Electrode Particle Degradation Characterization

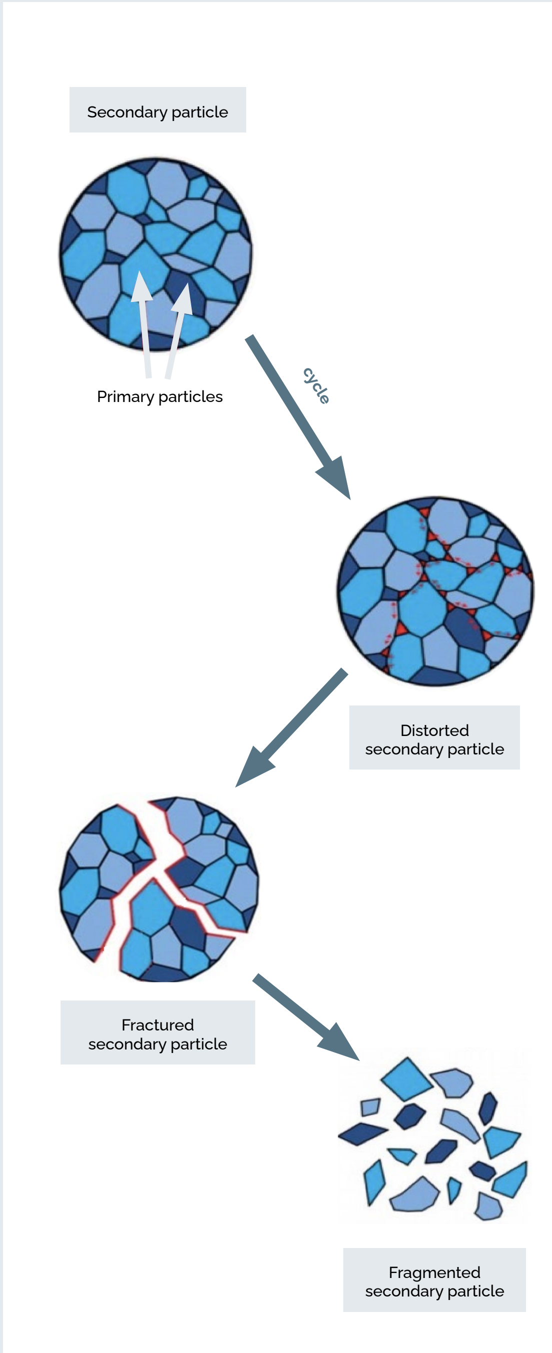
Introduction

Lithium-ion batteries have revolutionized the world of portable electronics and electric vehicles, providing high energy density and long cycle life. However, as the demand for these power sources continues to grow, so does the urgency to understand and mitigate their failure mechanisms. Among the many factors that contribute to lithium-ion battery failure, electrode particle degradation stands out as a crucial concern.

Electrode particle degradation is the process of physical and chemical changes that occur within the active materials of the battery's positive and negative electrodes. This phenomenon can lead to capacity loss, increased internal resistance, reduced charge-discharge efficiency, and even safety hazards such as thermal runaway. The degradation of electrode particles is primarily driven by the cycling process, elevated temperatures, and the potential for unwanted side reactions resulting in the deactivation of active materials and loss of lithium inventory.

The common lithium-ion battery anode typically consists of graphite particles as the active material and their degradation based on exfoliation is a unique aspect of lithium-ion battery behavior. Exfoliation refers to the separation of graphite layers within individual particles, caused by the intercalation and deintercalation of lithium ions during charge-discharge cycles. As lithium ions are inserted into the graphite layers, they cause the layers to expand. Upon discharge, these layers contract, and over time, this repeated expansion and contraction can lead to exfoliation, where the layers may partially or fully separate from each other. This exfoliation process results in structural damage, loss of electrical contact, increased internal resistance, and new surfaces for solid electrolyte interface growth consuming lithium. All of these factors contribute to reduced battery capacity and overall performance deterioration.

Cathode particles are generally composed of lithium metal oxide material (NMC - lithium nickel manganese cobalt oxide, LCO - lithium cobalt oxide, LFP – lithium iron phosphate, etc.). During cycling, as lithium ions move in and out of the particles, chemical reactions take place, and volume changes occur, causing mechanical strain. These reactions and strain can result in the cracking and breaking of the particles (see Figure 1), leading to a decrease in structural integrity



▲ **Figure 1:** Scheme of NMC cathode particle degradation during the cycling and electrical conductivity. The fractured and fragmented particles not only reduce the cathode's capacity but can also lead to increased internal resistance and limited ion diffusion, negatively impacting primarily the capacity and subsequent lifespan of the battery.

