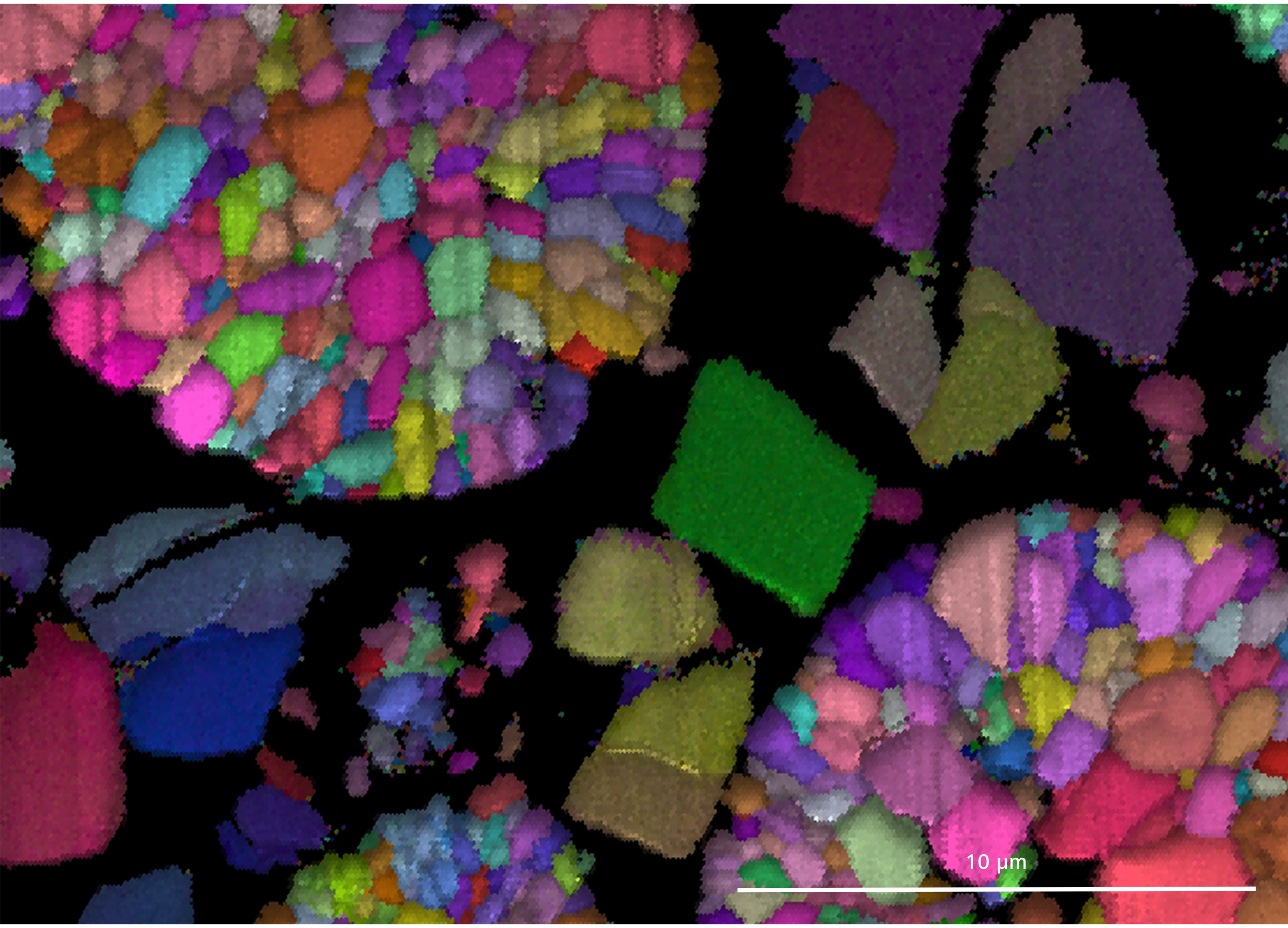
White Paper



EBSD-analysis for the visualization of crystal orientation and the granulate sub-grain size of blended cathode active material for 18650 lithium ion batteries

ZEISS Crossbeam 550

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Secondary or rechargeable batteries are nowadays not only of interest for low power applications, but also for high power applications such as electric transportation systems or large scale intermediate storage systems for energy produced by fluctuating energy sources. In search of a promising battery technology providing high cell voltage, this application note considers some potential options.

Introduction

Lithium is a useful anode material due its very low electrochemical potential. However, the high chemical reactivity of Li restricts the choice of further components to set up a complete battery. Moreover, using anodes of Li metal provokes the formation of lithium dendrites during cycling.

