



Diagnostic Studies to Improve Abuse Tolerance and the Synthesis of New Electrolyte Materials

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Overview

Timeline

- **Start: 10/01/2007**
- **Finish: 09/30/2010**
- **60% complete**

Budget

- **Funding received in FY08**
DOE: \$350k
- **Funding received in FY09**
DOE: \$350k

Barriers addressed

- **Li-ion and Li-metal batteries with superior performance**
- **Li-ion and Li-metal batteries with long calendar and cycle life**
- **Li-ion and Li-metal batteries with superior abuse tolerance**

Collaborators

- **MER Corporation (Arizona)**
- **Argonne National Lab. (ANL)**
- **LG Chemical Corp., South Korea**
- **Duracell (P&G)**
- **Beijing Institute of Physics**
- **Hydro-Québec (IREQ)**
- **Lockheed Martin Space System**

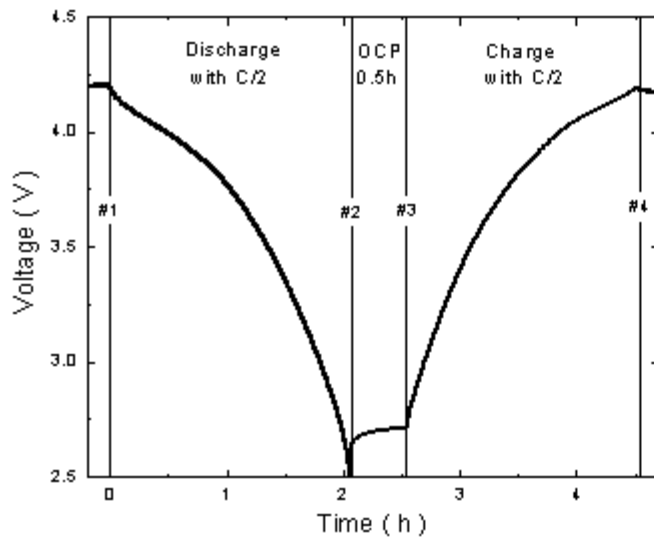
Milestones

Month/Year	Milestones
Oct/08	Complete <i>in situ</i> XRD studies on the structural changes of the LiMn_2O_4 - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite cathode in both Li-half and Li-ion full cells during charge-discharge cycling (in collaboration with LG Chem.). ↪ Completed.
Apr/09	Complete the synthesis and selections of boron based new salts for low temperature Li-ion battery electrolytes. ↪ Completed.
Apr/09	Complete time resolved X-ray diffraction and in situ X-ray absorption spectroscopy (XAS) studies of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (G2) cathode material during heating for thermal stability studies (safety related issues) ↪ Completed.
Sep/09	Complete time resolved X-ray diffraction and in situ X-ray absorption spectroscopy (XAS) studies of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (G3) cathode material during heating for thermal stability studies (safety related issues) ↪ On schedule.
Sep/09	Complete the synthesis and selections of boron based anion receptors (BBAR) as additives for high voltage Li-ion battery electrolytes. Study the solubility, conductivity and Li^+ transference number studies using BBAR-LiF and BBAR- $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2$ electrolytes. ↪ On schedule.

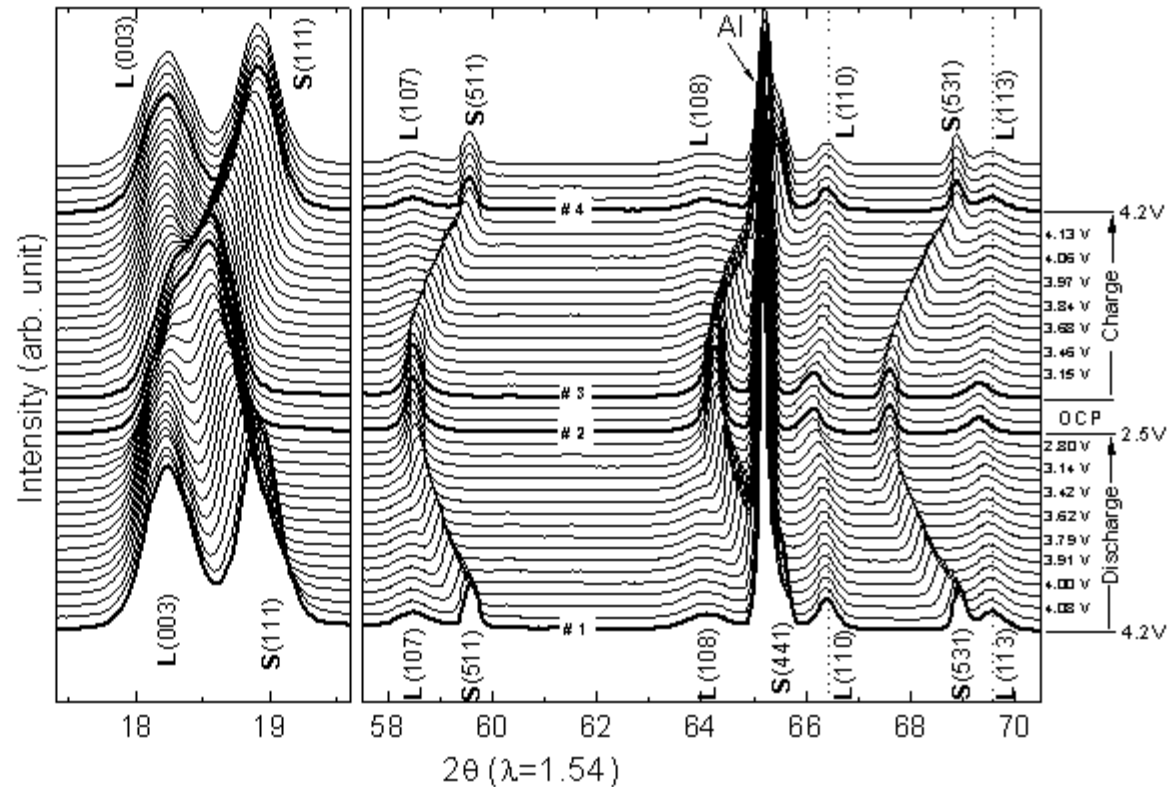
Approaches

- ▣ A combination of time resolved X-ray diffraction (XRD) and *soft and hard* X-ray absorption (XAS) techniques during heating to study the thermal stability of the electrode materials.
- ▣ Hard and soft XAS studies of new electrode materials during electrochemical cycling to perform the diagnostic studies to extend the calendar and cycling life of Li-ion batteries.
- ▣ In situ XRD to study the structural changes of the electrode materials during charge-discharge cycling to understand the power and energy density fading mechanism for longer cycling life of Li-ion batteries.
- ▣ New electrolyte system development through molecular design and organic synthesis, study their effects on the formation and stability of the solid electrolyte interphase (SEI) layer.
- ▣ Extended collaboration with other US and international academic institutions and US industrial partners.

**In situ XRD of Mixed $\text{LiMn}_2\text{O}_4 + \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode (1:1 wt%) in *Li-ion cell*
: Collaboration with LG chemical.**



In Li-ion cell (with MCMB anode)
Voltage: 2.5 ~ 4.2 V, C/2 rate
Capacity = 10 mAh

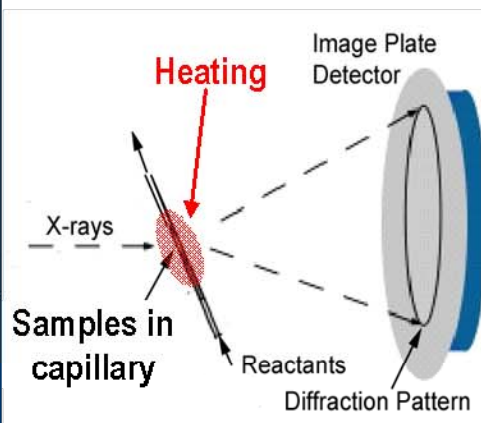


- ↳ *In situ* XRD tracks well the structural changes of each component
- ↳ Structural changes in Li-ion cell is dominated by spinel phase with much less changes in layered phase during charge-discharge in a voltage range of 2.5 ~ 4.2V.
- ↳ Critical parameters for the cell performance using mixed cathode
; *Cell voltage, anode and cathode capacities, wt% of each component in mixed cathode.*
- ↳ The results provide valuable information regarding how to design a Li-ion cell using the mixed cathode.

