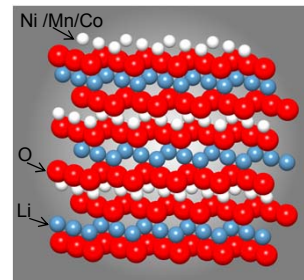


Magnetron sputtered Li-Ni-Mn-Co-O thin film cathodes for lithium-ion batteries

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Portfolio Elektrochemische Speicher im System 2014, 14. Oktober 2014, Karlsruhe, Germany

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



Outline

Motivation

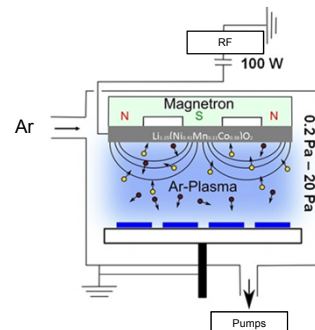


www.infinitepowersolutions.com (2014)

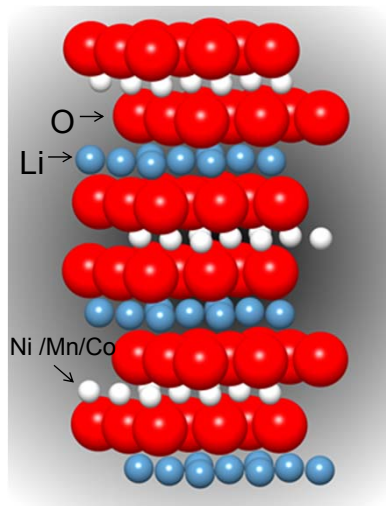
Thin film synthesis & characterisation

Selected results

Summary and outlook



Layered structure – $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$



Structure and properties:

- Theoretical capacity: 290 mAh/g
- Voltage versus Li: 2.5 V – 4.3 V
- Space group: $\bar{R}3m$
hexagonal lattice
 $a = b = 0.2867 \text{ nm}$
 $c = 1.4246 \text{ nm}$
 $\alpha = \beta = 90^\circ \quad \gamma = 120^\circ$
- Layers of closed packed oxygen ions are separated by alternating layers of lithium and transition metal ions

Goals for materials development

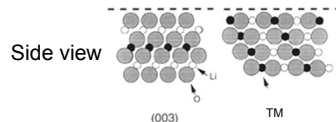
Fabrication of Li-Ni-Mn-Co-O layered structure with high capacity and enhanced Li^+ diffusion

- Nanocrystalline material with optimised chem. composition

Optimization of grain orientation

- Variation of deposition and growth kinetics

→ pressure variation during sputtering



Diffusion coefficients $\text{Li}_{0.8}\text{CoO}_2$:

(003) orientation: $\sim 1 \times 10^{-14} \text{ cm}^2\text{s}^{-1}$

(104) orientation: $\sim 1 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$

"Orientation dependence of Li-ion diffusion kinetics in LiCoO_2 thin films prepared by RF magnetron sputtering" J. Xie, N. Imanshishi, 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. Hackney, Journal of The Electrochemical Society, 2000

- Increase of the crystallinity

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

Characterisation Methods



- 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

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Experimental procedure 2-Step process

Deposition conditions:

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

Thin film constitution:

Li(Ni-Mn-Co)O ₂	1 – 1.5 μm
Si / SS	



Deposition parameters:

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

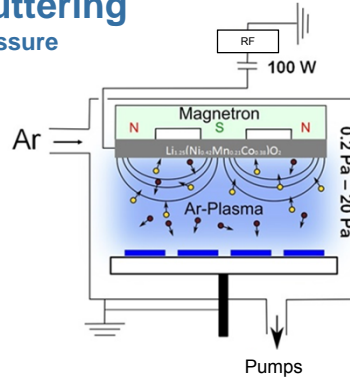
Heat treatment:

- Temperature: 600 °C
- Atmosphere : Ar / O₂ (80:20)
- Pressure range: 10 mPa, 10 Pa, 150 Pa, 80 kPa
- Time: 1 h

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1. Step: Magnetron sputtering

