

# リチウムイオン電池正極材料の XAFS 解析

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層状構造を有する  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  は次世代のリチウムイオン電池正極材料の有力な候補の一つである。本材料は、現在広く利用されている正極材料  $\text{LiCoO}_2$  に比べて低コスト且つ高出力であるというメリットを有する。しかしながら、長期の利用により電池容量が低下し、且つ反応抵抗が増大するという電池劣化問題が未だ解決されていない。本研究の目的は、電池劣化に伴う Ni, Co 周辺の電子状態変化、局所構造変化を明らかにすることにより、容量低下・反応抵抗増大の原因を究明することである。本研究では、表面敏感性(分析深さ約 90 nm)を有する転換電子収量法 XAFS とバルク敏感な透過法 XAFS の両方を用いることによって、Ni, Co の価数・局所構造が、正極粒子の表面とバルクで違いがあるか否かについて調査した。その結果、作製直後の電池においては、Ni, Co の価数・局所構造が表面とバルクで同じであるのに対して、サイクル耐久試験(60、1000 サイクル)および高温保存耐久試験(60、1年間保存)後の電池では、粒子表面の Ni, Co の価数がバルク平均価数に比べて低くなっていることがわかった。また、電池充電に伴う Ni 価数の変化量も低下した。EXAFS 解析による局所構造の結果もこれらの価数に関する観測結果を支持するものであった。これらの観測事実は、粒子表面に低価数(2価)の Ni が存在していること、さらには一部の Ni 原子が電池充電に伴う系の電荷補償に関与しなくなっていることを示唆している。本研究およびその他の分析手法による観測結果から、劣化後の正極粒子の表面において、電気化学的に不活性な Ni 原子を含む低価数 Ni 相(NiO 様相)が形成されていることが推定された。NiO は本材料に比べてイオン導伝性・電子導伝性が著しく劣ることから、この NiO 様相の形成が電池容量低下・反応抵抗増大の要因になっている可能性が提案された。

The slide features a blue header with the 'SPring-8' logo on the left and the date '2007/09/11' and event name '第4回SPring-8産業利用報告会' on the right. The main title 'リチウムイオン電池正極材料の XAFS解析' is centered in a large orange box. Below the title, the presenter's name '(株)豊田中央研究所 野中 敬正' is written in red. At the bottom right, the 'TOYOTA CENTRAL R&D LABS., INC.' logo is displayed.

## Outline

1. General Introduction
2. Surface-sensitive XAFS Study on  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$
3. Effect of Mg doping on Electrochemical and Structural Properties of  $\text{LiNi}_{0.75}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mg}_{0.05}\text{O}_2$

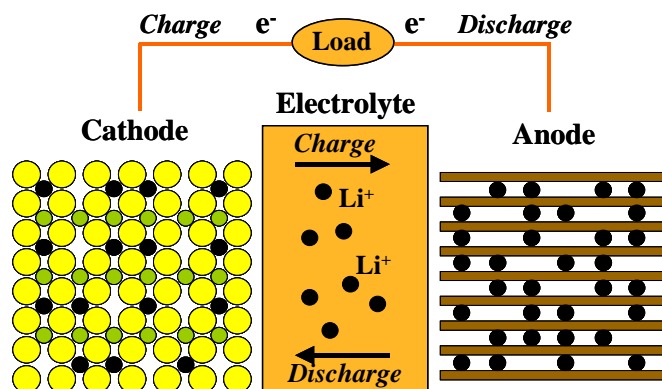


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## Li-ion battery



Schematic diagram of Li-ion battery



## Performances required for practical applications

- 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

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## A promising cathode material

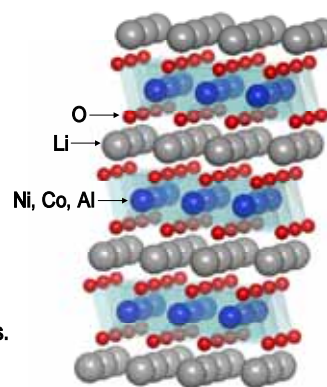


as a substitute for  $\text{LiCoO}_2$

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

Stabilization produced by substituting Co and Al for Ni sites.