Synchrotron based X-ray diffraction and absorption spectroscopy during heating

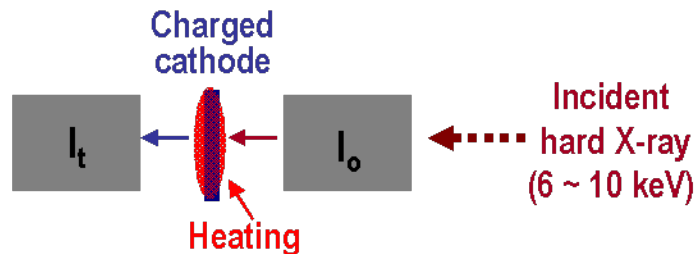
Studies on thermal decomposition (*thermal abuse tolerance*) of cathode materials

1. *Time-resolved XRD* study of charged cathode materials



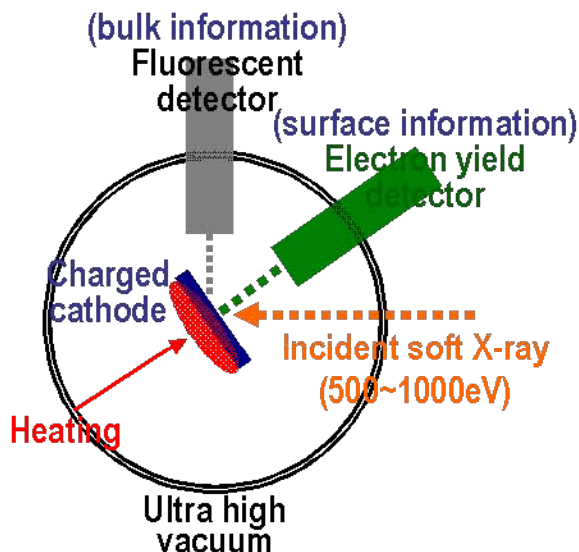
- **Average structural information** (long range order) during heating

2. *Hard X-ray absorption spectroscopy* study of charged cathode materials



- **Local structural and electronic structural information (bulk)** in elemental-selective way during heating

3. *Soft X-ray absorption spectroscopy* study of charged cathode materials

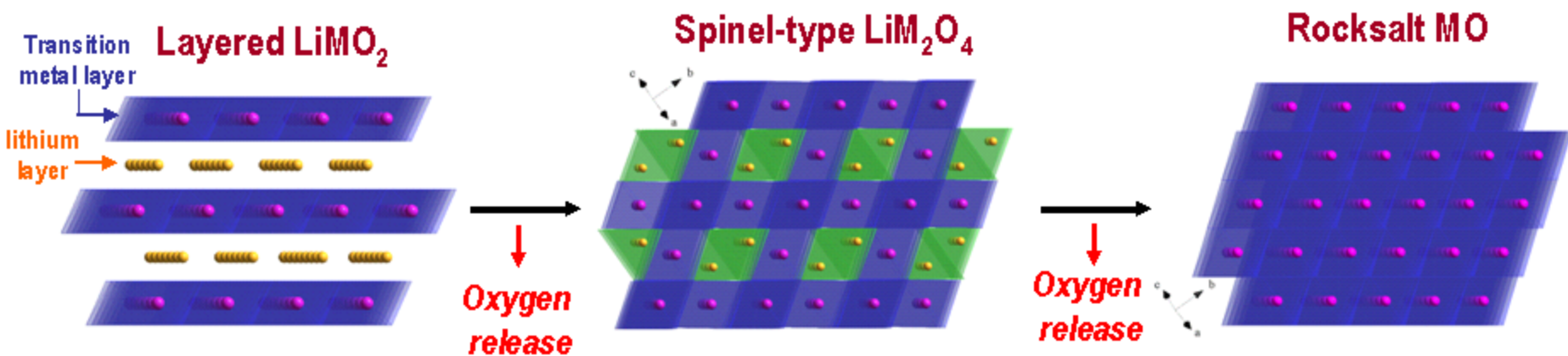


- **Electronic structural information at the surface** (~ 50Å) and in the bulk (~ 3000Å) in elemental-selective way during heating

↳ Combination of these techniques will clearly provide valuable information about thermal stability of various types of cathode materials and help designing cathode materials with superior thermal abuse tolerance !!

Thermal stability study of layered cathode materials (safety related issue)

Temperature induced structural changes of charged layered cathode materials



When $x = 0.5$ (50% of SOC) in Li_xMO_2

$\text{Li}_{0.5}\text{M}^{(3.5+)}\text{O}_2$ (layered, $R-3m$) \Rightarrow $\text{Li}_{0.5}\text{M}^{(3.5+)}_{1.0}\text{O}_2$ (disordered spinel, $Fd3m$) ; no oxygen loss

$\text{Li}_{0.5}\text{M}^{(3.5+)}_{1.0}\text{O}_2$ (disordered spinel, $Fd3m$) \Rightarrow $\text{Li}_{0.5}\text{M}^{(2.5+)}_{1.0}\text{O}_{1.5}$ (rock salt, $Fm3m$) + 0.25 O_2 ; oxygen release!!

When $x = 0.33$ (67% of SOC) in Li_xMO_2

$\text{Li}_{0.33}\text{M}^{(3.67+)}\text{O}_2$ (layered, $R-3m$) \Rightarrow $\text{Li}_{0.33}\text{M}^{(3.21+)}_{1.0}\text{O}_{1.77}$ (disordered spinel, $Fd3m$) + 0.115 O_2 ; oxygen release!!

$\text{Li}_{0.33}\text{M}^{(3.21+)}_{1.0}\text{O}_{1.77}$ (disordered spinel, $Fd3m$) \Rightarrow $\text{Li}_{0.33}\text{M}^{(2.33+)}_{1.0}\text{O}_{1.33}$ (rock salt, $Fm3m$) + 0.22 O_2 ; oxygen release!!

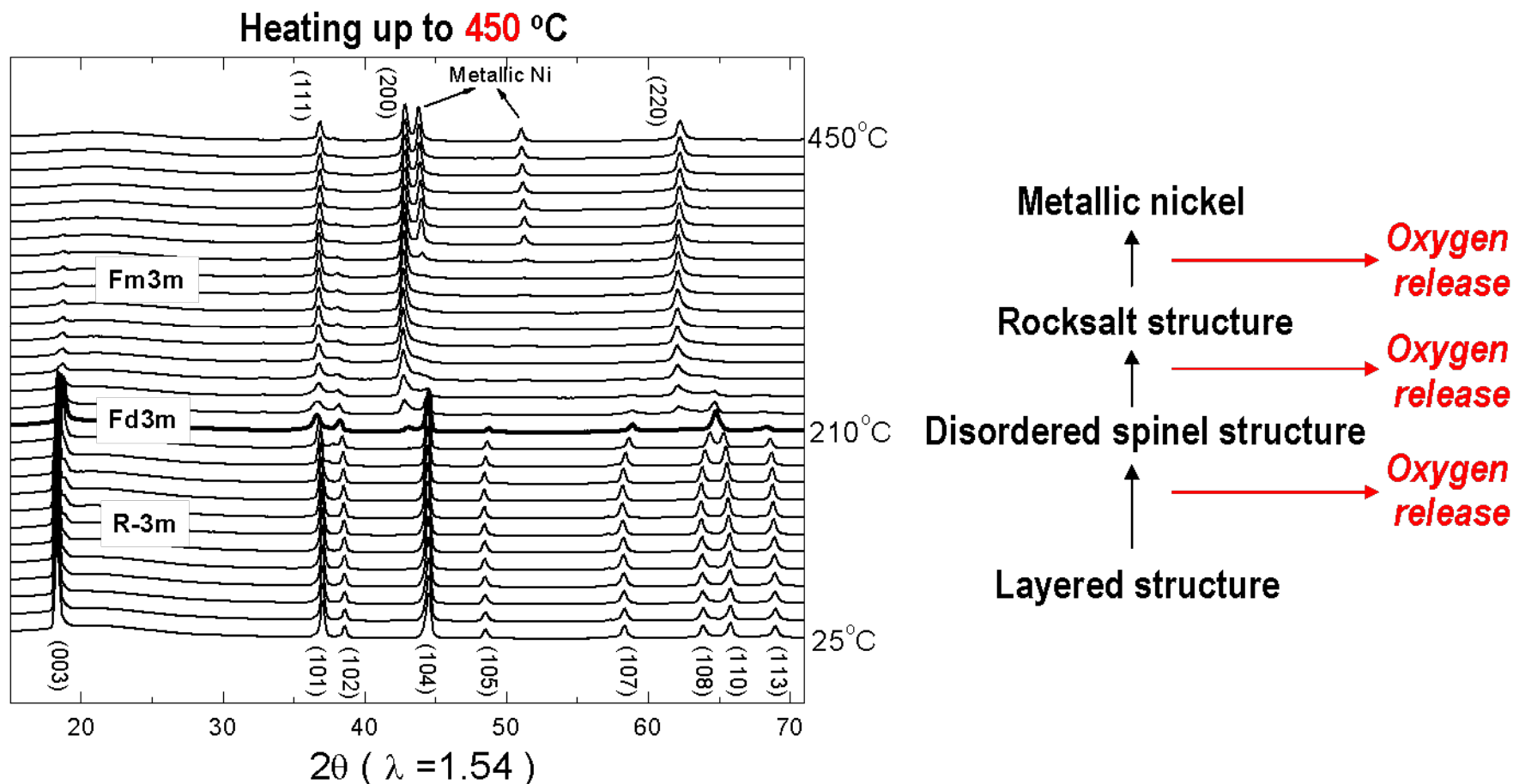
↳ More charged state, more thermally unstable.

