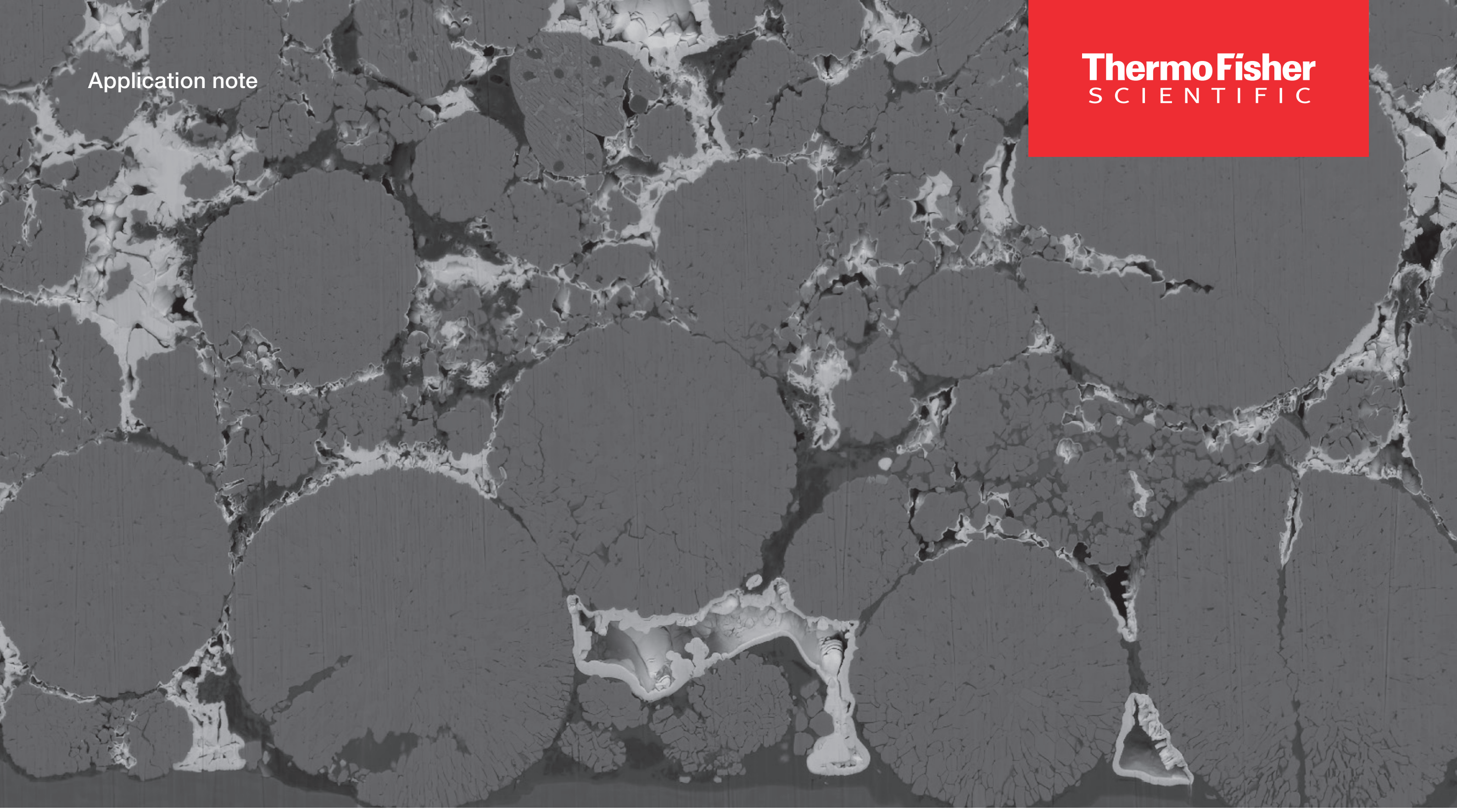
Application note



Kintsugi imaging of battery electrodes with plasma FIB-SEM

Authors

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The Helios Hydra DualBeam.

