Thin film cathodes for lithium ion batteries in the material system Li-Ni-Mn-Co-O

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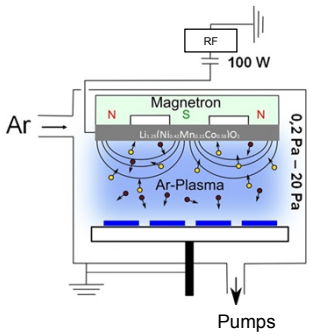
Outline

- Motivation and goal
- Synthesis
- Selected results
- Summary and outlook

www.infinitepowersolutions.com (2014)



Thin Film LIB

www.frontedgetechnology.com (2014)

www.avesodisplays.com (2014)

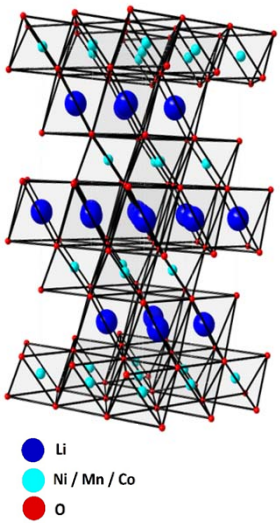
- Very high cycle life time
- Flexible
- Not flammable
- High temperature application

- Micro systems
  - Sensors
  - Smart cards
  - Medical technology

Advantage of thin film technology for material science?

- Fabrication of active cathode material without additives possible
- Homogeneous and dense films
- Films with preferred crystal orientation

Layered Structure – $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ NMC

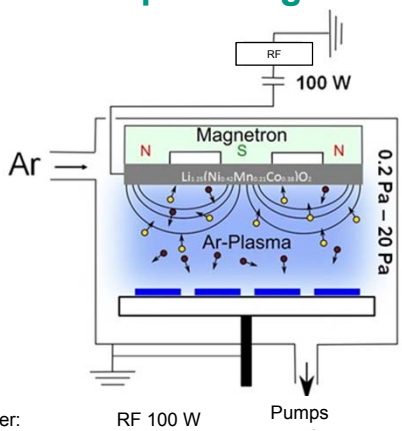


Structure and properties:

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

- Space group: $R\bar{3}m$
  hexagonal lattice
  a = b = 0.2867nm 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

Magnetron sputtering



- Power: RF 100 W
- Pressure range: 0.2 ; 0.5 ; 2 ; 4 ; 7 ; 10 ; 20 Pa
- Working gas: Ar
- Temperature: ~ 80°C
- Substrate: Si (001) /stainless steel

Goals for materials development
Chemical composition

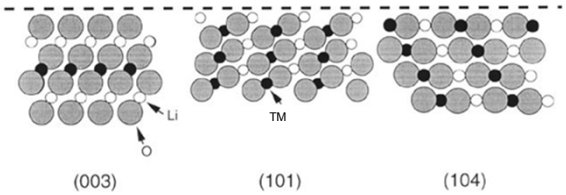
- High Capacity: > 160 $mAhg^{-1}$
  → Ni ↑
- High cycle life time: min. 85 % of the output capacity after 100 cycles
  → Li ↑
- High voltage material: voltage range between 2.8 V- 4.9 V
  → Li ↑

⟹ Used target material: $Li_{1.25}(Ni_{0.42}Mn_{0.21}Co_{0.37})O_2$

Goals for materials development
Micro structure of the film

- Fabrication of nanocrystalline, single phase NMC layer structure with optimized chem. composition
  - High theoretical capacity, good but directional Li^+ diffusion
- Optimization of grain orientation
  - Variation of deposition and growth kinetic

