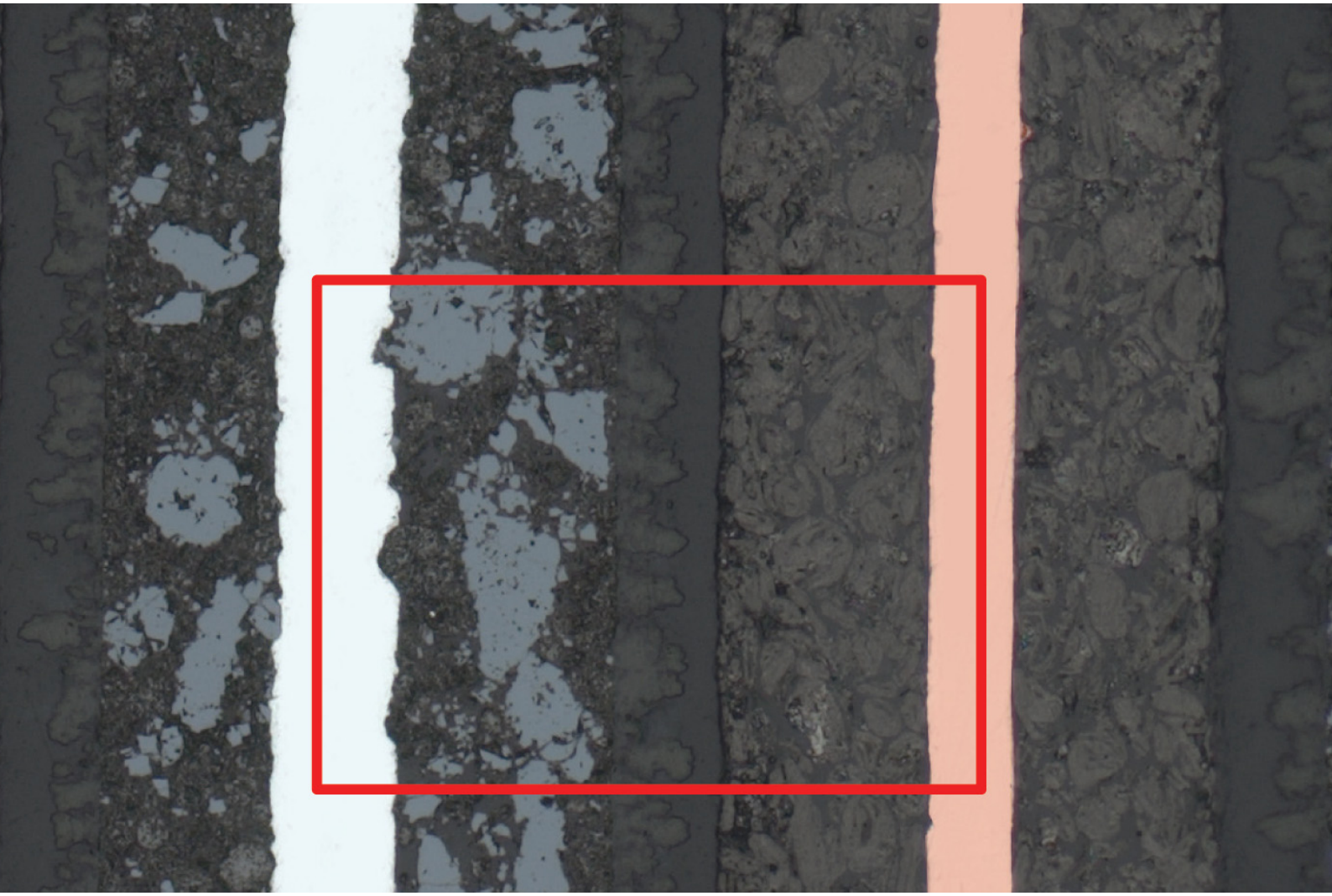
White Paper



Fast Structural and Compositional Analysis of Aged Li-Ion Batteries with "Shuttle & Find"

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Fast Structural and Compositional Analysis of Aged Li-Ion Batteries with "Shuttle & Find"

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Introduction

The development of efficient storage technologies for electrical energy plays an important role in the progress of electromobility. They will help to reduce emissions and allow efficient usage of renewable energy as they are implemented in smart grids. Li-ion batteries are attractive candidates for these applications since they can provide high energy and power densities with the latest developments.