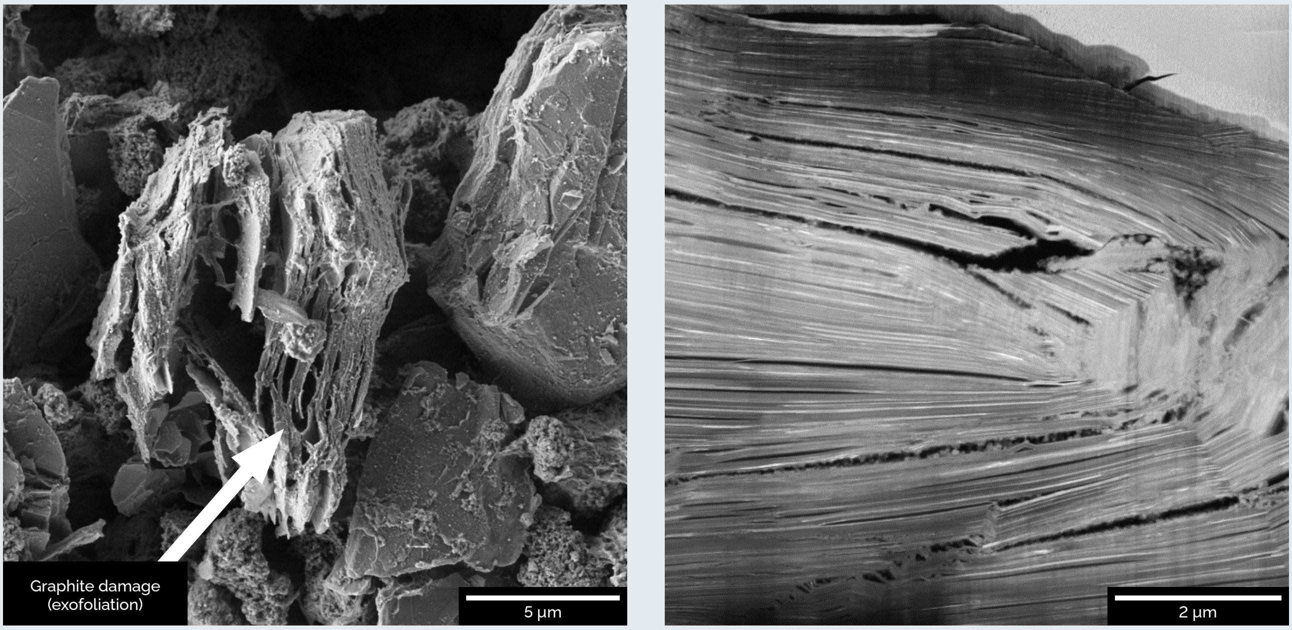
As stated above, electrode particle degradation is a process that significantly influences the battery's overall performance, lifespan, and safety. However, the size of the particles is at the microscale and the defect size is at the nanoscale. For these reasons, the electrode particle degradation study utilizing a FIB-SEM (Focused Ion Beam Scanning Electron Microscope) is a valuable approach for gaining insights into the structural and chemical changes that occur within electrode materials. FIB allows for the preparation of a high-quality cross section through electrode and SEM for high-resolution imaging and analysis of electrode particles, enabling researchers to examine various aspects of degradation. In this application note, we demonstrate multimodal analysis of degraded anode and cathode particles using TESCAN AMBER X system.