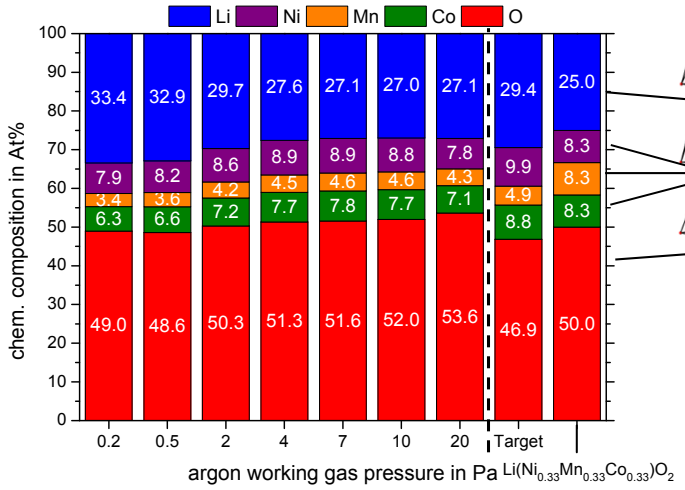
  ⟶ pressure variation during sputtering



"Preferred Orientation of Polycrystalline LiCoO2 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

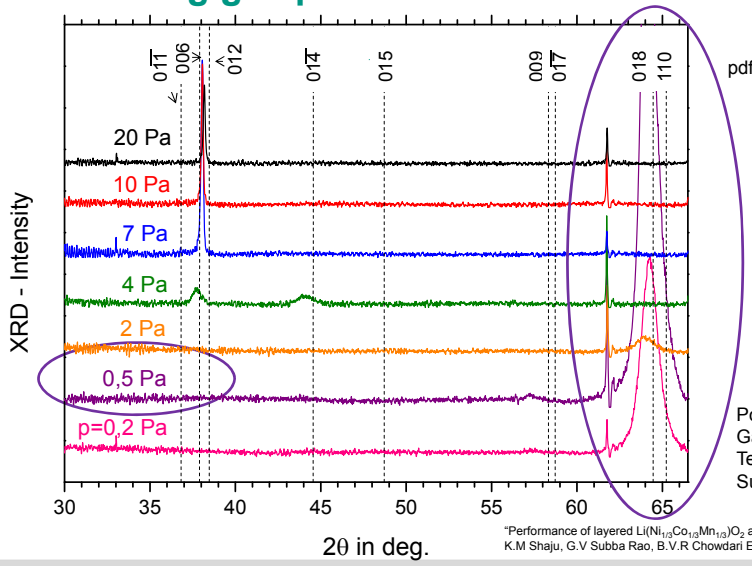
  - Increase of the crystallinity
  - Heat treatment of the films (T,t)
  - Influence of heat treatment pressure on the chem. composition

Chem. composition
(ICP-OES / CHGE) (as deposited)



Power: 100 W
Working gas: Ar
Temperature: RT
As deposited
Substrate: Si

XRD pattern
Ar working gas pressure variation



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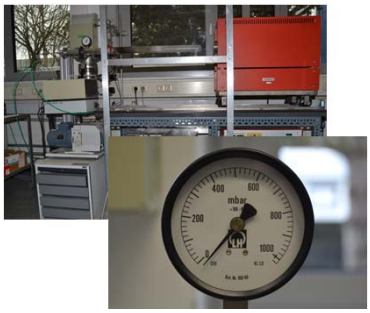
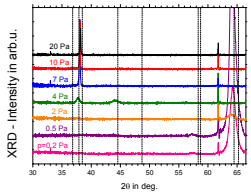
Power: 100 W
Gas: Ar
Temperatur: ~80°C
Substrate: Si

"Performance of layered $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ as cathode for Li-ion batteries"
K.M Shaju, G.V Subba Rao, B.V.R Chowdari Electrochimica Acta 2002

