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SPring-8グリーンエネルギー研究会

Ni系リチウムイオン電池正極材料のXAFS解析

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本日の内容

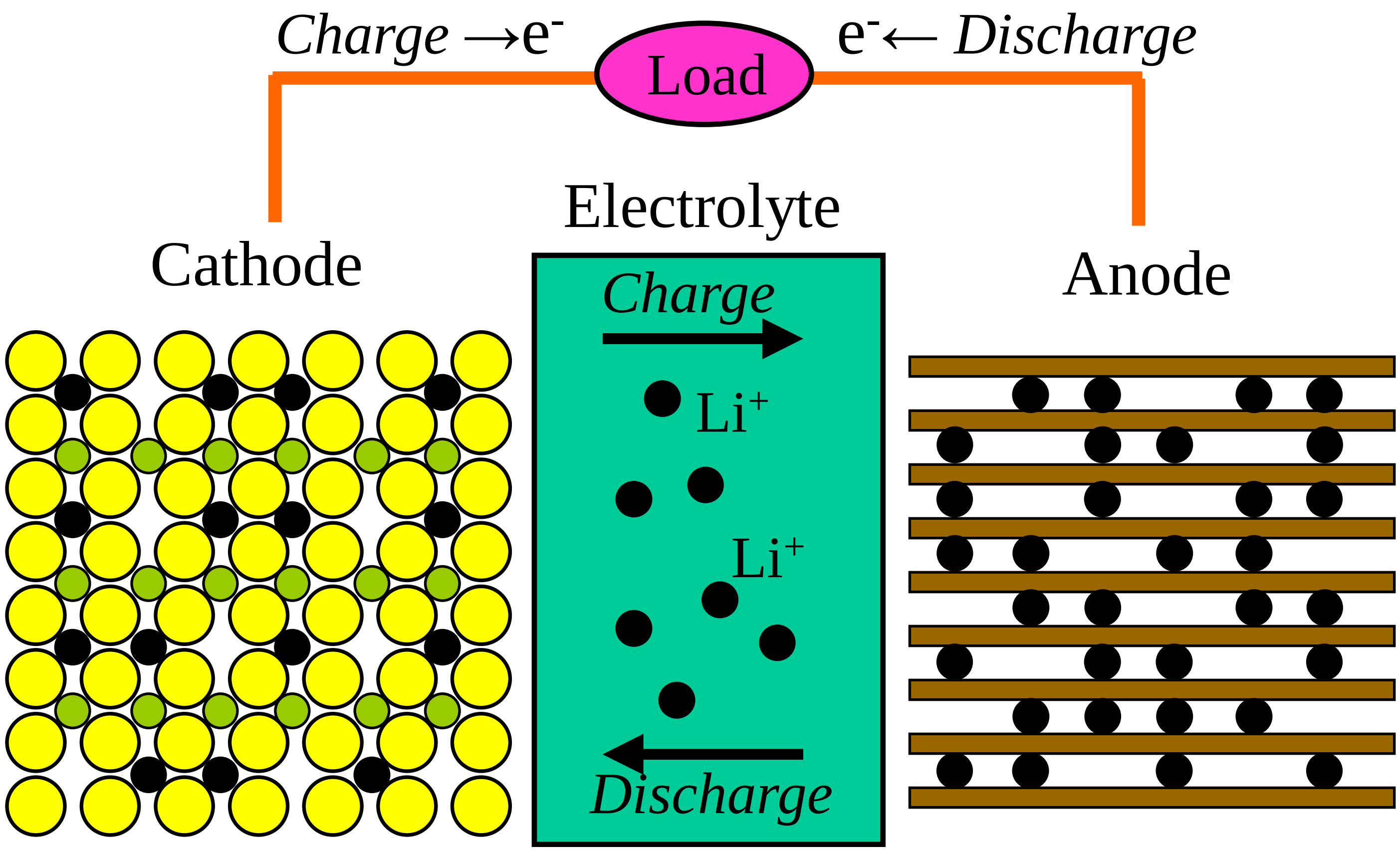
1．はじめに

2．実験①　$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$のXAFS解析

3．実験②　XAFSによる電池劣化の定量的評価

4．まとめ

リチウムイオン電池



Schematic diagram of Li-ion battery

実利用において求められる性能

- High Power
- High Capacity
- Long Life
- Low Cost
- Safety

Li-ion batteries consist of Cathode, Anode, Electrolyte, Separator, Charge Collector, etc.

Cathode material is one of the key components that decide such performances

正極材料

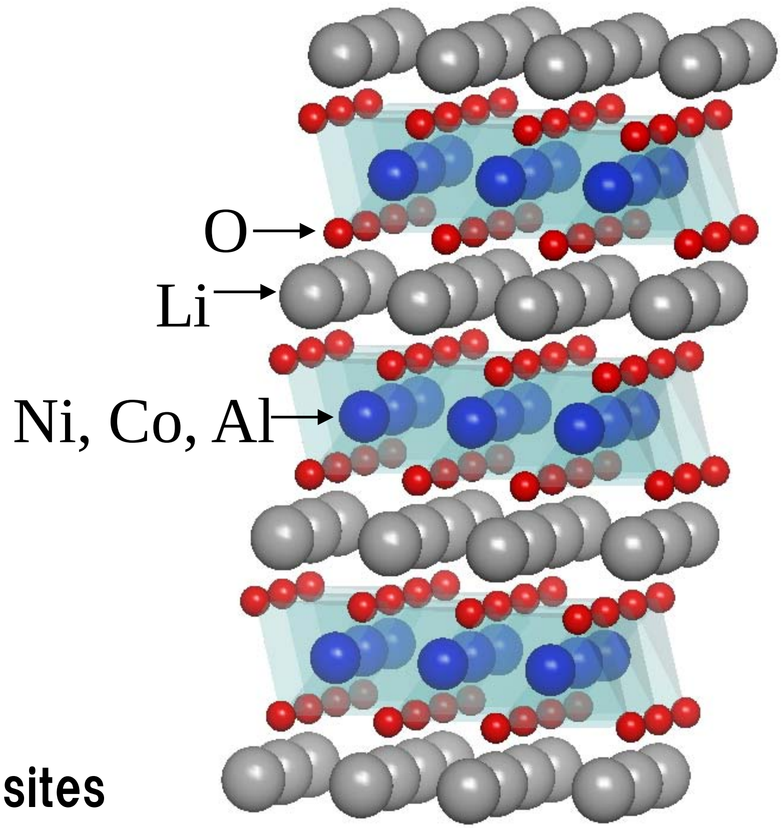
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

as a substitute for $LiCoO_2$

- High Power
- High Capacity
- Low Cost

Structural stabilization by substituting Co and Al for Ni sites

No phase transition during charge/discharge (R3m)



Structure of $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$

克服すべき問題

Capacity fade
Impedance rise

during charge/discharge cycles

storage at high temperatures

⇩

What is the main source of the deterioration of batteries?