Materials and Methods

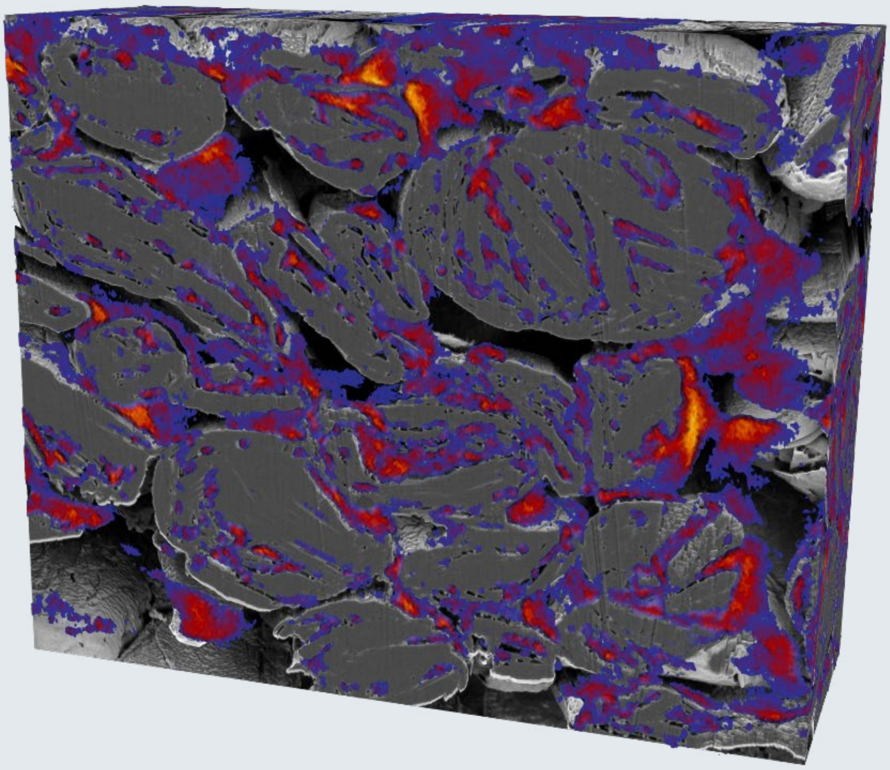
For this application note, the particle degradation within the cycled commercial graphite anode was analyzed with SEM imaging including STEM (Scanning Transmission Electron Microscopy) capability, in volume using 3D FIB-SEM and 3D ToF-SIMS tomography. All these analyses were performed in a TESCAN AMBER X Plasma FIB-SEM equipped with inert gas transfer for the safe transfer of an air-sensitive battery sample between the glove box to the microscope vacuum chamber. The same microscopy system was utilized for the characterization of pristine/(un)cycled NMC cathode particle degradation. In addition to SEM observation, ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and Raman spectroscopy, all integrated into one system, were used as well.

Results and Discussion

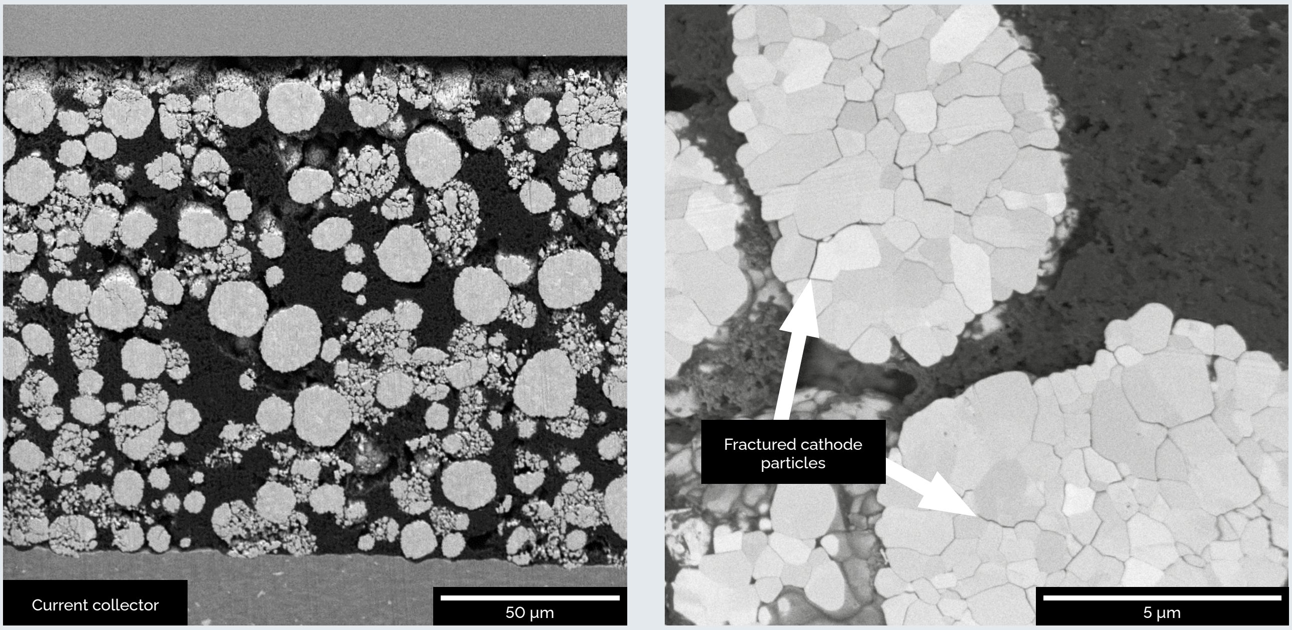
The degradation of graphite anode particles was studied with SEM on the electrode surface and on TEM (Transmission Electron Microscopy) lamella prepared within the same microscopy system. The multiple exfoliation observable from the surface and lamella is shown in Figure 2. Analysis of thin lamella in STEM imaging mode also allows for resolving non-native structures created within exfoliated areas. From volume analysis using 3D FIB-SEM tomography combined with 3D ToF-SIMS tomography, it is apparent that exfoliated areas within graphite particles are occupied by lithium-based chemical compounds (see Figure 3). This observation offers valuable insights into the composition and structural changes occurring during the degradation process.