No phase transition during charge/discharge (R3m).



Structure of  $\text{Li}_{1.3}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

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## Remaining problems - Battery deterioration -

- Capacity fading
- 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

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## 2. Surface-sensitive XAFS Study on $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

2007/09/11

### Introduction

- The deterioration at the **near-surface region** of cathode particles...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.

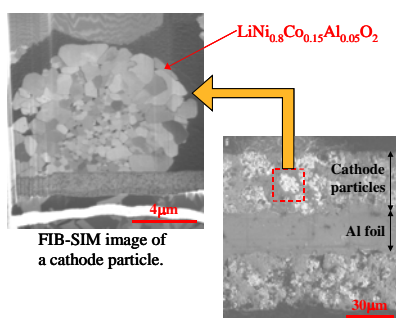


## 2. Surface-sensitive XAFS Study on $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

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### Samples

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



FIB-SIM image of a cathode particle.

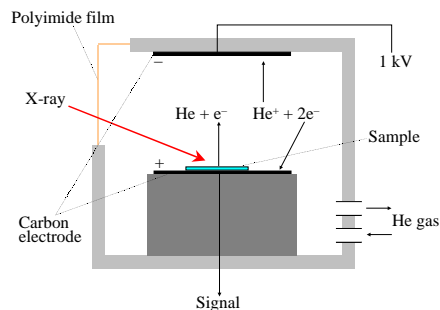
FIB-SIM image of a cathode sheet.

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

\*Constant current mode, 2 mA cm<sup>-2</sup> 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<sup>-2</sup>, (3.2V cut-off)



## XAFS in conversion electron yield mode



Schematic diagram of a conversion electron yield XAFS (CEY-XAFS) detector.

- Electrons emitted from a sample surface (KLL Auger electrons) are multiplied through the cascade ionization reactions with He atoms.

- Probing depth...?90 nm

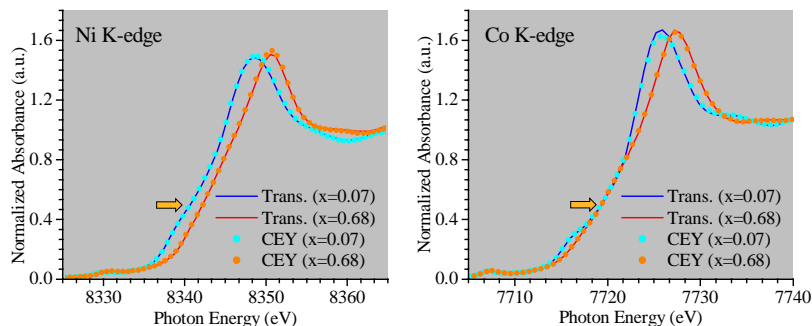
(S.L.M. Schroeder et al., *Surf. Sci. Lett.*, 324, 371(1995))

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2. Surface-sensitive XAFS Study on  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 

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## XANES



Representative normalized XANES spectra for  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  obtained in transmission XAFS (Trans.) and conversion electron yield XAFS (CEY).

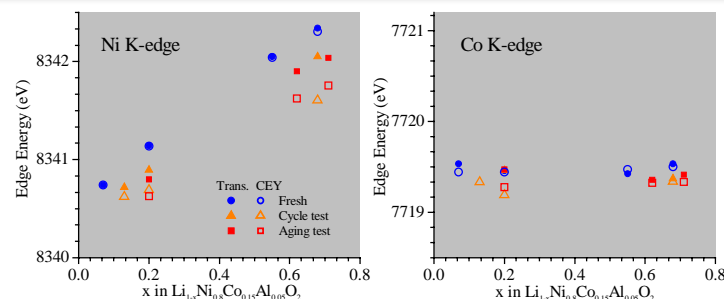
- Data qualities of two different modes are identical.
- Quantitative comparison is possible.