Cathode material (Y. Itou et al., *J. Power Sources*, 146, 39 (2005))

⇩

Extensive characterizations of cathode materials are required.

SEM, TEM, XPS, XRD, ICP, …, …, …, XAFS

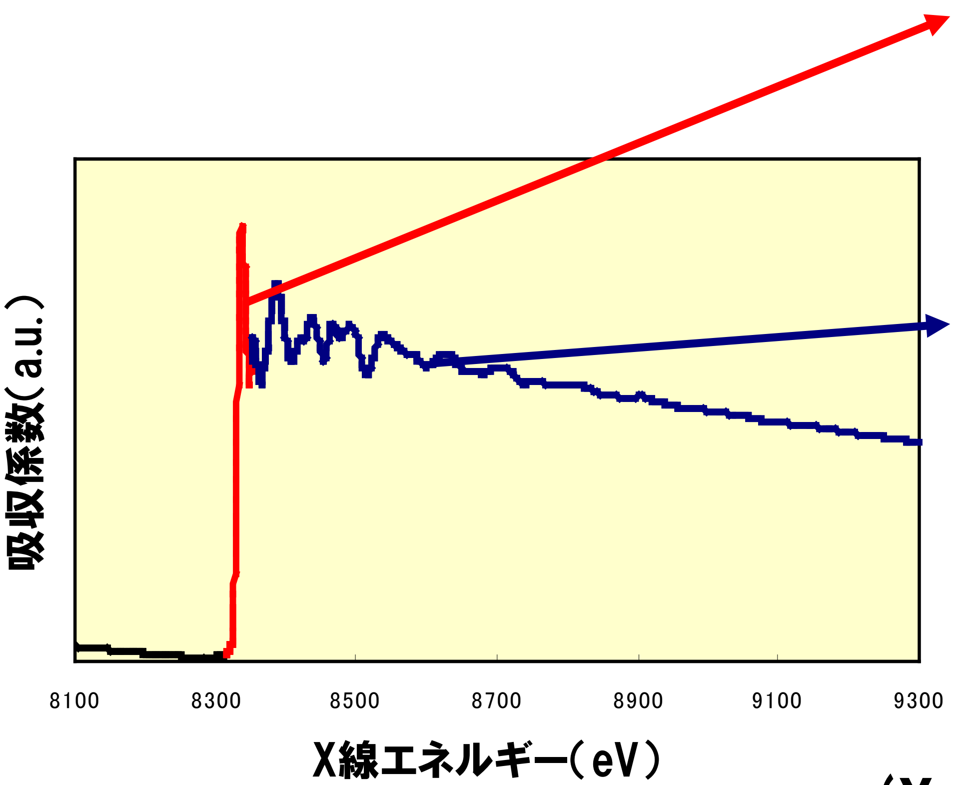
実験① 背景・目的

- The deterioration at the near-surface region of cathode particles is considered to be a main source of the capacity fade and impedance rise.

⇩

- The electronic and structural changes accompanied by battery deterioration have been investigated using Ni and Co K-edge X-ray absorption spectroscopy in the surface-sensitive conversion electron yield mode and the bulk-sensitive transmission mode.

XAFSとは？



Ni K吸収端XAFSスペクトル

XANES
(X-ray Absorption Near Edge Structure)
吸収原子周辺の電子状態

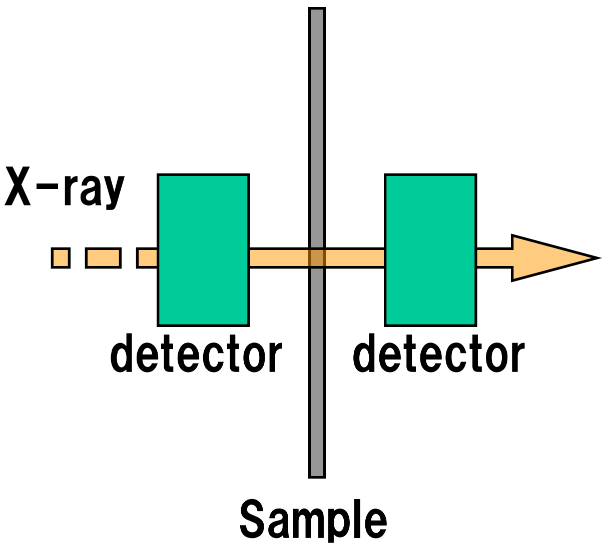
EXAFS
(Extended X-ray Absorption Fine Structure)
吸収原子周辺の局所構造

↓

XAFS
(X-ray Absorption Fine Structure)
X線吸収微細構造

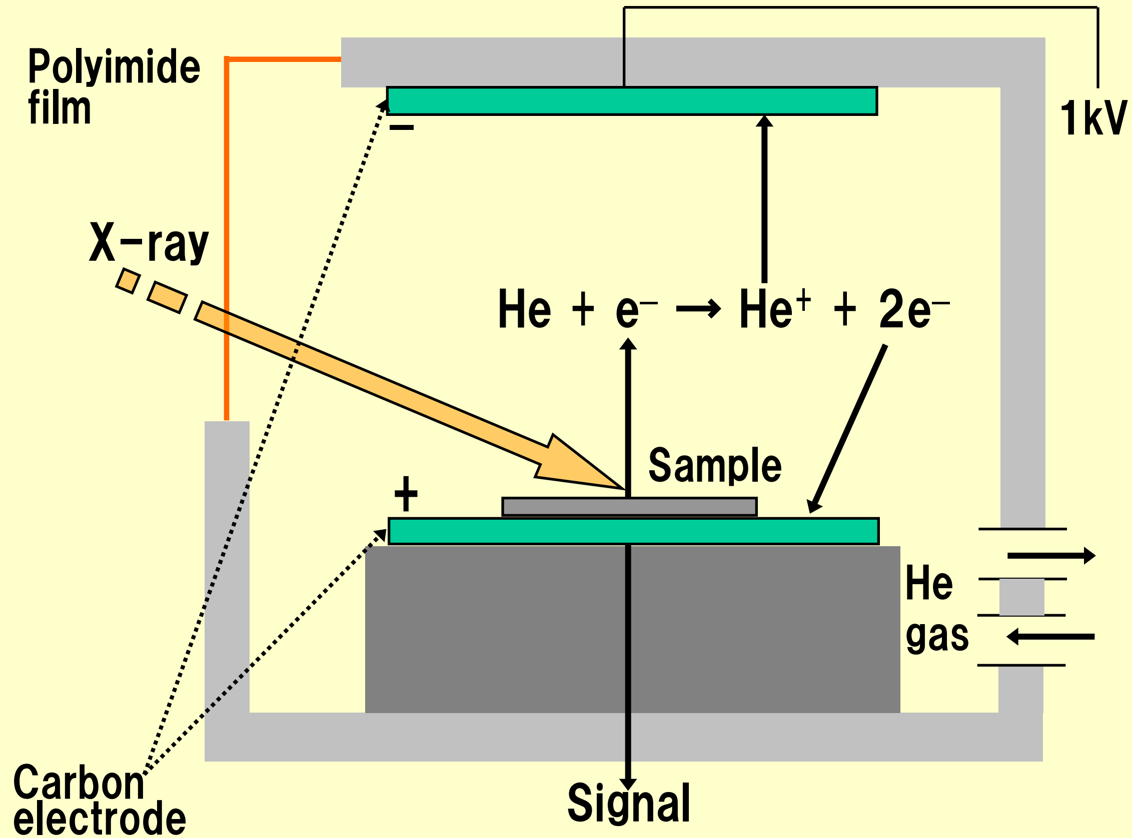
2種類のXAFS測定手法

透過法 (Trans.)