Introduction

The meso-structure of the porous electrodes in lithium ion batteries strongly influences their performance.[1] Accurate imaging of the phase distribution in these electrodes could be used to construct simulations that help us better understand this relationship.[2] However, imaging of the nanoscale features in these components is challenging. While scanning electron microscopy (SEM) is able to achieve the required resolution, it has difficulties imaging porous media. This is because the flat imaging planes prepared using focused ion beam (FIB) milling will intersect with the pores, making the images collected inside the walls of the pores hard to interpret. To help resolve this issue, porous media can be infiltrated with resin prior to imaging,[3] but both the nanoscale porosity of battery materials and their chemical similarity to resins make this approach poorly suited for most electrodes.

In this application note, a technique is demonstrated which uses in situ infiltration of platinum to fill the pores in order to enhance their contrast during imaging. As it is reminiscent of the Japanese art of repairing cracked ceramics with precious metals, this technique has come to be known as the kintsugi method.[4] This technique was applied to a conventional porous cathode and the resulting images were segmented using a U-Net convolutional machine learning (ML) trainable neural networks.[5] It was found that while some cracks in the cathode particles were filled with the carbon binder phase, others were empty, which has implications for the rate performance of the cell. Energy-dispersive X-ray (EDX) spectroscopy was used to validate the phase distribution determined with image analysis, and also suggested a graded distribution of the binder relative to the carbon additive.

As the equipment required to use the kintsugi method is commonly available in major research facilities, we hope that it will be rapidly adopted to improve the imaging of electrode materials and porous media in general.

Methods and results

Kintsugi imaging originates from a method used to suppress curtaining effects during plasma FIB (PFIB) serial sectioning of metals with pores and cracks,[6] as well as SEM-assisted platinum deposition of nano-porous matter.[7] Figure 1 shows experimental details for cross-sectioning and spin milling.

The main components of the kintsugi imaging method

Bowl restored using the traditional art of kintsugi.

- Fill the pores with platinium and increase the contrast of material constituents
- Increase segmentation robustness and reduce the ML training effort
- Auto Slice & View 5 Software and AutoScript automation (cross-section or planar)
- Large area Pt deposition (SEM- and/or PFIB-assisted)
- PFIB large area polishing
- Multi-detector SEM acquisition
- Avizo machine learning segmentation approach

Details of the ML-trainable segmentation approach are described in Avizo manual.

A fifth-generation Thermo Scientific™ Helios Hydra™ DualBeam was used for these experiments, which features a fast switching plasma ion source that can swap between Xe^+, O^+, Ar, and N. The system was equipped with a piezoelectric stage that allows for negative stage tilts to -38°, which is critical for planar spin milling of sub-mm^2 areas.[8-9]

Image processing was performed in Thermo Scientific™ Avizo™ Software (Figure 2) using an AI-powered image segmentation algorithm. The annotations used to train the algorithm were also created in Avizo Software, taking advantage of automatic segmentation to accelerate the process along with manual finetuning of the data. In the final annotation (or ground truth), the different phases of the sample were separated into: active material (red), pores (dark blue), CBD (light blue), and support layer (green), if present.

These annotations were then used to train a machine learning model using the Avizo Deep Learning Segmentation module. The model was then applied to other images, which were segmented automatically using the Avizo Deep Learning Prediction module.

Avizo Software enables users to accelerate their image data processing, segmentation, and classification using traditional image processing tool along with advanced machine- and deep-learning approaches.

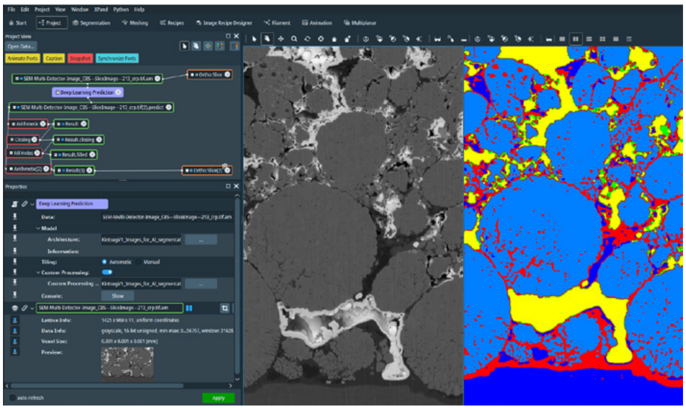

Figure 2. Avizo Software user interface showing the data processing workflow.

