APPLICATION NOTE

Application of Electron Microscopy to Lithium-ion Batteries II: an Electric Vehicle Battery

INTRODUCTION

Lithium ion batteries (LIB) are playing an important role in our daily life by charging the phones, computers, and electric vehicles (EV). The demand of LIB is keeping on increasing. According to Bloomberg 2019 Electric Vehicle Outlook, EV including commercial and passenger EV will dominate the demand of LIB market in next ten years.

Although LiCoO$_2$ is a very good materials for phone in term of energy density (See the part I of this application note), other factors like stability, safety, cost and lifetime will be important for EV batteries.

The energy density of LiCoO2 based LIB will increase when the charge voltage increase, however its structure will get damaged and the capacity will drop very fast. Cobalt is expensive in cost. Ni rich cathode material is currently a hot choice especially for EV battery due to its higher capacity and cheaper in cost. In Ni rich cathode, Mn or Al usually are added to stabilize the structure. Once the Ni content increases, the energy density will increase, however, Ni rich cathode also has the cycling stability issue. In order to improve the performance of battery, it is necessary to understand why the capacity drops and what causes the battery's degradation.

OVERVIEW OF THE EV LITHIUM ION BATTERY BY SEM/EDS

In this application note, multi techniques were used to characterize a lithium ion battery from an EV LIB including, SEM/EDS and AC-STEM/EDS/EELS. Similar as the phone battery, the EV battery also has a jelly roll structure. Multi layers were observed on the cross-section images. Based on SEM/EDS results, there are carbon-based anodes on both sides of Cu current collector. SiOx particles were also detected inside the anode electrode. Cathode is consisted of high Ni and O on Al current collector. Co and Al from the cathode however are not detected due to low SEM/EDS detection limit. Only the Al from current collector was detected. Between the anode and Cathode, is the polymer-based separator (Fig. 1).

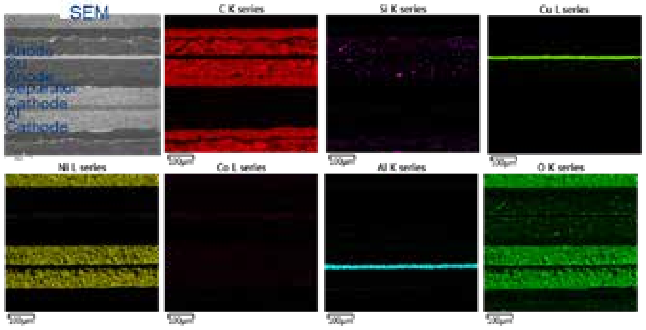

Figure 1. SEM image and EDS elemental maps of an EV battery shows the presence of C and SiOx on Cu current collector in Anode, and Ni/O on Al current collector in Cathode.

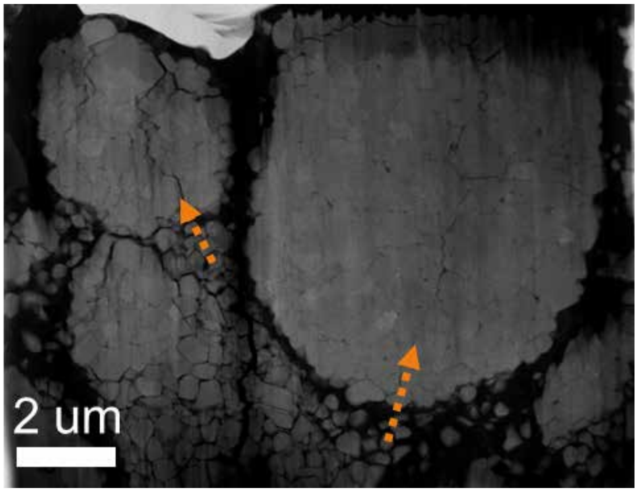

Figure 2. STEM image of typical primary and secondary particles inside the EV battery cathode.

MORPHOLOGY AND COMPOSITION OF CATHODE BY STEM/EDS

STEM image of the cathode shows there are nanosized primary particles and tens of um sized secondary particles (Figure 2). Microcracks were also observed inside the secondary particles. Beside the secondary particles, there are also some loose primary particles. In this application, particles at different positions will be studied to understand their structure and composition difference.

