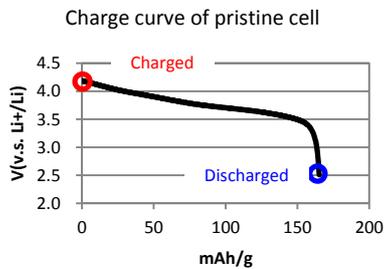


XAFS and STEM analysis of high resistance phase increased in NCA cathode of LIB

III-1

To clarify degradation mechanism in cathode active materials under various test conditions, we provide analysis services of surface valence state, local valence state and crystal structure distribution in active materials of test cells at controlled states of charge.

Samples



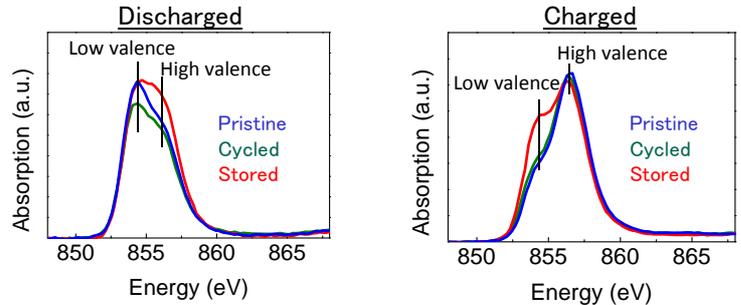
Laminate cells (1100 mAh)

- Cathode: $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (NCA)
- Anode: graphite
- Electrolyte: 1M LiPF_6 + EC/DEC (3/7) + VC

1. Pristine (Electrochemically activated)
2. Cycle-tested (0.5C x 200cycles at RT)
3. Stored (4.1V for 2 months at RT)

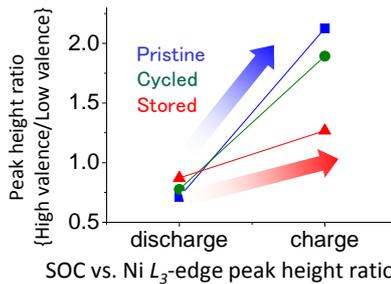
→ Cathodes extracted from samples 1-3 were charged or discharged in half cells and analyzed by XAFS and STEM.

Results of XAFS



Ni L_3 -edge XANES spectra of NCA cathode surface (Total electron yield)

- Ni oxidation by charging process was clearly observed
- Stored sample showed less change in valence population than the other two samples

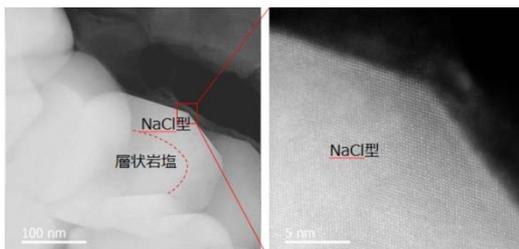


Slope: Pristine > Cycled >> Stored

Cycle and storage tests increased the amount of resistance phase which doesn't contribute to redox reaction.

HAADF-STEM images

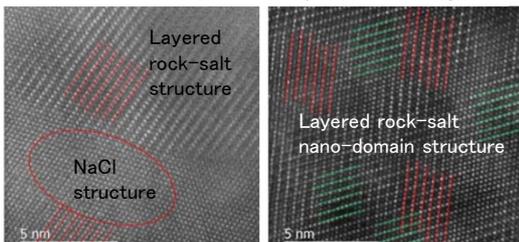
Stored and discharged sample



Inactive NaCl structure was observed at the surface of NCA down to ca. 50nm deep.

Cycled and discharged

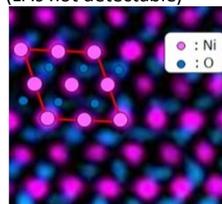
Cycled and charged



Structural difference dependent on SOC was observed.

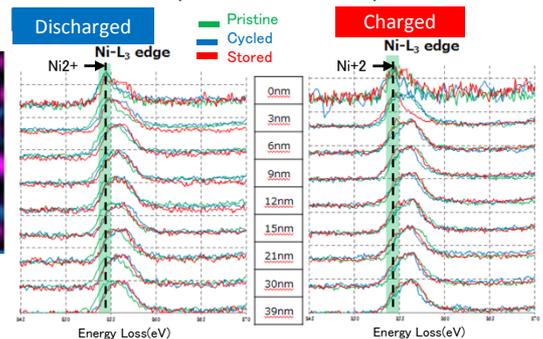
EDS atomic column mapping (NCA[010]) and EELS

EDS mapping of Ni_K + O_K (Li is not detectable)



NaCl structure was observed.

EELS spectra at various depths



- Consistent result with XAFS.
- Stored and discharged sample had an NaCl structure but showed higher valence state of Ni than bivalence.

- Stored and discharged sample had a thick surface layer of NaCl structure with a thickness of ca. 50nm where Ni was nearly trivalent ($\text{Li}_x\text{Ni}_{1-x}\text{O}$, $X=0.5$).
- Cycle-tested sample had nano-domain structure, whose repeated growth and granulation might result in the gradual increase in the domain of NaCl structure.