# Magnetron sputtered Li-Ni-Mn-Co-O thin film cathodes for lithium-ion batteries

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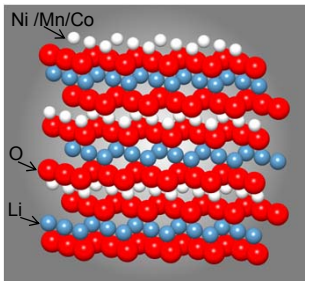
Institute for Applied Materials – Applied Materials Physics IAM-AWP, Department Composites and Thin Films

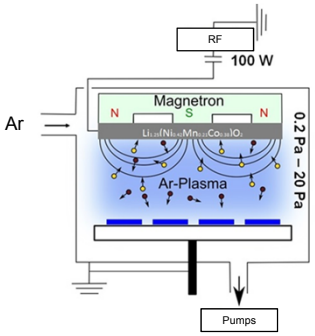

## Outline

Motivation


www.infinitepowersolutions.com (2014)

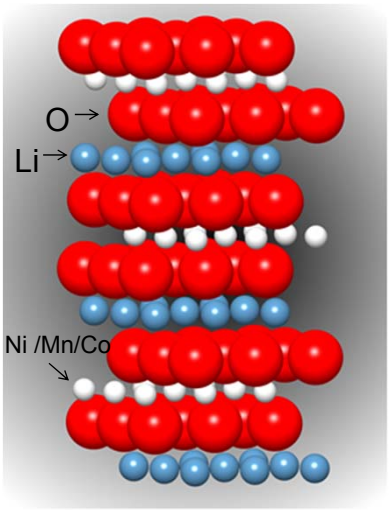
Thin film synthesis & characterisation

Selected results




Summary and outlook

## Layered structure – $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$




Structure and properties:

- Theoretical capacity: 290 mAh/g
- Voltage versus Li: 2.5 V – 4.3 V

- Space group: $R\bar{3}m$
  hexagonal lattice
  a = b = 0.2867 nm
  c = 1.4246 nm
  α = β = 90° γ = 120°

- Layers of closed packed oxygen ions are separated by alternating layers of lithium and transition metal ions



## Goals for materials development

Fabrication of Li-Ni-Mn-Co-O layered structure with high capacity and enhanced $Li^+$ diffusion

- Nanocrystalline material with optimised chem. composition

Optimization of grain orientation

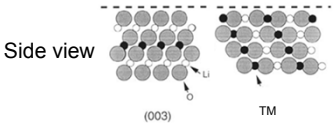
- Variation of deposition and growth kinetics

  ⟶ pressure variation during sputtering

Diffusion coefficients $Li_{0.8}CoO_2$:

(003) orientation: ~ 1 x $10^{-14}$ $cm^2s^{-1}$
(104) orientation: ~ 1 x $10^{-12}$ $cm^2s^{-1}$

"Orientation dependence of Li-ion diffusion kinetics in LiCoO2 thin films prepared by RF magnetron sputtering" J. Xie, N. Imansishi, T. Matsumura, A. Hirano, Y. Takeda, O. Yamamoto, Solid State Ionics, 2008




Picture redesigned "Preferred Orientation of Polycrystalline $LiCoO_2$ Films" J. B. Bates, N. J. Dudney, B. J. Neudecker, F. X. Hart,b H. P. Jun, S. A. Hackneyc, Journal of The Electrochemical Society, 2000

- Increase of the crystallinity
  - Heat treatment of the films (T = const., t = const.)
  - Influence pressure during heat treatment in $Ar/O_2$ (80:20) atmosphere on crystallization process

## Characterisation Methods


"iCap 7600", T. Bergfeldt, Chemical Analysis Group, 2014

- X-ray diffraction (XRD)
- Raman-spectroscopy
- Chemical analysis
  - Inductively coupled plasma optical emission spectrometry (ICP-OES)
  - Carrier gas hot extraction (CGHE)
- Electrochemical analysis
  - galvanostatic cycling



## Experimental procedure 2-Step process

Deposition conditions:

- Leybold Heraeus Z 550 PVD
- Argon - atmosphere (non reactive)

Thin film constitution:


1 – 1.5 µm

Deposition parameters:

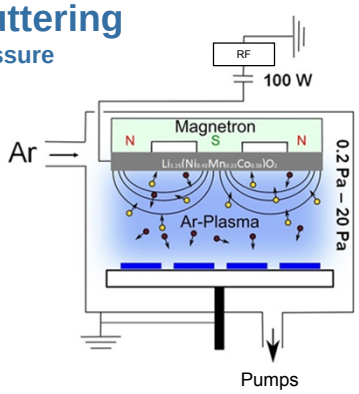
- Power: RF 100 W
- Pressure: 0.2 ; 0.5 ; 2 ; 4 ; 7 ; 10 ; 20 Pa

Heat treatment:

- Temperature: 600 °C
- Atmosphere : Ar / $O_2$ (80:20)
- Pressure range: 10 mPa, 10 Pa, 150 Pa, 80 kPa
- Time: 1 h

# 1. Step: Magnetron sputtering

## Variation of argon working gas pressure

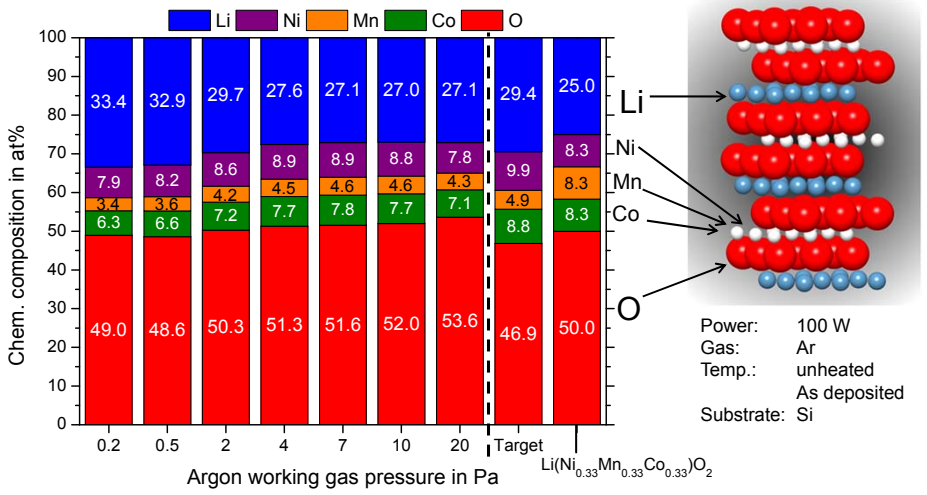



- Target: Li-Ni-Co-Mn-O (Li-rich)
- Power: RF 100 W
- Pressure range: 0.2 ; 0.5 ; 2 ; 4 ; 7 ; 10 ; 20 Pa
- Working gas: Ar
- Temperature: unheated (RT)
- Substrate: Si (001) / stainless steel