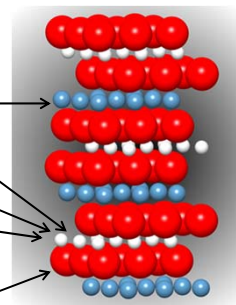
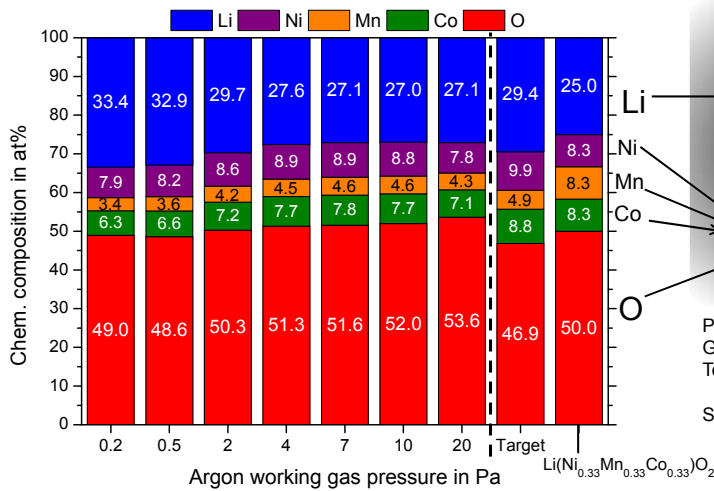
Variation of argon working gas pressure



- 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

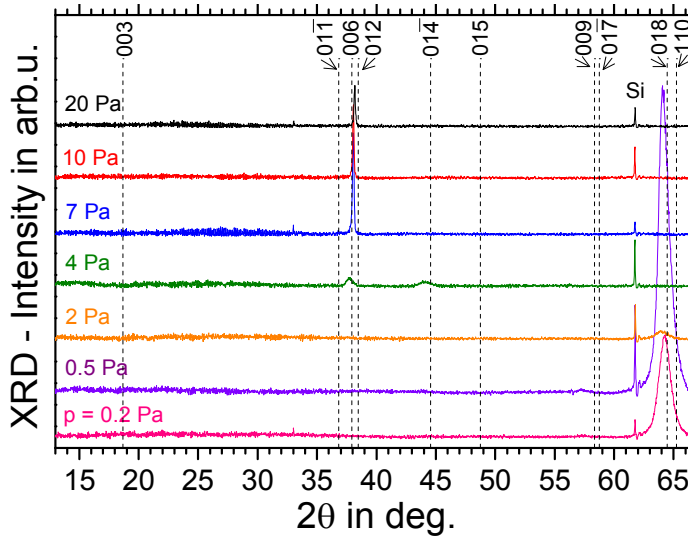
Chem. composition (ICP-OES / CHGE) – variation of working gas pressure



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

As deposited thin films

Microstructure (XRD) – variation of working gas pressure

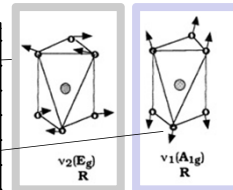
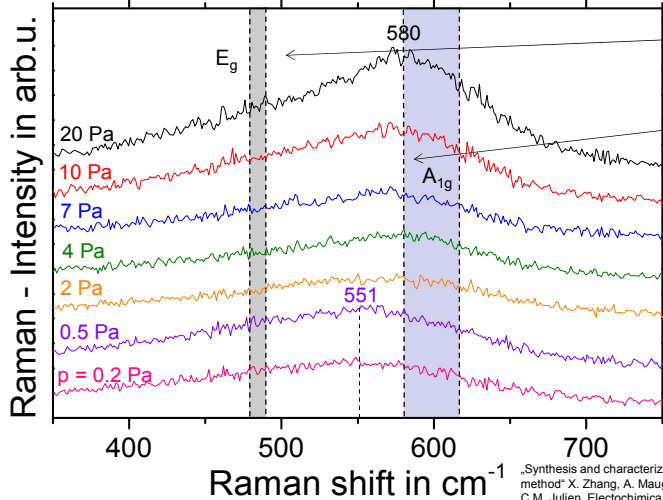


Layered structure
 $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$
 JCPDS: 00-056-0147

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

"Synthesis and characterization of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by wet-chemical method" X. Zhang, A. Mauger, Q. Lu, H. Groult, L. Perrigaud, F. Gendron C.M. Julien, Electrochimica Acta, 2010