To avoid dendrite formation Li has to be stored in stable host material. The application of many of the materials available that hold promise at first glance are in fact hampered by a severe aging phenomena. Si, for example, is able to store large amounts of Li (up to 3,75 Li atoms per Si atom) but this is accompanied by a huge volume increase leading to fast aging in terms of material destruction. Graphite is a low cost alternative with a much lower uptake capability for Li (only 1 Li atom per 6 C atoms) and also benefits from a higher durability. Graphite has so far been established as the most common anode material in commercial Li based batteries [1].

In order to investigate bulk materials in general or the interior of battery materials in particular by optical or electron microscopy and related methods, processes have to be developed to make these regions of interest accessible to visible light or an electron beam. A special issue in this context is the high need for smooth and well-defined surfaces. A classical method in this context is a combination of embedding in resin, cutting, grinding and mechanical polishing. However, due to the high sensitivity of lithium ion battery materials to air and moisture, the water assisted processes of grinding and polishing are more likely to cause problems when applied to LIB materials.

A promising, water free and oxygen free alternative to obtain the desired surface quality for LIB materials is the preparations of cross sections by means of a focused ion beam (FIB) implemented into an electron microscope. Appropriate electron microscopes feature – in addition to the electron gun – an ion gun which is constructed to emit a focused beam of metal ions such as gallium (Ga^+). Due to their much higher atomic weight, and a typical acceleration voltage of 30 kV, these ions feature much higher energy than the electrons usually used in electron microscopes for imaging the sample.

Provided there is a sufficiently high current, the ion beam removes the specimen material. In this way, a focused ion beam allows the preparation of defined cuts and cross sections of the sample material. However, the removal of material by FIB is limited to very small amounts of material. Thus, the method is commonly applied for microscopic slope cuts or TEM lamella preparation. For EBSD measurements, however, free-standing, exposed surfaces are needed.

To prepare the desired cross sections of the battery, a much thinner removal of specimen material is needed. To realize this, a laser system can be applied. The laser pre-treatment of the cathode foil sample allows the removal of even large parts of the sample to yield free-standing, exposed cross section surfaces of the cathode foils from quasi everywhere across the foil. This laser-made cross section required post processing by FIB milling to obtain the desired smooth surface required to perform EBSD measurements.

Experiment

The cathode material investigated was extracted from commercial 18650 type lithium-ion-batteries featuring composite cathode active material composed of equal amounts of spinel-type lithium manganese oxide $LiMn_2O_4$ (LMO) and lithium manganese cobalt nickel oxide (1:1:1 $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ (NMC). The anode active material was based on graphite.

In this example, a Trumpf Trumark 6000 laser system adapted on the pre-vacuum chamber of ZEISS Crossbeam 550 (Figure 1a) was used. A pulsed laser characterized by high power and outstanding beam quality, was also used (Figure 1b). The laser parameter settings for this work were: Trackwidth: 0.030 mm, Power: 80%, Velocity: 150 mm/s, Pulse Frequency: 15 mHz).

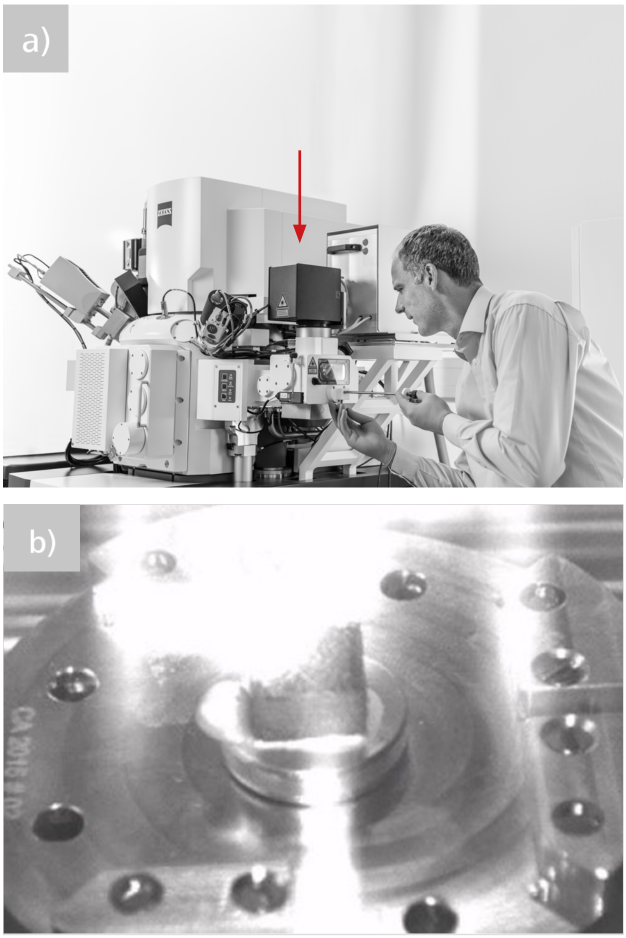

Figure 1 *a) ZEISS Crossbeam 550 with Trumpf Laser (red arrow). b) Sample inside the Laser chamber with active laser.*