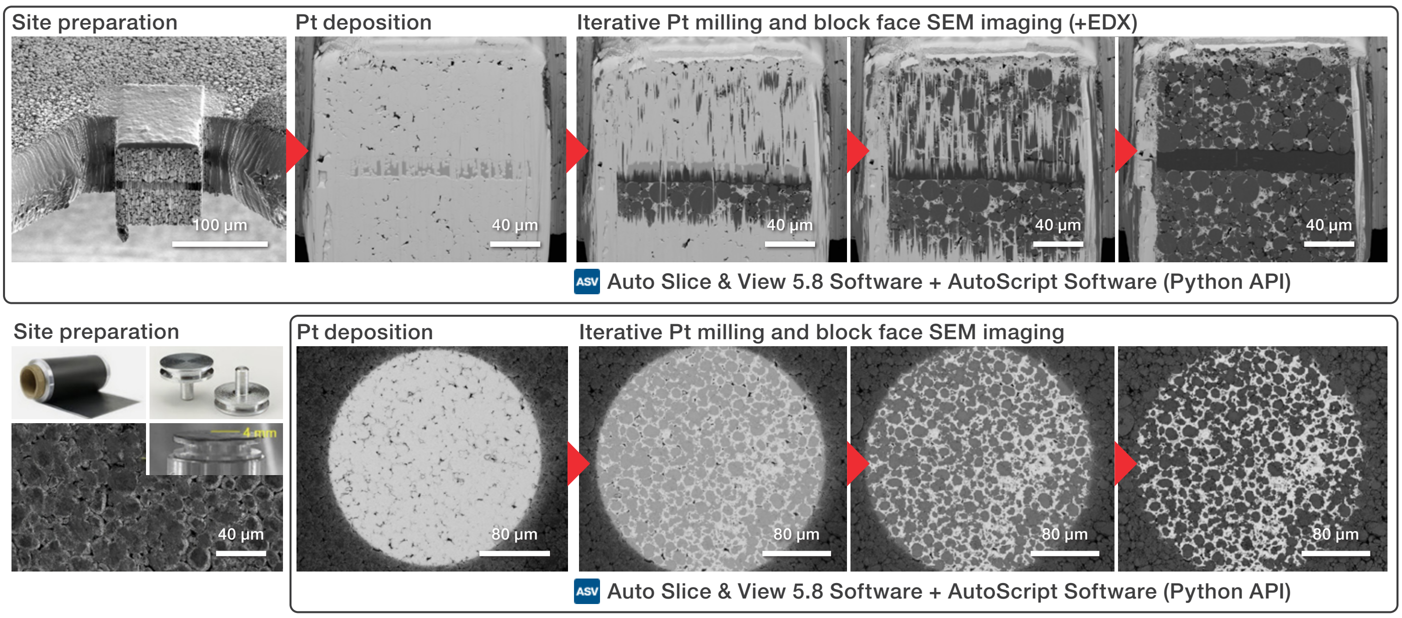

Figure 3. Experimental procedure for kintsugi imaging with the Helios Hydra DualBeam. Cross-section configuration (top), and spin milling (bottom).

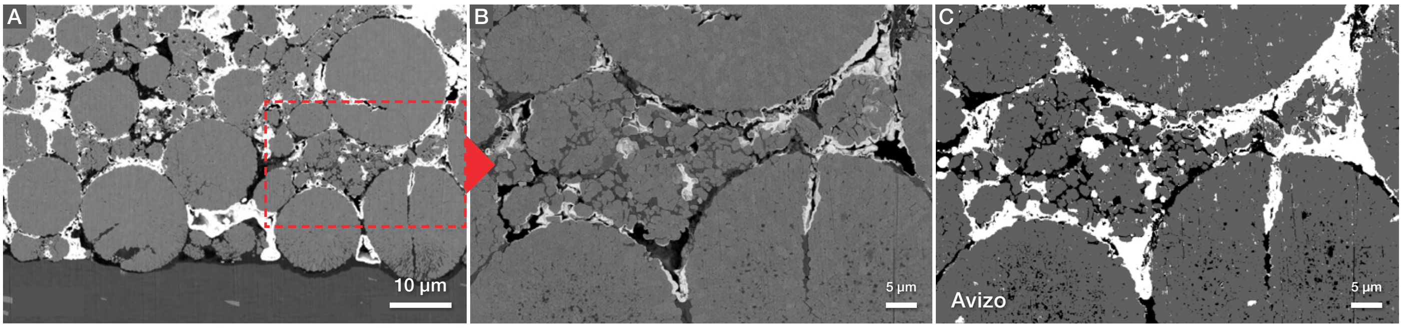

Figure 3. A) SEM-BSE cross section collected with a CBS detector. B) Close-up SEM-BSE cross section showing microstructural details. C) Deep learning segmentation results applied to the SEM cross section, showing: active material (grey), pores (white), CBD (black).

