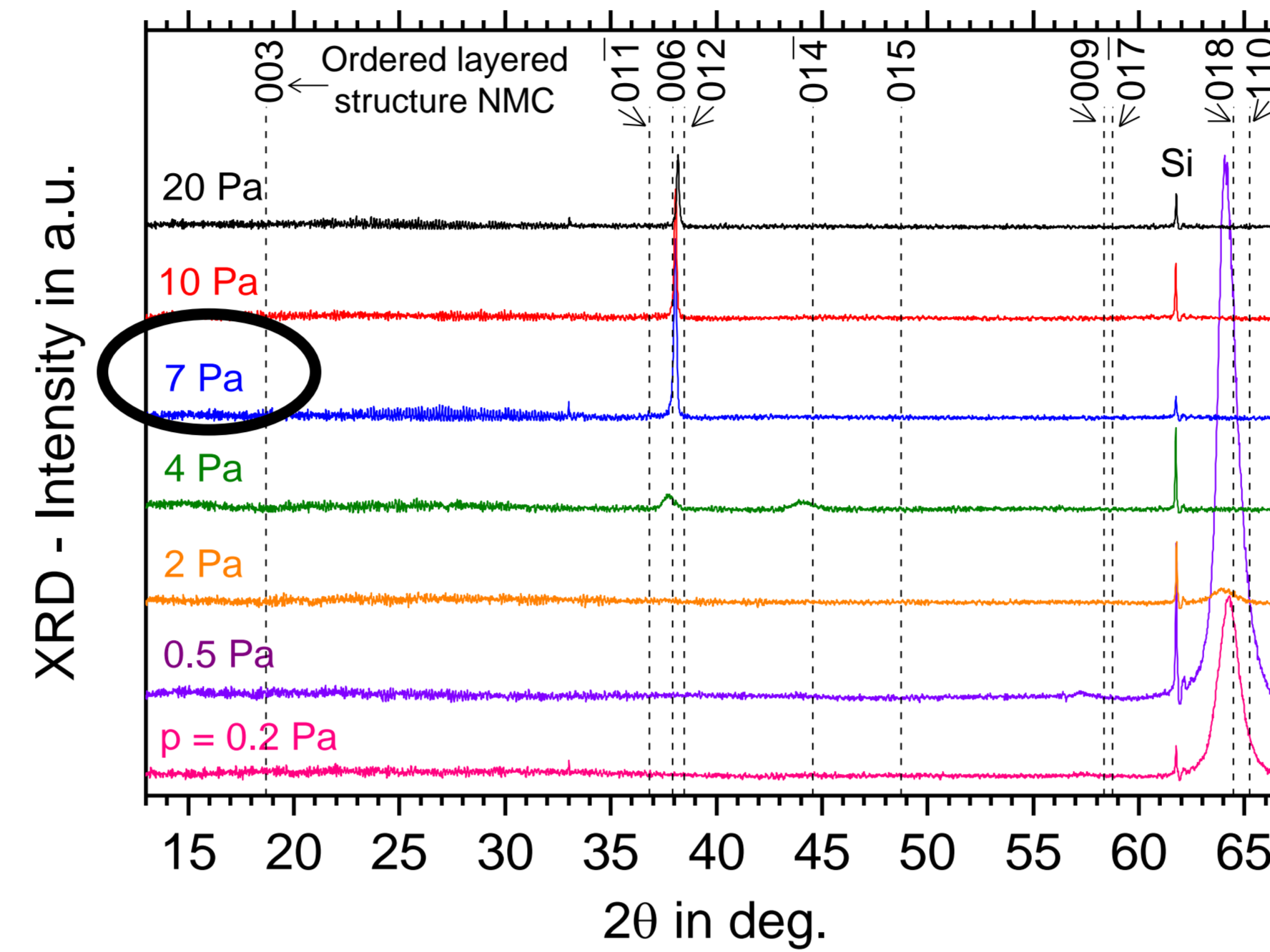
M. Strafela, J. Fischer, K. Seemann, H. Leiste, H.J. Seifert, S. Ulrich

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 $\text{Li}_{1.11}(\text{Ni}_{0.37}\text{Mn}_{0.19}\text{Co}_{0.33})\text{O}_{1.77}$ 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 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ for one hour at 10 mPa in Argon / Oxygen (80 : 20).

