

## Diagnostic analysis of Li battery cathode by EELS, first principles calculation and spectrum-imaging with 2D multi-variate analysis

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Although LiNiO<sub>2</sub> based materials are expected for cathodes of Li rechargeable batteries in high-power use, the electrochemical properties of the cathodes are degraded by charge-discharge cycles at elevated temperatures[1]. Small amounts of Al and Mg are doped so as to suppress the degradation. The purpose of this study is a cathode diagnostics by two different approaches. The one is the local environment analysis of the dilute dopants by TEM-EELS and first principles calculations. The other is STEM-EELS imaging with a multi-variate analysis for spatial distribution of the degraded areas in the cathode active materials.

The samples were LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>(Mg<sub>0.05</sub>)O<sub>2</sub> cathode materials, taking a form of secondary particles composed of aggregating primary grains of approximately 1 μm size (Fig.1). After the charge-discharge cycling tests on battery cells, the cells were disassembled to take out the cathode. *K*-shell ELNES of the dopants Al and Mg were measured from the ion-milled sample. Their theoretical spectra were calculated by the first principles APW+lo band method. In order to image electrochemically degraded areas included over an entire secondary particle, samples prepared by FIB were analyzed by STEM-EELS.

In Fig. 2 are shown the typical Ni-*L*<sub>2,3</sub> and O-*K* ELNES of the sample. Ni *L*<sub>2</sub>/*L*<sub>3</sub> relative intensity ratio is known to become higher as Ni more oxidized. The broken line spectrum is responsible for Ni<sup>2+</sup>, while the solid line corresponds to Ni<sup>3+</sup> in LiNiO<sub>2</sub>[2,3]. The O-*K* spectra differ correspondingly. Because Ni<sup>2+</sup> is electrochemically inactive, the areas responsible for the broken line spectra should be degraded.

Regarding the Ni *L*<sub>2</sub>/*L*<sub>3</sub> relative intensity ratio as a measure of the degradation, the dopants spectra were collected at the normal and anomalous areas. Representative Mg- and Al-*K* spectra are shown in Fig 3-a and b, respectively. We use the calculated spectra as theoretical fingerprints (Fig. 3-c and d). Comparing the experimental spectra with the theoretical, in the normal LiNiO<sub>2</sub> area, we find that both Mg and Al mainly occupy the Ni site. In the anomalous areas, the chemical state of Mg is estimated as Mg in NiO. Similarly, Al in degraded area 1 corresponds to Al in NiO. The spectrum profile of degraded area 2 is consistent with the theoretical one of Al in LiAlO<sub>2</sub>, which has the same crystal structure as LiNiO<sub>2</sub>.

Our EDX and x-ray absorption spectroscopy analyses on the dopants indicated that the charge-discharge cycles decreased the Mg concentration at least at the surface of the secondary particles. Our first principles calculation for the dopants in LiNiO<sub>2</sub> indicated that Al-O bonds are much stronger than Mg-O, while Mg reinforced the Ni-O bonds of the nearest neighbor Ni. Combining these findings to the fact that some Al atoms have chemical states similar to LiAlO<sub>2</sub>, we can see different characters of Mg and Al, that is, the doped Mg would be eluted out from the cathode active material while the Al would stay at the Ni site in LiNiO<sub>2</sub>, depending on their local chemical bonding.

In the presentation, we will discuss the degradation process based on the dopants chemical bonding and the degraded areas distributed in the secondary particle, which were revealed for the first time by a multi-variate analysis on the STEM-EELS results.

### References

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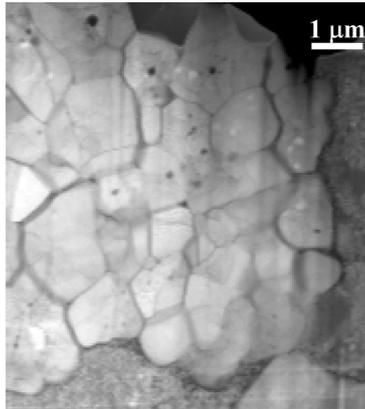


FIG. 1. STEM dark field image of the cathode material prepared by FIB

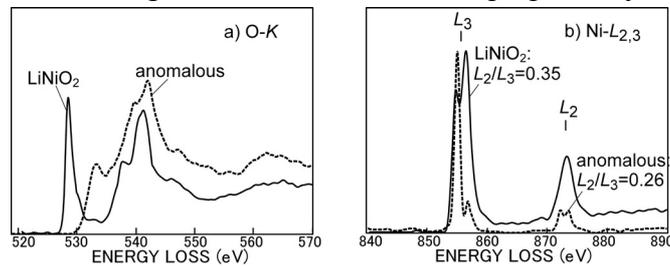


FIG. 2. Typical O-K (a) and Ni- $L_{2,3}$  (b) ELNES of the cathode

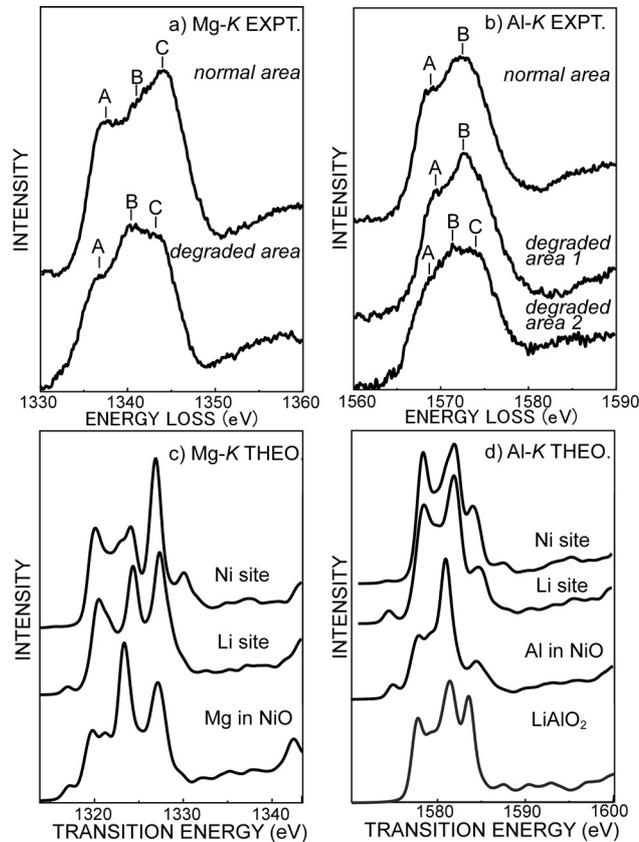


FIG. 3. Experimental Mg-K (a) and Al-K (b) ELNES and theoretical ones for possible chemical states of Mg (c) and Al (d)