

EAG Laboratories

APPLICATION NOTE

# Application of Electron Microscopy to Lithium-ion Batteries I: A Cell Phone Battery

#### **INTRODUCTION**

Lithium ion batteries (LIB) are playing an important role in our daily life by charging the phones, computers, and electric vehicles. Three scientists have been awarded Nobel Prize in Chemistry for the development of lithium-ion batteries in 2019. Similar as other types of batteries, lithium ion batteries store chemical energy and transform chemical energy into electrical energy. It is rechargeable, and it can be charged and discharged and repeat the cycles. Currently a typical phone LIB can last 500 to 1000 cycles. The capacity of LIB will drop with time and eventually will stop working. To understand the degradation of LIB is critical to improve the performance of LIB.

Different techniques have been used to characterize the LIB. XRD could provide phase information, XPS and FTIR/Raman can provide composition and chemical bonding information. SEM can provide morphology of grains. However, all these techniques are for bulk materials with poor resolution. It is not possible to get information from grain levels from such bulk techniques. But degradation usually starts from grain level or start from atom level. Conventional TEM/STEM/EDS/EELS can provide information like morphology, structure, composition and chemical analysis. However, the spatial resolution is limited by the lens aberration. In academia area, Aberration-corrected STEM and EDS/EELS are widely used in characterization of lithium ion battery. But there is not much aberration-corrected system in industry service lab. At Nanolab, we have aberration corrected system, with such aberration corrected system, it is possible to understand the structure and composition including chemical state at atomic level.

### OVERVIEW OF THE LITHIUM ION BATTERY BY SEM/EDS

In this application note, multi techniques were used to characterize a lithium ion battery from a cell phone including X-ray imaging, SEM/EDS and AC-STEM/EELS. X-ray image shows the battery has a jelly roll structure (Fig. 1a, b). Multi layers were observed on the cross-section images (Fig. 1c, d) by optical microscope and SEM. Based on SEM/EDS results, there are carbon-based anodes on both sides of Cu current collector. Cathode is consisted of Co and O on Al current collector. Between the anode and Cathode, is the polymer-based separator (Fig. 2).







Figure 2. SEM image and EDS elemental maps of phone battery shows the presence of C on Cu current collector in Anode, and Co/O on Al current collector in Cathode.

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## ATOMIC STRUCTURE ANALYSIS BY AC-STEM

The cathode is consisted of grains with size from a few um to tens of um (Fig. 3a). In order to get more information about the cathode materials, TEM samples were extracted from the cathode film (Figure 3b). AC-STEM images (Figure 3c, d) show the materials has good crystalline structure. Figure 3c and d show two grains with different orientation. Image (c) clearly show the layered structure along the 003 direction. While image (d) is from another direction to show the atom arrangement in a-b plane. The surface of the grain shows a different structure from the core part even from a fresh new phone battery.



Figure 3. (a) SEM image shows the cathode particles size in the range of a few um to tens of um. (b) STEM image and (c, d) atomic HAADF images from the two regions labeled inside image (b) from two grains with different orientation.

Atomic level HAADF image clearly shows the surface structure changed from the core layered structure to rock-salt structure (Figure 4). The bright spots in the HAADF images here are the Co atom column. Li channels are between the Co layers, however not visible in HAADF image. As shown in the image (Fig. 4a), Co atom moved into the lithium positions at the surface and blocked the Lithium channel. Once the Co completely entered the lithium positions, the layered structure changed into a rock-salt structure. At the surface that is at the end of the Li channels, such rock-salt structure is uniform with a flat interface with the core layered structure (Fig. 4a). At another surface that is parallel to the lithium channels, the surface also has a rock-salt structure. At this direction, the interface between layered structure and rock-salt structure is rough with steps (Fig. 4b). The transition mechanism from core layer structure to surface rock-salt structure at these two surfaces is different. The formation of the strain will be direction depended on the uniform or rough interface, and lead

to the formation of crack eventually. This surface rock-salt layer protects the particle from further degradation, but it also reduces ionic and electronic conductivity.



Figure 4. HAADF images from the grain with surface: (a) at the end of the lithium channels and parallel to the lithium channels.

### COMPOSITION AND CHEMICAL STATE ANALYSIS BY EELS

EELS confirmed the presence of O and Co inside the cathode oxide as shown in the elemental maps (Figure 5a). An EELS spectrum from the core part of the particle also confirm the presence of the lithium as indicated by Figure 5b. Line profile (c) along the yellow line in (a) shows the O/Co is around 2. Based on such results, the cathode oxide is determined to be  $Li_xCOO_2$ .



Figure 5. (a) STEM image of a part of a cathode particle shows the presence of the O and Co. (b) an EELS spectrum from the core area shows the Li K edge overlaps with Co-M edge. (c) line profile across the yellow line in (a).

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For the rock-salt surface, EELS near edge fine structures revealed the change of Li, Co and O at different positions of the surface (Fig. 6a). As shown in Fig.6b, no Li was detected at the surface of the rock-salt layer. At the surface, Co L edge shifted to lower energy loss which means the Co's oxidation state changed (c) and was reduced to a lower valence state. By comparing the edge position and shape, the Co from surface changed into CoO. The prepeak of O from the surface area is much lower than that from the core area, which indicates the formation of oxygen vacancies (d). The loss of oxygen also supports the phase change from Li<sub>2</sub>CoO<sub>2</sub> to CoO. The formation of CoO is likely starting with the extraction of lithium during charging, then the Co moved into the empty lithium position, at the same time, oxygen gets released. Such CoO phase will block the lithium moving in and out, increase the ionic and electrical resistance of the lithium ion battery, and is responsible to the irreversible capacity loss.



Figure 6. (a) STEM image of a cathode particle surface. (b) Li K-edge, Co M-edge, (c) Co L-edge and (d) O K-edge at different locations as labeled inside image (a).

### SUMMARY

Different types of electron microscopy were applied for the characterization of a phone lithium ion battery. SEM/EDS provides large field of view morphology and composition distribution. AC-STEM provides atomic level structure information about the cathode oxide. Rock-salt like structure was observed on the surface of the particles, different from the layered structure inside the oxide particles. Inside the rock-salt layer, no lithium was observed, and the Co moved to the Lithium position and was reduced to 2+ from the 3+. Overall, AC-STEM/EELS provide atomic structure, composition and chemical state information of the cathode oxide.