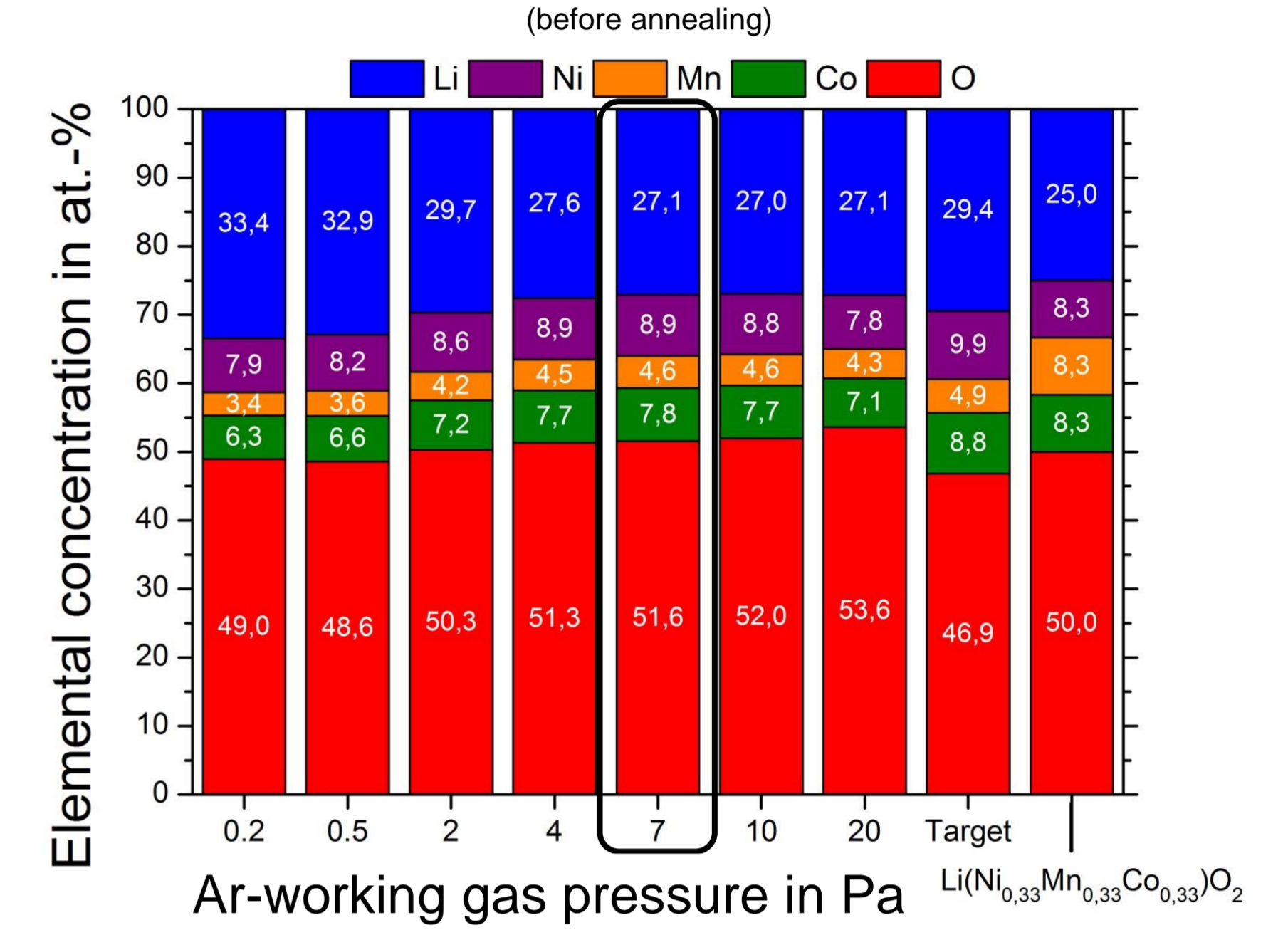
Film deposition



X-Ray diffraction as deposited

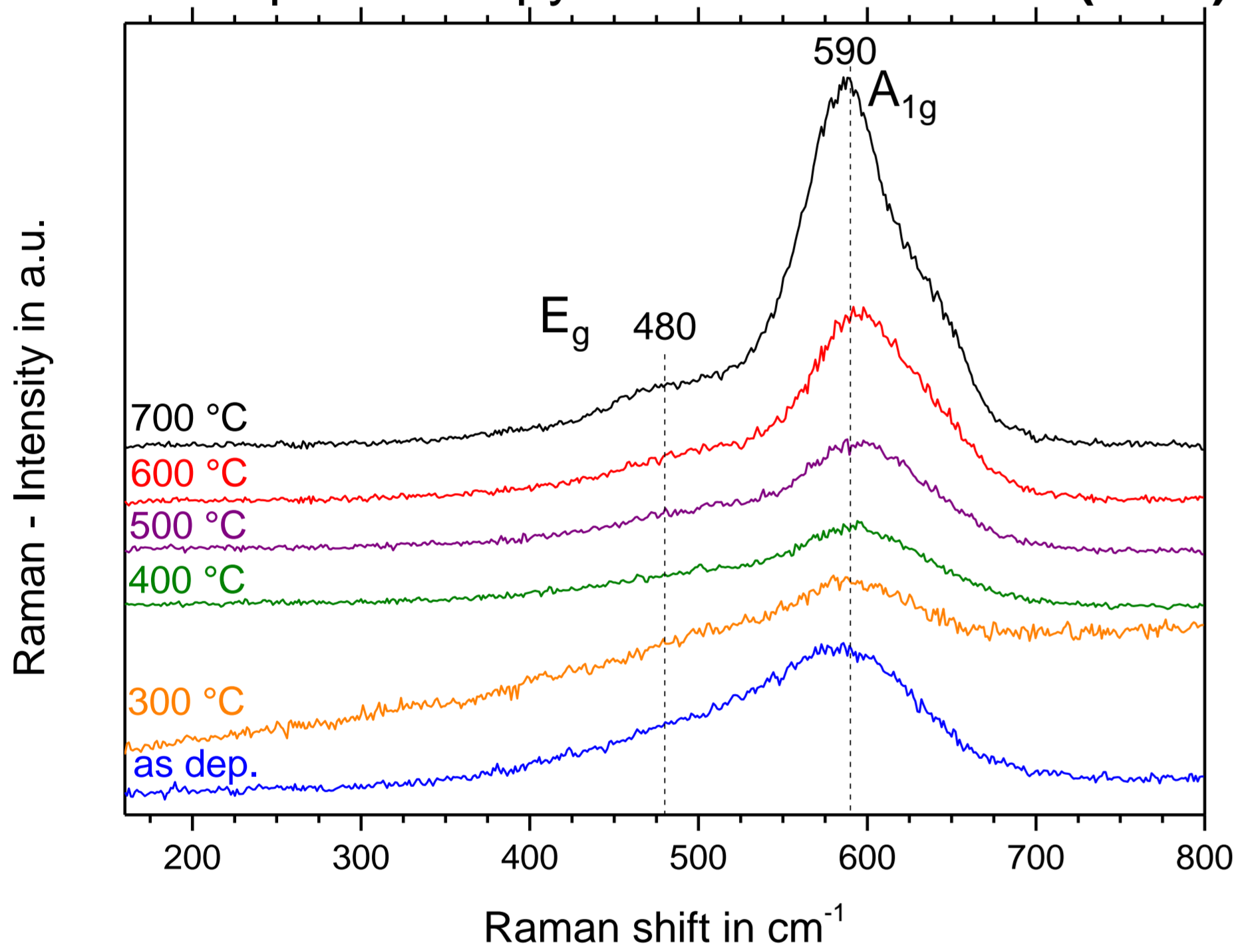