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2. Surface-sensitive XAFS Study on  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 

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## Comparison of the edge positions of XANES spectra



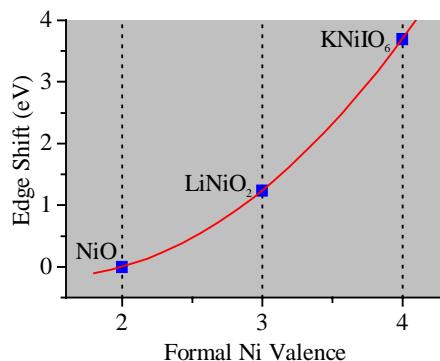
The edge energy measured at the half-step height of XANES spectra for Ni and Co in  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ .

- 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.

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

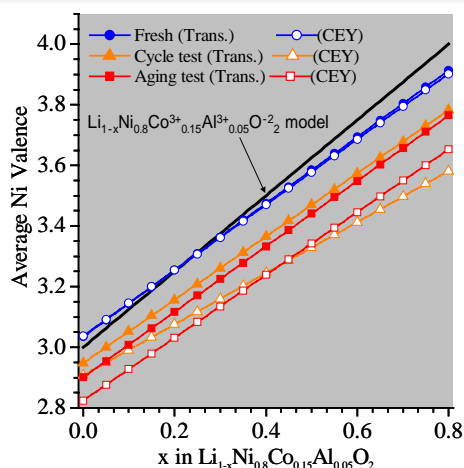
(A.N. Mansour et al., *J. Electrochem. Soc.*, **146**, 2799 (1999))



Edge position  
↓  
Average Ni valence

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### Average Ni valences estimated using the edge positions

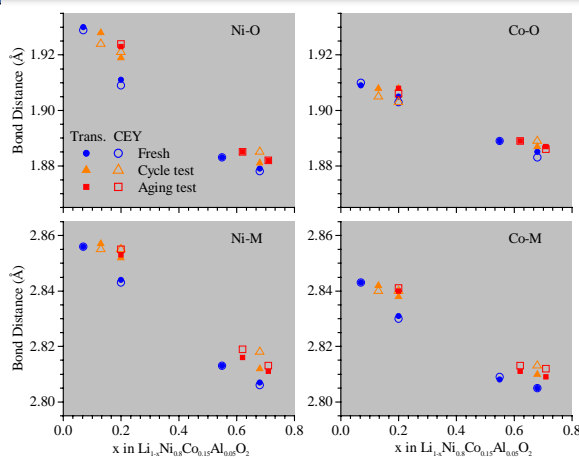


Approximate lines obtained by least-squares fits to average Ni valences.

- 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.

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### Bond distances

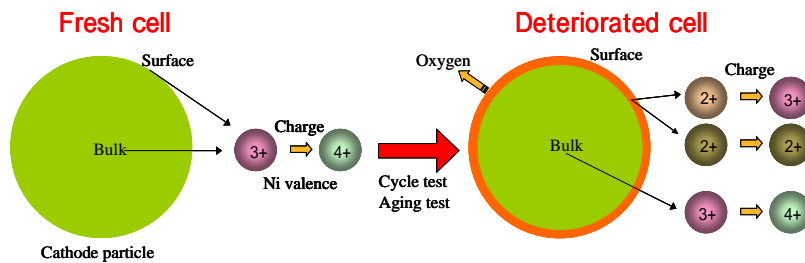


Variations of structural parameters obtained by the fitting to the first two peaks of the Ni and Co K-edge FTs.

- The bond distances for the tested cells are longer than those for the fresh cell.  
→ The presence of divalent Ni atoms.

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## A possible mechanism of battery deterioration



- **Growth of NiO-like surface layer including inactive Ni atoms**
  - ⇒ may reduce electronic and ionic conductivities.
  - ⇒ a possible main cause of capacity fading and impedance rise.