The performance of a Li-ion battery is determined by its energy density, battery power and capacity, charge and discharge rates as well as its lifetime. The functionality, schematically shown in Fig. 1, is based on the change of active materials due to diffusion processes [1,2]. Hence, microstructural parameters of the materials have a strong influence on the battery performance next to geometrical aspects like design and the components of the cell or the thickness of the electrodes or physical properties like diffusion coefficient, thermal capacity and expansion, volume change or resistance. Within the microstructure of the battery material, the size and shape of the grains, surface area and volume fraction of phases are the most important parameters.

Therefore, microstructure characterization of Li-ion batteries is essential to achieve a deeper understanding of the battery performance. It makes it possible to analyze relations between cell design and battery performance. The extraction of quantitative microstructure data then allows the development of physical models. Furthermore, the visualization of microscopic phenomena due to aging history is very important for reliability analysis, which helps to prevent critical accidents caused by short circuit failures.

Correlative Light and Electron Microscopy (CLEM) is essential for this application since it allows combining defect identification and the optical properties of Light Microscopy (LM) with detailed structural analysis in the Scanning Electron Microscope (SEM). While LM gives a fast overview of morphology, optical appearance of phases and damaging effects, SEM images deliver information about particle size, shape and chemical composition within the same region. This enables multimodal data extraction from the micro-structural context. Therefore, CLEM is essential for a complete characterization of battery materials.

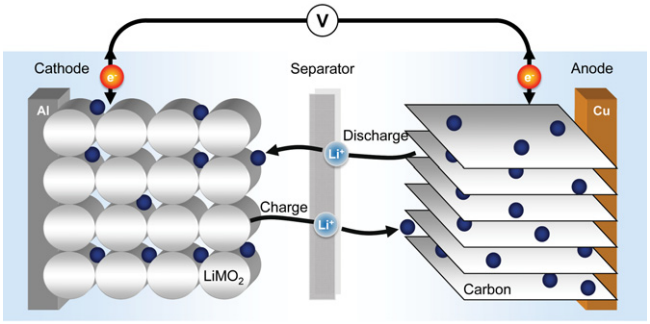

Figure 1
Schematic setup of a Li-ion battery. The functional principle is based on diffusion of Li-ions through the separator between the two active materials of cathode and anode.

Sample Preparation and Imaging

A cylindrical standard Li-Ion consumer cell (Type 18650) was aged for 50 days with 4.2 V constant voltage at 65° C. Then it was discharged and opened in a glove box under argon atmosphere. After removal of the electrolyte the sample was embedded in epoxy resin and prepared in accordance with high-end materialographic sample preparation protocols. Thus, the resulting sample is a polished cross-section of the battery.

The sample was placed into the "Specimen Holder CorrMic Mat Universal A" which is a universal materials sample holder especially designed for CLEM by Carl Zeiss. This holder can be used in LM as well as SEM so that the sample is fixed in the holder during the whole imaging process. The holder has three fiducial markers which define a coordinate system that can be calibrated very fast and semi-automatically in the Shuttle & Find module of the AxioVision Software.

LM imaging of the sample was performed in an Axio Imager.Z2 (Carl Zeiss Microscopy GmbH), a compound light microscope for materials analysis. 20 x and 50 x objectives (EC Epiplan-Neofluar 20 x / 0.5 HD DIC and 50 x / 0.8 HD DIC) as well as an AxioCam HR camera were used for imaging. With this setup brightfield images in the reflected light mode were obtained with and without polarization contrast. Regions of interest (ROI) for further investigation were defined in the LM images with the Shuttle & Find software module.
Then the sample was transferred to a SUPRA® 40 VP FE-SEM (Carl Zeiss Microscopy GmbH) controlled by the same software. After the semi-automatic calibration of the sample-holder and subsequent fine calibration the ROIs in the LM images were relocated within a few seconds at a precision below 5 µm. SEM imaging was done at an acceleration voltage of 15 kV with the 4 quadrant angular selective backscattered electron (AsB®) detector.

Subsequently, an energy dispersive X-ray spectroscopy (EDS) mapping of the same area was performed with the SEM and a Bruker Quantax 200 XFlash-Detector with 133 eV spectroscopic resolution.