STEM/EDS (Fig. 3) with a higher sensitivity clearly show the presence of Al and Co beside Ni and O inside the cathode electrode. F and P from SEI were also detected surround the secondary particle and along the crack inside the particle. Apparently, electrolyte was penetrated the secondary particle as a result of a serious degradation.

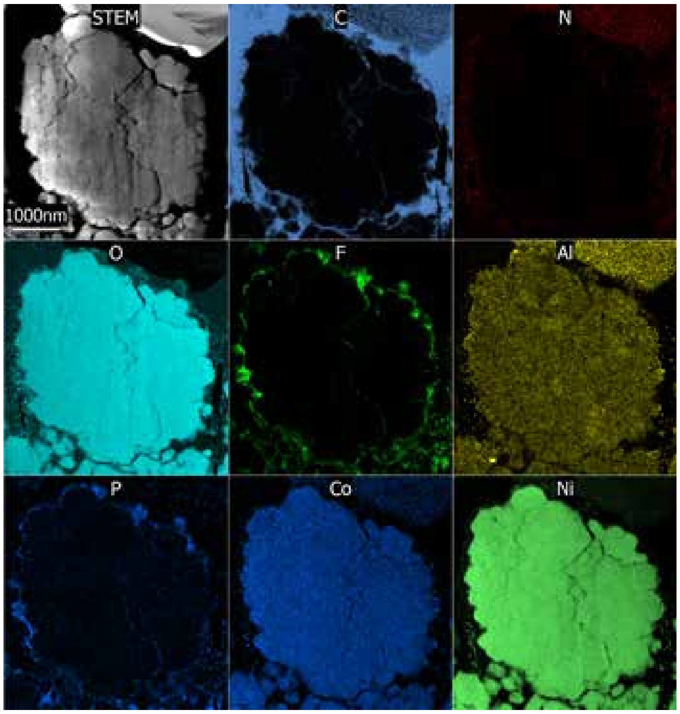

Figure 3. STEM/EDS show the cathode contains Ni, Co, Al and O. F and P surrounded the secondary particle and along the crack inside which was likely from SEI layer.

ATOMIC STRUCTURE ANALYSIS BY AC-STEM

As the lithium moves in or out of the electrode during charge/discharge, the electrode volume will change, and stress will be formed. Then there will be some crack inside the cathode. Figure 4a shows a particle near the microcrack inside the secondary particle. A shell layer was observed on the grain near the crack; however such shell is not visible in the surface away from the crack. For this 20nm shell, the very top surface 2nm has a rock-salt structure, and beneath the 2nm surface is a mixed structure of both rock-salt and layer structure (Fig. 4b). In the core area (Fig. 4c), no contrast in the lithium channel indicated the transition metal did not enter to lithium position. In the surface area (Fig. 4d), transition metal occupied all the lithium positions. Such 20nm shell layer is observed on EV battery cathode, but is not observed on the phone battery cathode, based on it, EV battery has been degraded a lot.

As shown in Figure 4, the shell-like surface at the end of the Li channel is uniform. For the direction that parallel to the lithium channel (Fig. 5), rock-salt structure was also formed on the surface with a rough interface, similar as that observed on phone LiCoO2 cathode. In the layer structure in Fig. 5a area, bright contrast was observed in the lithium position indicates part of the Li/Ni cation mixing due to the degradation.