## Conclusion

- **After the cycling and aging tests**
  - The amount of divalent Ni atoms increased prominently at the surface.
  - Electrochemically inactive Ni atoms were created.
  - The bond distances (Ni-O, Ni-M, Co-O and Co-M) increased.
- These electronic and structural changes which occur prominently at the surface of cathode particles are probably main causes of capacity fade and impedance rise.
- Our combined probing method using both CEY and transmission XAFS can be a powerful tool to evaluate the state of cathode materials.

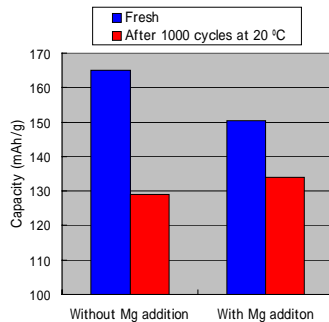
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## Introduction

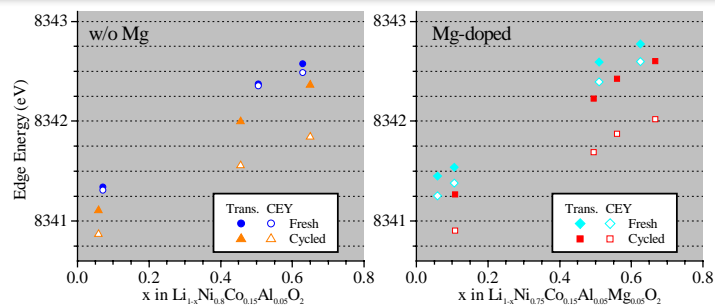
- Capacity fading can be suppressed by  $\text{Mg}^{2+}$  substitution for Ni sites.  $\text{LiNi}_{0.75}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mg}_{0.05}\text{O}_2$

What is the mechanism of this suppression?



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## Comparison of the edge positions of Ni K-edge XANES

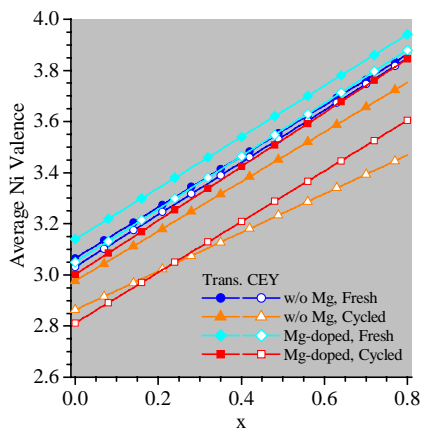


The edge energy measured at the half-step height of Ni K-edge XANES spectra.

- Ni oxidation states are increased by Mg-doping.
- The loss of Mg at the surface?

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## Average Ni valences estimated using the edge positions



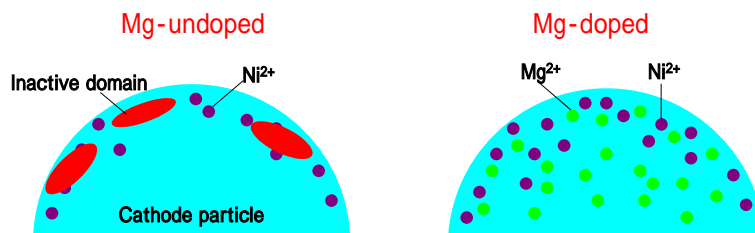
Approximate lines obtained by least-squares fits to average Ni valences.

- Mg-doped cell... The ranges of Ni valence change upon charging maintain the original value after the cycle tests.

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## A possible mechanism of the suppression of capacity fading



- Local structural stabilization around  $\text{Mg}^{2+}$  ions.
  - ⇒ The growth of inactive NiO-like domains can be suppressed.

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## Conclusion

## Effects of Mg doping

- The Ni valence is increased by the  $\text{Mg}^{2+}$  substitution for Ni sites.
- The surface-averaged Ni valence for the fresh cell is lower than the bulk-averaged one, implying the loss of  $\text{Mg}^{2+}$  ions at the surface.
- After the cycling test, the reductions of Ni atoms are observed especially at the surface. However, the ranges of Ni valence change upon charging maintain the original value, indicating that the creation of electrochemically inactive Ni atoms can be suppressed by Mg substitution.

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