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OPTIMIZING THE CATHODE MATERIAL LNMO SYNTHESIZED USING DIFFERENT PRECURSOR CHEMISTRIES AND CALCINATION PARAMETERS

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MOTIVATION

The cathode material $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a promising next generation active material for Li-ion-batteries. A wide range of synthesis routes, precursors and calcination profiles for the synthesis of LNMO has been reported in literature. Nevertheless, the correlation between electrochemical properties and the synthesis parameters is not fully understood. Therefore, in this study the influence of the variation of selected synthesis parameters on the properties of LNMO is analyzed and discussed.

EXPERIMENTAL

LNMO was prepared by using a spray drying method. Different metal salts were dissolved in EtOH:
- nitrates → "precursor 1"
- acetates → "precursor 2"

The solution was spray dried in a "Büchi" spray drying machine to produce the precursor. The precursor was then calcinated in a muffle furnace for 5 h at 800 °C. Finally the samples were calcinated a second time for 5h at 800 °C. To optimize the second calcination a grinding step between the calcinations was added and optimized:
- hand grinding → "not opt. calcination"
- PKM grinding → "opt. calcination"

For the preparation of the electrode foil 80 % active material (LNMO), 10 % carbon (Super P, Timcal) and a binder (PVDF, Solef) were mixed and coated on an Al-foil (Hydro). The foil was tried in an oven and calendared to reach a porosity of 30 %.

Coin cells were assembled by using the prepared foil, vs lithium with a Wahtmann separator and LP40 (1M $LiPF_6$ in EC:DEC 1:1 w/w, BASF) as an electrolyte.
The coin cells were rested for 24 h and afterward the electrochemical measurements were started.

Figure 1: "Büchi Mini Spray Dryer B-290".

Figure 2: Coin cell parts.

MATERIALS

After the spray drying the precursors show different properties. For a higher nitrate amount the precursor is highly hydrophilic (similar to the individual salts) whereas acetates do not show such properties.

After the calcination LNMO is a black powder which shows different tap density depending on the precursor used. This can be correlated to different crystal size and agglomerates after the calcination.

The FESEM pictures (figure 5) show the different appearances of the LNMO from different precursors. LNMO synthesized from nitrate based precursor shows smaller crystals, a branched network and agglomerates in different shapes. The crystals show an undefined morphology. LNMO synthesized from acetate based precursor show lager crystals and big agglomerates. The crystal morphology appears with octahedron crystal planes. Those pictures indicate why the powders have a different tap density.
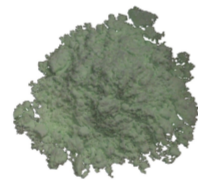

Figure 3: precursor consisting of different metal salts.

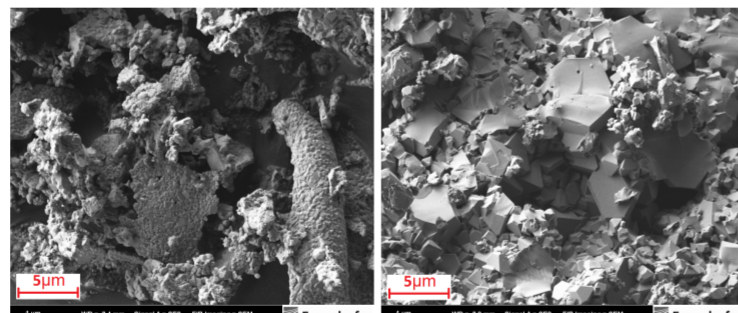
Figure 4: LNMO after two step calcination.

Figure 5: FESEM of LNMO synthesized from "precursor 1 not opt. calcination"(left) and "precursor 2 not opt. calcination" (right).

RESULTS

Figure 6 shows the electrochemical properties of the synthesized LNMO. The as prepared coin cells where charge and discharges with specific C-rate from 0.1 C to 2 C and afterwards cycled 60 times at a C-rate of 1C/1C. At a C-rate of 0.1C the precursor 1 (nitrates) shows a higher specific capacity with 131 mAh/g compared to LNMO from from precursor 2 (acetates) with 119 mAh/g. Through die optimizing of the grinding between the calcinations the specific capacity of precursor 1 can be significant improved and reach a specific capacity of 133 mAh/g at 0.1 C. On the other hand the optimized LNMO shows the largest capacity drop during the cycling of 5 %, while the other samples specific capacity only drop between 2 and 3 %.

Figure 7 shows the discharge curve for LNMO. Three plateaus are visible. The expected ones at a voltage of 4.7 V, which describe the reduction of Nickel(IV) to Nickel(II) and the plateau at 4.1 V which can be attributed to by the reduction of manganese(IV) to manganese(III). Through comparing the capacity values for the different plateau it can be seen, that throw the optimization of the grinding the amount of manganese(III) can be reduced significantly for precursor 2. The amount decreases from 14 % to 9 %. This reduction results in an increase in the energy density. The reduction is based on a better interaction of the samples with the atmosphere during the second calcination, which can occur because of a higher surface resulting from the grinding process.[1] Therefore oxygen can better interact with the sample and manganese(III) can be better oxidized to manganese(IV).

