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ToF-SIMS and XPS Characterization of R.F. Magnetron Sputtered Li-Mn-O Thin Films for Li-Ion Batteries

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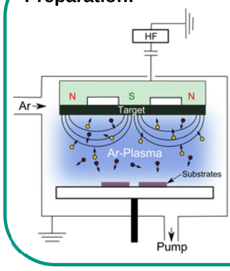
Most of currently available lithium-ion batteries operate with toxic and highly flammable liquid electrolytes bearing risks of leakage, ignitability and undesirable side-reactions. To overcome these problems a very promising approach is the development of all-solid-state-LIBs by means of thin-film technology. Such batteries consist of a solid multilayer stack of cathode, electrolyte and anode thin films of about 3 µm overall thickness [1]. The present study focusses on the surface analytical characterization of environmental friendly Li-Mn-O based thin film cathodes fabricated by means of combined R.F. magnetron sputtering and furnace annealing [2]. ToF-SIMS and XPS allows for quantitative information on the uniformity of the as prepared thin films as well as of the atomic and/or ionic inter-diffusion of the layer constituents at the contact interface (cathode and current collector) during annealing. Special care was taken to widely guarantee atmosphere-contact-free sample transport.

Preparation:



Film deposition by R.F. magnetron sputtering

Substrates: stainless steel discs
12 mm diam. x 0.5 mm thickness

Interlayer: 100 nm Gold

Targets: $LiMn_2O_4$ (CERAC Inc., USA)
Li_2MnO_2 (MaTecK GmbH, Germany)

Annealing: 100 nm thick films using the ***$LiMn_2O_4$*-target:**
30 min at 700 °C in ambient air (~1000 hPa)
100 nm thick films using the ***Li_2MnO_2* -target:**
30 min at 665 °C under vacuum (5×10^{-3} Pa)

Characterization:

X-ray Photoelectron Spectroscopy (XPS):
Thermo Fisher Scientific K-Alpha spectrometer
- Micro-focused mono-AlKα X-ray source
- 1 keV Ar^+ sputter depth profiles

Time-of-Flight Secondary Mass Spectrometry (ToF-SIMS):
ION-TOF GmbH ToF.SIMS[5] spectrometer
- Bi^+, pos. & neg. polarity
- 2 keV Cs^+ sputter depth profiles

Atmosphere-contact-free sample handling

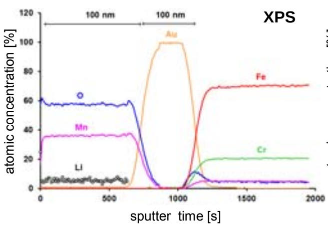
$LiMn_2O_4$ - Target

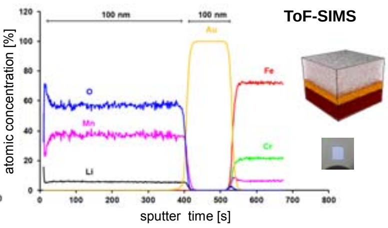
Deposition Parameters
16 Pa Argon, 100 W R.F. power

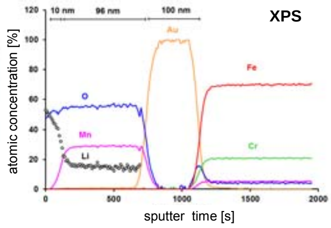
Li_2MnO_2 - Target

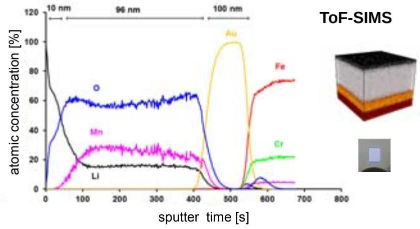
Deposition Parameters
4 Pa Argon, 100 W R.F. power

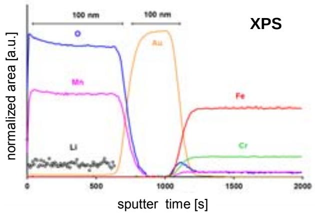
as deposited







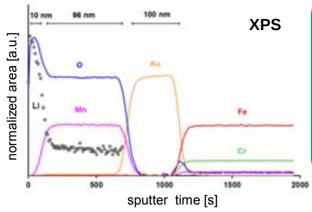




XPS binding energies [eV]:

Li 1s	=	55.7 (Li_2CO_3),	54.9 (Li-Mn-O)
Mn $2p_{3/2}$	=		641.4 (Li-Mn-O)
O 1s	=	532.7 (Li_2CO_3),	529.8 (Li-Mn-O)
Au $4f_{7/2}$	=	84.0 (Au°)	
Fe $2p_{3/2}$	=	706.8 (Fe°)	
Cr $2p_{3/2}$	=	574.1 (Cr°)	

ToF-SIMS fragments/ions: MCs^+ and O_2^-



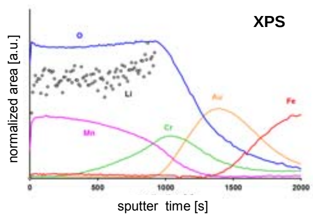
XPS cross talk: Li 1s, Au $5p_{3/2}$, and Fe 3p
Mn $2p_{3/2}$ and Au $4p_{1/2}$

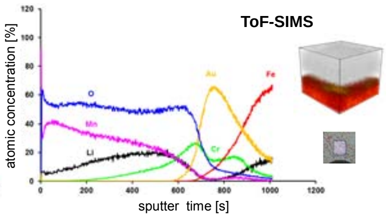
XPS detection limit: insufficient Li 1s cross section
Li 1s = 0.06 ⇔ C 1s = 1.00

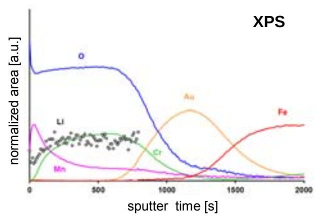
➔ **XPS** sputter depth profiles using normalized area
➔ **ToF-SIMS** sputter depth profiles calibrated by XPS

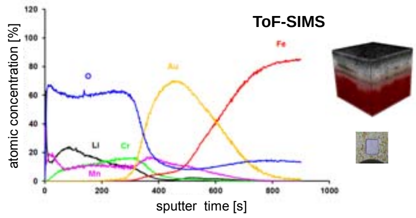
➔ Sharp multilayer interfaces

annealed









- ➔ Quantitative depth resolved elemental composition of thin film cathodes, anodes and solid state electrolytes
- ➔ Detailed information on elemental diffusion processes between substrate, interface and thin film cathode
- ➔ Influence of ambient air on the topmost surface of the battery active materials

Combined **ToF-SIMS** and **XPS** measurements can help to improve:
- the adhesion and electrical contact between current collector and electrode materials
- the solid electrolyte interface (SEI) and artificial SEIs
- protective coatings to prevent Mn^{2+}-dissolution into acidic liquid electrolytes
- Li^+ diffusion barriers, Li^+ transport processes, and corrosion behavior

Conclusions

- ❖ Combined ToF-SIMS and XPS allows for quantitative information on the uniformity of the *as prepared* thin films as well as on diffusion processes during annealing
- ❖ The depth profiles give hints on reaction layers at the thin film surface and the substrate to cathode interface
- ❖ Post mortem analysis for investigation of the degradation mechanisms after electrochemical cycling are possible

References

[1] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, Solid State Ionics, 135 (2000) 33-45.
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