ICP-OES and CGHE analysis

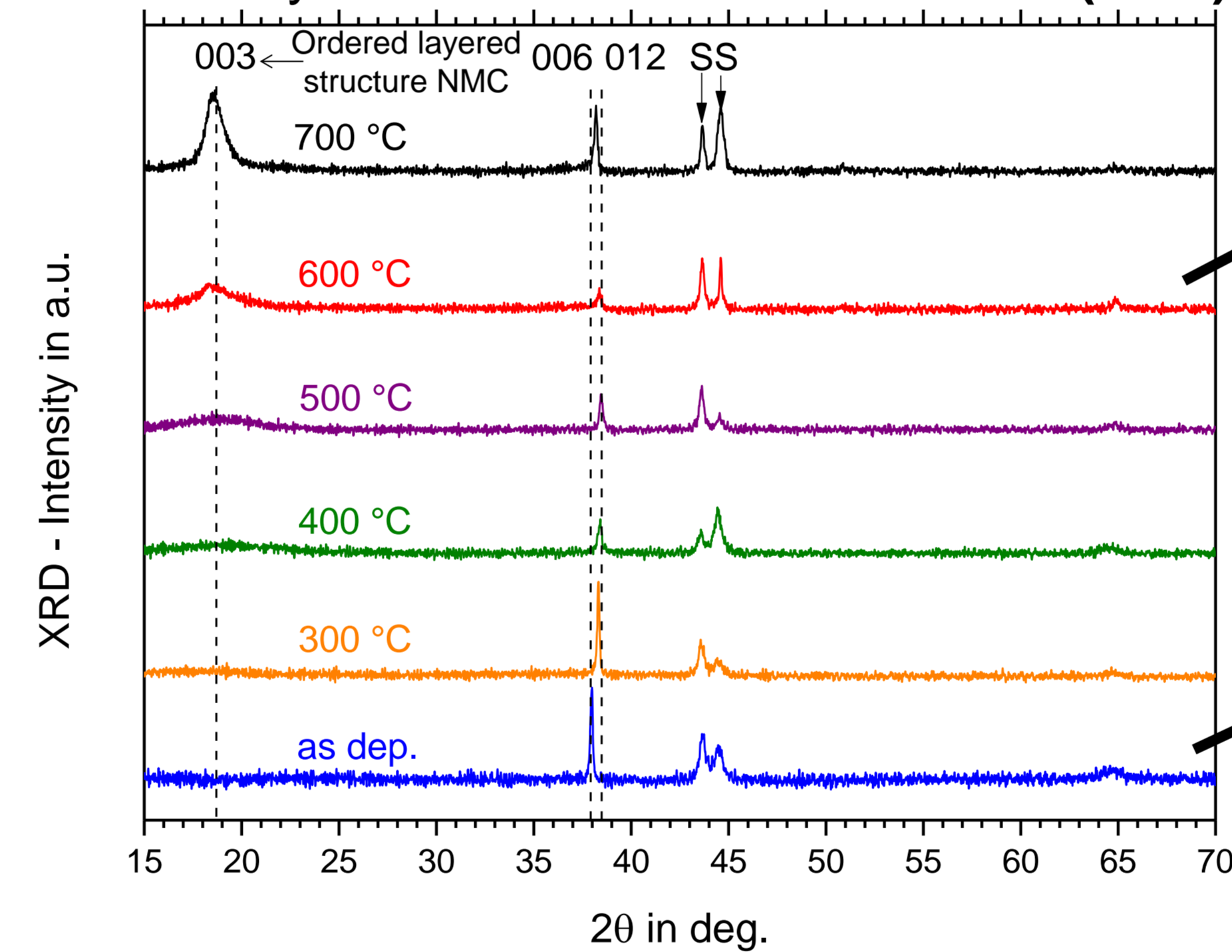


Heat treatment of selected film (7 Pa)

