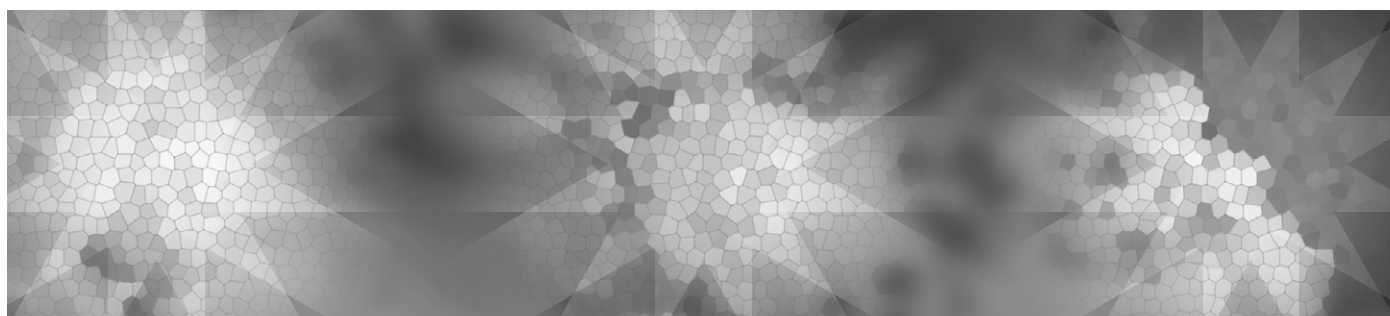


Large area automated sample preparation for batteries

Spin milling using plasma FIB-SEM

Author

Bartłomiej Winiarski, Zhao Liu, Brandon B. Van Leer, Mikhail Dutka, Herman Lemmens



Introduction

In the past decade, the rapid growth of the consumer electronics and electric vehicle markets has focused significant attention to Li-ion batteries. Currently, two important industries, the energy and automobile industries, are involved in intensive research to improve current Li-ion battery technology and develop technology beyond Li-ion batteries [1–3]. As the energy revolution gathers pace, more advanced batteries will be needed for energy storage in order to equalize the fluctuating power production of photovoltaic solar systems or wind turbines. The trend for electromobility also creates a lot of pressure to advance battery research.

Higher energy density and better safety is achieved by a fundamental understanding of battery materials' structures and chemistry throughout the battery life cycle. In order to fully understand battery structures, multimodal information via different characterization techniques (e.g., SEM, EBSD, EDS, Raman, SIMS) is collected at multiple length scales using a correlative approach in 2D and 3D [4–6]. Although 3D analysis can provide more comprehensive structural information than 2D analysis, 3D imaging analysis usually requires a considerable amount of effort involving complex data collection and analysis procedures. In most cases, 2D characterization from a well-prepared surface area of battery material can deliver substantial quantitative and statistical information, such as phase distribution, feature size and shape, defects, and grain orientations, which are all commonly employed in batteries characterizations.

2D area preparation techniques: cross-sectional polishing vs. plasma FIB-SEM

In order to collect high-quality 2D information, an effective 2D area preparation method is essential. Broad ion beam (BIB) polishing is a well-accepted method for large 2D surface area preparation in the battery industry. An optical microscope is used for sample alignment and can prepare surface areas up to mm² with site preparation time (SPT) of a couple of hours via Ar ion beam polishing. Another method is a focused ion beam microscope (FIB) with integrated SEM (FIB-SEM). The introduction of plasma FIB-SEM (PFIB-SEM) opened up fast access to cross-sections of hundreds of microns wide and deep, allowing collection of multimodal information with nanometer resolution. Compared to BIB polishing, PFIB-SEM performs both milling and imaging at the same location, which reduces sample transfer steps and provides high accuracy for locating regions of interest on the sample. In this current study, a new large area (≤ 1 mm²) or large volume acquisition technique, namely plasma FIB spin milling (PFIB-SM), is introduced and shown to polish areas of a Li-ion battery sample comparable to what can be achieved in the BIB [7].

Experimental method and results

As an example, a generic NMC cathode from a Li-ion battery cell was mounted on a regular SEM flat stub and spin mill polished in a PFIB-SEM via focused ion beam using 30 kV high tension and 60 nA (Xe^+) and 120 nA (Ar^+) currents, where areas of 500 μm in diameter were prepared within dozens of minutes. Figure 1 illustrates the experimental setup. The SEM stub with specimen is mounted on a spin mill post positioned in the center of the stage rotation axis, where the plasma ion beam is positioned at the glancing angle of 0.5–1 degree to the sample surface. During the PFIB-SM process, the stage rotates to several stationary positions at which the ion beam mills the sample. The FIB polishes superficial layers of the specimen surface and requires only minimum SPT (~50 min - Xe and ~35 min - Ar). The PFIB-SM technique allows collection of data from on-axis of the SEM stub (Figure 1 (a)) and off-axis location via compucentric stage rotation (Figure 1 (b)), enabling access to areas of about 50 mm^2 . The geometry of EDS and EBSD measurements on the prepared sample are shown in Figure 1 (c)–(d). Figures 2 and 3 show the PFIB-SM results. The spin milling process results in a flower-like pattern on the sample surface. SEM images and EBSD maps revealing the high-quality flat surface prepared via FIB-SM technique are presented in Figures 2 (d)–(e) and 3. Argon PFIB-SM at higher beam currents reduces the site preparation time by about 30%, while keeping similar quality of the microstructure as obtained by Xe^+ beam (as indicated by EBSD data in Fig. 3). Such a well-prepared, large, 2D area with short SPT enables multimodal information collection with statistics for electrode structural-performance analysis.