バルク敏感（平均情報）

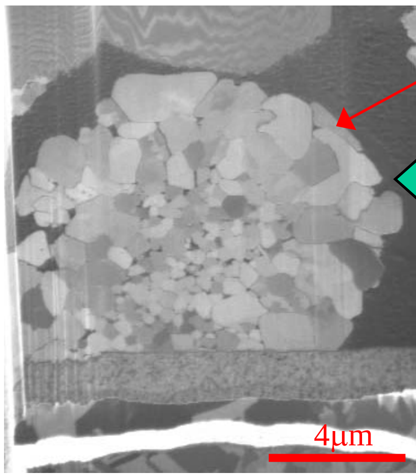
転換電子収量法 (CEY)



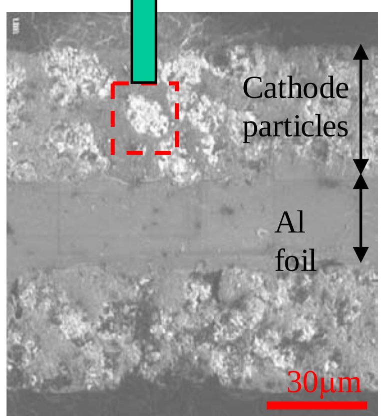
表面敏感（分析深さ:～90 nm）

試料

Cathode sheets extracted from 18650-type cells which exhibit various levels of capacity fading



FIB-SIM image of a cathode particle.



FIB-SIM image of a cathode sheet.

Cell condition	Capacity† (mAh/g)
Fresh: One charge/discharge cycle	160.0
Cycle test : 1000 charge/discharge cycles at 60 °C*	122.6
Aging test: Stored at 60 °C for a year**	125.0

*Constant current mode, 2 mA cm^{-2} between 4.1 V and 3.0 V
**Storage in air with the voltage held at 4.1 V (charged state)
†Discharge capacity obtained at 0.20 mA cm^{-2}, (3.2V cut-off)

実験手順

電池作製

耐久試験(1000サイクル@60℃、1年保存@60℃)

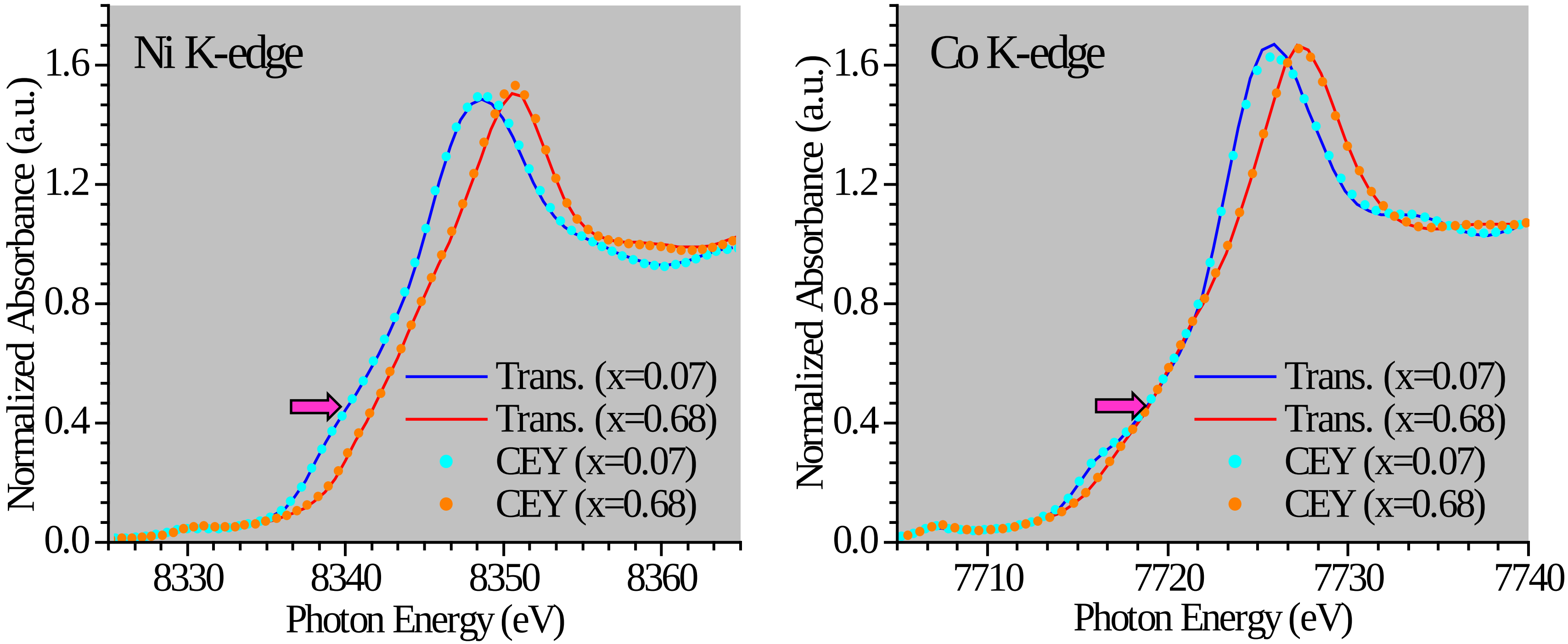
解体・正極取出し

単極評価(容量、抵抗)

SOC※調整　　SOC※:充電状態(State of Charge)

XAFS測定(透過法、転換電子収量法)
@SPring-8 BL16B2 (サンビーム)
ICP組成分析(Li量)

