
# High-quality cross polishing of Li-ion battery cathodes with the CleanMill Broad Ion Beam System

## Introduction

It is often said that the main challenge of high-quality scanning electron microscopy (SEM) is sample preparation. Specifically, material characterization is heavily influenced by the preparation of the surface/cross-section, including polishing. For instance, metallographic characterization with SEM requires a high-quality, flat, mirror surface. Historically, such samples would be prepared by specialized mounting, mechanical grinding, and fine polishing using ceramic slurries of decreasing particle size. This process could be imperfect, introducing surface damage such as an amorphous layer and/or dislocations. Removal of the damaged surface layer was then achieved by the additional use of finer slurries, chemical polishing, or ion polishing.

To achieve a high-quality sample surface, ions with an energy as low as 0.1 kV can be used to sputter the damage away; this approach has been proven to leave a damage layer much smaller than traditional mechanical polishing. In this application note, an argon ($Ar^+$) broad ion beam (BIB) is used to prepare a large area cross-section for SEM characterization. The sample is inclined towards the beam to achieve a “glancing angle” near 90 degrees (the sample is typically inclined between 0 to 10 degrees in ion polishing methods).

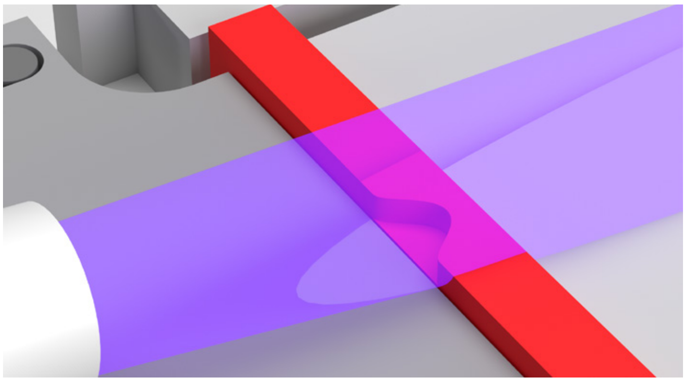
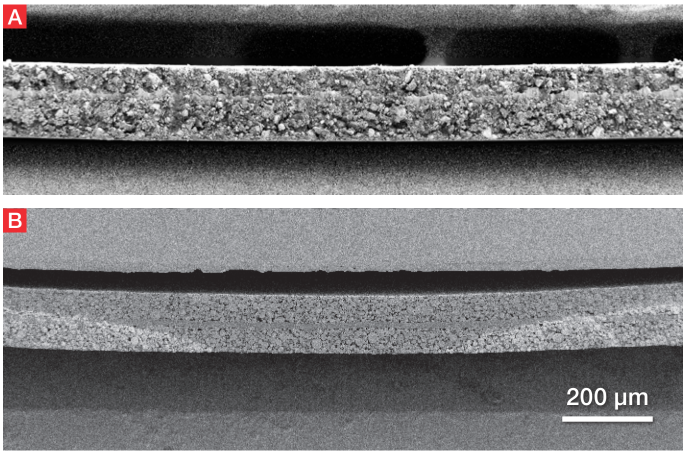


Figure 1. Schematic of the CleanMill Broad Ion Beam System preparing a cross-section.

As with a focused ion beam (FIB), the quality of the surface and the introduced ion damage is dependent upon:

- The energy of ions
- The ion current
- The angle of incidence (glancing angle)




Figures 2. Li-NMC cathode before (A) and after (B) broad ion beam cross-polishing.

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## SEM of Li-ion battery materials

SEM characterization is often applied to Li-ion battery materials in order to verify the quality and composition of the resulting cathodes and anodes. As with most SEM analyses, results are highly dependent on the quality of the sample, particularly the surface. With high-quality surface/cross-section preparation, it is possible to determine a range of different physical attributes for the cathode layer, including:

- Layer thickness
- Particle size
- Particle crystallography
- Particle cracking
- Porosity
- And more

Figure 3. The CleanMill Broad Ion Beam System with the CleanConnect Sample Transfer System.

## CleanMill Broad Ion Beam System

The Thermo Scientific™ CleanMill™ Broad Ion Beam System is a cross-polisher (CP) designed for the rapid preparation of high-quality surfaces and cross-sections for a variety of materials. Beyond sample surface quality, it is also important for many battery samples to be protected from air and moisture. Litheated cathode or anode materials, for instance, will often react with ambient oxygen or water, complicating accurate characterization of the material. The CleanMill System can be combined with the Thermo Scientific™ CleanConnect™ Sample Transfer System, creating a full inert-gas sample-transfer (IGST) workflow that protects these sensitive materials from ambient conditions (with an argon environment), generating higher quality results.