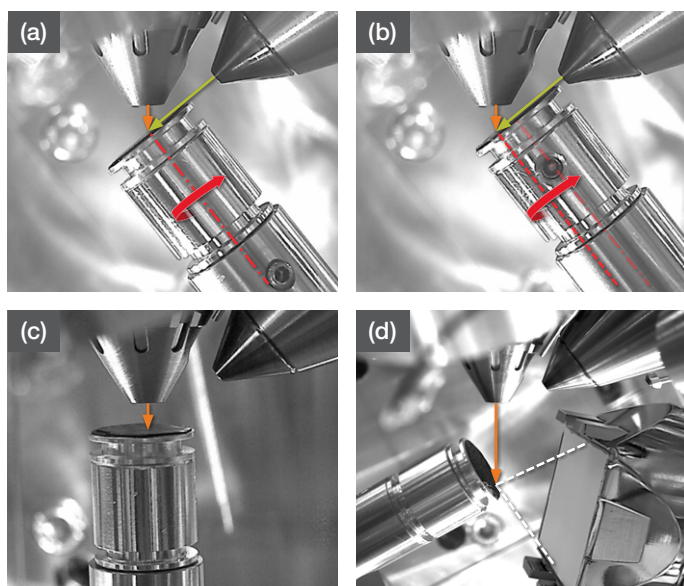


Figure 1. The experimental setup of PFIB spin milling. (a) Stage on-axis rotation and (b) off-axis compucentric rotation; (c) SEM/EDS data collection and (d) EBSD data collection geometries.

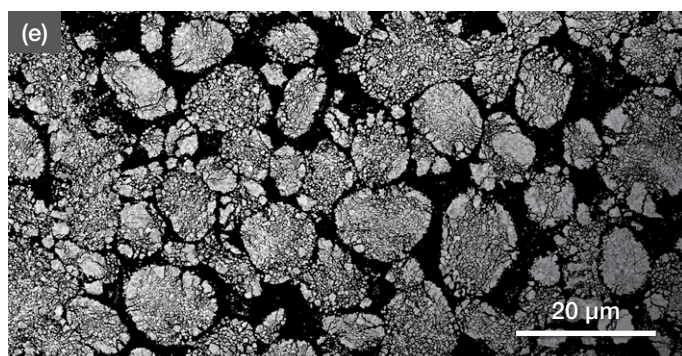
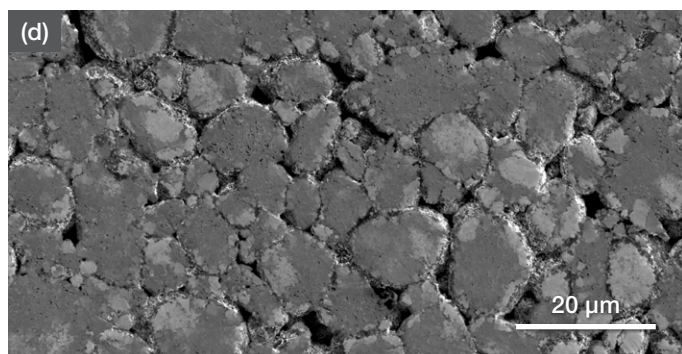
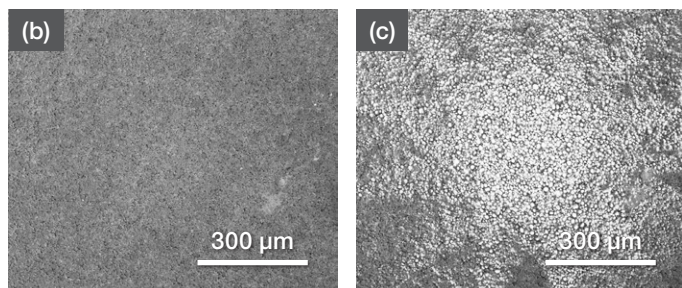
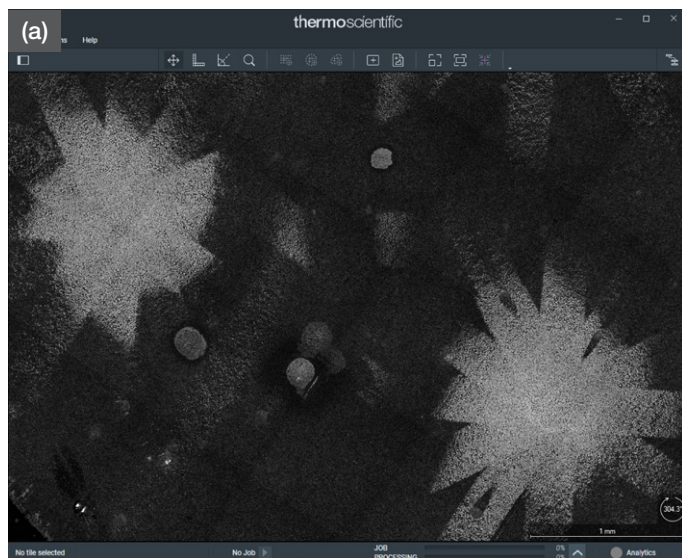