# As deposited thin films

## Chem. composition (ICP-OES / CHGE) – variation of working gas pressure



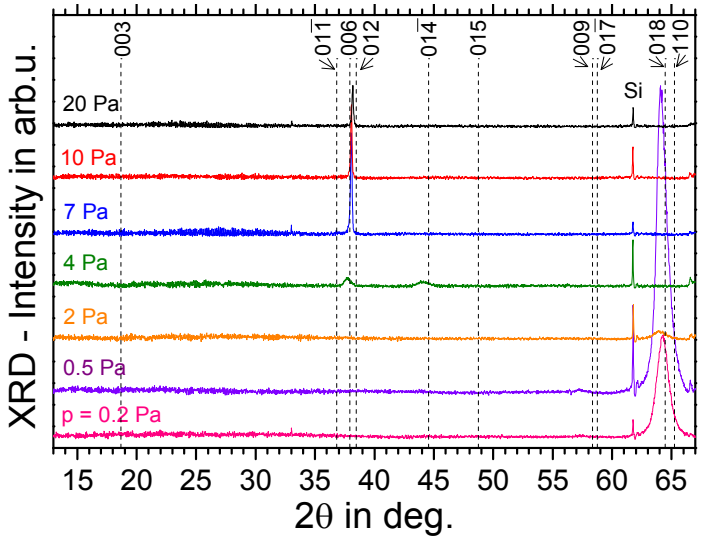




Power: 100 W
Gas: Ar
Temp.: unheated
As deposited
Substrate: Si

# As deposited thin films

## Microstructure (XRD) – variation of working gas pressure



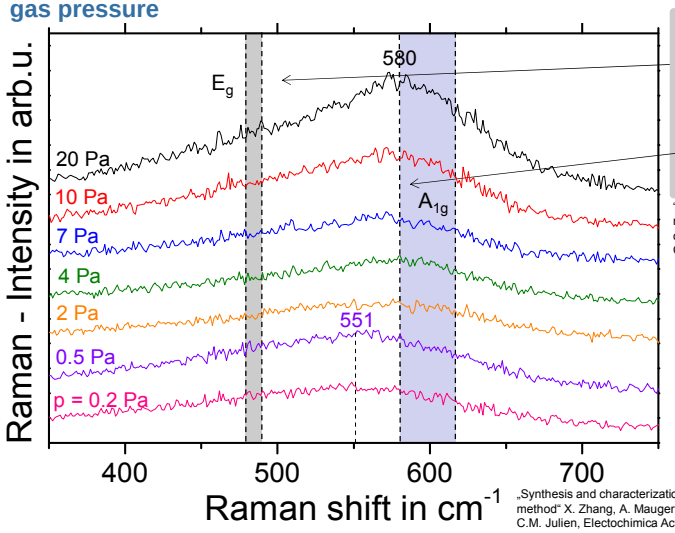

Layered structure
$Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$
JCPDS: 00-056-0147

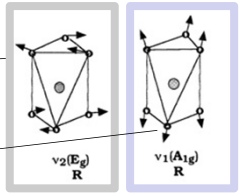
| | |
|---|---|
| Power: | 100 W |
| Gas: | Ar |
| Temp.: | unheated<br>As deposited |
| Substrate: | Si |



# As deposited thin films

## Microstructure (Raman spectroscopy) – variation of working gas pressure




"Local cationic environment in lithium nickel–cobalt oxides used as cathode materials for lithium batteries", C. Julien, Solid State Ionics 2000

| | |
|---|---|
| Power: | 100 W |
| Gas: | Ar |
| Temp.: | unheated<br>As deposited |
| Substrate: | Si |

„Synthesis and characterization of Li $Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ by wet-chemical method" X. Zhang, A. Mauger, Q. Lu, H. Groult, L. Perriguard, F. Gendron C.M. Julien, Electochimica Acta, 2010

- Battery test (as dep. at 7 Pa): 20 $\mu Ahcm^{-2}\mu m^{-1}$

## 2. Step: Heat treated thin films 7 Pa

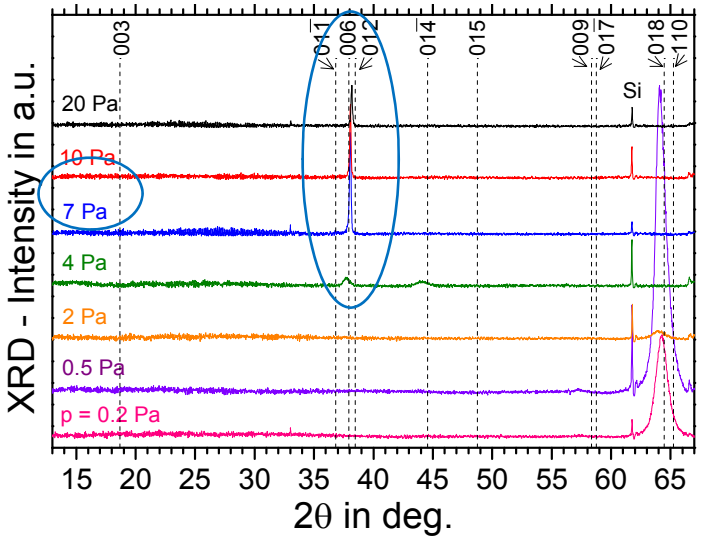
### Variation of heat treatment pressure


- Sample: Deposited at 7 Pa
- Temperature: 600 °C
- Atmosphere: Ar / $O_2$ (80 : 20)
- Pressure : 10 mPa, 10 Pa, 150 Pa, 80 kPa
- Time: 1 h
- Substrate: Stainless steel S 30400