↳ Released oxygen causes safety problems (e.g., thermal runaway) by reacting with flammable electrolytes.

Thermal stability of $\text{Li}_{0.33}\text{NiO}_2$ with electrolyte (as a reference)

- $\text{Li}_{0.33}\text{NiO}_2$

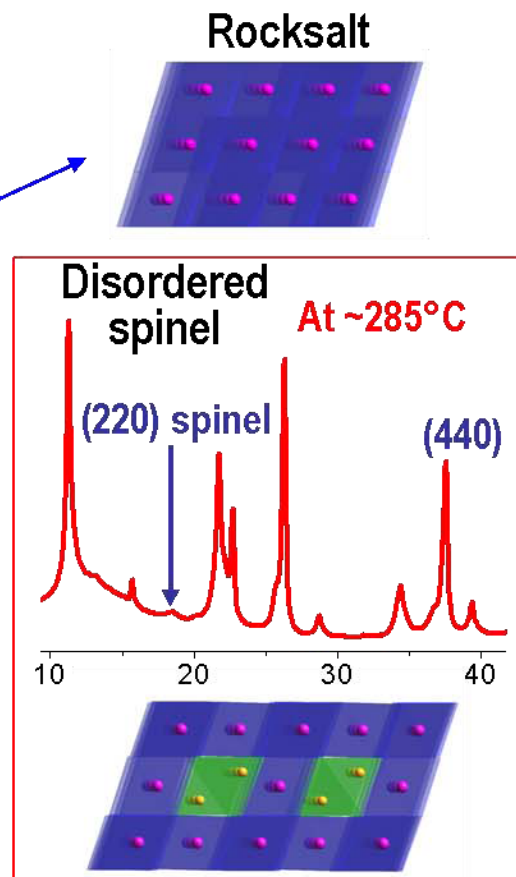
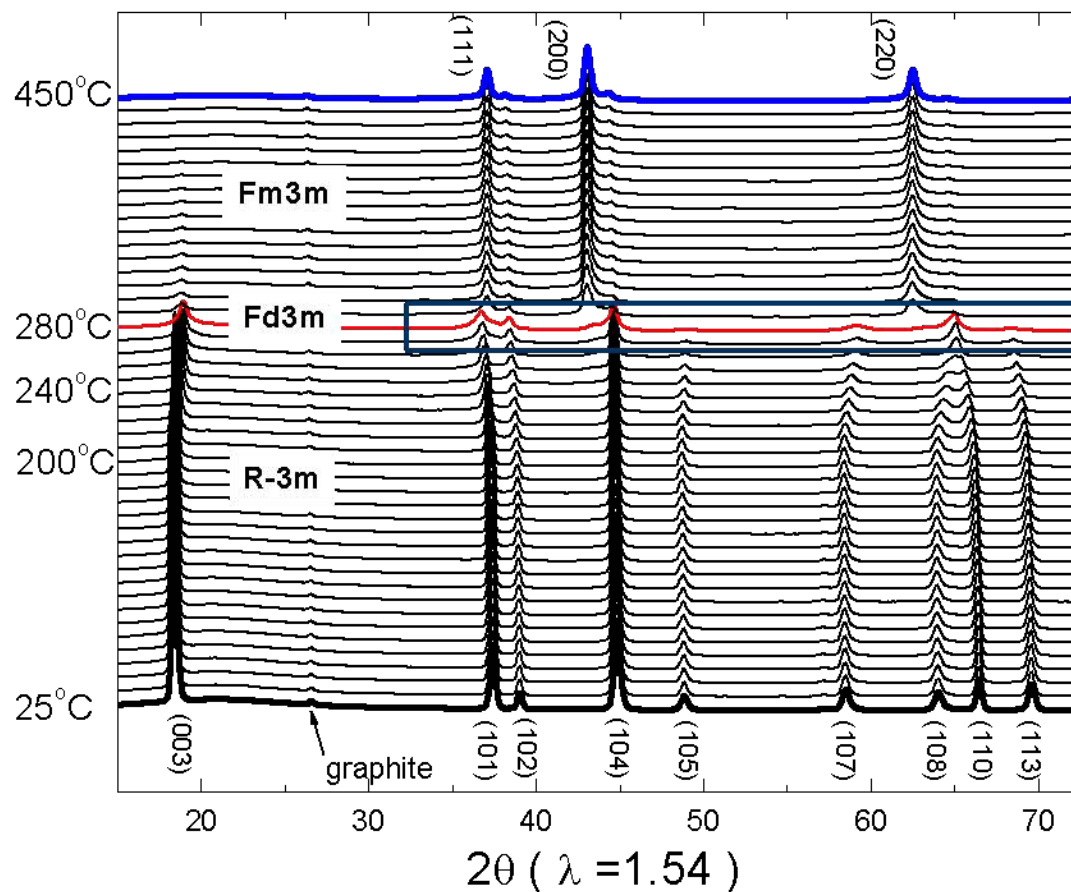
↪ A good road map for the structural changes of nickel-based cathode materials during heating.



↪ $\text{Li}_{0.33}\text{NiO}_2$ goes through a whole series of phase transitions (i.e., thermal decomposition) when heated from 25 to 450 °C.

Thermal stability of charged $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (*Gen2*) with electrolyte