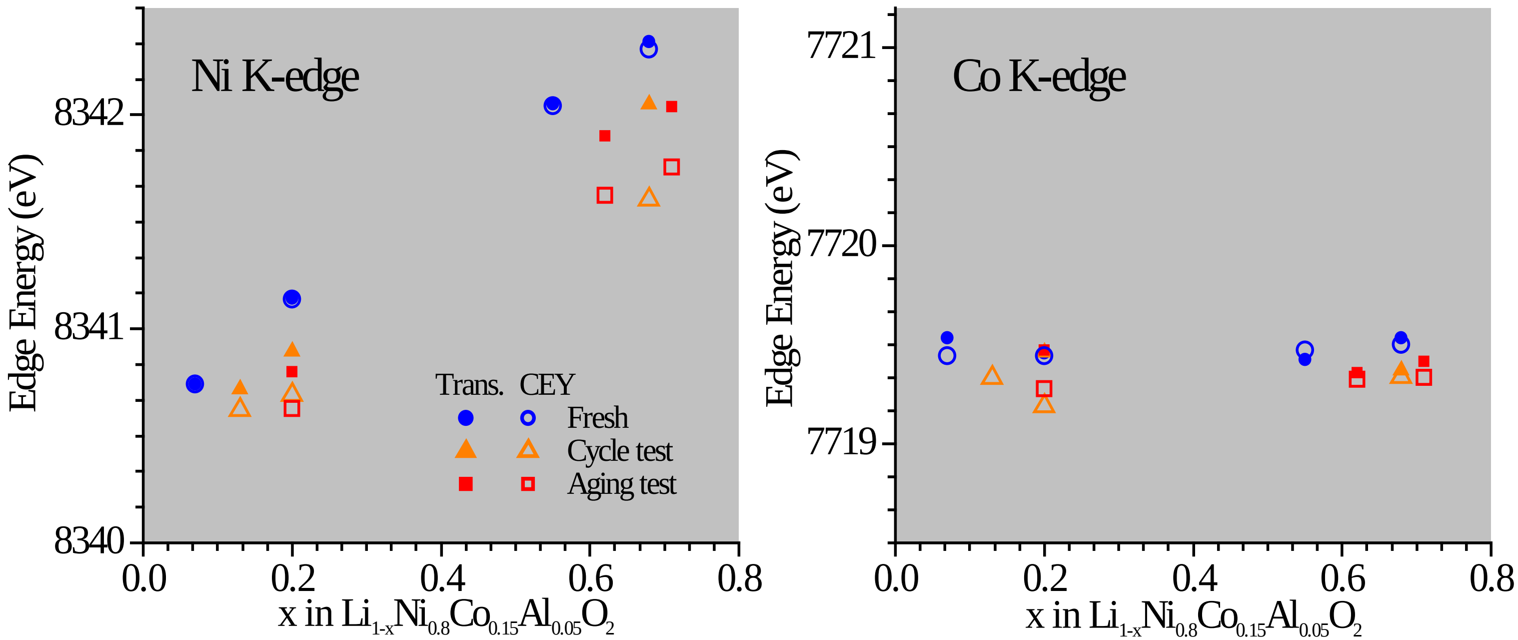
XANESスペクトル



Representative normalized XANES spectra for $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ obtained in transmission XAFS (Trans.) and conversion electron yield XAFS (CEY).

Data qualities of two different modes are identical.
⇨ Quantitative comparison is possible.

Edge Energyの比較



The edge energy measured at the half-step height of XANES spectra for Ni and Co in $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$. ¥

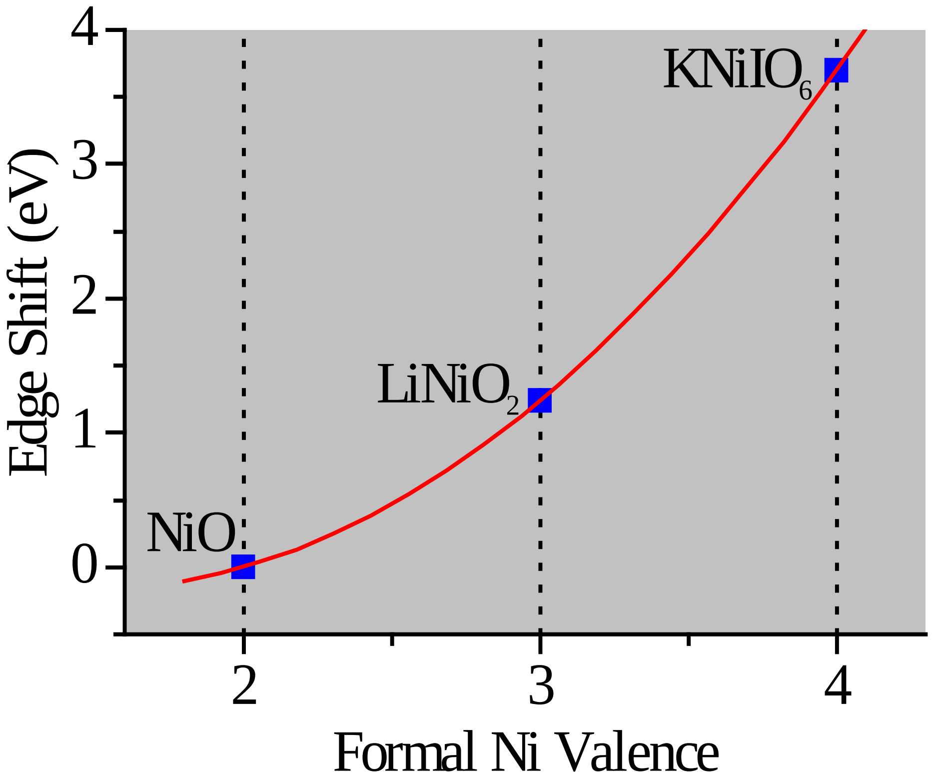
Ni…oxidizes upon charging, and exhibits different behaviors depending on the cell condition and the probing mode.

Co… hardly changes upon charging. Slight reductions after the tests.

Ni価数とEdgeシフトの関係

Quadratic relationship between formal Ni valence and the edge shift of XANES spectra.

(A.N. Mansour et al., *J. Electrochem. Soc.*, 146, 2799 (1999))