In this application note, cross-sections of a cycled $LiMnNiCoO_2$ (Li-NMC) cathode were prepared using the CleanMill BIB System with and without the IGST workflow in order to exemplify the protection provided by the CleanConnect System.

Figure 4 shows a cross section of a Li-NMC cathode sample that was introduced into the CleanMill BIB System from an argon filled glovebox using the CleanConnect System.

The sample was processed using 16 kV $Ar^+$ ions and a glancing angle of 88.7° (sample inclined 1.3°); a 40° rocking polish was applied for 90 minutes at room temperature. As seen in Figure 2B and Figure 4, more than 500 µm of the full cathode layer could be rapidly processed into a high-quality surface.

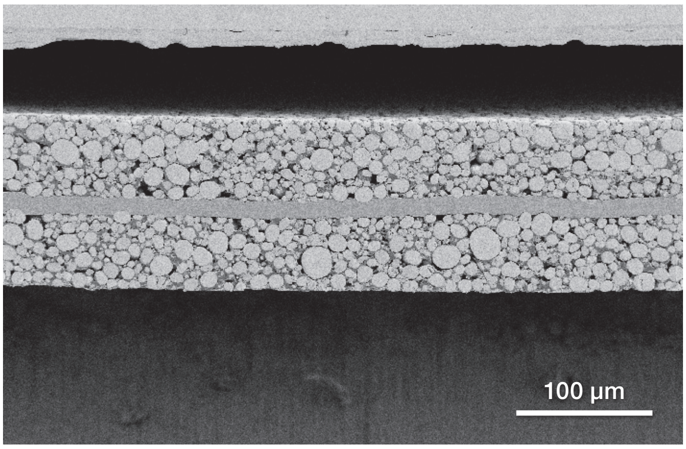



**Figure 4. Backscattered electron image acquired in the Apreo 2 SEM at 2 keV with a horizontal field width of 500 µm.**

Once the cross-section was complete, the sample was transferred using the CleanConnect System to a Thermo Scientific™ Apreo™ 2 Scanning Electron Microscope for ultra-high-resolution imaging. One benefit of the CleanConnect System is that it can be backfilled with argon directly at the CleanMill System or at the Apreo 2 SEM. A positive pressure of inert gas inside the CleanConnect System provides an extended time for transfer, if needed. Additionally, it allows you to return for further BIB processing under argon gas without a vacuum transfer,  avoiding possible air contamination. (All vacuums are inherently poor if active pumping is not applied.)

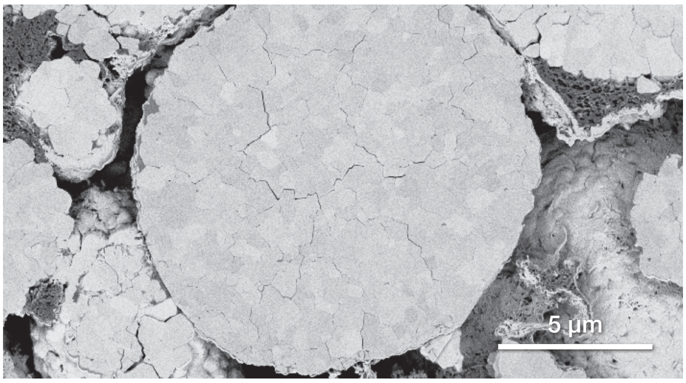
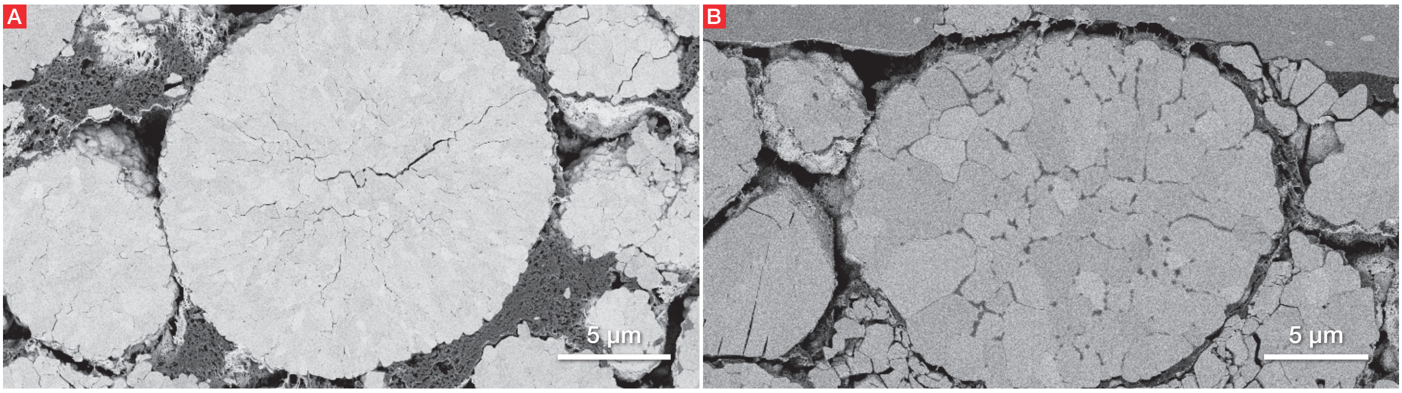