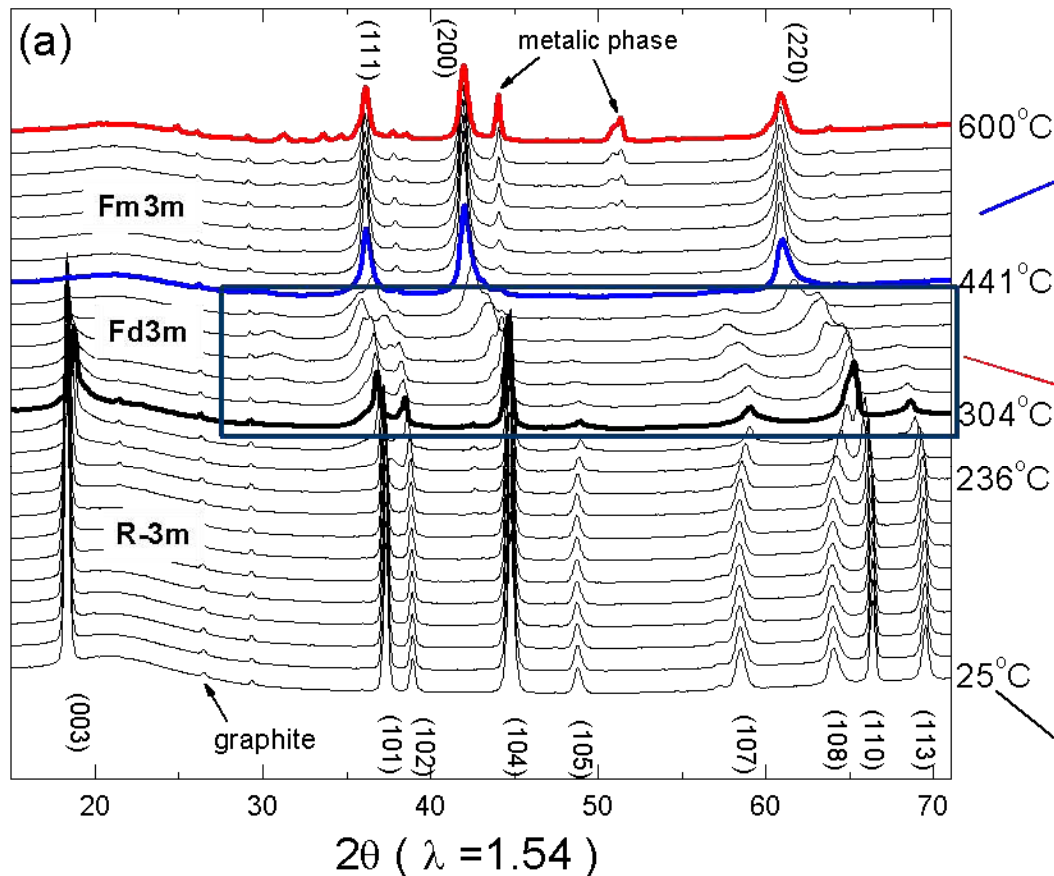
Heating up to 450 °C



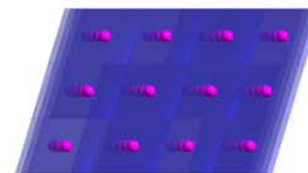
- ↳ Much better thermal stability than $\text{Li}_{0.33}\text{NiO}_2$.
- ↳ Narrow temperature range (~20 °C) for the disordered spinel region. (boxed region)

Thermal stability of charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (*Gen3*) with electrolyte

Heating up to 600 °C

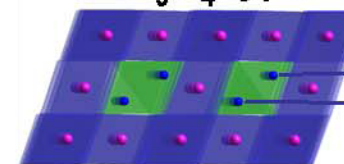


Rocksalt



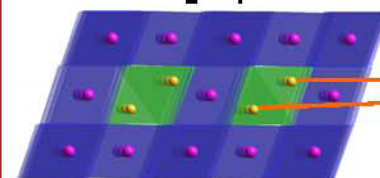
2 types of disordered spinel

M_3O_4 type



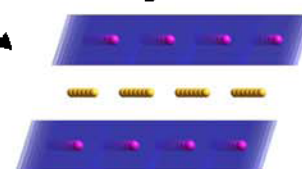
8a
tetrahedral site
: Mostly
transition metal

LiM_2O_4 type



8a
tetrahedral site
: Mostly lithium

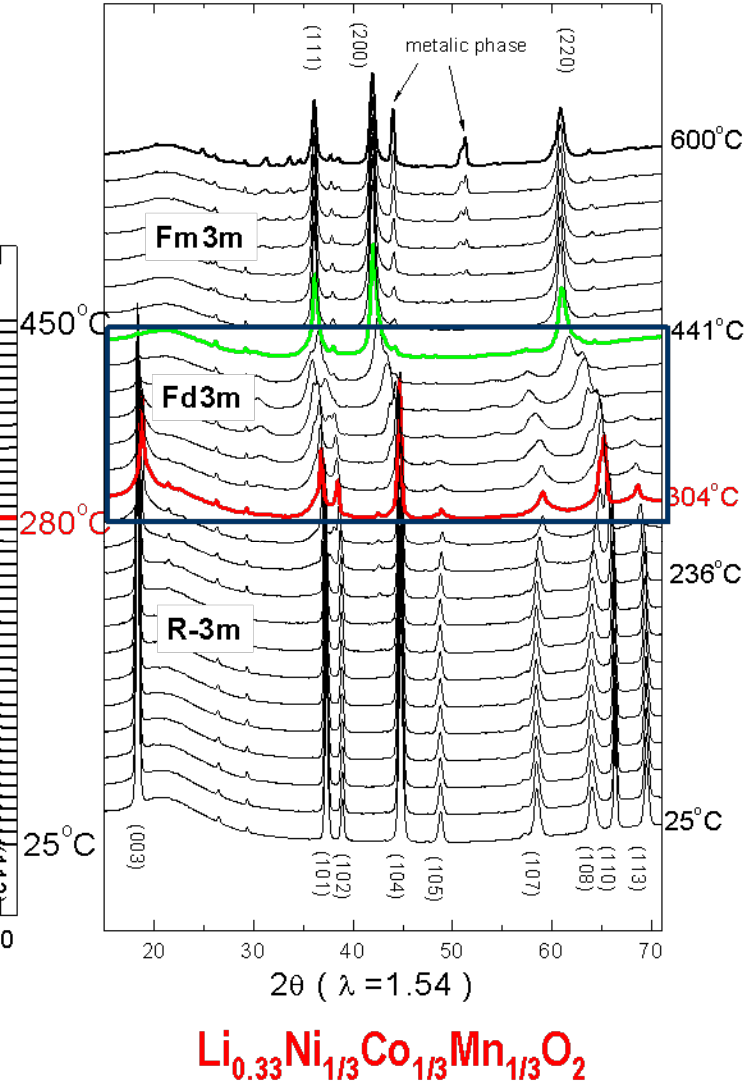
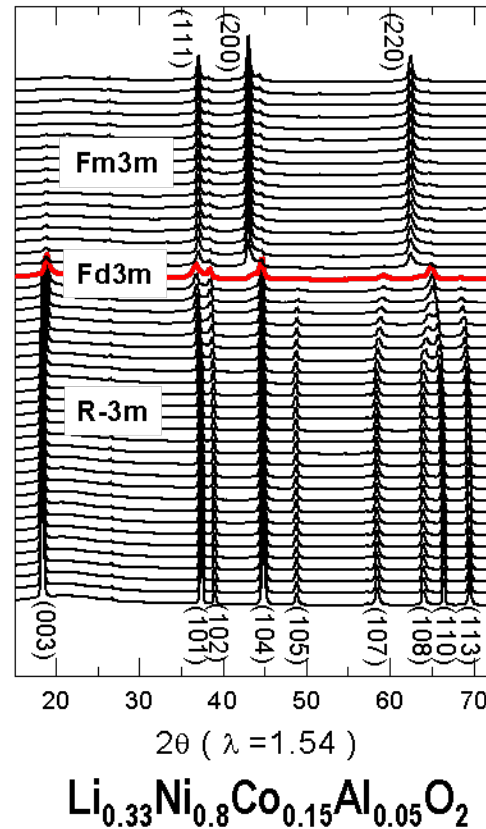
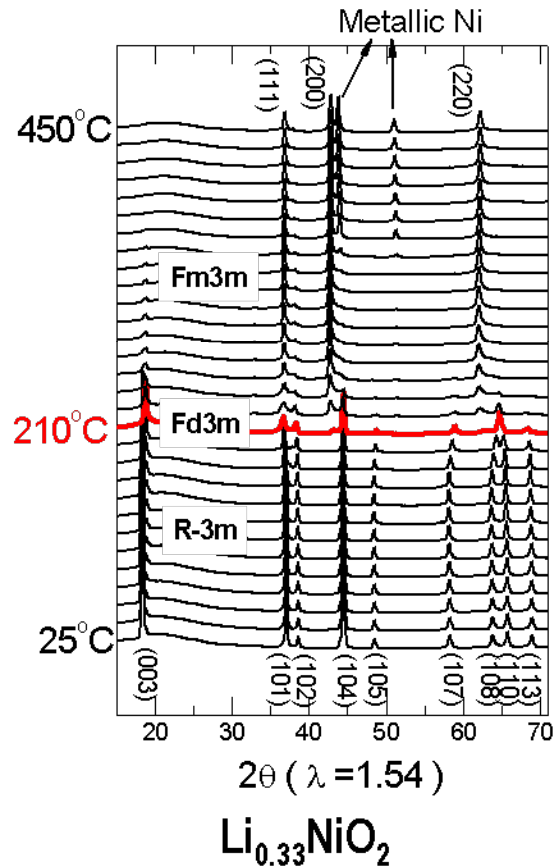
layered



↳ Much wider temperature range (~140 °C) for the disordered spinel region. (boxed region) due to the existence of two different types of spinel structures.

