Design of cathode materials for improved capacity, stability and safety for lithium ion batteries based on the system $LiMO_2$ (M = Co, Mn, Ni)

Applications for thin film lithium ion batteries:

Thin film cathodes for lithium ion batteries (LIB) offer an enormous application potential. Thin film LIB's can be fabricated very thin (total thickness below 10 µm), ultra lightweight, leak-proof, flexible, pressure resistant and optimized cells can be used in a wide temperature range (-50 – 150 °C). Furthermore they show a low self-discharge rate and an excellent cycling stability leading to a very long service life. The range of applications for this kind of batteries is very large. Wherever self-sufficient microsystems are used, thin film batteries could supply the energy. Examples are RFID-Chips for product identification, Smart Card applications and safety relevant micro sensors in the automotive or medical industry.

Scientific Motivation:

Thin film batteries are interesting not only due to their large range of possible applications, they also offer an enormous research potential. By r.f. magnetron sputtering it is possible to produce pure active materials for cathodes or anodes without any impurities like carbon blacks or binders, which enables the study of the intrinsic material properties. Moreover thin films represent ideal two dimensional model systems for the investigation of ionic or electronic conductivities. Thin films can also be coated with different protective layers to reduce the chemical reactions with liquid electrolytes. This increases the safety of the battery.

Current project status:

In the material system Li-Ni-O thin films were produced by r.f magnetron sputtering of a $LiNiO_2$ Target in pure argon atmosphere and the following process parameters were changed systematically. Three different target powers (50 W, 100 W, 150 W) and five different working gas pressures (0.5 Pa, 2.0 Pa, 4.0 Pa, 7.0 Pa, 10.0 Pa) were investigated. All films were subjected to a post deposition annealing process under high vacuum or air (300 °C, 400 °C, 500 °C, 600 °C, 700 °C). The same systematic study was carried out in the system Li-Mn-O using two different targets ($LiMnO_2$ and $LiMn_2O_4$) and the results were compared.

The films were characterized by the following methods:
Scanning electron microscopy (SEM), X-Ray techniques (XRD, XRR), Raman spectroscopy and electrochemical investigations like galvanostatic and potentiostatic measurements.

By now several parameter fields for the fabrication of the high temperature phase of $LiCoO_2$, of orthorhombic $LiMnO_2$ and of $LiMn_2O_4$ spinel have been elaborated. In the following section selected results for the orthorhombic $LiMnO_2$ will be shown.

Orthorhombic - $LiMnO_2$ (*o*-$LiMnO_2$):

o-$LiMnO_2$ is characterized by a high theoretical specific capacity of 285 mAh/g and a possible voltage window during charging and discharging between 2.0 and 4.3 V against metallic lithium. The reversible capacity that can be practically achieved lies between 120 – 180 mAh/g. In comparison to nickel or cobalt based oxides the manganese based cathodes are cheaper, less toxic and the worldwide resources that will be needed for a future mass production are larger.