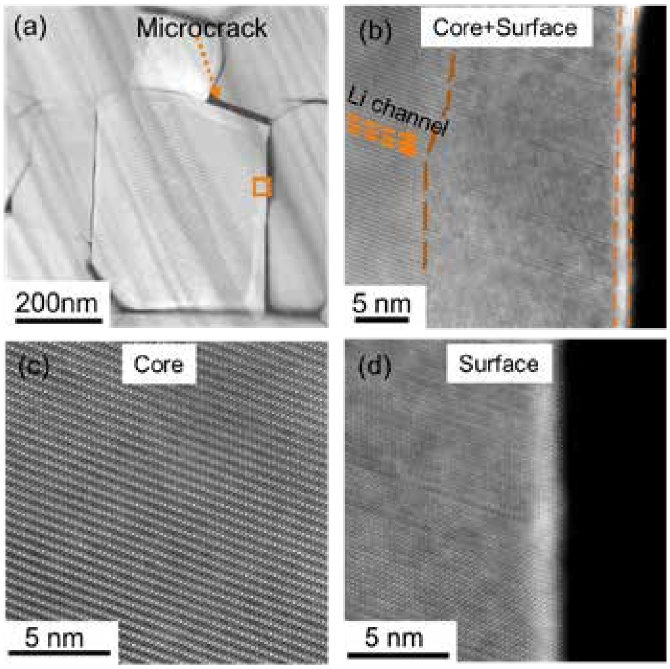

Figure 4. (a) STEM image of a cathode particle near a microcrack inside secondary particle. (b) zoom in STEM image from the box area of (a) show the different atomic structure inside the core and surface area. (c, d) atomic HAADF images from the core and surface area show more details of the structure.

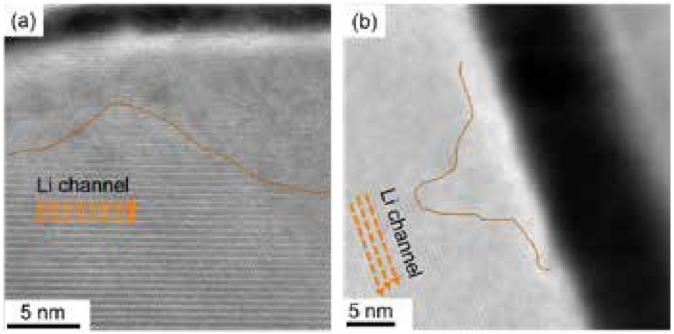

Figure 5. HAADF images from the grain with surface parallel to the lithium channel.

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COMPOSITION AND CHEMICAL STATE ANALYSIS BY EELS

EELS from multi grains were collected and quantification confirmed the EV battery cathode oxide is Ni rich NCA with Ni about at 90% of the metal, Co about 6 at% and Al around 4at%. Further EELS analysis revealed Li was present inside the core part of the particle, however, no Li was detected in the 20nm thick shell surface. The transition metal Ni, Co, Al and oxygen are present inside the whole area of the grain (Figure 6).

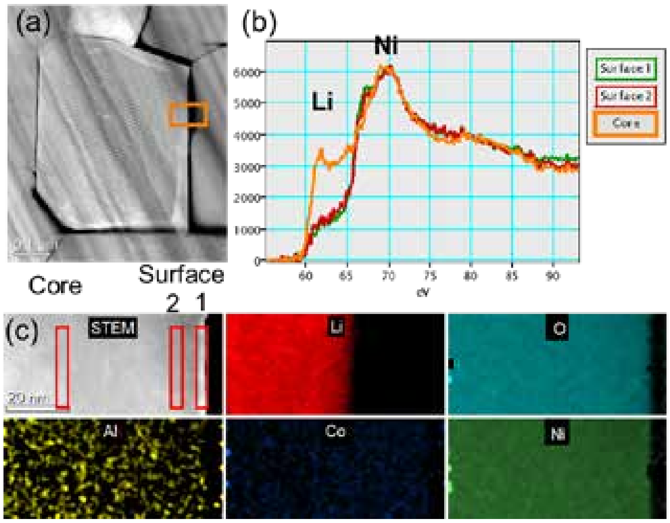

Figure 6. (a) STEM image of a cathode particle with shell surface near a microcrack. (b) Li K-edge and Ni-M edge from three locations labeled from (c). Elemental maps of Li, O, Al, Co and Ni.

More analysis was performed on the surface for the chemical state of Ni at the surface and the core of the grain. At the very top 2nm shell surface, the Ni L edge shifts to left, lower energy loss (Fig. 7b). The left shift indicates the Ni valence state drops from 3+ into 2+. At the surface, O-K edge pre-edge intensity drop a lot (Fig. 7c), and O/Ni ratio drops at the shell surface (Fig. 7d). This all indicates the formation of NiO at the surface. But inside the mixed layer of the 2nm-20nm of the surface, The Ni valence state keeps same as that inside the core of the grain. This is different from the Lithium distribution which was absent in the whole shell of the 20nm layer. Li and Ni have a different degradation in the shell surface.