⇒ **much better thermal stability!!**

Comparison of thermal stability of charged layered cathodes *with* electrolyte

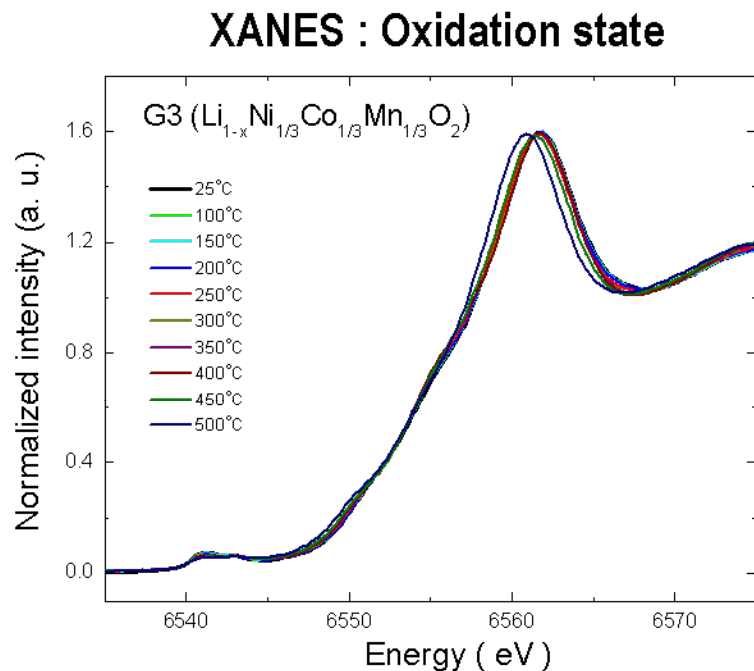


↳ **G3 cathode shows the best thermal stability** due to the large spinel stabilized temperature region.
 why? ⇒ **Solution: Soft & Hard X-ray absorption spectroscopy !!**

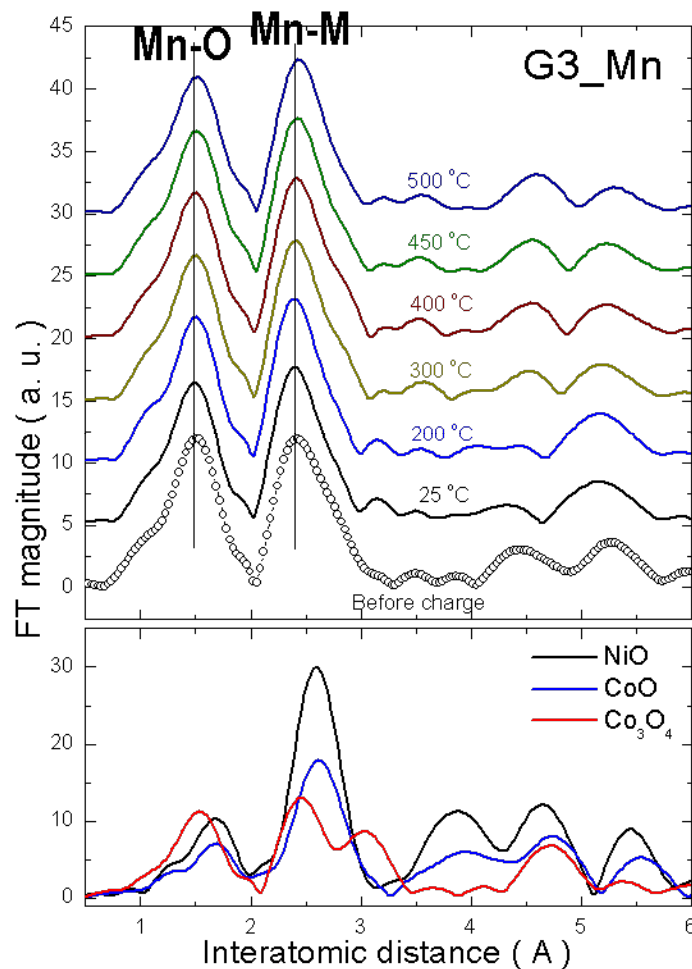
Mn K-edge XANES and EXAFS of charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Gen3) during heating

In depth analysis of better thermal stability of G3 cathode using XAS

EXAFS : local atomic structure



⇒ **No reduction of Mn ions during heating.**



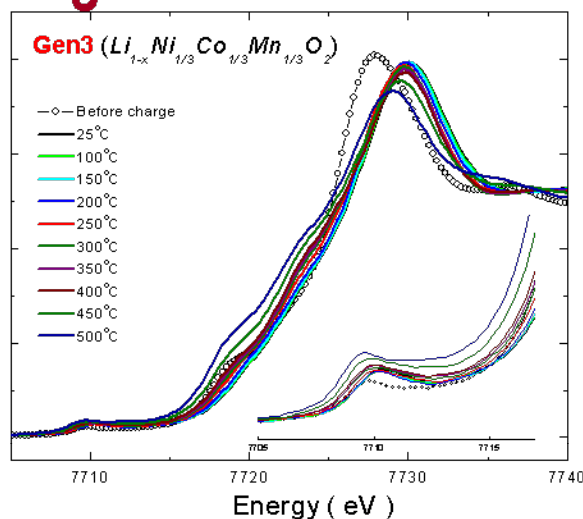
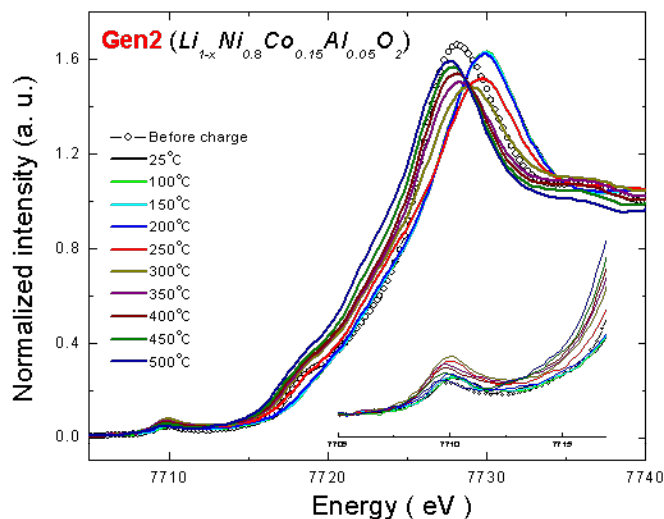
⇒ **Preserving local structure around Mn during heating.**

↳ Excellent thermal stability of Mn^{4+} ions in the charged $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode.

⇒ **likely due to the high preference of octahedral coordination of Mn^{4+} ions.**

