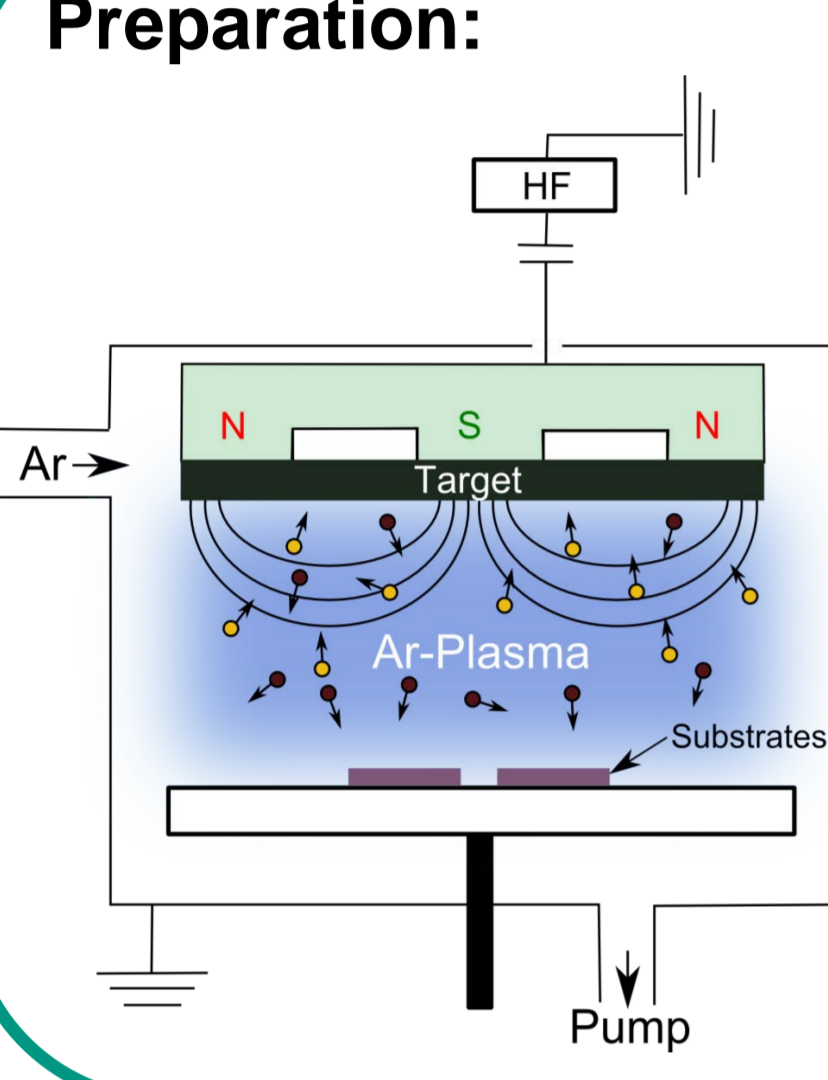


R.F. Magnetron Sputtered Li-Mn-O Films for Li-Ion Batteries: Combined XPS and ToF-SIMS Characterization

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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):
ThermoFisher Scientific K-Alpha spectrometer

- Micro-focused mono- $\text{AlK}\alpha$ X-ray source
- 1 keV Ar^+ sputter depth profiles

Time-of-Flight Secondary Mass Spectrometry (ToF-SIMS):
ION-TOF GmbH ToF.SIMS⁵ spectrometer

