APPLICATION NOTE

# Towards Atomic Elemental Mapping of Lithium-ion Materials by Low Count Electron Energy Loss Spectroscopy

## INTRODUCTION

With the increasing demand of lithium-ion batteries, it is critical to understand the structure and composition of lithium-ion materials with high spatial resolution. STEM/EELS has been a routine technique to understand the structure-property of various materials. However, lithium-ion materials are susceptible to electron beam damage. Their crystalline structure would be modified and chemical composition including bonding information can be changed with electron beam. Aberrated-corrected STEM are reported to characterize the atomic level structure of lithium-ion materials. (Please refer to another application note of STEM/ABF to directly visualize light element atoms including lithium atoms in crystalline phase) However, chemistry information at atomic level is still missing from STEM. Though EELS has been frequently used for beam robust materials, it is challenging to get atomic level EELS results on lithium-ion materials due to the beam effect.

## LOW COUNTS EELS

In order to avoid or limit the beam effect, a weak electron beam and short exposure time are essential to control the beam dose to the area of interest. In consequence EELS counts and its signal to noise ratio (S/N) will be low. Dark noise needs to be removed accurately and multi frames are needed to increase the EELS counts and S/N. In the default EELS collection mode in Gatan DigitalMicrograph Software, gain normalization way is used in which the dark reference is collected based on one frame (Method 1). However, the S/N cannot be improved when adding up multi frames using such one-frame dark reference [1]. A high quality dark reference is necessary to enhance the S/N which was found as effective as average gain reference. Gatan GMS 3 has introduced a new option of "apply HQ dark correction" that could remove noise effectively with a high quality dark reference (Method 2) [2]. Such function uses an averaged dark reference with frame/pixel number of 3 times square root of N (the number of the total frame/pixel). Recent study shows the noise standard deviation could become much less than one when the number of the dark references is above a critical sample size (i.e. 5000) (Method 3) [3]. Such ultra low counts even single count EELS is claimed to be possible. In Method 3, EELS was collected in unprocessed mode and then dark reference and the gain reference were removed manually.

Commercial lithium-ion battery cathode material, $LiCoO_2$ and $LiMn_2O_4$ powders, were ordered from MSE supplies, LLC (Tucson, AZ) and thinned down by FIB after was embedded into a carbon matrix. A probe-corrected FEI Titan equipped with Gatan Enfinium EELS spectrometer was operated at 200kV for STEM imaging and EELS analysis. First, EELS spectra of O-K and Co-L edge were collected using a weak beam and short pixel time by three methods with 10k frame (Figure 1). The averaged spectra were shifted along y-axis in purpose for a better view. The S/N of the average spectrum with counts less than 5 by Method 3 was obviously much higher than those obtained by Method 1 and 2. The beam effect to the sample is negligible with the low counts EELS techniques.

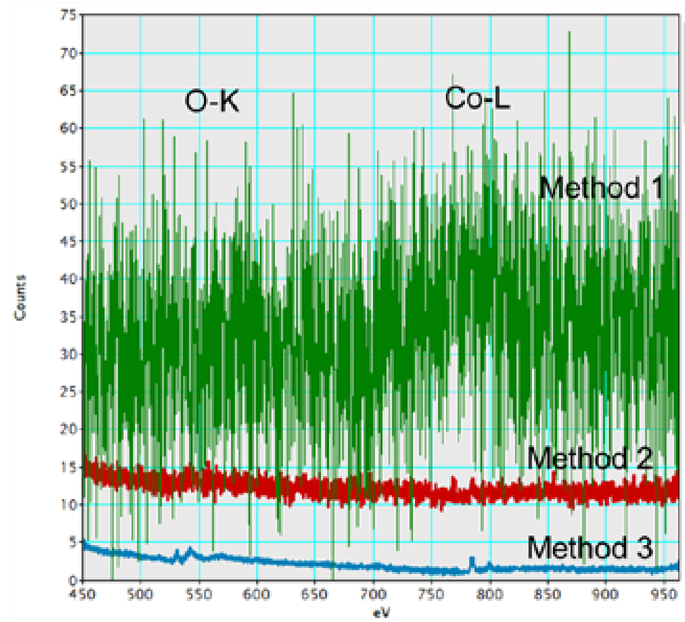


**Figure 1. Averaged EELS of O-K and Co-L edge of LiCoO2 by Method 1, 2 and 3 with frame of 10k. The spectra of Method 1 and 2 were shifted up 30 and 10 counts respectively in purpose for view. This figure shows the dramatically increase of S/N by Method 3 low counts EELS.**

Figure 2 shows Li-K and O-K edge using Method 3 with different frame numbers and strong beam. Clearly, the S/N increases with the frame number from 200 to 10k for both Li and O edges. The intensity of Li-K edge (62 eV) dropped when a strong beam was used. The O-K edges from weak and strong beams had a similar shape except the shoulder on the 2nd peak was more obvious with the weak beam. Both results confirm weak beam is necessary to keep the EELS near-edge fine structure to better understand their bonding.