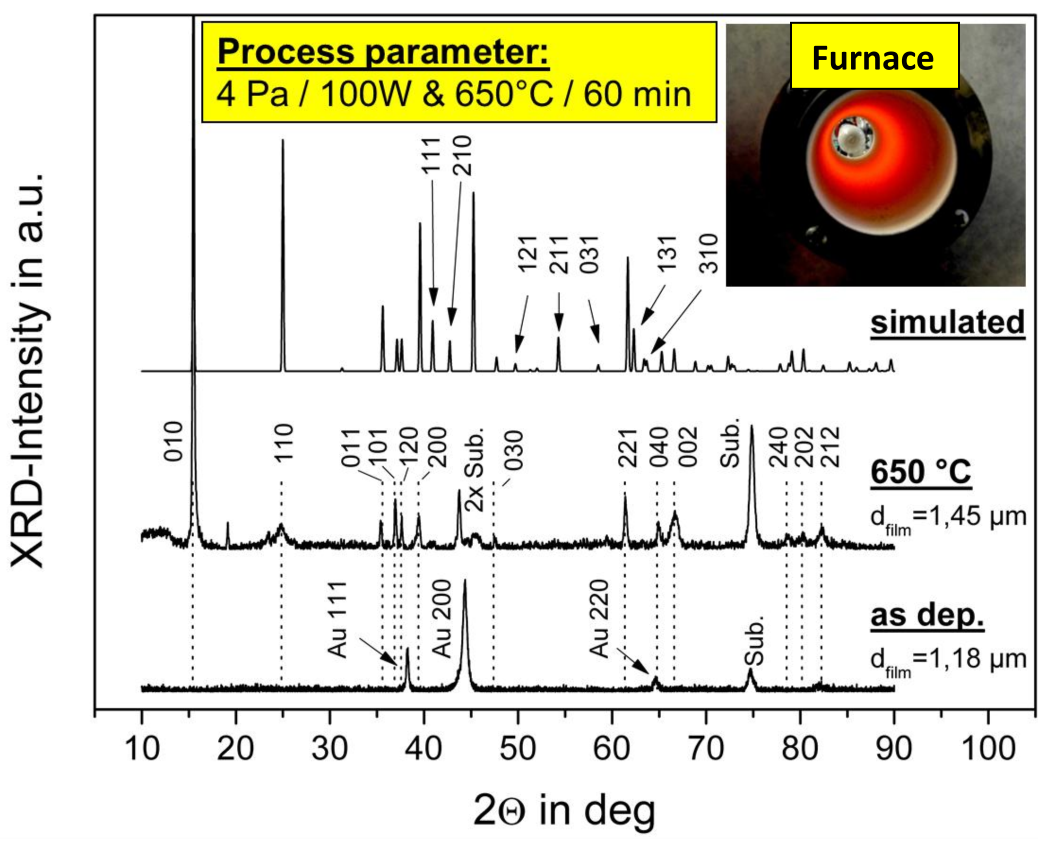

Figure1

o-$LiMnO_2$ thin films can be deposited by r.f. magnetron sputtering of a $LiMnO_2$ target in pure argon discharge with a working gas pressure of 4 Pa followed by a post deposition thermal annealing at 650°C for 60 min under vacuum atmosphere. Figure 1 shows three X-Ray diffraction patterns. The bottom curve shows the diffraction pattern of the as-deposited thin film on a stainless steel substrate coated with a thin gold layer. The deposited Li-Mn-O film is X-ray amorphous.

The next pattern belongs to the annealed thin film, in which 13 reflexes show a good agreement with the simulated pattern of orthorhombic $LiMnO_2$ (top pattern) and data from the JCPDS database (card # 35-749).

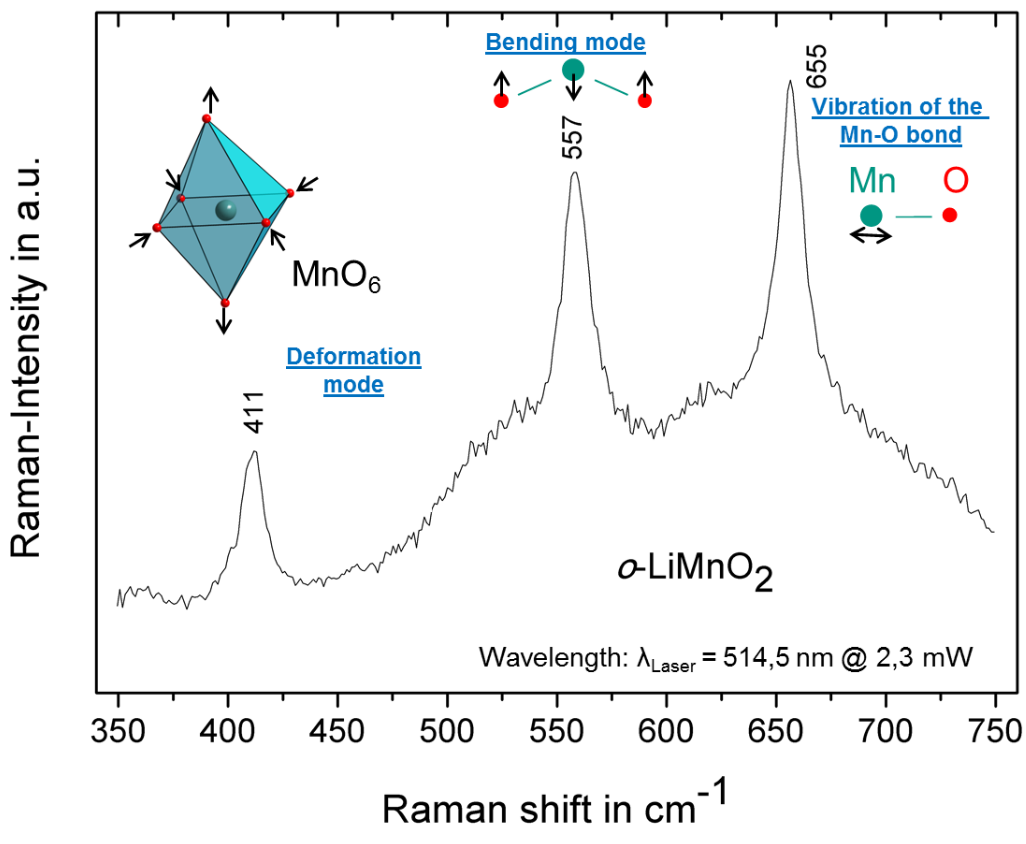

Figure 2

In the Raman spectrum (Figure 2) signals of the o-$LiMnO_2$ can be identified as well. The three bands at $411 cm^{-1}$, $557 cm^{-1}$ and $655 cm^{-1}$ can be assigned to the deformation vibration of the MnO_6 octahedron cage, the O-Mn-O bending mode and the strongest Mn-O bond respectively.

Next steps:

The next steps will consist of achieving a better understanding of the correlation between process parameters, microstructure and properties of the materials. Moreover concepts for the stabilization of the orthorhombic $LiMnO_2$ structure during cycling tests will be developed (at the moment a cycle induced transformation into the cubic spinel phase is observed). With all experimental data we are working in close contact, to our project partners in Aachen and our thermodynamics group in Karlsruhe.