After aging of the electrochemical cell (e.g. by battery cycling or storage under defined conditions) the cells were discharged and then opened in an argon filled glovebox to ensure there was a protective atmosphere – oxygen and moisture. Subsequently, the jelly roll was unrolled; the electrode foils were separated from the separator, washed with dimethyl-carbonate (DMC), and dried in an oven at 70 °.

From the cathode foil obtained in this way, small pieces were cut using scissors and mounted on a SEM stub with the edges extending beyond the stub. To yield a projecting surface for EBSD measurements the selected piece of cathode foil was precut by a laser system (Trumpf Trumark 6000) (Figure 2).

Subsequently the projection was fine-cut by a FIB-milling procedure involving several preparation steps which were characterized by successively decreasing FIB currents to yield a smooth surface with only little residues of so called curtaining, a kind of waviness of the cross section surface introduced by the FIB.

A smooth surface without artefacts is crucial for reliable EBSD measurements due to EBSD analysis being a very surface-sensitive method of sampling (only the topmost 40 nm of the specimen [4]).

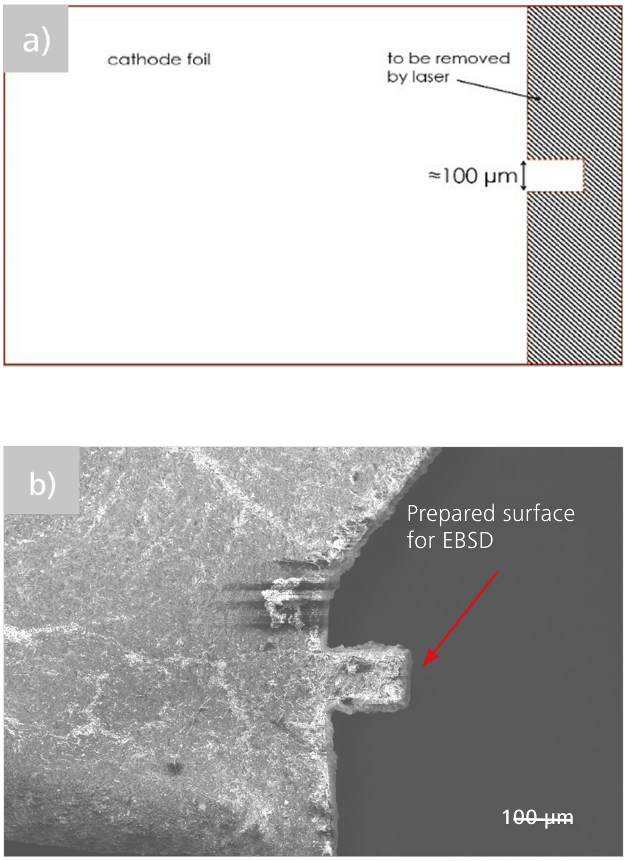

Figure 2 *a) schematic picture of the Laser precut b) SEM image of the Laser precut of the electrode foil sample, 100x, InLens*

NMC/LMO LIB cathode active material microstructure

The FIB cross-section (Figure 3) shows the NMC as well as the LMO particles as marked with red arrows. Both particle-types are very compact and are arranged with relatively low pore space. The LMO particles in this cross-section do mainly occur at the surface of the section. The NMC particles exhibit a subgrain structure (Figure 3b).

ESBD measurements

The EBSD measurements were performed by means of a ZEISS scanning electron microscope (SEM) equipped with FIB functionality (Crossbeam 550). For analysis of the EBSD data the software OIM v7.2.1 (Orientation Imaging Microscopy) distributed by EDAX company was used. The EBSD camera is also made by EDAX (EDAX Hikari). The acceleration voltage for the EBSD measurements was 20 kV, a current of 20 nA, a step size of 0.1 µm and a magnification of 3000x.