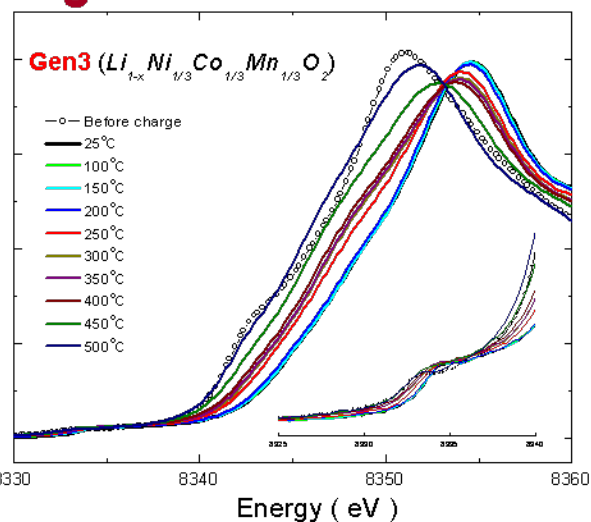
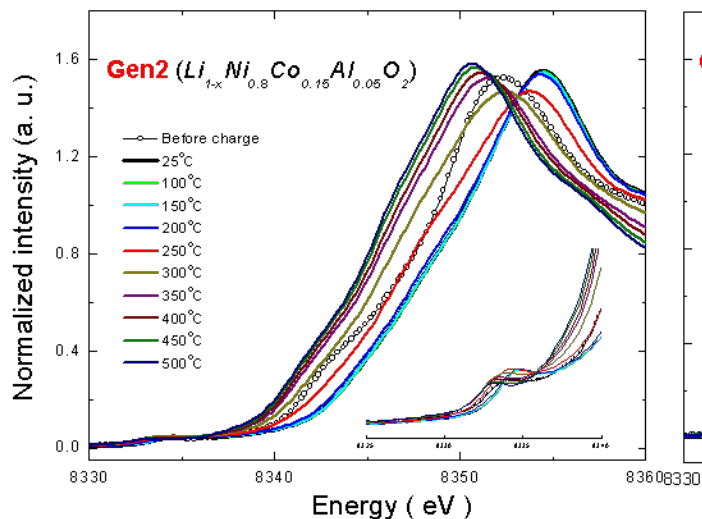
Co & Ni K-edge XANES of charged $Li_{0.33}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2) and $Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Gen3) during heating

Co K-edge



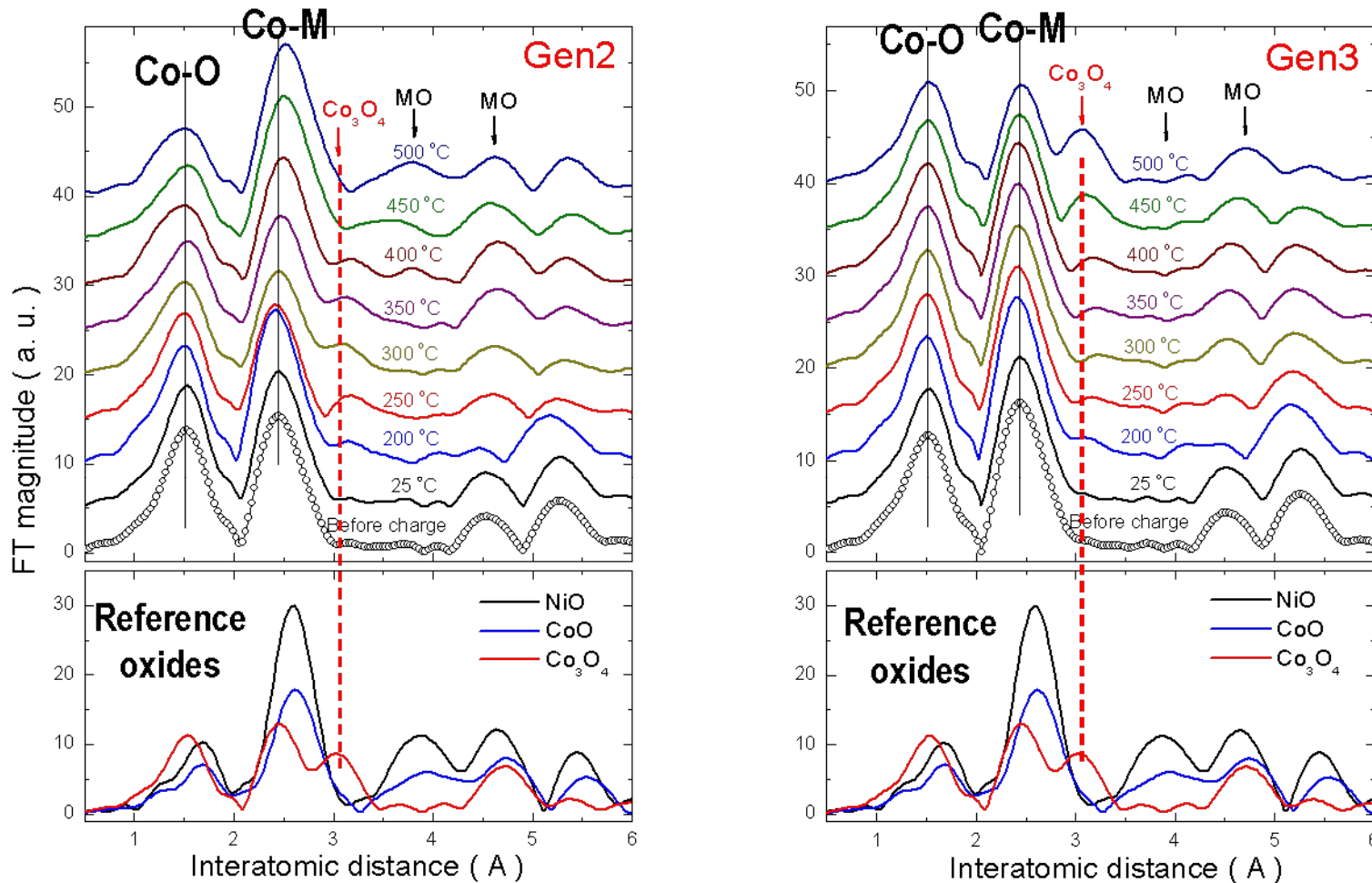
- ➔ Much slower reduction in oxidation state of Co ions in Gen3 than Gen2 during heating.
- ➔ Better thermal stability of Co ions in Gen3 is likely due to the stabilization of Co_3O_4 type-spinel phase prevent further thermal decomposition to CoO type-rock salt phase.
- ➔ New observation of the Co_3O_4 type-spinel phase formation in Gen 2 which was not detected in TR-XRD during heating. (Pre-edge region in Gen2)

Ni K-edge



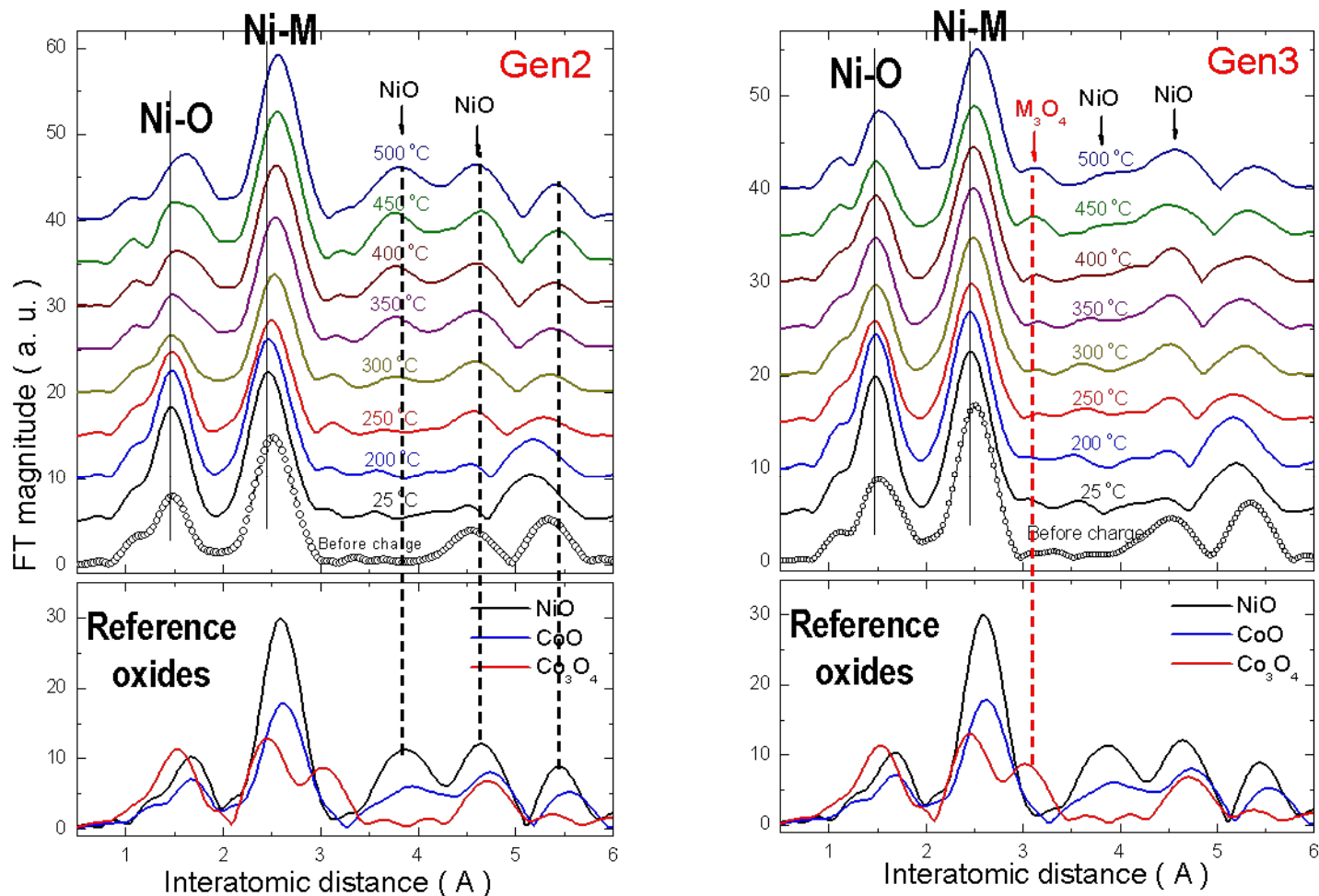
- ➔ Much slower reduction in oxidation state of Ni ions in Gen3 than Gen2 during heating.
- ➔ Better thermal stability of Ni ions in Gen3 is likely due to the combined effects of the stabilization of spinel type-phase and excellent thermal stability of Mn ions near Ni ions.

