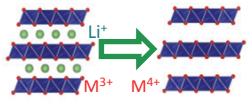
Structural analysis of LIB cathode material using Chemical Delithiation/Lithiation

We can prepare model active materials of various SOC alone by chemical delithiation / lithiation, without influence from the other components in an actual cell. It enables us to examine their thermal stability, crystal structure and local environment around Li ions at various charging / discharging states.

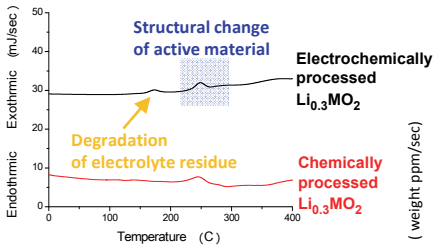
【Example : NCA($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)】

【Charged model samples:Chemical Delithiation】 to simulate / evaluate various SOC-cathodes



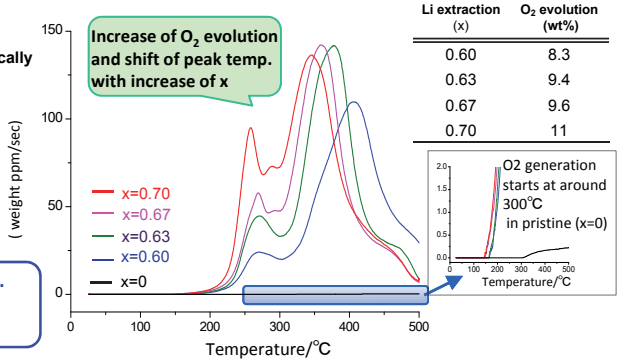
$LiMO_2 + xNO_2BF_4 \rightarrow Li_{(1-x)}MO_2 + x\ LiBF_4 + x\ NO_2\uparrow$ (M:Ni,Co,Al etc) $LiMO_2$ is delithiated by oxidant.

DSC profiles of $Li_{0.3}MO_2$ (x=0.7)



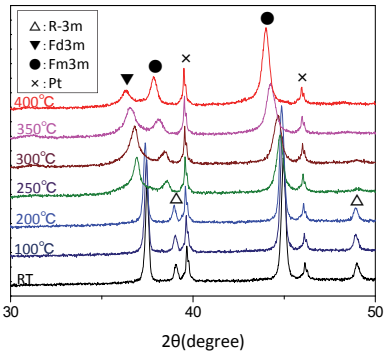
Exothermal behaviors are slightly different.
⇒ Influence from the other components should be eliminated.

Oxygen generation rate of $Li_{(1-x)}MO_2$ by TPD-MS



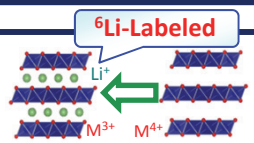
Li extraction (x)	O_2 evolution (wt%)
0.60	8.3
0.63	9.4
0.67	9.6
0.70	11

HT-XRD patterns of $Li_{0.3}MO_2$ (x=0.7)



✔Chemical Delithiation enables us to evaluate thermal stability/crystal structure without influence of other components.

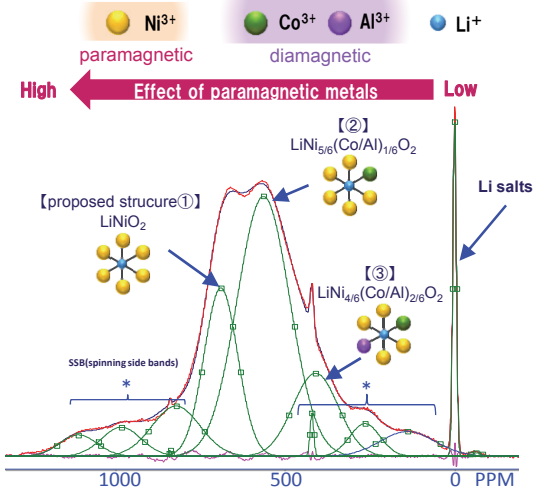
【Discharged model samples:Chemical Lithiation】 to reveal inserted Li sites



$Li_{(1-x)}MO_2 + x\ LiI \rightarrow LiMO_2 + x/2\ I_2$ (M:Ni,Co,Al etc) $Li_{(1-x)}MO_2$ is lithiated by reductant.

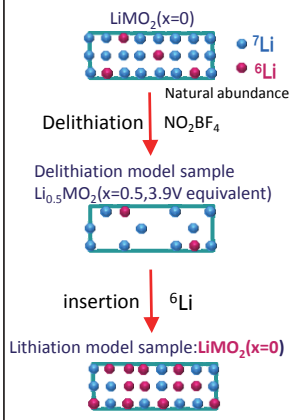
-Local structural analysis around Li ion by solid-state NMR-

^7Li MAS NMR spectrum of $LiMO_2$ (x=0)



Chemical shifts are influenced by paramagnetic metals around Li.
(Ref.: Journal of The Electrochemical Society,162 (7) ,A1315-A1318 (2015))

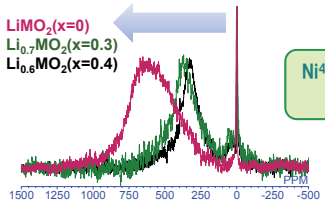
Chemical Delithiation/Lithiation



The other 2 intercalation-levels:
$Li_{0.7}MO_2$(x=0.3), $Li_{0.6}MO_2$(x=0.4)

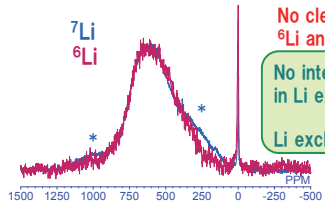
^6Li,^7Li MAS NMR spectra of Chemical Lithiated samples

^6Li NMR spectra at various ^6Li inserting states



$Ni^{4+} \rightarrow Ni^{3+}$ redox reaction with ^6Li insertion

^6Li,^7Li NMR spectra of ^6Li inserted $LiMO_2$(x=0)



No clear difference between ^6Li and ^7Li spectra.

No intercalation site selectivity in Li extraction/insertion or Li exchanged among Li^+ sites

✔Chemical Lithiation enables us to analyze local structural change around Li ion in ^6Li-labeled cathode materials.

Chemical Delithiation/Lithiation is useful for analyzing charge-discharge reaction in cathodes and designing materials.

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