A special challenge in performing EBSD measurements at the material system under discussion is the fact that the two components of the electrode's active material, $LiMn_2O_4$ (LMO) and $LiMn_{1/3}Co_{1/3}Ni_{1/3}O_2$ (NMC), feature different crystal structures based on different crystal systems and space groups. Since it is not possible to determine the crystal structure of the material under investigation by the method of EBSD, crystallographic data has to be provided and preset in to the software. In this case this was: crystallographic data of LMO, space group Fd 3m, and of NMC, space group R-3m.

Although the two unit cells seem to be sufficiently different to allow clear distinction, wrong automatic assignment was frequently observed during the measurements. Measuring-spots within a LMO particle were assigned to the crystal structure of NMC and vice versa. However, the Chi Scan functionality of the TEAM software by EDAX allows correcting these misassignments by correlating the results of EBSD and EDX measurements.

A specific phase identified in an EDX map of the surface under investigation which is characterized by the chemical composition determined by EDX can be manually assigned to a preset crystallographic phase from the EBSD map.
By this method, the correct assignment of one of the preset crystal structures to a measured diffraction pattern is significantly facilitated. Thus, the appearance of the EBSD map changes on applying the Chi Scan functionality of the TEAM software (Figure 4b) [2,3].

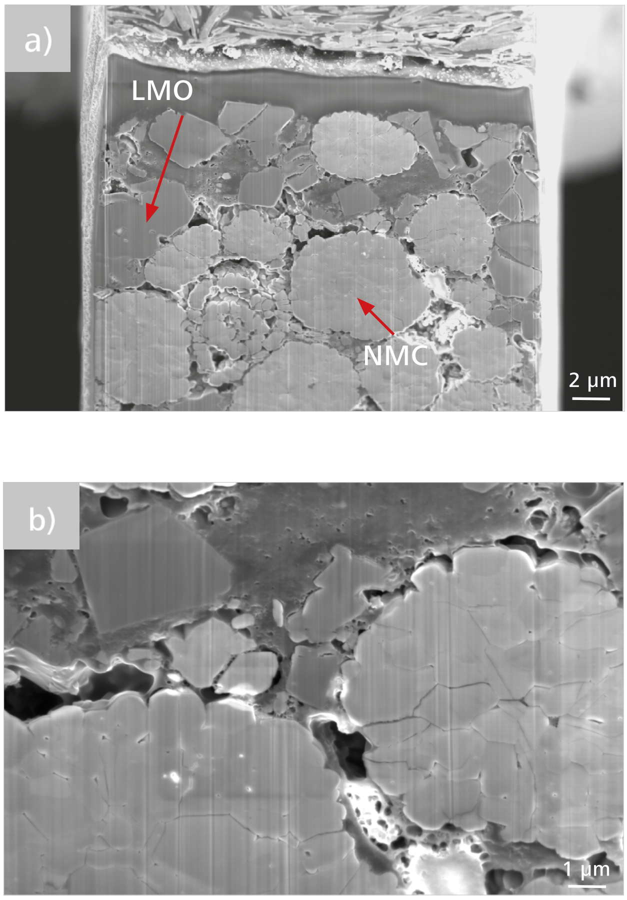

Figure 3 *FIB Cross section of Laser precut surface a) overview with NMC/LMO particles, 1.500x, InLens b) NMC particles with subgrain structure, 7.500x, InLens*