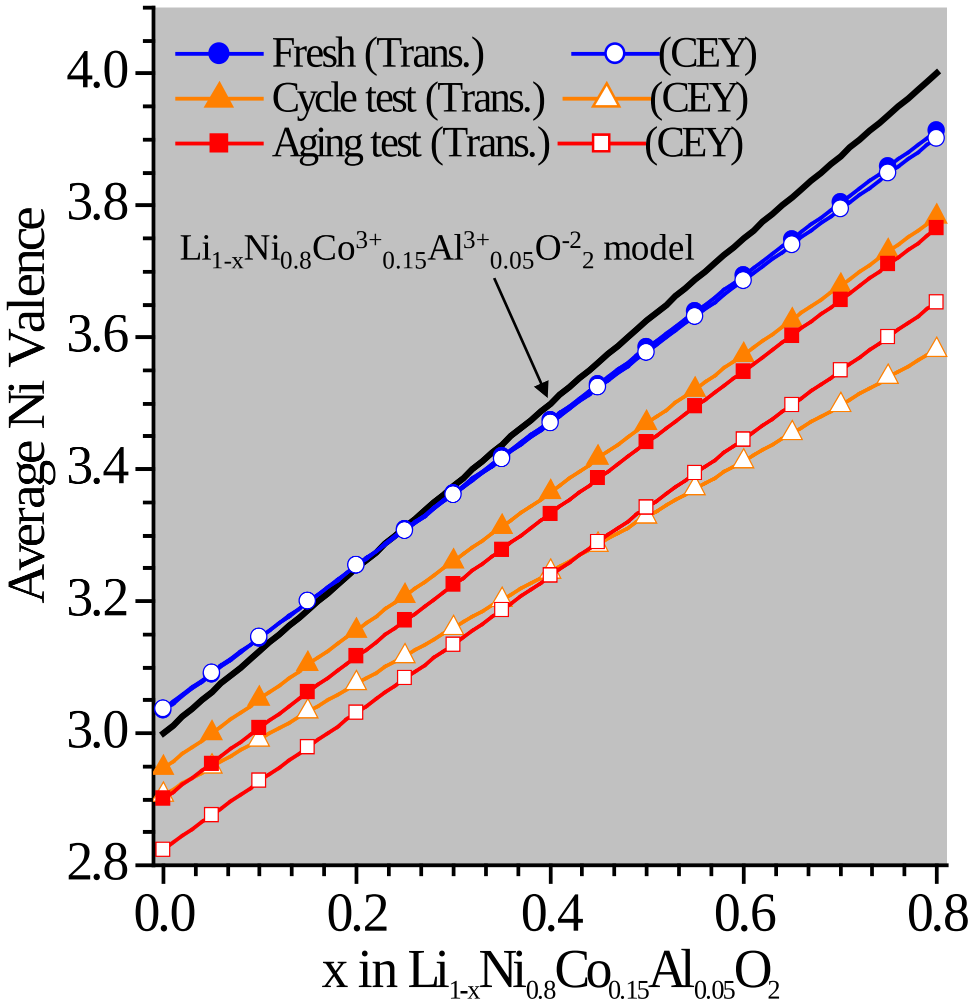


Edge energy

⇩

Average Ni valence

Edgeから導出されたNi平均価数



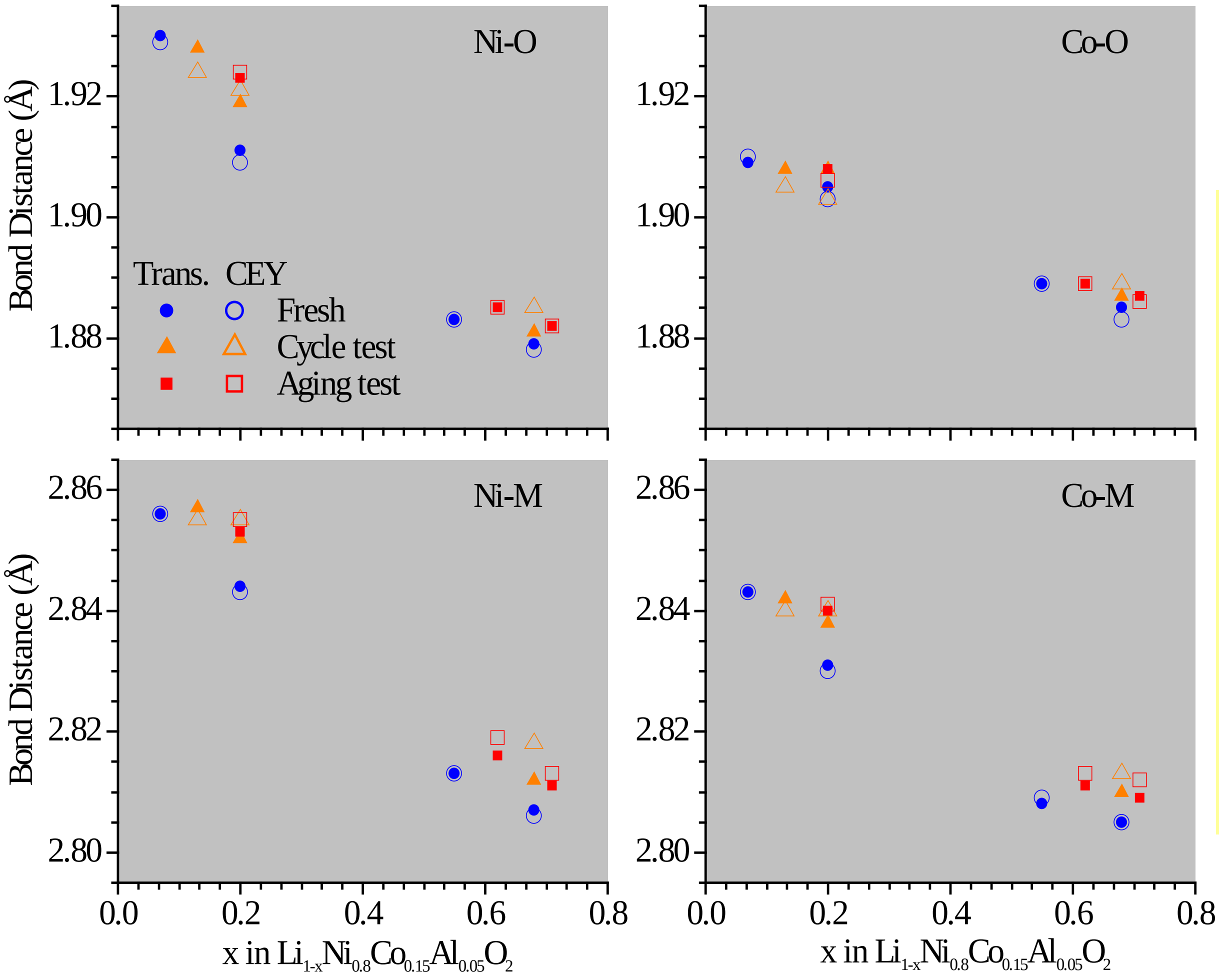
Approximate lines obtained by least-squares fits to average Ni valences.

Fresh cell…Ni oxidizes from 3+ to 4+ upon charging.

No difference between bulk（Trans.）and surface（CEY）.

Tested Cells…Ni valences are lower than that for the fresh cell prominently at the surface. The slopes of the lines for the surface are more gradual, implying the presence of the Ni atoms that do not oxidize upon charging.

