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

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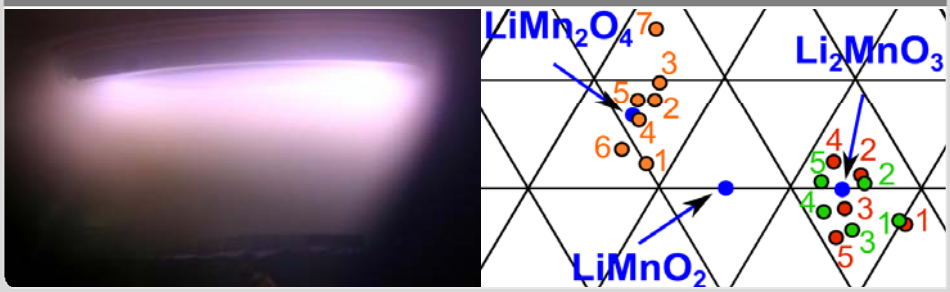


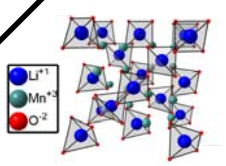
Outline

- Motivation
- Li - Mn - O structures and properties
- Experimental setup
- Results of Li - Mn - O thin films
- Summary and outlook

Scientific Motivation
for cathode development with thin film technology

- Preparation and characterization of pure active materials without carbon black or binder
- Realization of an two dimensional model system (conductivities)
- Investigation of texturing effects
- Combinatorial materials approach (stoichiometry, microstructure)
- Specific development of protective coatings for the cathode materials possible

Li - Mn - O Structures and Properties

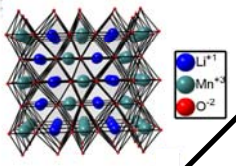


Properties of $LiMn_2O_4$

- **Theoretical capacity :** 148 mAh/g
- **Practical capacity:** 80 - 135 mAh/g
- **Voltage window:** 3.0 V - 4.3 V
- **Space group:** Fd3m
- **Color:** grey - blue
- **Li and Mn atoms occupy octahedral and tetrahedral sites**

Properties of *o*-$LiMnO_2$

- **Theoretical capacity :** 285 mAh/g
- **Practical capacity:** 120 - 180 mAh/g
- **Voltage window:** 2.0 V - 4.3 V
- **Space group:** Pmnm
- **Color:** black - grey
- **LiO_6 and MnO_6 octahedra are arranged in corrugated layers.**



Experimental Setup
R.F. magnetron sputtering

$LiMn_2O_4$ - Target

Selected Parameter:
Deposition: 16 Pa 100 W r. f. power
Annealing: 300 – 700 °C (30 min) : Atmosphere

$LiMnO_2$ - Target

Selected Parameter:
Deposition: 4 Pa 100 W r. f. power
Annealing: 350 – 650 °C (20 - 60 min) : Vacuum

Systematic parameter study:
50 , 100 , 150 W with **0,5 , 2 , 4 , 7 , 10, 13, 16 Pa**
Pure argon – working gas pressures

Annealing:
Used temperatures: 300 - 700 °C
Annealing durations: 20-100 min (air / vacuum)

Thin film concept:

Li-Mn-O
Stainless steel / Si

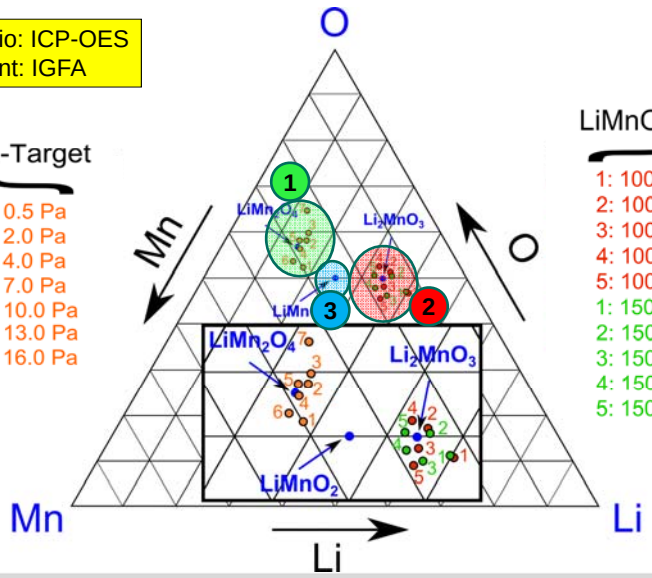
Thin film concept:

Li-Mn-O
Au 80 nm
Stainless steel / Si

Chemical Composition (after deposition)

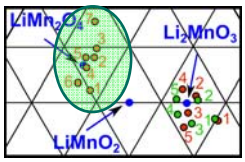
Li/Mn ratio: ICP-OES
O_2 content: IGFA

$LiMn_2O_4$-Target
1: 100 W 0.5 Pa
2: 100 W 2.0 Pa
3: 100 W 4.0 Pa
4: 100 W 7.0 Pa
5: 100 W 10.0 Pa
6: 100 W 13.0 Pa
7: 100 W 16.0 Pa

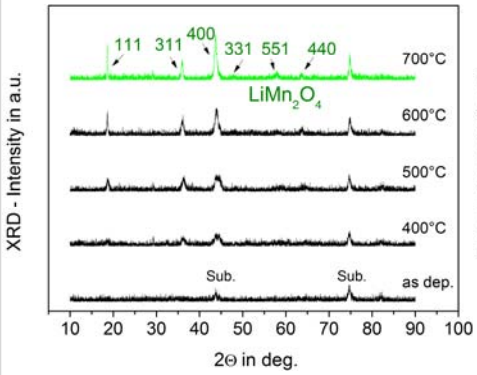


$LiMnO_2$-Target
1: 100 W 0.5 Pa
2: 100 W 2.0 Pa
3: 100 W 4.0 Pa
4: 100 W 7.0 Pa
5: 100 W 10.0 Pa
1: 150 W 0.5 Pa
2: 150 W 2.0 Pa
3: 150 W 4.0 Pa
4: 150 W 7.0 Pa
5: 150 W 10.0 Pa

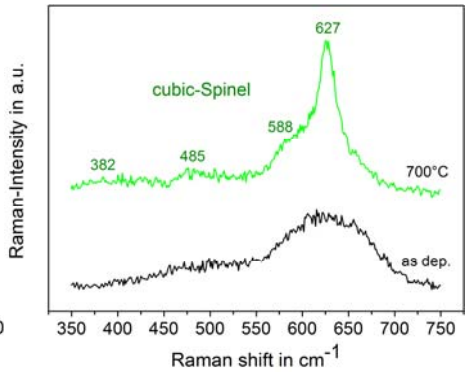
1 $LiMn_2O_4$ - Spinel



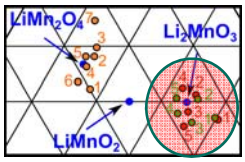
XRD



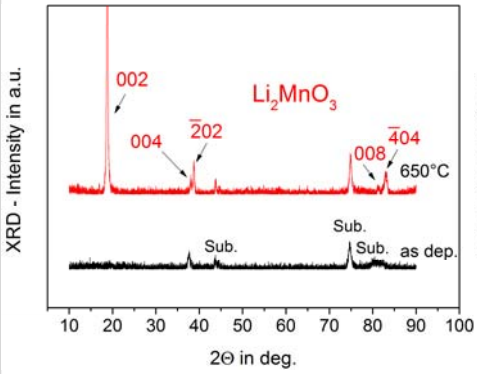
Raman



2 Inactive Li_2MnO_3



XRD



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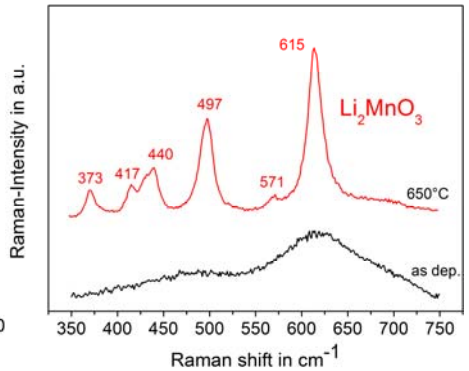
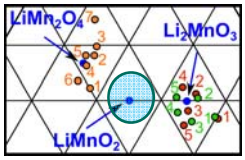


3 o-$LiMnO_2$



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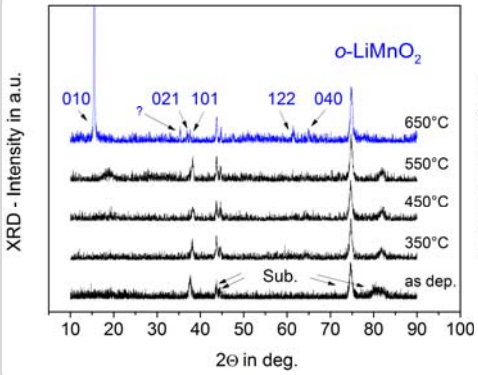