**Figure 5. Higher magnification BSE image reveals particle cracking, which was likely caused by the calendaring step during fabrication.**

Another cycled Li-NMC cathode sample was processed in the CleanMill System using the same processing conditions described previously. This time, the sample was transferred to the Apreo 2 SEM without the air protection of the CleanConnect System. As shown in Figure 6B, darkening on the grain boundaries within the NMC particle reveals that the sample has been contaminated due to air exposure.




Figures 6. 2 keV BSE images of a Li-NMC oxide acquired in the Apreo 2 SEM. A) Image of a sample that was transferred to the Apreo 2 SEM with the CleanConnect System. B) Image of a sample that was transferred to the Apreo 2 SEM without air protection.

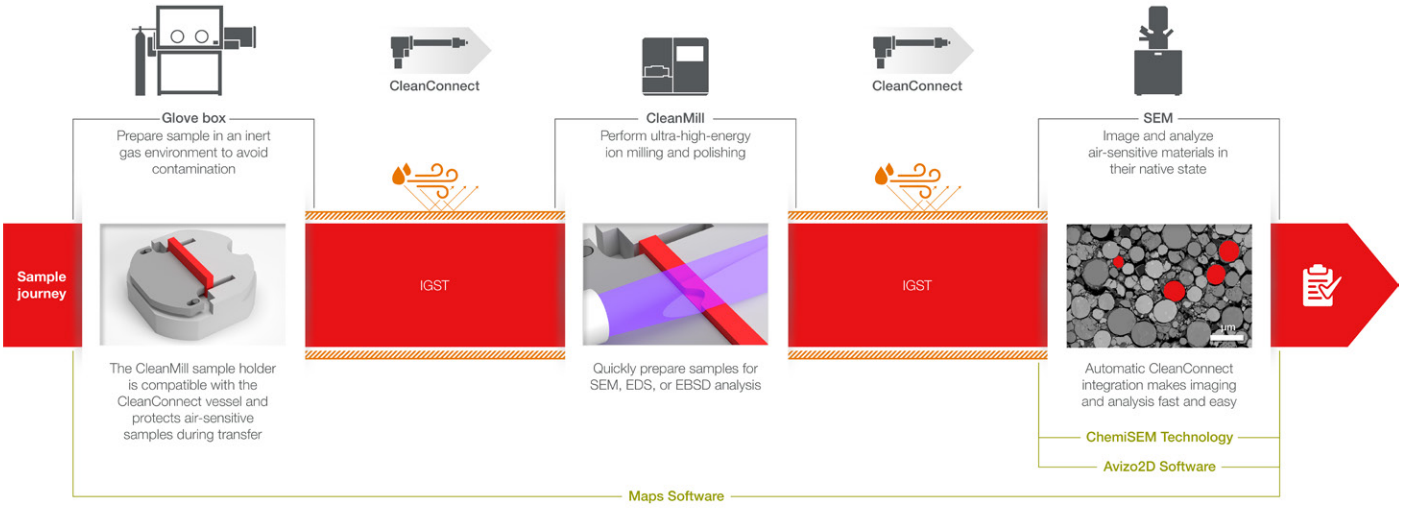



Figure 7. The Thermo Scientific IGST Workflow.

## Conclusions

The Thermo Scientific CleanMill System allows you to rapidly prepare high-quality surface and cross-section samples of cathode materials, characterizing a variety of attributes including layer thickness, particle size, porosity, and even particle cracking. When combined with the Thermo Scientific IGST Workflow and the CleanConnect Sample Transfer System, accurate SEM characterization is ensured for air-sensitive samples.


### Acknowledgements

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Learn more at **thermofisher.com/cleanmill**