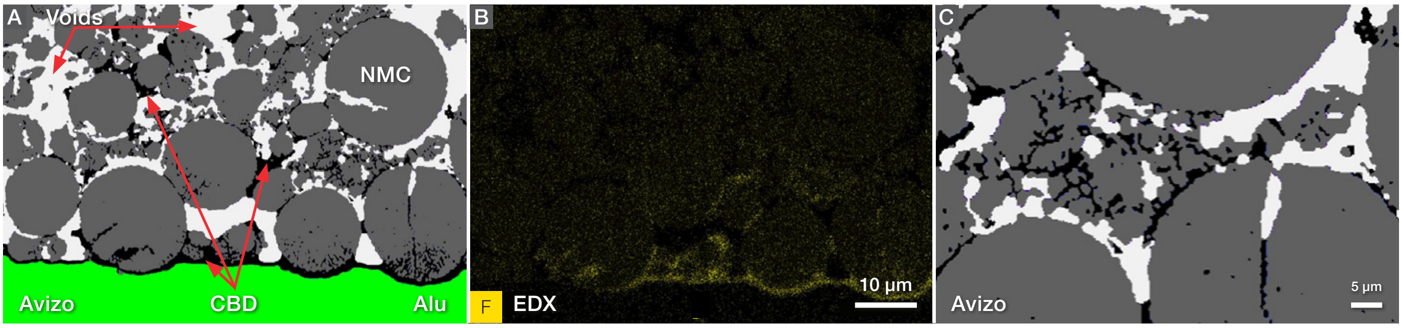

Figure 4. A) Deep learning segmentation results applied to the SEM cross section, showing: active material (grey), pores (white), and CBD (black), and the electric current collector (green). C) EDX maps shows distribution of fluorine. C) Close-up image of deep learning segmentation from A, that corresponds to high resolution segmentation results from Figure 3C.

Avizo Software provides a rich pre- and post-processing toolbox that supplements manual and supervised segmentation. The result is enhanced annotation that can be used to train the prediction module that performs the remaining segmentation. The trained model can be integrated into a workflow or recipe to automate all processing, segmentation, and measurement tasks.

The deep learning training modules feature a highly configurable tool for training models using state-of-the-art architectures, such as Unet with Resnet or VGG backbones, data augmentation, as well as a selection of loss and metric functions. The training can occur from scratch (random weights) or from pre-trained weights. It is monitored in real time using TensorBoard to track metrics such as loss and accuracy, or to visualize the model's architecture.

Advanced users can customize both the Deep Learning Training and Prediction modules through a plugin system, allowing for the definition of custom model architectures, loss, or metric functions. Predictions can also be customized from pre- to post-prediction processing.

Conclusions

This application note demonstrates a novel approach for enhancing the quality of PFIB-SEM-derived images of porous media. Kintsugi imaging utilizes *in-situ* infiltration of platinum (or other metal-deposition precursors) into the pores, significantly reducing the ambiguity of different materials on the imaging plane and on the back wall of pores.

Imaging and machine-learning-based segmentation was performed on a cross-section of a porous lithium-ion battery cathode. The segmented data provides direct insight for qualitative interpretation of electrode structure performance. This method is also compatible with PFIB spin milling, and could possibly be further enhanced by standard PFIB-SEM serial-sectioning techniques used to generate 3D volumes. Additionally, while this method has previously only been applied semi-automatically, improvements to Thermo Scientific™ Auto Slice & View™ Software now allow for custom Python programming in Thermo Scientific™ Autoscript™ Software, which can be used to automate the entire procedure.

Acknowledgements

Sample courtesy of Dr. Philipp Müller, BASF SE, Ludwigshafen am Rhein, Germany.

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