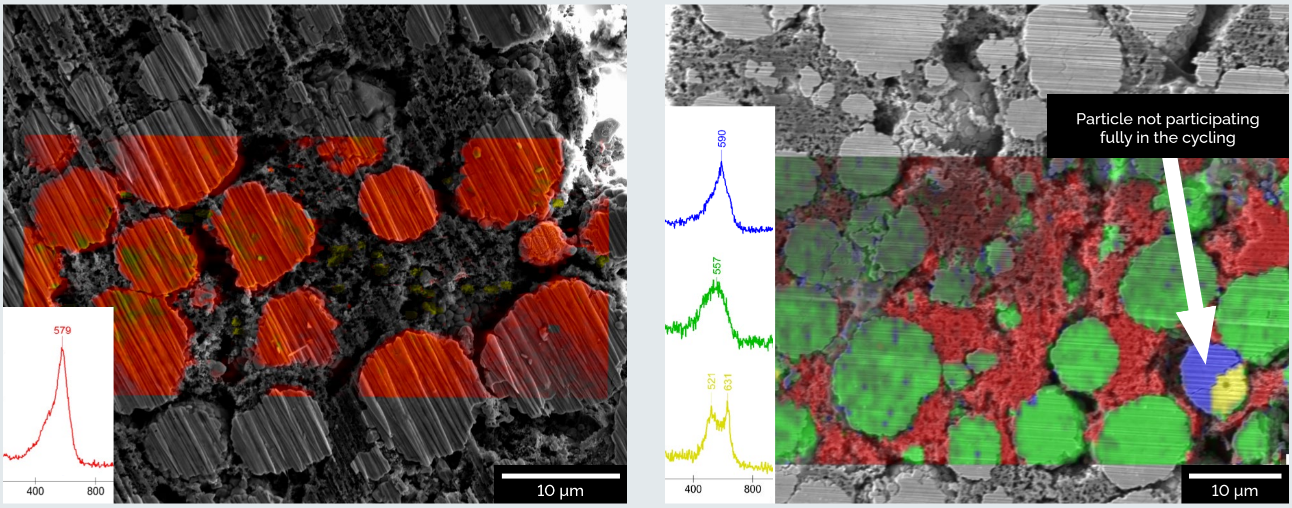
▲ **Figure 2:** Graphite particle degradation based on exfoliation observed on the anode surface (left) and in TEM lamella (right)



▲ **Figure 3:** Result of 3D FIB-SEM and 3D ToF-SIMS tomography showing the relationship between lithium distribution and the defects inside graphite particles (analyzed volume 60 x 50 x 20 µm^3)



▲ **Figure 4:** Example of the cross section through the whole NMC cathode prepared by FIB with apparent fractured and fragmented particles (left); detailed SEM observation of NMC particles with initial fracturing (right)



▲ **Figure 5:** Raman spectroscopy comparative analysis of pristine (left) and cycled (right) NMC cathode cross section; the Raman spectroscopy maps, correlated with SEM topography images, are presented through the use of distinct colors assigned to specific spectral peaks.

NMC particle degradation was evaluated by SEM observation of the cross section prepared through the whole electrode (see Figure 4). Detailed imaging of cycled cathode particles shows initial fracturing (see Figure 5). A similar kind of cathode was analyzed by Raman spectroscopy as well. This technique was applied for comparison of the optical response of pristine and cycled NMC cathode material. The internal structural changes including Li-NMC material composition and its inhomogeneity within analyzed particles associated with cycling are represented by broadening and peak shift, and significant variation within single particles (see Figure 5). Raman spectroscopy mapping also allows the identification of particles that are not fully participating in the cycling.

Conclusion and outlooks

The combination of ultra-high-resolution SEM observation including STEM detection, ToF-SIMS chemical mapping, and Raman spectroscopy in the TESCAN AMBER X Plasma FIB-SEM system offers a powerful and comprehensive approach to understanding particle degradation in lithium-ion battery electrodes. The FIB capability further facilitates meticulous sample preparation, priming them for subsequent subsurface analysis, even in volume using 3D FIB-SEM tomography combined with 3D ToF-SIMS tomography. Correlating microstructural and chemical data allows gaining deeper insights into the degradation processes and their impact on battery performance. This knowledge is invaluable for the development of strategies to enhance the durability and efficiency of lithium-ion batteries in a wide range of applications.

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