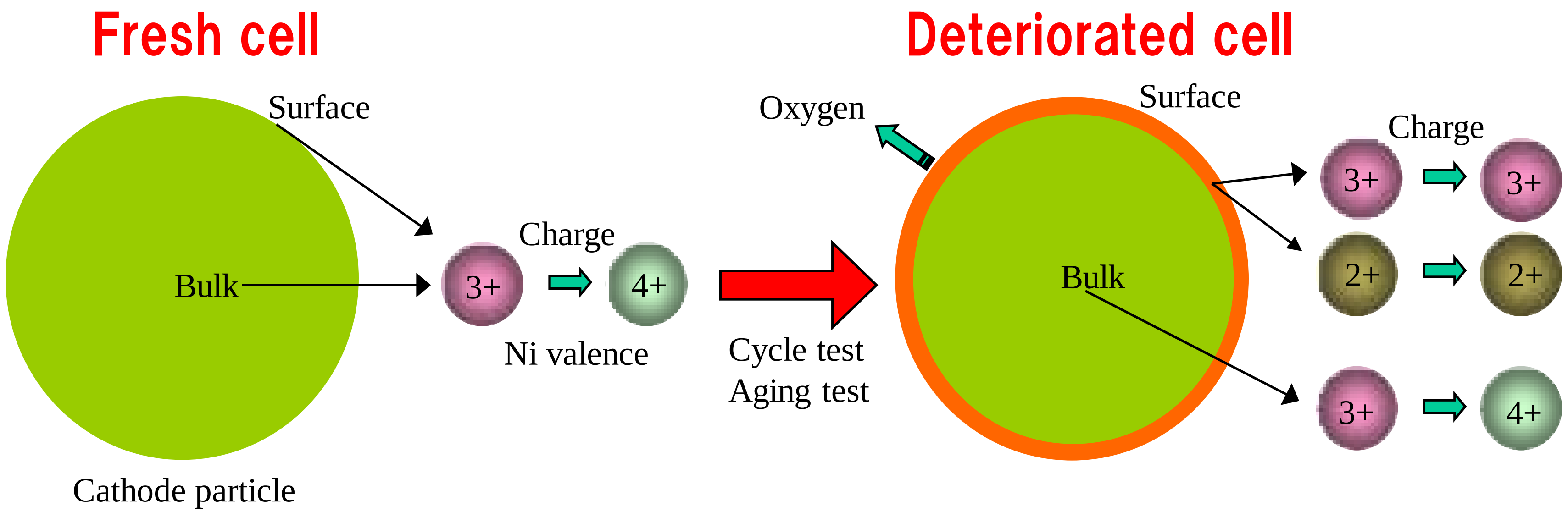
EXAFS解析から得られた結合距離



Variations of structural parameters obtained by the fitting to the first two peaks of the Ni and Co K-edge FTs.

The bond distances for the tested cells are longer than those for the fresh cell.
⇨ The presence of Ni atoms with lower valences.

本実験より得られた電池劣化モデル



Growth of surface layer including inactive Ni atoms

⇨ may reduce electronic and ionic conductivities.

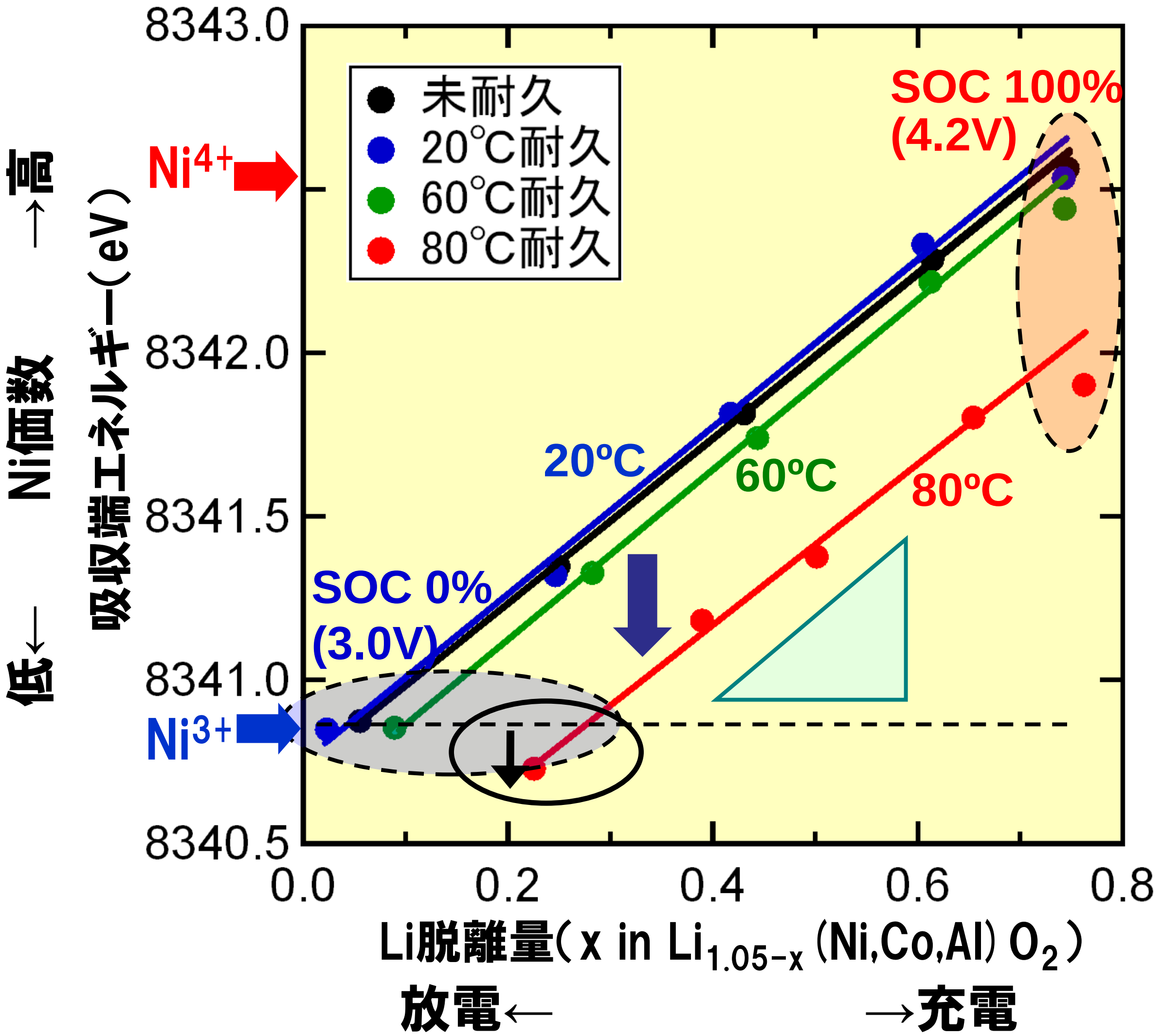
⇨ a possible main cause of capacity fading and impedance rise.