Co K-edge EXAFS of charged $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Gen2) and $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Gen3) during heating



- Gen2 shows thermal decomposition to MO type-rock salt phase in local structure around Co at above ~ 400°C, while Gen3 clearly shows the formation of M₃O₄ type-spinel phase in local structure around Co which prevent further thermal decomposition to MO type-rock salt phase.
- Co K-edge EXAFS clearly supports the better thermal stability of Gen3 than Gen2 due to the stabilization of spinel-type phase in Gen3.

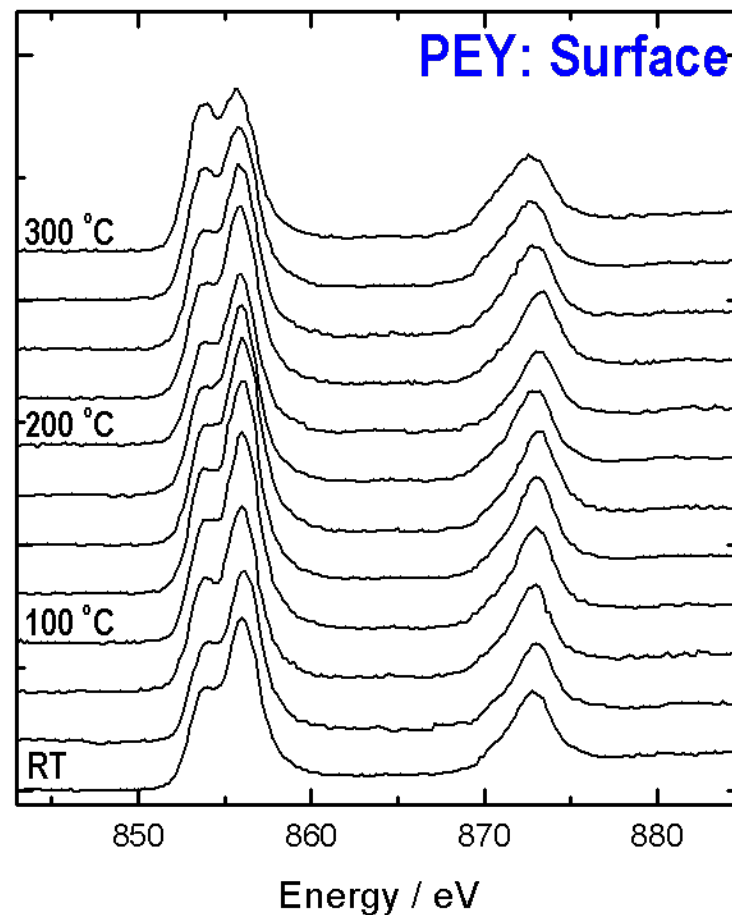
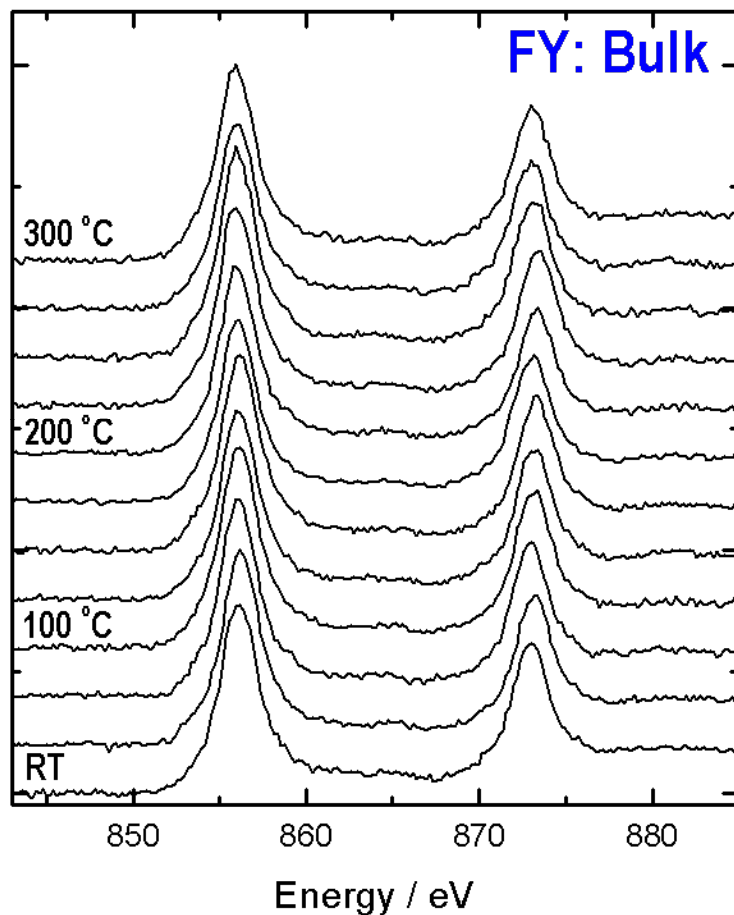
Ni K-edge EXAFS of charged $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Gen2) and $\text{Li}_{0.33}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Gen3) during heating



- ↳ Gen3 shows much slower thermal decomposition to MO type-rock salt phase in local structure around Ni compared to Gen2.
- ↳ Ni K-edge EXAFS clearly supports the better thermal stability of Gen3 than Gen2 due to the combined effects of the stabilization of spinel-type phase (likely Co_3O_4) and excellent thermal stability of Mn in Gen3.

Thermal Abuse: Element-selective technique (Soft X-ray absorption)

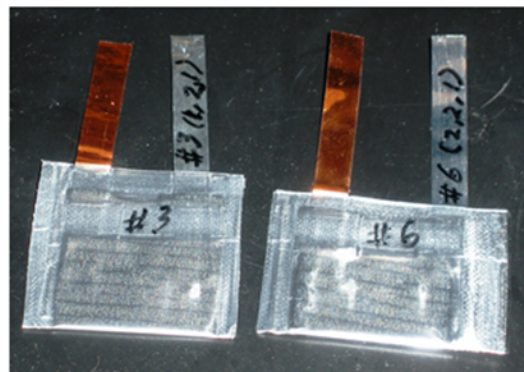
Ni L-edge XAS for $\text{Li}_{0.33}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode



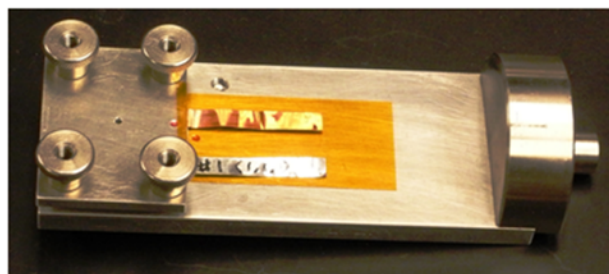
- ↳ Clear observation of the reduction of Ni^{4+} ions at the surface.
- ↳ The surface of the electrode is decomposed at much earlier temperature than the bulk.