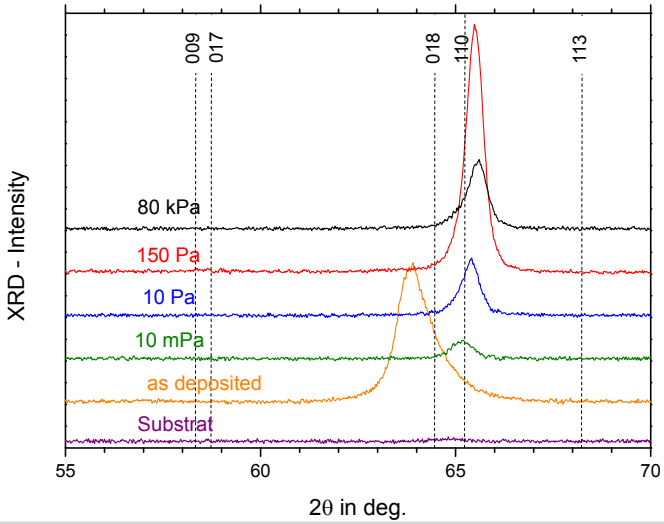
Second step :
heat treatment 0.5 Pa sample





- Sample: Deposited at 0.5 Pa
- Temperature: 600 °C
- Atmosphere: Ar / O_2 (80:20)
- Pressure range: 10 mPa, 10 Pa, 150 Pa, 80 kPa
- Time: 1 h
- Substrate: stainless steel S 30400

XRD pattern
heat treatment: pressure variation



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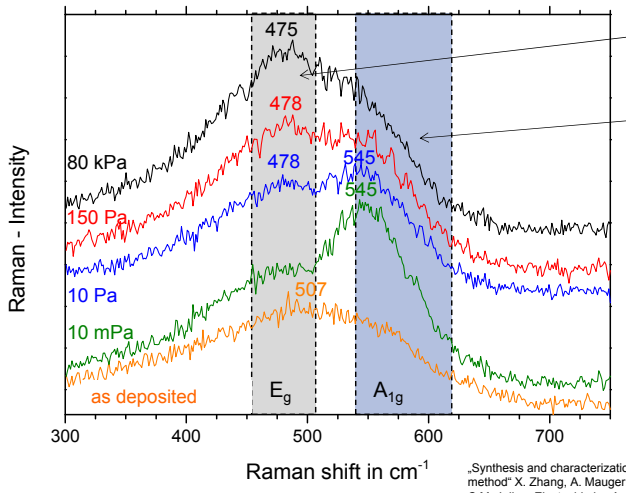
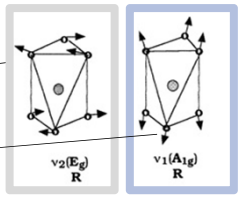
Sample: deposited at **0.5 Pa**
Temperature: 600 °C
Atmosphere: Ar / O_2 (80:20)
Time: 1 h
Substrate: stainless steel S 30400

Raman spectra
heat treatment: pressure variation





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

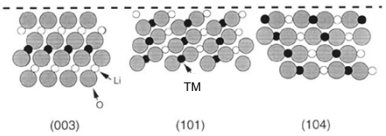
	E_g	A_{1g}
$LiNiO_2$	467	547
$LiCoO_2$	483	591
α-$LiMn_2O_4$	510	625

Sample: deposited at **0.5 Pa**
Temperature: 600 °C
Atmosphere: Ar / O_2 (80:20)
Time: 1 h
Substrate: stainless steel S 30400

„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

Summary

- Li-Ni-Mn-Co-O films were successfully deposited with different chemical compositions and microstructures
  - Variation of Li and O concentration up to 5 at.%
  - Pressure depending texture
    - 0,5 – 2 Pa: (018) / (110)
    - 4 – 20 Pa : (012)



- Heat treatment in Ar/O_2 atmosphere of the sample deposited at 0.5 Pa Ar working gas pressure
  - Microstructurel depending on the pressure during heat treatment
    - Same phase and texture
    - Different peak positions and grain sizes

Suggestions for cooperation

- Deviation from $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ stoichiometry
  - Influence of phase formation and crystallinity
- Metastable phases in thin films
  - Influence of composition, annealing temperature and pressure, grain size and film thickness on the layered structure stability

I would like to thank

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and you for your attention