Results

A brightfield LM image of the layer structure within an aged Li-ion battery is shown in Fig. 2. Cathode and anode are alternately layered, each with a separator in-between. The cathode consists of an aluminum collector coated by active lithium metal oxide material. The anode has a copper collector with graphite as active material. Aging effects can be observed within the separator, showing a layer growing

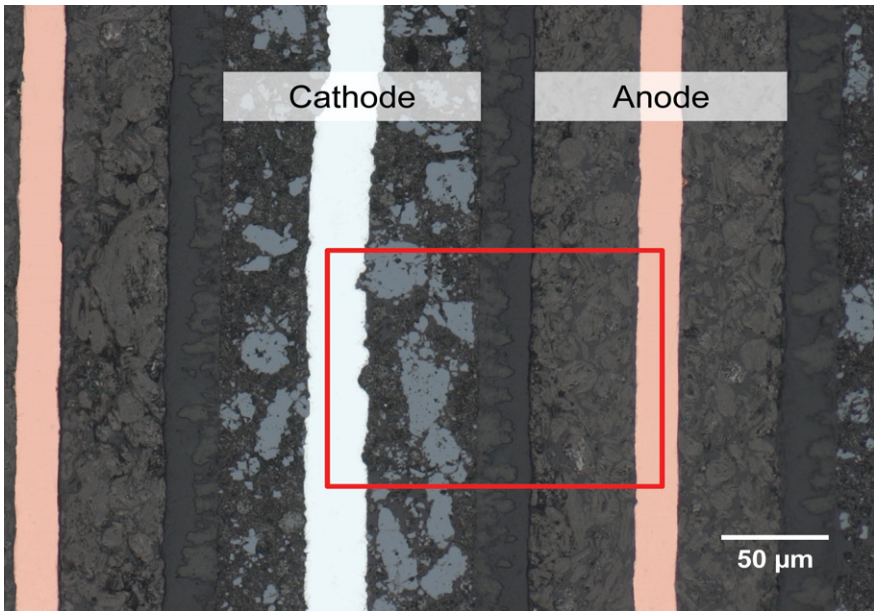

Figure 2
Brightfield LM overview within the layer structure of an aged Li-ion battery.