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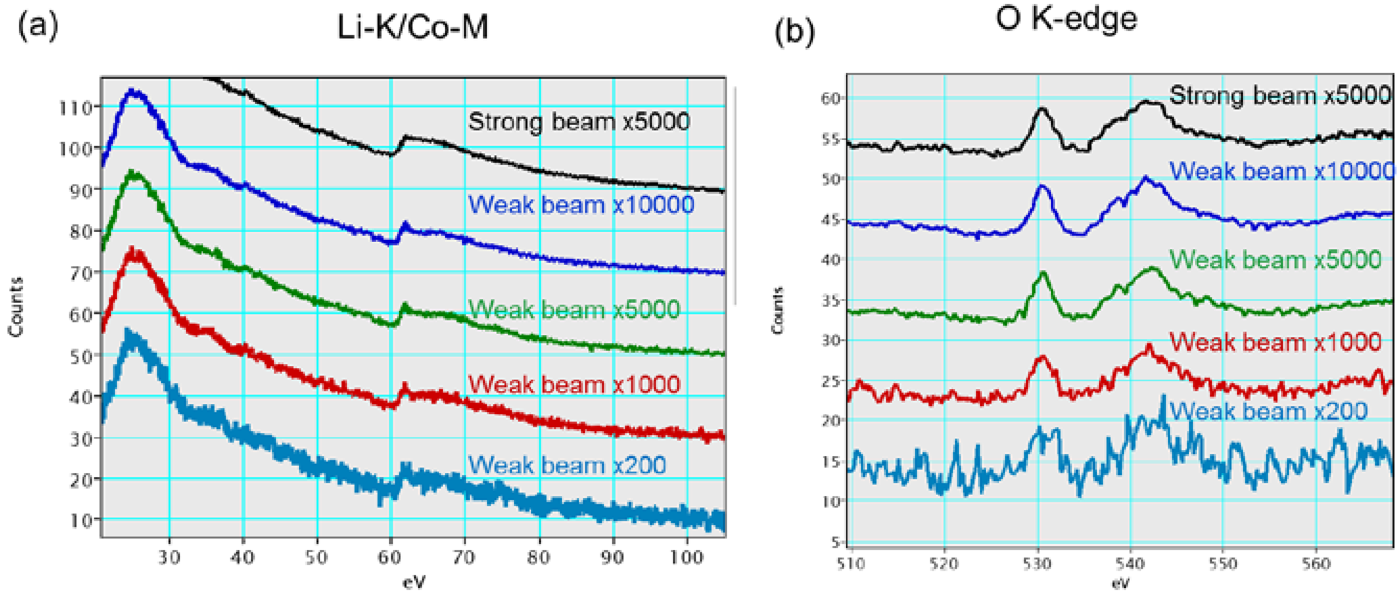


**Figure 2: Averaged EELS of (a) Li-K/Co-M edges and (b) O-K edges of $LiCoO_2$ by Method 3 with weak beam under different frames (x200, x1000, x5000, x10000) and strong beam under x5000 frames.**

With the low counts EELS (Method 3), it is possible to get atomic level elemental mapping of beam sensitive materials. One example of $LiMn_2O_4$ is shown in Figure 3. Multi EELS spectrum images (SI) with 50x100 pixels were collected in dual EELS mode from different areas, aligned according to their ADF images and added up together. EELS energy of the data was calibrated based on the zero-loss-peak. An averaged pixel spectrum over 10k pixel shows good S/N with a count around 20. The raw (Fig. 3c) and smoothed (Fig. 3d) Mn-L edge intensity maps matched well with their atomic ADF image (Fig. 3b). These results are quite promising and can be applied to other beam sensitive crystals.

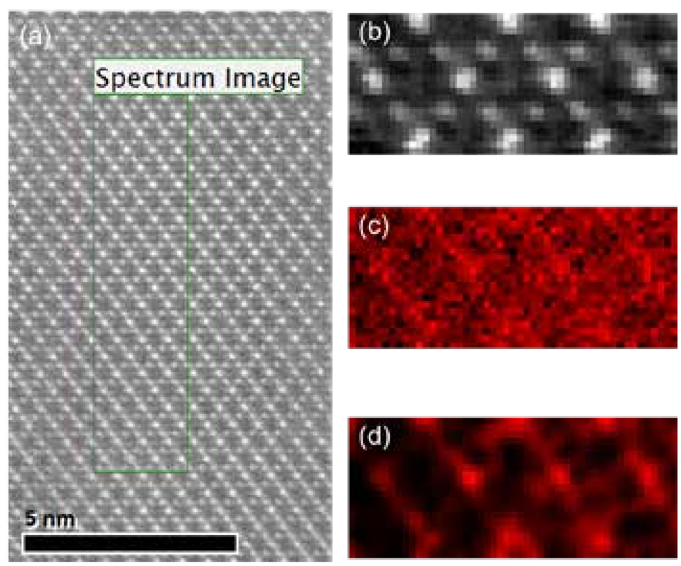


**Figure 3: (a) Overview STEM image of LiMn2O4 with the area for EELS Spectrum Image. (b) ADF image of final combined SI. Mn-L edge maps (c) raw intensity and (d) after smooth**

## SUMMARY

Besides providing advanced electron microscopy service to the society, Nanolab is also developing new methods for novel functional materials characterization. As shown in this application note, a new method of low count EELS was developed for beam sensitive lithium-ion materials detection to get pristine properties of the specimen itself.

## REFERENCES


[1] V Hou, Microsc. Microanal, 15 (S2) (2009), p. 226.

[2] Manual of Gatan Microscopy Suite (GMS) version 3.11. Gatan Inc.

[3] M Haruta et al, Ultramicroscopy, 207 (2019), p. 112827.