Variation of oxygen compostion of $Li(Ni_xCo_yMn_z)O_2$ cathode measured by TEM-EDS during FIB preparation

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Li ion batteries (LIBs) have been widely applied as rechargeable power sources of many personal electronic devices such as mobile phones, lap top computers, smart watches and digital cameras, etc. $LiCoO_2$ is a successfully commercialized cathode materials for the personal electronic devices due to high volumetric capacity and safe operation. Recently, LIBs have expanded their uses for large-scale applications including electric vehicles and energy storage stations. Layer structured $Li(Ni_xCo_yMn_z)O_2$ (x+y+z=1) have been regarded as one of the promising cathode materials for the large-scale energy storage due to great power density and lower materials cost compared to $LiCoO_2$. Higher demands for a market acceptance of these cathode materials keep requiring to improve the performance regarding power density, cycle life, fast charge ability, and safety. Although deep understandings for the operation mechanism of LIBs is essential to achieve the further improvements, the detailed mechanism has not been clear yet due to complicated structure of LIBs, composed of oxide electrodes, electrolyte solutions and many organic additives. Instability of Li related compounds in the ambient environments and limited detection techniques for Li ions are another obstacles to elucidate the operation mechanism. In recent years, atomic structure of the cathode materials and the atomic behavior during the battery operation have become key-issues and electron microscopy has more widely used to observe the atomic structures.

In this study, we introduce the error of element analysis for layer structured $Li(Ni_xCo_yMn_z)O_2$ cathode using electron microscope. The SEM and TEM samples for cross-sectional observation were routinely prepared by using Ar ion cross-sectional polishing and/or Ga ion milling in FIB. It has been found through many analysis that the oxygen concentration is measured differently depending on analysis methods and conditions of sample preparation even in the same specimens. Table 1 shows elemental compositions of the identical cathode materials measured by TEM-EDS depending on sample thickness prepared by FIB. The mild Ga ion beam conditions of 5kV acceleration voltage and 15pA currents were used for the final surface cleaning. Li contents were not included in the table because of the elemental detection limit of EDS technique. It is noted that measured composition of the cathode is different depending on the sample thickness and oxygen concentration, in particular, increases with decreasing sample thickness. In this presentation the tendency of the compositional change behavior depending on sample preparation conditions and analysis methods will be explained.

Table 1. Elemental composition of $Li(Ni_xCo_yMn_z)O_2$ cathode depending of the sample thickness measured by TEM-EDS.

Thickness (nm)	Elemental compositions (At.%)				Relative composition
	Ni	Co	Mn	O	O/(Ni+Co+Mn)
330	48.3	5.1	2	44.7	0.81
250	39.7	4.2	1.7	54.5	1.20
190	37.7	4.2	1.9	56.3	1.29
150	39.7	4.7	1.8	53.9	1.17
130	36.8	4.2	1.6	57.4	1.35
90	33.4	3.7	1.5	61.4	1.59
80	34.1	3.7	1.6	60.6	1.54
70	33.1	3.7	1.5	61.7	1.61