Al which is important to stabilize the whole structure of the NCA has a non-uniform distribution inside the grain. The Al concentration can change from 0 to 3% across the cathode oxide. However, the Ni and Co concentration are uniform across the grain. Multi grains were studied and all show the uneven distribution of Al inside the cathode oxide.

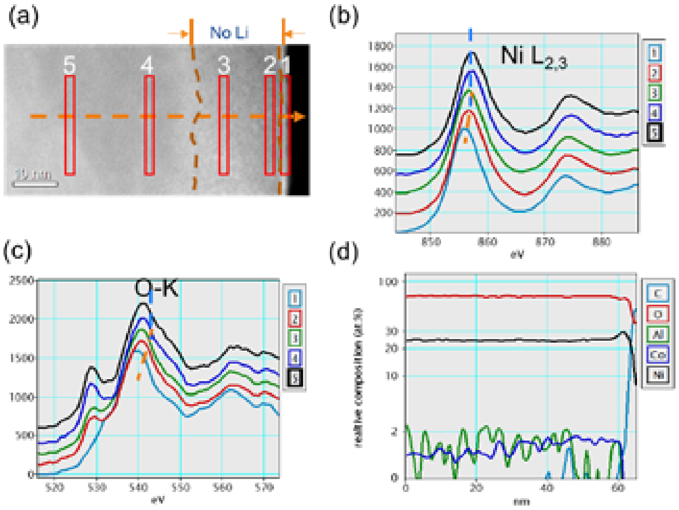

Figure 7. (a) STEM image of a cathode particle surface. (b) Ni M-edge, and (c) O K-edge at different locations as labeled inside image (a). (d) Relative composition profile along the line in (a).

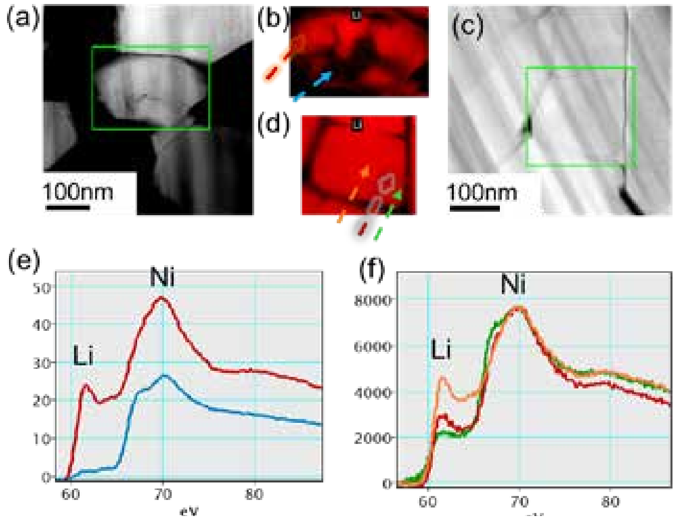

Figure 8. (a) STEM image of a loose particle and the lithium map (b). (c) STEM image of a core particle and its lithium map (d). (e) and (f) are EELS spectra from arrowed position in (b) and (d), respectively.

EELS analysis on a loose particle shows that almost half of the particle lost lithium (Fig. 8 a, b, and e). And at the area without lithium, the Ni L edge shift to the left and changed into NiO structure. For the particle near the core of the secondary particle, the lithium covers the whole grain (Fig. 8 c, d, and f). Likely because it was shielded from the direct contact with the electrolyte by surrounding grains. Structure and composition changes only occurred on the loose particle or near the crack that is contact with the electrolyte.

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SUMMARY

Different types of electron microscopy were applied for the characterization of an EV lithium ion battery. SEM/EDS provides large field of view morphology and composition distribution. Microcrack was seen inside the EV NCA grains. 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 Ni 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. In addition, Aluminum was not uniform for the EV NCA cathode.