In figure 8 the particle size distribution of precursor 2 is shown. The sample with no specific grinding show a broader range of the crystal size. It reaches from over 20 µm to 0.03 µm. By grinding the sample with a PKM between the calcinations the size distribution can be reduced. The samples shows crystals sizes which reaches from 4 µm to 0.03 µm. This correlates with the assumption that by the grinding the particle size can be reduced and therefore the surface which can interact with oxygen is higher. Furthermore in the cell the electrolyte can better interact with the active material and the cells can reach a higher specific capacity. It needs to be pointed out that the interaction with the electrolyte at high voltage can lead to side reaction, which lead to worse cycling properties.

The change in the particle size can be seen in figure 9 which compared to figure 5 (right) shows a smaller crystal size, which was already discussed for figure 8. The crystal size is more similar to those of the nitrate based LNMO in figure 5 (left) shown. In difference to the nitrate based precursor the sample shows a different particle morphology. The crystals show octahedral crystal planes, which are descripted to have better long life cycle stability than other crystal planes.[2]
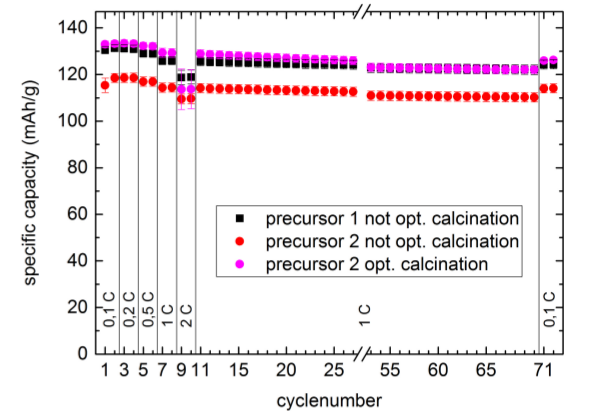

Figure 6: performance- and aging test for LNMO with different precursors and modified grinding between the two calcinations (average of 5 coin cells with standard deviation).
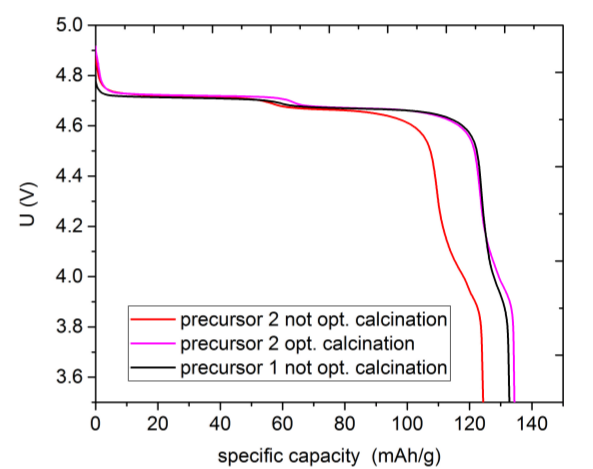

Figure 7: discharge curve for LNMO with different precursors and different grinding between the different calcinations (one selected coin cell).
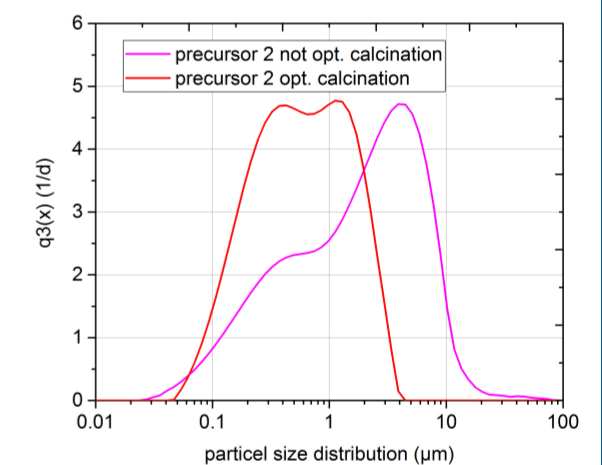

Figure 8: particle size distribution for LNMO with different precursors and different grinding between the calcinations.
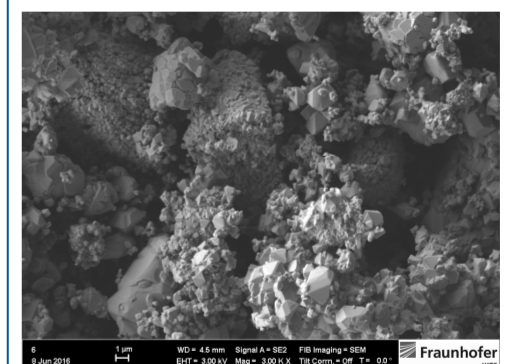

Figure 9: FESEM of LNMO synthesized from precursor "precursor 2 opt. calcination".

REFERENCES

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[2] K.R. Chemelewski, D.W. Shin, W. Li, A. Manthiram, Octahedral and truncated high-voltage spinel cathodes: the role of morphology and surface planes in electrochemical properties, J. Mater. Chem. A 1 (2013) 3347.

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SUMMARY AND OUTLOOK

It was shown that samples crystallized from different precursors consisting of different lithium and nickel compounds resulted in samples with unequal crystal morphology in the resulting product. Those samples have different electrochemical properties and the discharge curves indicate a different content of manganese(III).

By optimizing the grinding between the calcination the properties of the acetate based precursor can be enhanced significantly. Additionally the crystals now show octahedral planes, which are important to achieve in order to reduce side reaction with the electrolyte.

Following investigations will focus on improving the LNMO properties further, by reducing the particle size distribution, forming Octahedrons and by that improving the electrochemical properties. To achieve this the LNMO can be doped with different elements and the grinding of the samples will be further modified be using different methods and grinding mediums.

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