- Bi^+ , pos. & neg. polarity
- 2 keV Cs^+ sputter depth profiles

Atmosphere-contact-free sample handling

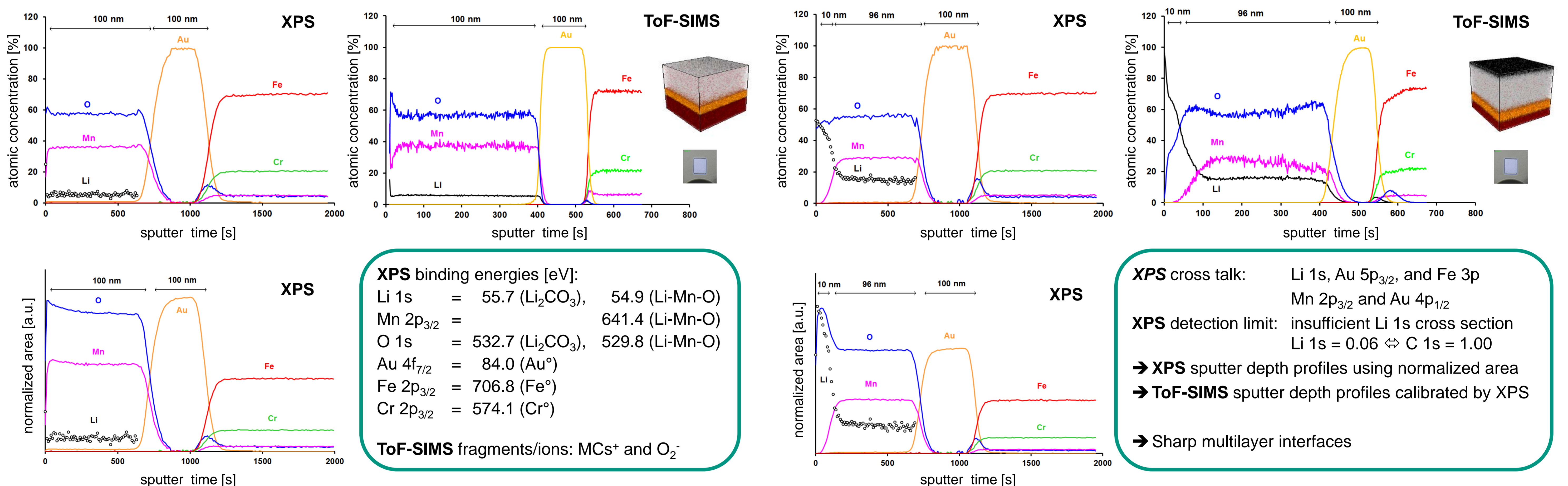
LiMn_2O_4 - Target

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

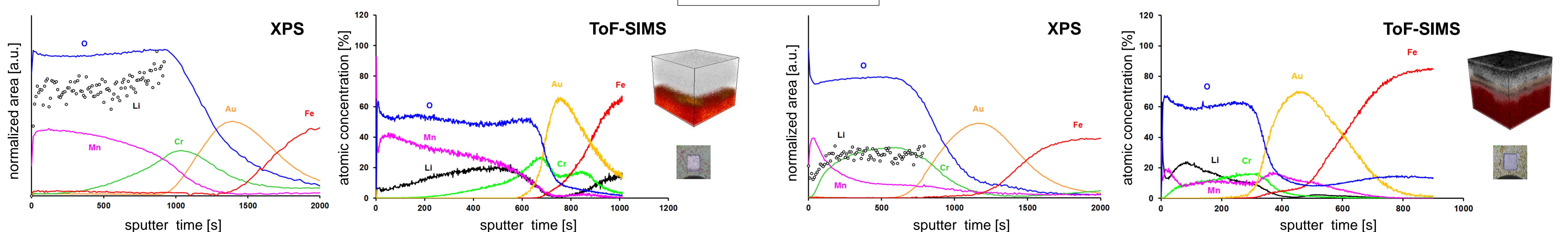
Li_2MnO_2 - Target

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

as deposited



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.
- [2] J. Fischer, C. Adelhelm, T. Bergfeldt, K. Chang, C. Ziebert, H. Leiste, M. Stüber, S. Ulrich, D. Music, B. Hallstedt, H.J. Seifert, Thin Solid Films, 528 (2013) 217-223.

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