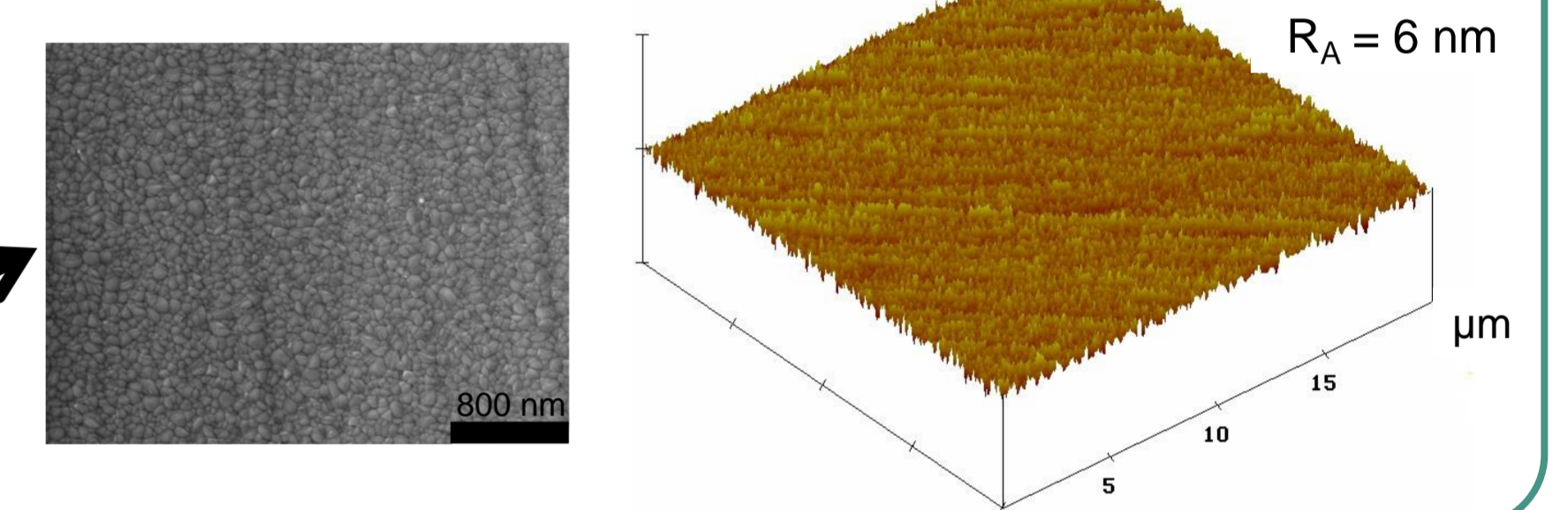
Raman spectroscopy heat treated films (7 Pa)



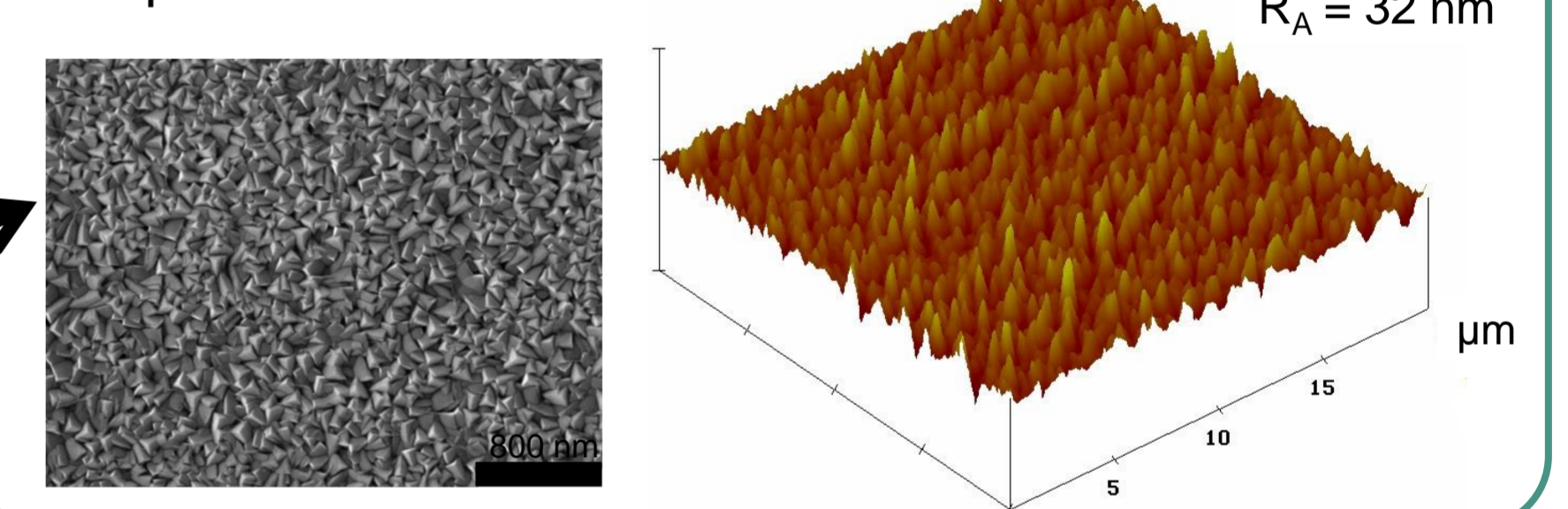
X-Ray diffraction heat treated films (7 Pa)



