An Advanced Quantitative Analysis of Li in LIB with AES Preparation For a Clean Cross Section with the Cross Section Polisher

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Since the introduction of the first consumer lithium ion battery (LIB) in 1991, it has become attracted considerable attention as a renewable energy source. Its demand is increasing yearly with increasing diffusion of a cell-phone and a laptop PCs, recently it is widely applied to not only small type but also middle-large type products such as hybrid vehicles. For the systematic, effective development aiming of higher-energy density, longer-life, and lower-cost, lithium distribution has earnestly been desired to be observed in active material of cathode and anode in less than one micrometer region. Ordinary energy dispersion spectroscopy (EDS) cannot detect lithium because the energy of its characteristic X-ray is out of the range of the detection limit of ordinary detectors. On the other hand, Auger electron spectroscopy (AES) is well known as the detectable method of Li like X-ray photoelectron spectroscopy (XPS), it has been widely used for research and development regarding Li in a minute area, especially since a field emission gun started to be used. Additionally AES has higher sensitivity for lithium than XPS. By comparing the peak intensity of the standard spectrum of Li LVV to C KLL measured under the same analysis conditions with AES, Li LVV has 4 times higher intensity than C KLL. On the other hand, by comparing the photoionization cross section for Al Kα of Li 1s with that of C 1s, Li 1s has 18 times lower intensity than C 1s. So, lithium sensitivity in AES is about 72 times higher than in XPS. But there are fewer applications to LIB with AES compared to those with XPS because of two disadvantages as below:

1. Sensitivity to the surface condition due to the short mean free path
2. Difficulty for the quantification

As for the first disadvantage, it is caused by the shorter mean free path of Li KVV Auger spectrum; the mean free path of Li KVV Auger spectrum is about 0.6 nm whereas that of Li Kα photoelectron spectrum with Al Kα line excitation is about 2.0 nm, so slight contamination makes it undetectable. Furthermore the chemical preparation for sampling could lead lithium to elute, so the sample preparation is critically important to analyze with AES. As for the second disadvantage, it is caused by the spectrum overlapping of the Li KVV with a MVV spectrum of transition metal used as active material for the cathode of LIB. This overlapping prevents the detection of the expected intensity of Li KVV spectrum for quantification as shown Fig. 1. Moreover Li KVV spectrum has various shapes depending on the chemical state of lithium [1], so the relative sensitive factor (RSF) value of lithium is not constant.

In this presentation, we report a suitable sample preparation method of LIB for AES, and the quantification for Li KVV regardless of the peak overlapping with another element. For the sample preparation, a cross section of a cathode of a lithium-ion battery was prepared for AES with Cross Section Polisher (CP): IB-09020CP. It uses an argon beam to mill or polish virtually any material and produces cross sections of samples: hard, soft, or composites, without smearing, crumbling, distorting, or contaminating them in any way. The Auger electron spectrometer used in this experiment was JAMP-9510F with a Schottky type field emission gun and a hemi-spherical analyzer with variable energy

resolution (0.05 - 0.5 %). As a clean cross section, a cathode of a LIB cut by the CP enabled clear Auger elemental maps including lithium to draw with high efficiency in a short time within 5 min for each element due to the high sensitivity. As to quantitative analysis for lithium with AES, we tried the peak deconvolution calculation with the help of the standard library of lithium, and then obtained the ratio corresponding to the concentration with referring the absolute spectrum intensity [2]. With the above quantitative method, a reliable quantitative value was obtained which is quite close to the stoichiometric value obtained with their conventional quantitative method.

References:

[1] Madden, H. H. *et al.*, Journal of Vacuum Science and Technology, Vol. 14(1977), 412-415
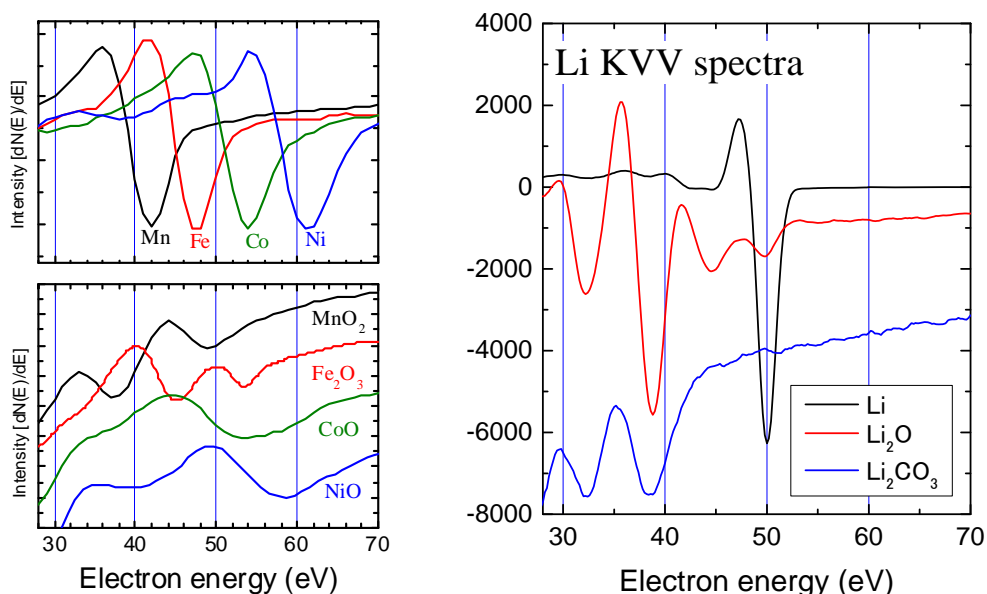[2] K.Tsutsumi *et al.,* Journal of the Surface Science Society of Japan Vol. 33(2012), No8, 431-436

Figure 1. Li KVV spectra and MVV spectra of transition elements for various chemical states: metal, oxide, and carbonate
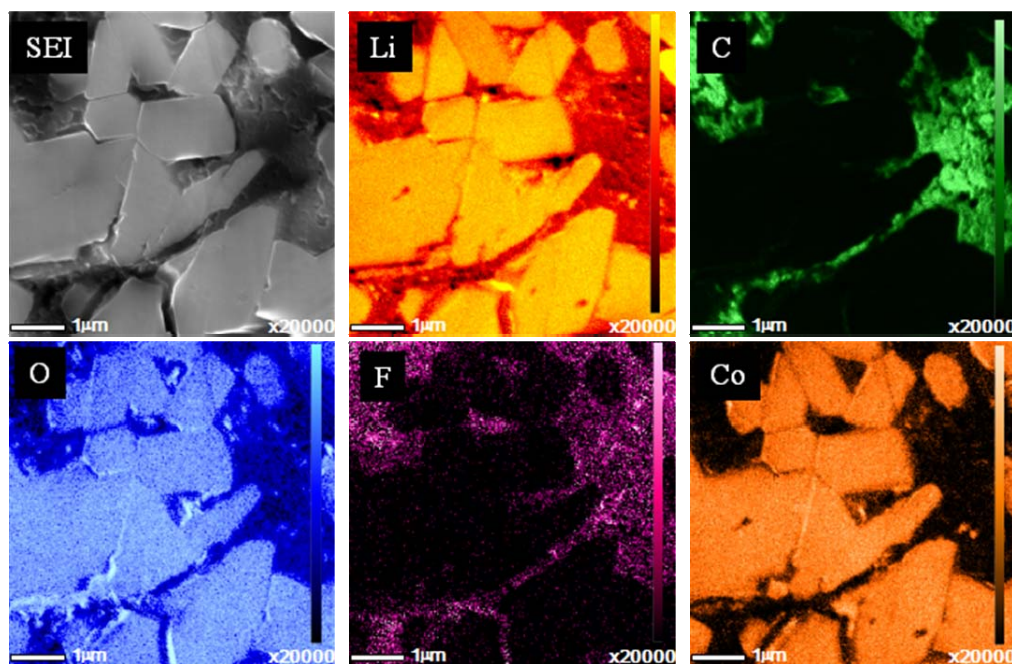

Figure 2. Auger elemental maps: Li, C, O, F, and Co of cross section of a cathode cut by CP (electron irradiation condition: 30kV, 10nA, magnification: ×20000)