## As deposited thin films

### microstructure (XRD) – variation of working gas pressure

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Power: 100 W
Gas: Ar
Temp.: unheated
As deposited
Substrate: Si

# Heat treated thin films 7 Pa

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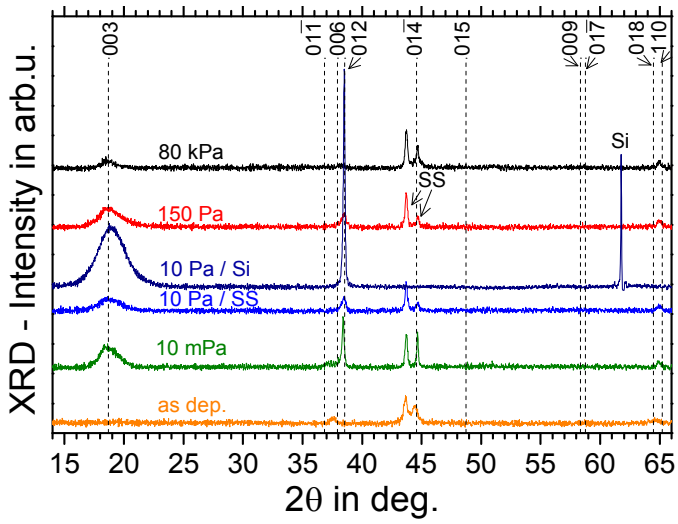


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Sample: dep. at 7 Pa
Temp.: 600 °C
Atmosphere: Ar / $O_2$ (80 : 20)
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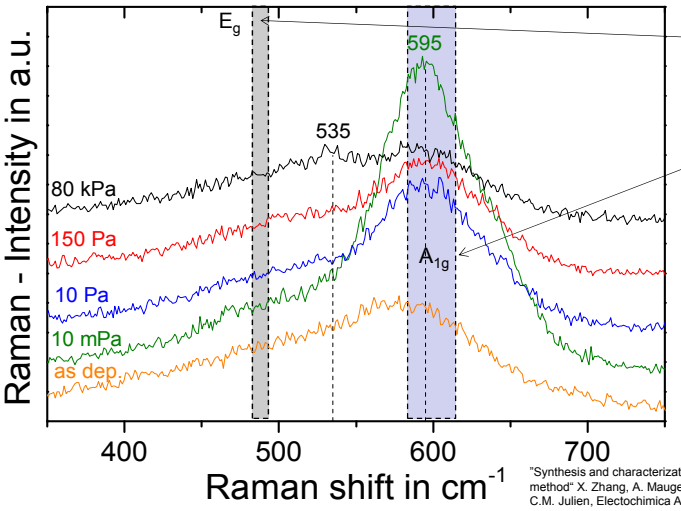
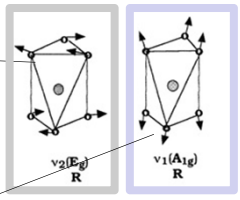
# Heat treated thin films 7 Pa

## microstructure (Raman spectroscopy) - variation heat treatment pressure




"Local cationic environment in lithium nickel–cobalt oxides used as cathode materials for lithium batteries", C. Julien, Solid State Ionics 2000

Sample: deposited at **7 Pa**
Temperature: 600 °C
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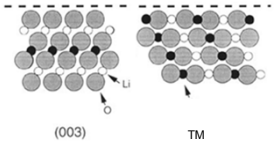
## Summary and Outlook

- Li-Ni-Mn-Co-O films were successfully deposited with different chemical compositions and microstructures
  - As deposited unordered layer structure showed discharge capacity of about 20 $\mu Ahcm^{-2}\mu m^{-1}$ Variation of Li and O concentration up to 5 at%
  - Texture depending on pressure
    - 0.2 Pa – 2 Pa: (018) / (110)
    - 4 Pa – 20 Pa : (012)




- Pressure during post annealing has an influence on the crystallisation process
  - During heat treatment the structure transforms into an ordered layer structure
- Battery tests and investigation of heat treated films and development of a one step process to deposit ordered layer structure
- Deposition on structured substrates and structuring by different deposition methods



I would like to thank

- the financial support by the BMBF Portfolio program
- Our chemical analysis group
- The members of the "Department for Composites and Thin Films" and IAM-AWP

You for your attention