実験② 目的

・実験①と同様な手法をより多くの状態の電池(サイクル温度、SOC)に適用し劣化現象についての理解を深める

・劣化を示すパラメータ(電池容量、反応抵抗)とXAFSにより得られるパラメータの間に定量的な相関関係がないか調査する

透過法XAFS(バルク情報)測定結果



高温耐久後:

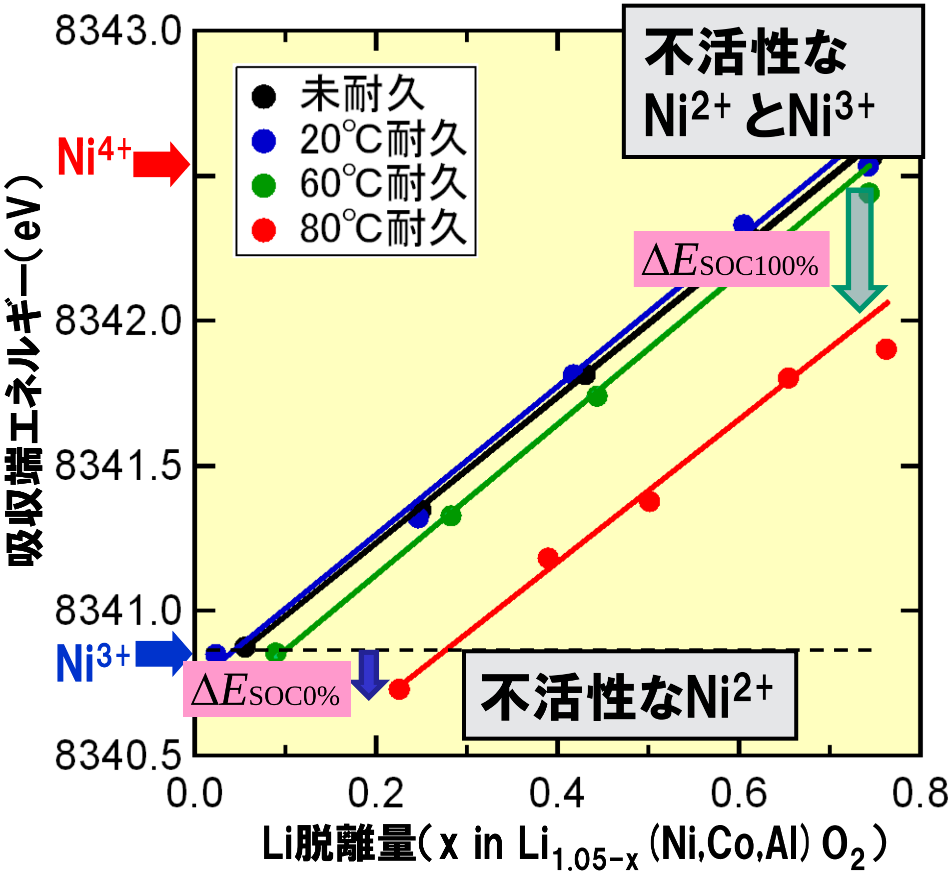
傾きは変化なし
⇒**酸化還元種はNi**

Ni価数低下
⇒Li欠損かつ低価数で
不活性なNiの生成

80℃サイクル後には
Ni^{2+}も顕著に生成

劣化は活物質自身の変質(Li-Ni価数関係)

バルク劣化に関する定量的な解析



①全Ni量を1としたときの不活性なNi^{2+}の量

$$Q_{\mathrm{Ni(II)}} = \Delta E_{\mathrm{SOC0\%}} / \Delta E_{\mathrm{Ni(II)Ni(III)}}$$

$$(\Delta E_{\mathrm{Ni(II)Ni(III)}} = 1.24[\mathrm{eV}])$$

②不活性なNi^{3+}によるEdge Energyの低下量

$$\Delta E_{\mathrm{Ni(III)}} = \Delta E_{\mathrm{SOC100\%}} - \Delta E_{\mathrm{Ni(II)Ni(IV)}} \times Q_{\mathrm{Ni(II)}}$$

$$(\Delta E_{\mathrm{Ni(II)Ni(IV)}} = 3.70[\mathrm{eV}])$$

③不活性なNi^{3+}の量

$$Q_{\mathrm{Ni(III)}} = \Delta E_{\mathrm{Ni(III)}} / \Delta E_{\mathrm{Ni(III)Ni(IV)}}$$

$$(\Delta E_{\mathrm{Ni(III)Ni(IV)}} = 2.46[\mathrm{eV}])$$

④全不活性Ni量

$$Q_{\mathrm{total}} = Q_{\mathrm{Ni(II)}} + Q_{\mathrm{Ni(III)}}$$

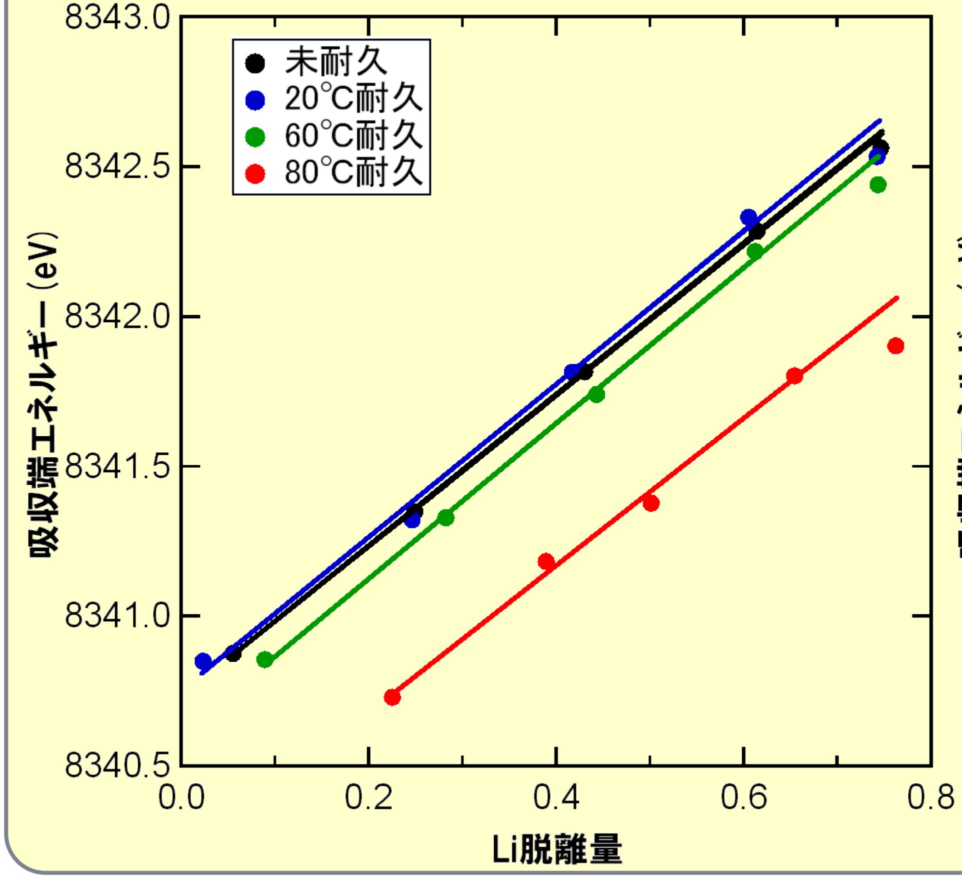
定量解析の結果

Cycling temperature (℃)	$Q_{Ni(II)}$ (%)	$Q_{Ni(III)}$ (%)	Q_{total} (%)	Estimated capacity fade (mAh/g)	Measured capacity fade (mAh/g)
60	1.61	2.57	4.18	9.33	10.6
80	11.8	9.16	20.9	46.7	47.8