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



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



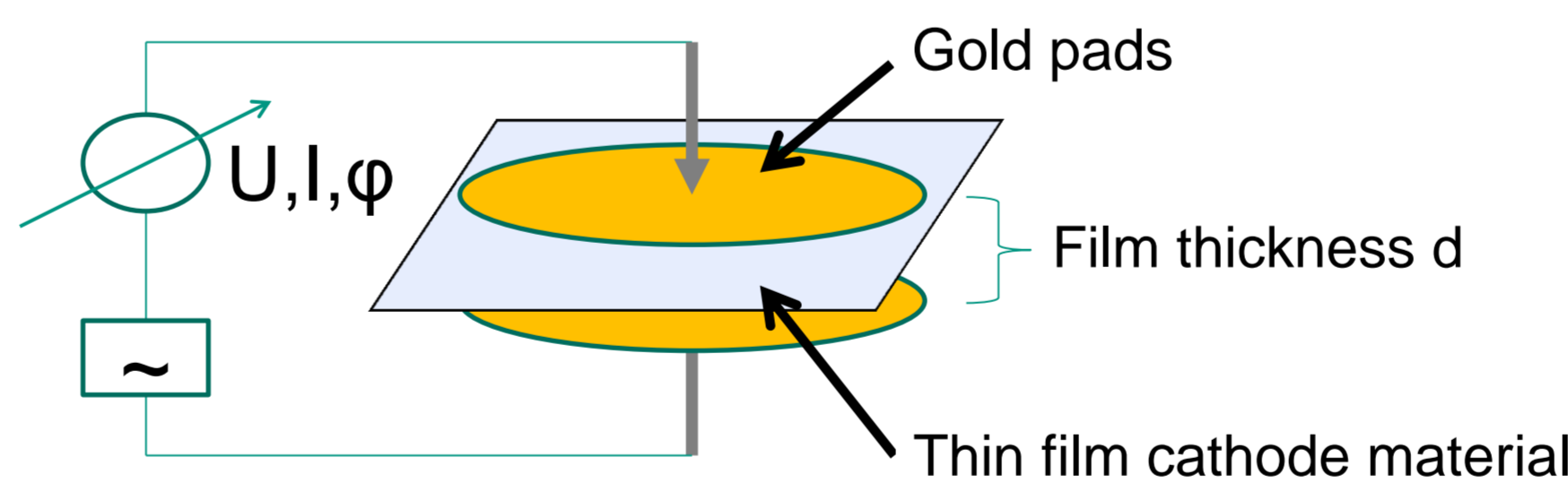
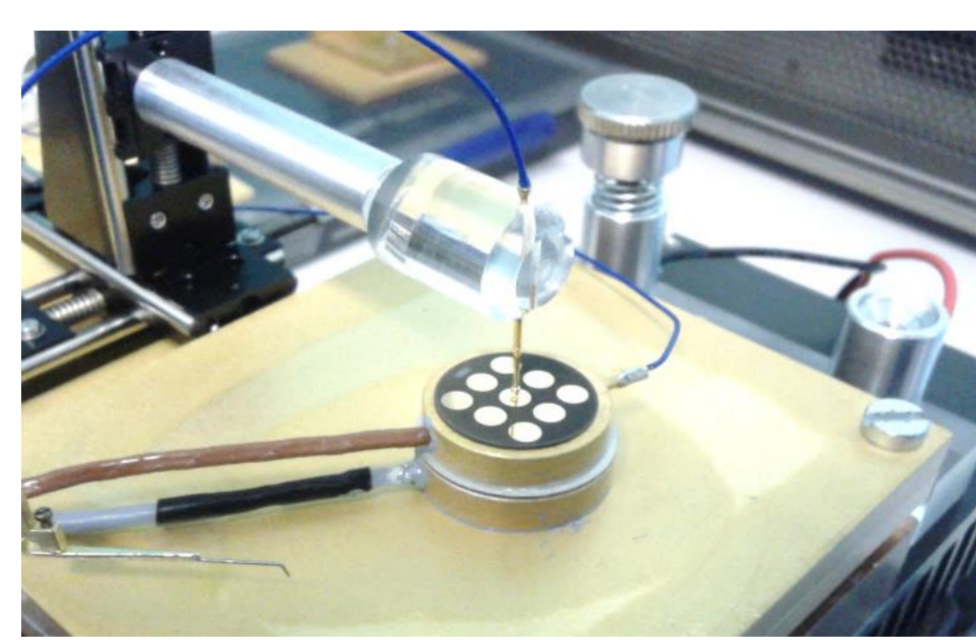
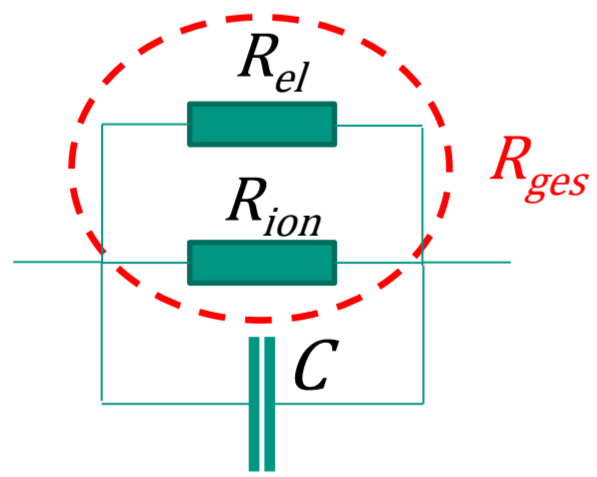
AC-impedance spectroscopy of heat treated film at 600 °C