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

2. Step: Heat treated thin films 7 Pa

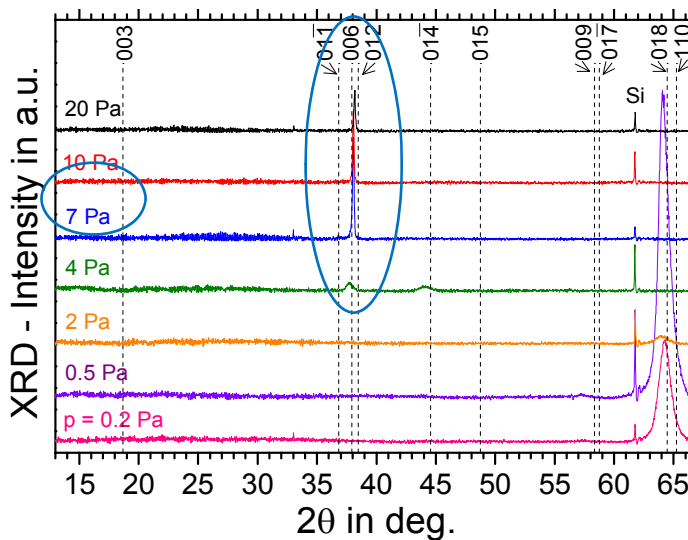
Variation of heat treatment pressure



- Sample: Deposited at 7 Pa
- Temperature: 600 °C
- Atmosphere: Ar / O₂ (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

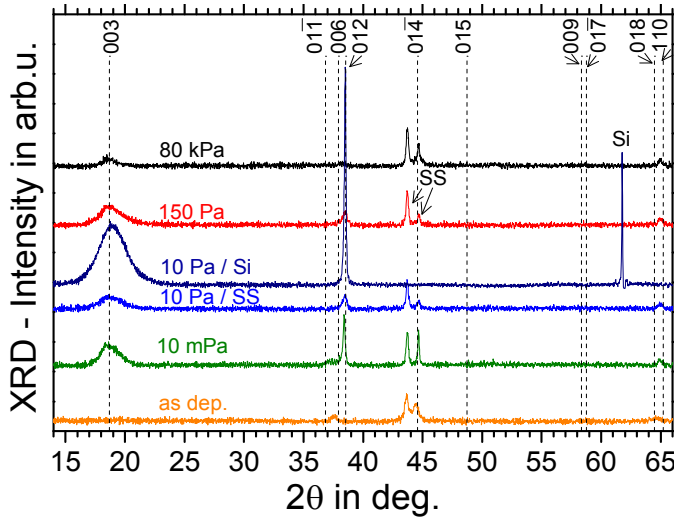


Layered structure
Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂
JCPDS : 00-056-0147

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

Heat treated thin films 7 Pa

microstructure (XRD) – variation of heat treatment pressure

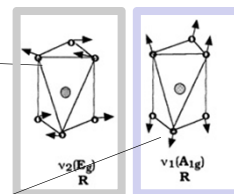
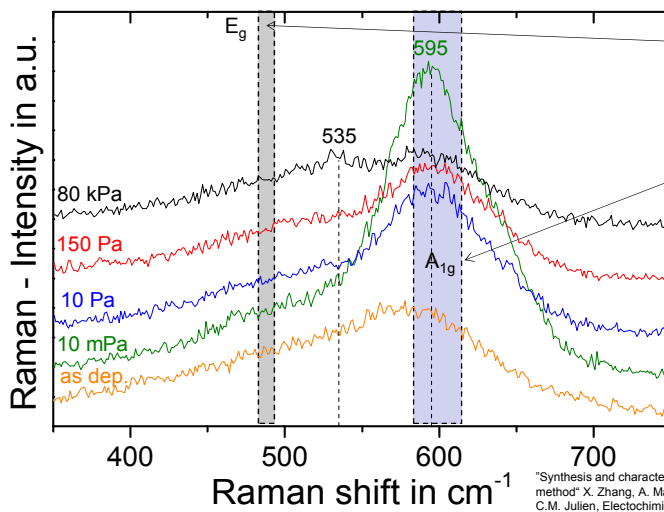


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Sample: dep. at 7 Pa
 Temp.: 600 °C
 Atmosphere: Ar / O₂ (80 : 20)
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Heat treated thin films 7 Pa

microstructure (Raman spectroscopy) - variation heat treatment pressure



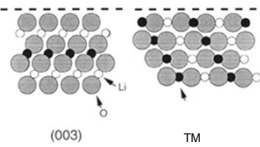
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Summary and Outlook

- 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 $20 \mu\text{Ahcm}^{-2}\mu\text{m}^{-1}$
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