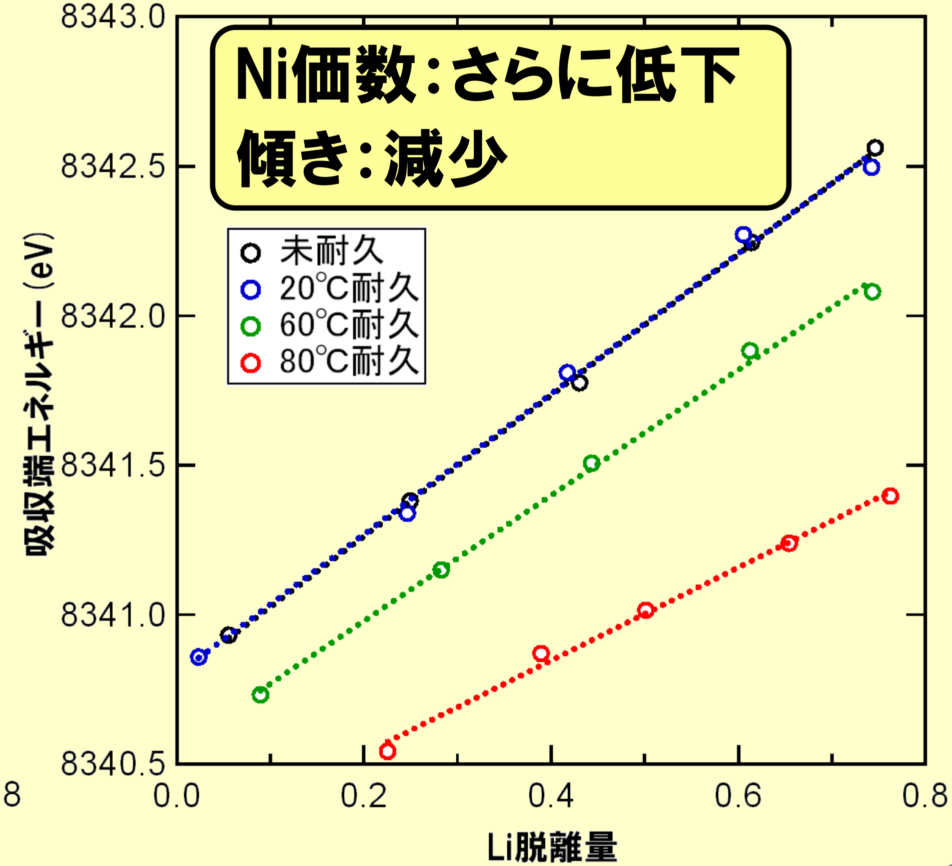
不活性Ni量と電池容量低下の間に良い相関

転換電子収量法XAFS 測定結果

透過法
（⇒バルクNi価数）

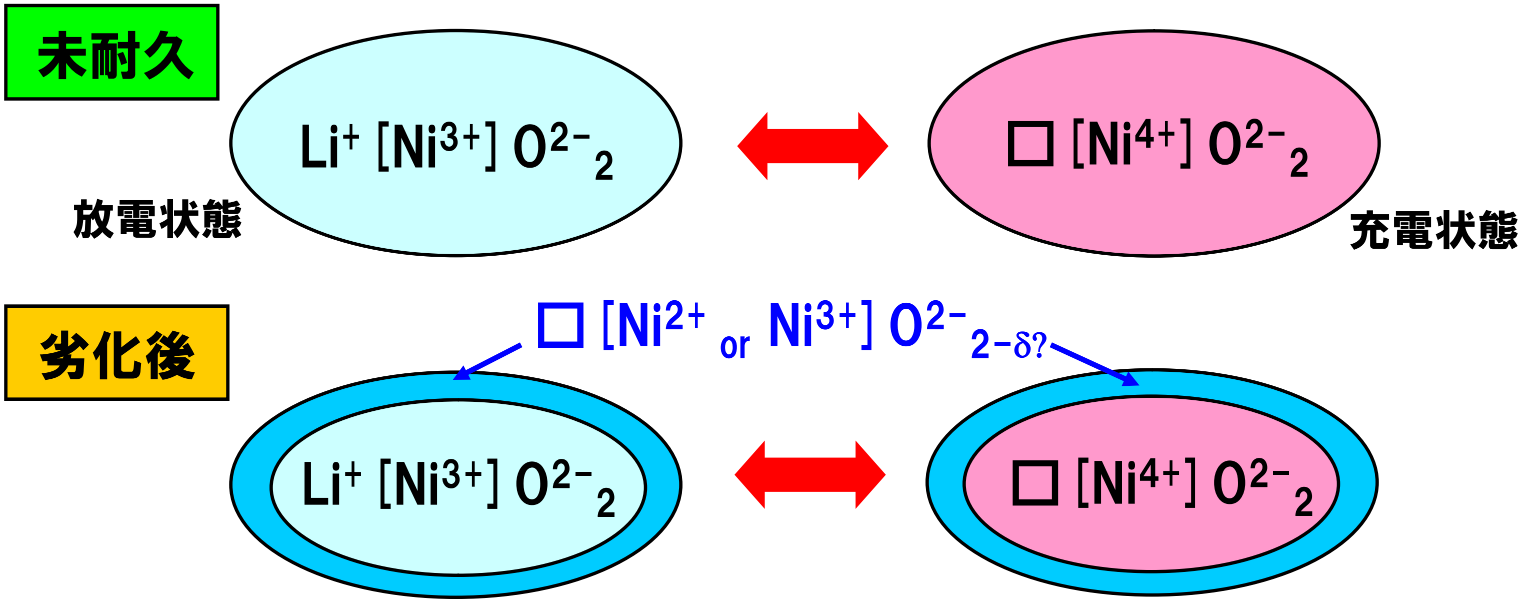


転換電子収量法
（⇒表面Ni価数）



低価数で不活性なNiの表面局在を示唆

まとめ



正極活物質中に低価数な不活性Niが生成
⇒可逆容量減少

不活性Niの生成は活物質表面で顕著
⇒反応抵抗増加の原因?