Assumed Model:

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

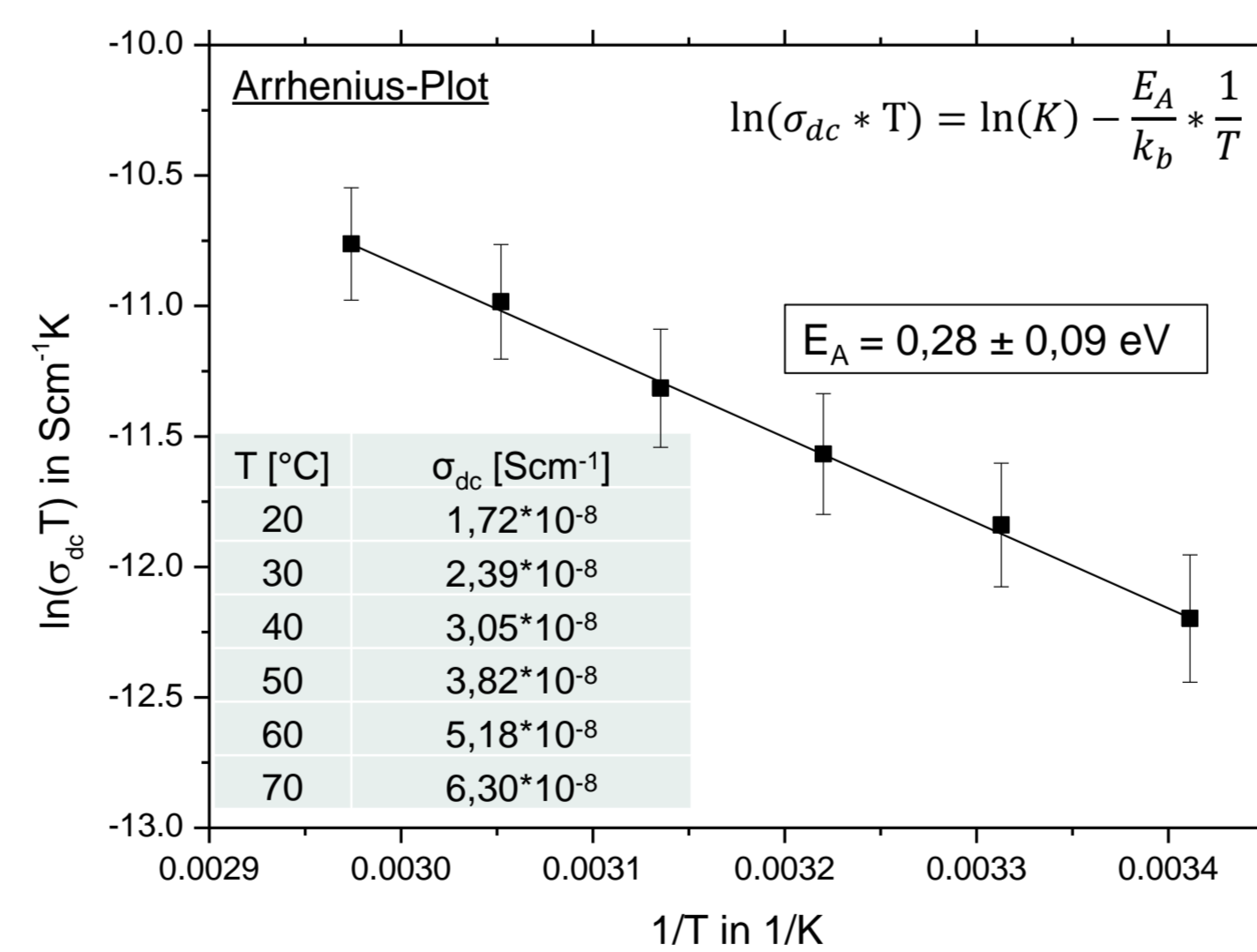
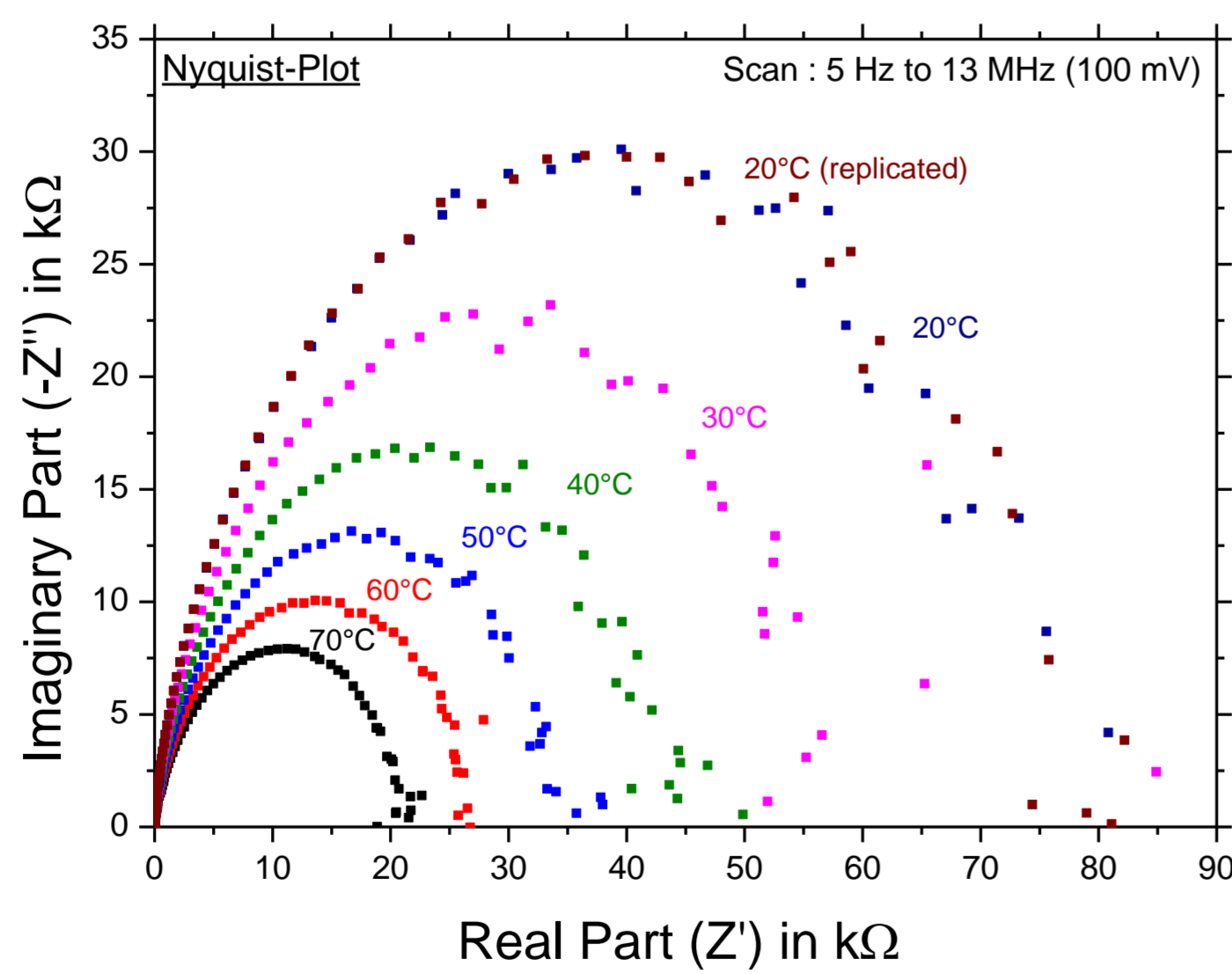
$$\sigma''(\omega) = \omega \cdot C \cdot \frac{d}{S}$$