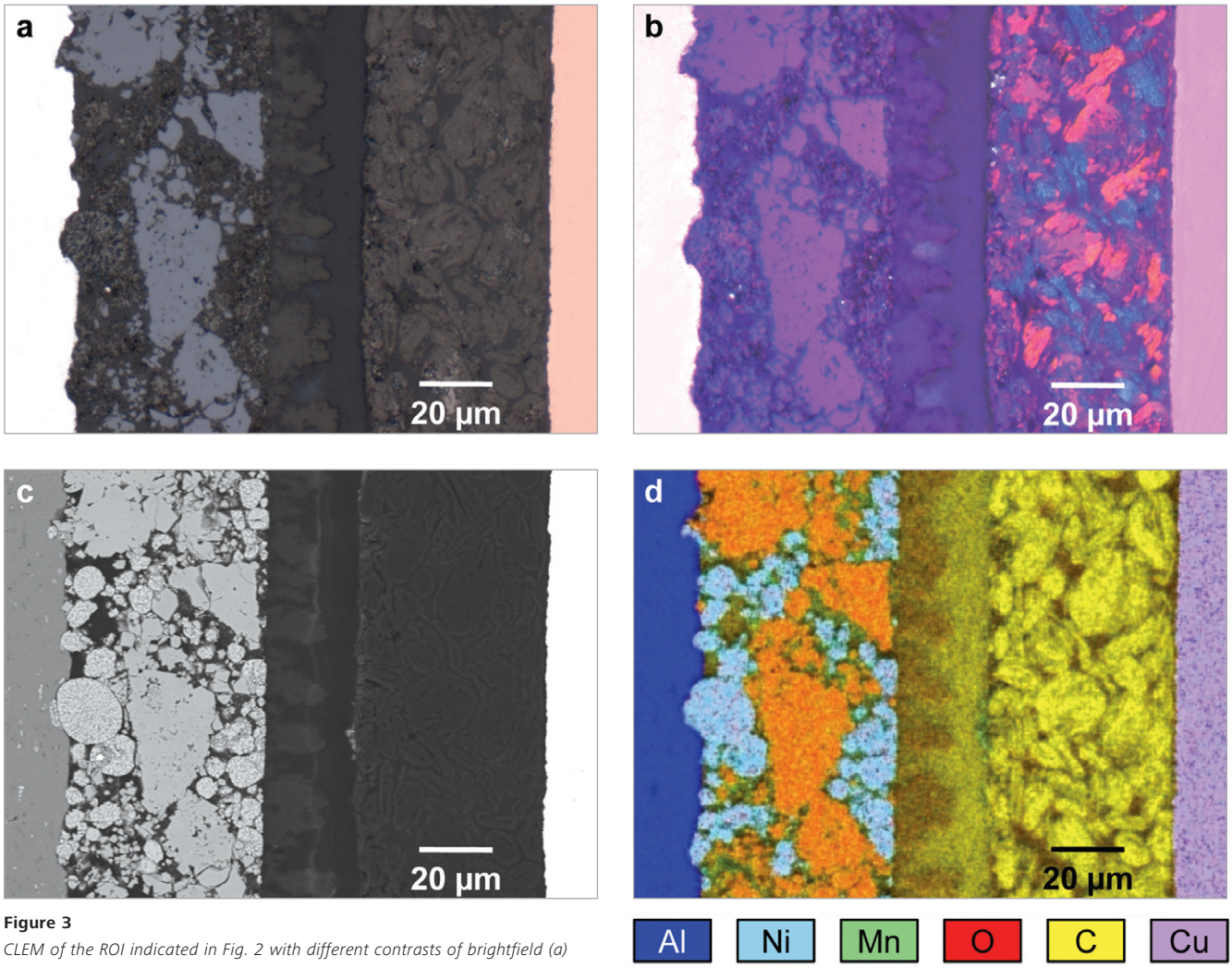

Figure 3
CLEM of the ROI indicated in Fig. 2 with different contrasts of brightfield (a) and polarized light (b) in LM as well as BSE signal (c) and EDS mapping (d) in SEM.

from the cathode into the separator. A ROI (red rectangle) is chosen containing a complete unit cell of the battery with aging effects in the separator.

The selected ROI is displayed in more detail in Fig. 3: Whereas Fig. 3a is a brightfield LM image at a higher magnification, Fig. 3b shows the polarization contrast in LM. Fig. 3c is a backscattered electron (BSE) image of the same area in the SEM and Fig. 3d pictures an EDS mapping with the distribution of the 6 chemical elements of highest concentration. These contrasts complement each other; only the combination allows a detailed microstructural analysis of this battery cell. Brightfield LM gives a good overview of the geometry and morphology within the electrodes as well as of the aging effects within the separator.

In polarized LM different phase orientations of the graphite within the anode can be observed, whereas the BSE image makes the detailed grain structures within the cathode material visible. This contrast also allows segmentation of the cathode using image analysis so that grain size and distribution can be quantified. The additional EDS mapping completes the correlative imaging and provides explicit qualitative information on the chemical elements. Aluminum and copper collectors, graphite (carbon) anode and organic separator foil can clearly be identified. Due to physical limitations lithium cannot be detected in EDS directly. However, based on the functional principle it can be worked out qualitatively that the sharply edged grains within the cathode active material are composed of $LiMn_2O_4$ whereas the roundly shaped grains consist of $LiNi_xCo_yO_2$ [3,4].

Conclusion and Outlook

The Shuttle & Find interface for CLEM enables productivity in structural analysis of Li-ion batteries due to a fast, reliable and precise workflow. The workflow is sped up significantly as the process of searching the same ROI in both microscopy modes is now automated. Therefore, failures can be identified quickly and the development cycle time can be reduced. This leads to a considerable increase of sample throughput. The solution also enables new possibilities especially for quantitative image data analysis from one and the same ROI in different microscopes, which can now be carried out systematically.

As Shuttle & Find is compatible with CrossBeam® workstations, the sample can also be transferred there for further detailed investigations. Then specific structures, e.g. migrations, can be selected and 3D inspection can be performed by Focused Ion Beam (FIB) milling. Furthermore, it is also possible to fabricate a thin lamella from the selected structure for high resolution Transmission Electron Microscopy (TEM) imaging. This enables Electron Energy Loss Spectroscopy (EELS) analysis by which the local distribution of Lithium can be detected directly.

References

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