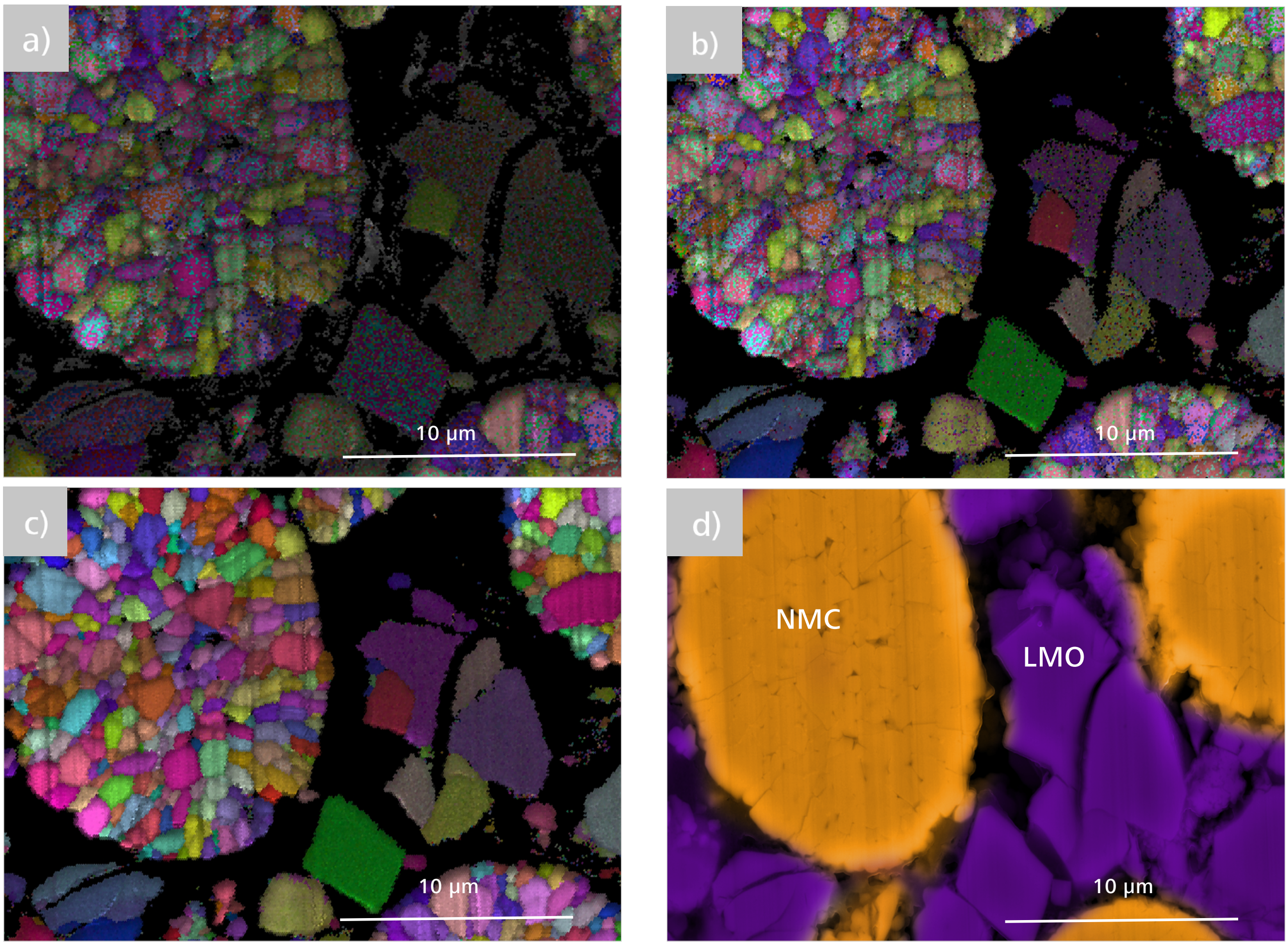

Figure 4 *BSD Inverse Pole Figure Map a) as measured, b) after correct attribution of structures and phases by Chi-Scan in TEAM, c) after pseudo symmetry cleanup and additional grain dilation clean-up by the OIM software, d) EDX phase map of the section with clear distinction between NMC and LMO particles.*

Following the correction for misassignments in crystal structure described above, further analysis was conducted by means of the OIM software. The analysis of the orientation relations for various obviously cohering grains containing surprisingly two different colors (suggesting to different orientations) in the inverse pole figure image yielded the same result for several spot checks within different grains. The observed misorientation angle was 90 °. This result pointed to the presence of a pseudo-symmetry. The OIM software allows compensating for such pseudo-symmetries by an implemented clean-up procedure. The execution of this procedure corrects the image data straightening out the inverse pole figure image. In addition, a single step grain dilation cleanup in the OIM software can help to further smooth the inverse pole figure image especially near the grain boundaries (Figure 4c).

Conclusion

The procedure presented allows for electron backscatter diffraction measurements at cross sections on thin foils such as lithium ion battery cathodes to access the crystallographic microstructure of the materials the foil consist of. In the model case described it was possible to resolve the isotrop orientation distribution within NMC agglomerates used in mixed NMC / LMO (1:1) LIB cathodes.

References:

[1] A. Schoppa et al. Electric Drives Production Conference (EDPC), 2013 3rd International, 2013, pp. 1–5.

[2] D. Schuller, T. Grubesa, T. Schubert, R. Löffler, T. Bernthaler, D. Goll, G. Schneider, 7th International Conference On Magnetism And Metallurgy (WMM16), Rom, Italien, 13.-15. Juni 2016, pp. 431-441.

[3] D. Hohs, D.Schuller, T. Grubesa, T. Schubert, R. Löffler, T. Bernthaler, D. Goll, G. Schneider, 50. Metallographietagung, Berlin, Deutschland, 21–23. September 2016.

[4] A. J. Wilkinson et al., Materials Today 15, 2012, pp. 366–376.

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