Figure 2. Xe PFIB spin milling results. (a) SEM data is collected in a Thermo Scientific Maps™ Software project; the cathode before (ETD-BSE) (b) and after spin milling (ETD-BSE) (c) at 30 keV, 60 nA, 0.5° glancing angle, total data collection time <60 min; (d) SEM ETD-SE 2keV, 0.8nA; (e) SEM CBS 5 keV, 1.6 nA.

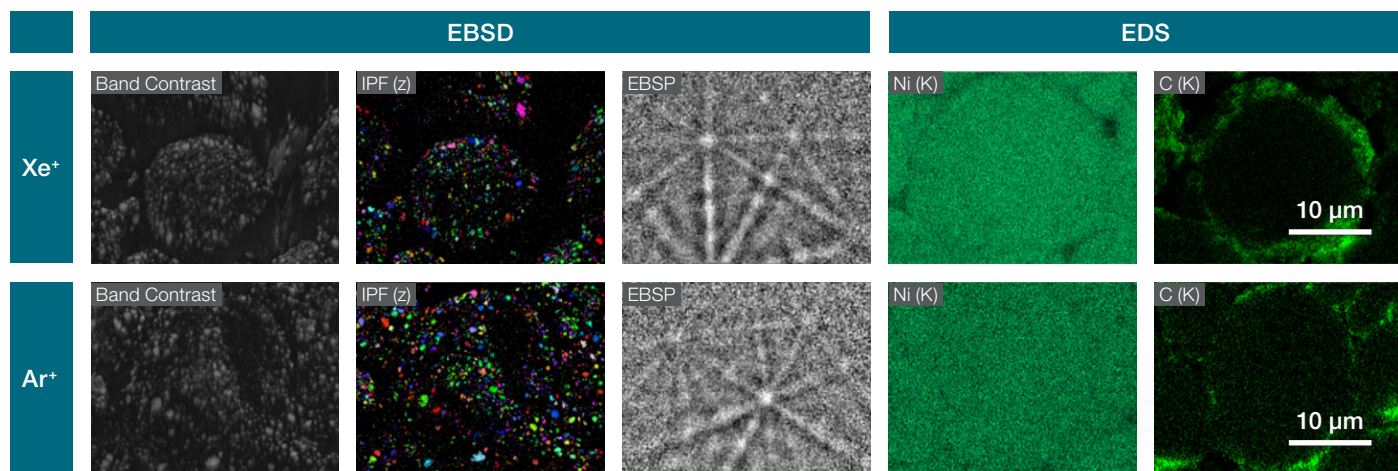


Figure 3. Comparison results of EBSD (left) and EDS (right) after xenon (top) and argon (bottom) PFIB spin milling on NMC cathode.

Conclusion

This work presents the application of the PFIB-SM method for battery research. It is a powerful technique that is well suited for rapid polishing of large area surfaces and allows acquisition of multimodal information. Argon at higher beam currents reduces the site preparation time by about 30%, while keeping similar quality of the microstructure as obtained by Xe⁺ beam. Furthermore, the latest Thermo Scientific™ Helios™ 5 Hydra PFIB features the capability for fast switching between different primary ions (Xe⁺, Ar⁺, O⁺, N⁺), thus giving even more control for surface preparation strategies based on different types of battery material needs.

Keywords

Plasma FIB-SEM, spin milling, lithium-ion battery, cathode

Acknowledgements

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

Reference

- [1] J Nanda, C Wang, et al. MRS Bulletin 43(10):740-745.
- [2] G Blomgren. Journal of The Electrochemical Society 164(1): A5019-A5025.
- [3] M Liu, P Zhang at al. Nature Communications, (2019) 10:3917.
- [4] R Moroni, M Börner at al. Scientific Reports 2016; 6: 30109.
- [5] B Winiarski, G Pyka, at al. Microscopy and Microanalysis, Nano Supp, Dec 2017.
- [6] B Winiarski, G Pyka, at al. Microscopy and Microanalysis 24(S1) 2018:366-367.
- [7] B Winiarski, C Rue, at al. Microscopy and Microanalysis 25(S2) 2019:350-351.

Find out more at thermofisher.com/HeliosPFIB