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



Nyquist plot:

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.

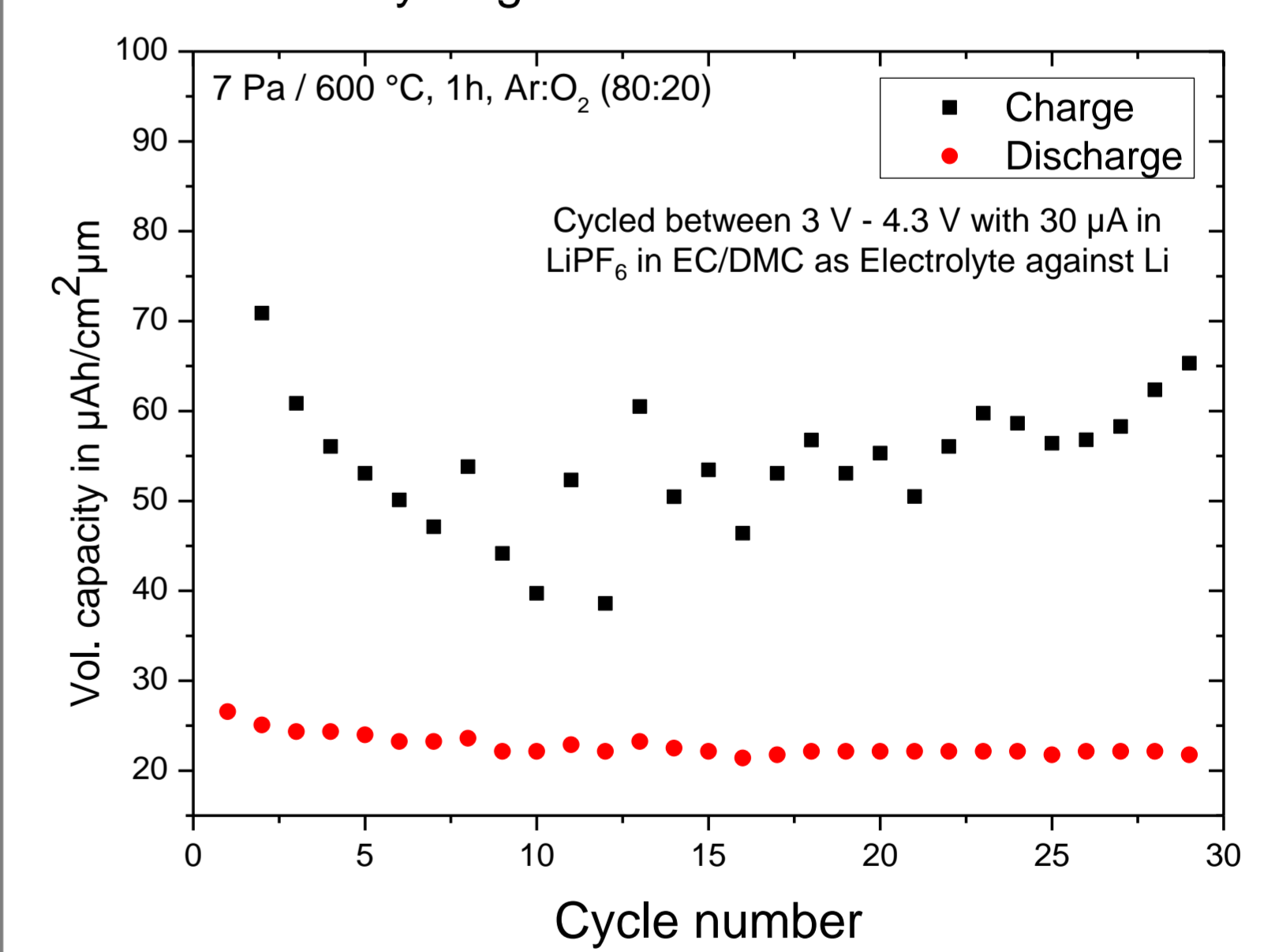


Arrhenius-Plot:

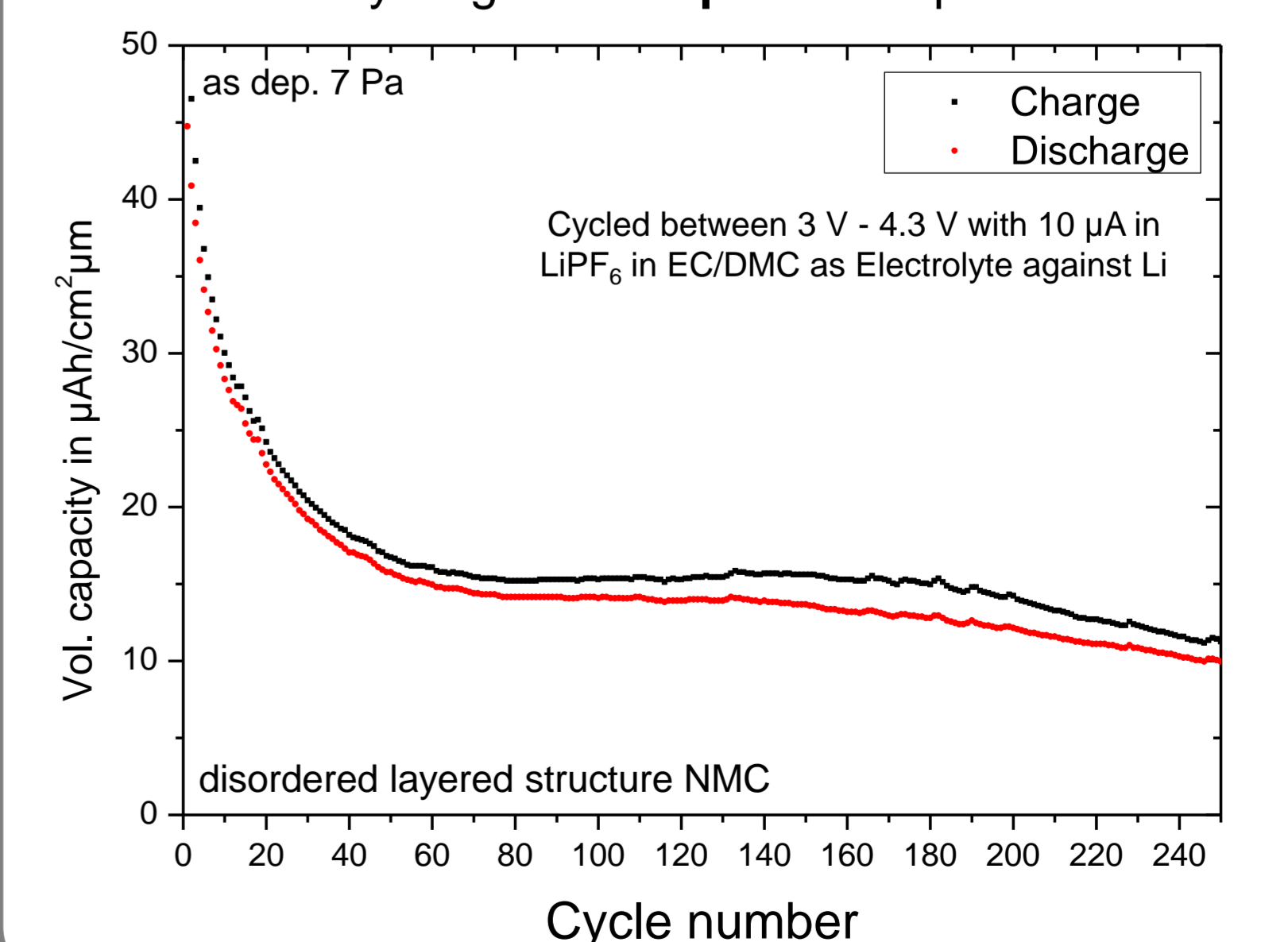
The measurements depending on the temperature allows the determination of the activation energy E_a of the ionic hopping mechanism.

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 induced from a disordered to an ordered layered structure by post deposition heat treatment.
- As deposited and heat treated films at 600 $^{\circ}\text{C}$ are battery active.
- Heat treated thin film cathodes show a lower loss of discharge capacity at first cycles.

Acknowledgment:

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