AMTC Letters
Vol. 2 (2010)

Local chemical changes associated with cycling tests in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ studied by STEM-EELS

Yuji Kojima[1], Shunsuke Muto[1], Kazuyoshi Tatsumi[1], Hiroki Kondo[2], Kayo Horibuchi[2], Yoji Takeuchi[2]

[1] Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464-8603, JAPAN
[2] Toyota Central R&D Labs., Nagakute, Aichi, 480-1192, JAPAN

In order to reveal 'where' and 'how' the degradation occurs, we have applied spectrum imaging (SI) using electron energy-loss spectroscopy (EELS) attendant on scanning transmission electron microscopy (STEM) to O, Co and Ni EELS for $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ after cycling at 80°C [1,2]. In the present study, we examine similar samples after 500 cycling at 70℃ using the same method but this time other elements involved, including Li, are also analyzed.

The sample preparation and data analysis procedures are the same as our previous studies [1,2]. STEM-EELS-SI was performed using JEM2100 and 2100F S/TEM equipped with a Gatan ENFINA1000, respectively measuring O-K, F-K, Co-$L_{2,3}$, Ni-$L_{2,3}$ ELNES and Li-K, Co-$M_{2,3}$, Ni-$M_{2,3}$ ELNES by the STEM-EELS-SI mode. The multivariate curve resolution (MCR) technique [2] applied to the obtained datasets, which enables spatial distribution mapping of the constituent chemical components underlying the SI data.

Figure 1 shows the result of MCR for the sample after 500 cycles at 70℃. From the spectral shapes and their distributions, we identified that component **a** is the normal $LiNiO_2$-based phase, and component **b** is a degraded (NiO-like) phase, as reported in the previous study [1]. Compared between the samples before and after cycling, it turned out that the thickness of the degraded phase was increased at grain surfaces. From a number of SI datasets obtained on the samples we roughly estimated the volume fractions of the degraded phase relative to the normal phase in the samples before and after cycling tests at 70 and 80℃. We found that the rough tendency of the degraded phase increase accounted for the most amount of capacity fading. This result suggests that formation of NiO-like phase is mainly responsible for the capacity fading of the positive electrode.

Figure 2 shows the result of MCR for Li-K ELNES after cycling. Component **c** could be Co and Ni $M_{2,3}$ ELNES by their peak positions and spectrum shape. We identified that component **d** is the normal $LiNiO_2$-based phase. Component **e** exhibits the peak shifted to the high energy side compare with the first main peak of the normal $LiNiO_2$-base phase. This component was mainly distributed at the secondary particle surfaces, consistent with the distribution of fluorine, possibly derived from the $LiPF_6$ electrolyte. We thus assigned this component as a lithium fluoride.

We integrate our previous results and the present observations to build a closed picture of degradation mechanism of the electrode during cycling at elevated temperatures.

References
[1] S. Muto *et al. J. Electrochem Soc.* 156 A371 (2009).
[2] S. Muto *et al. Mater. Trans.* 50 A964-969 (2009).

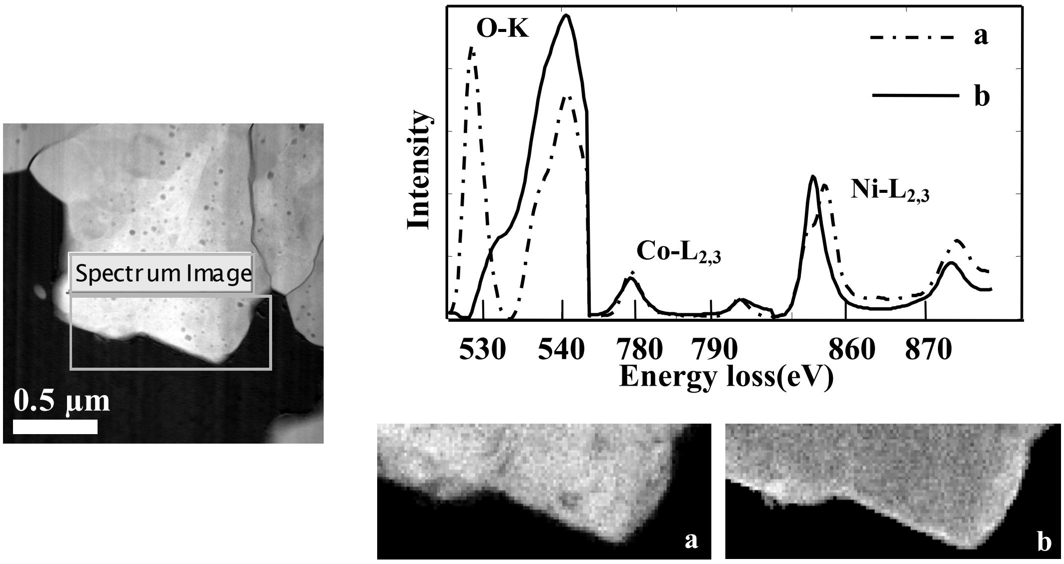

Fig. 1 Result of MCR for O-K, Co-$L_{2,3}$, Ni-$L_{2,3}$ ELNES after 500 cycling at 70℃
(Spatial distributions of resolved components and pure spectral profiles are shown on the right side.)

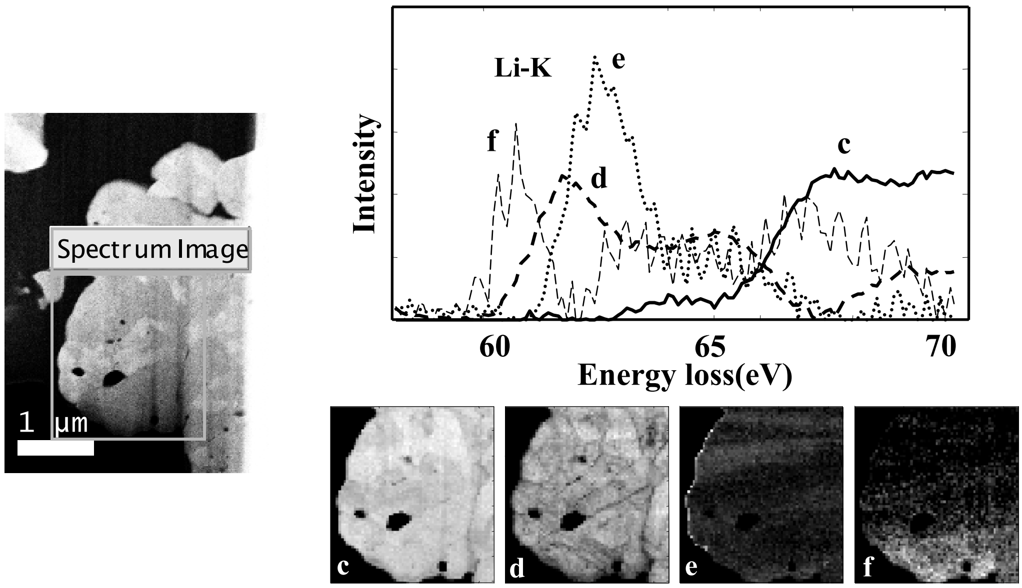

Fig. 2 Result of MCR for Li-K ELNES after 500 cycling at 70℃