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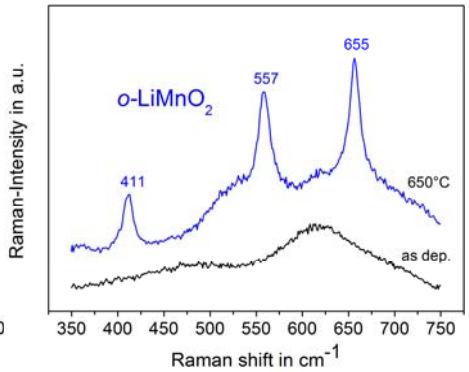
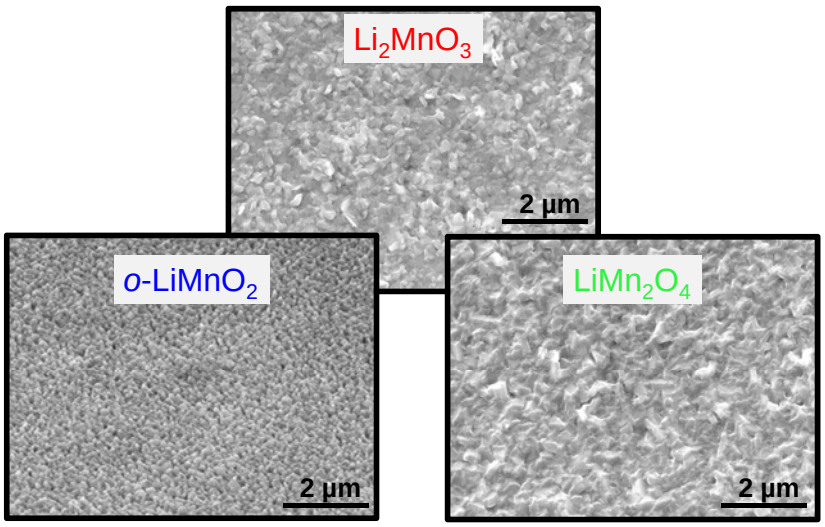
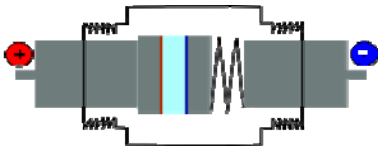


SEM- Investigations

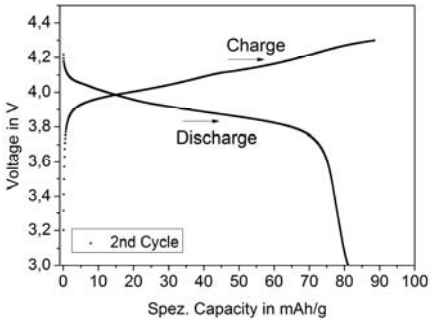


Electrochemical behavior

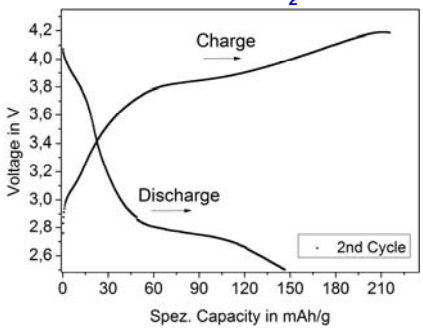
- Swagelok assembly
- Anode: Lithium ribbon
- Separator: Glass fiber filter
- Electrolyte: $LiPF_6$ EC/DMC (1:1)



$LiMn_2O_4$



o-$LiMnO_2$



Summary

- Successful deposition of different thin film cathodes in the Li-Mn-O system, and determination of the chemical composition
- Improvement of the crystallinity of the films with post deposition annealing and realization of three different microstructures ($LiMnO_2$, $LiMn_2O_4$, Li_2MnO_3)
- Successful electrochemical investigations on both active cathodes with approximately 70 - 80 % of the reversible capacity
- Now we can provide these films for further investigations in the priority program

Outlook

- Chemical investigations of selected films after annealing
- Investigations on the transformation from the *o*-$LiMnO_2$ phase to the cubic-spinel phase and work on stabilization concepts
- Investigation of the film - substrate interaction and adhesion

Finally, I would like to thank

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and of course you for your attention!