In situ XRD of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at NSLS X18A

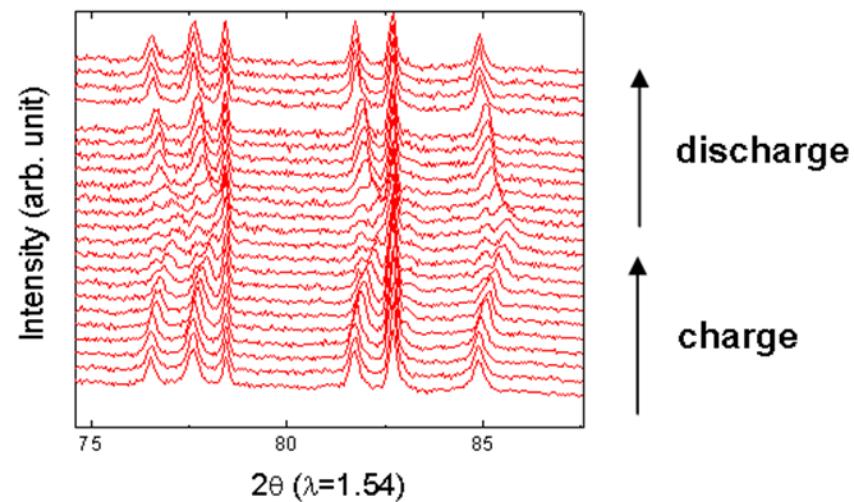
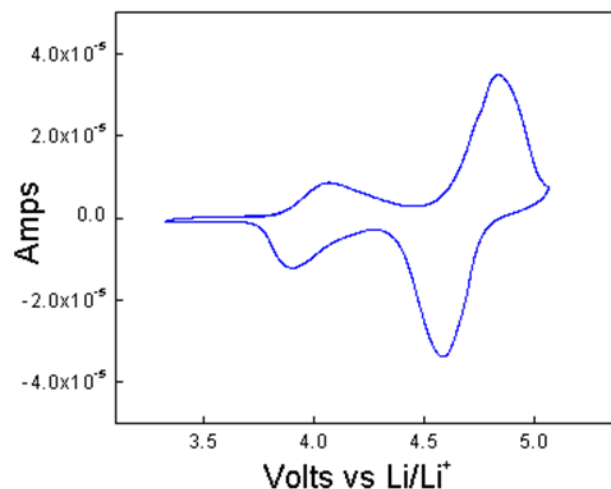
In collaboration with Duracell



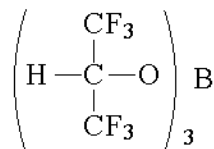
Pouch cells
(Duracell R&D)



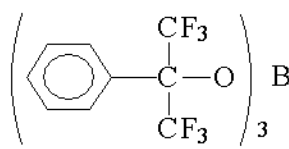
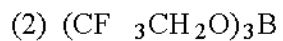
Cell holder for the
goniometer at X18A



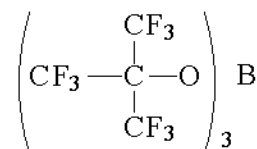
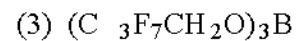
Chemical structures of boron based anion receptors



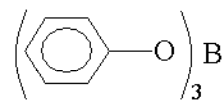
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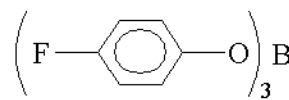
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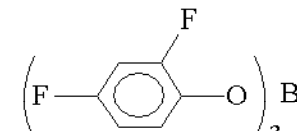
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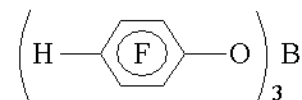
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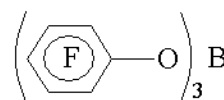
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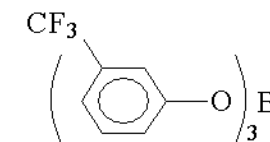
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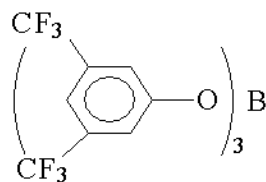
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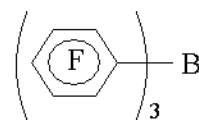
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(12)



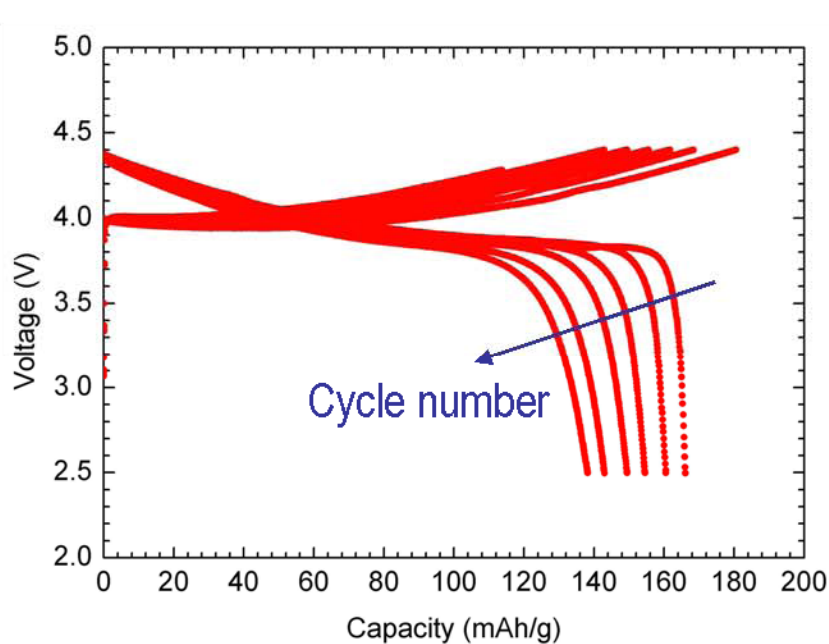
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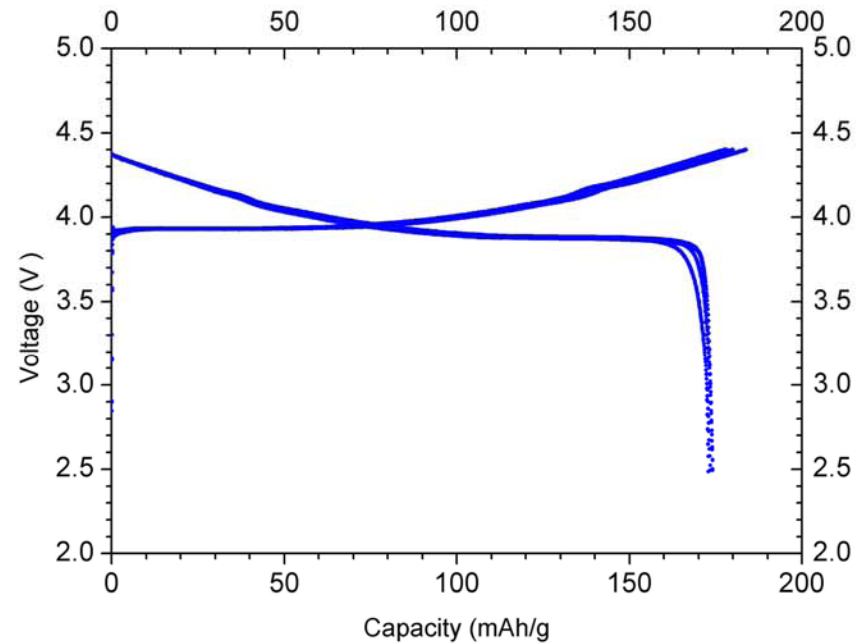
TPFPB as an additive for the electrolytes

The cyclability of a Li/LiCoO₂ cell using B-based additive



Electrolyte:

1.0 M LiBF₄ in PC:DMC(1:1)



Electrolyte:

0.2 M TFPFB + 1.0 M LiBF₄ in PC:DMC(1:1)

The capacity retention **improvement by TFPFB addition is quite impressive!**

LiF-TPFPB based electrolytes

Transfer number measurement on electrolytes

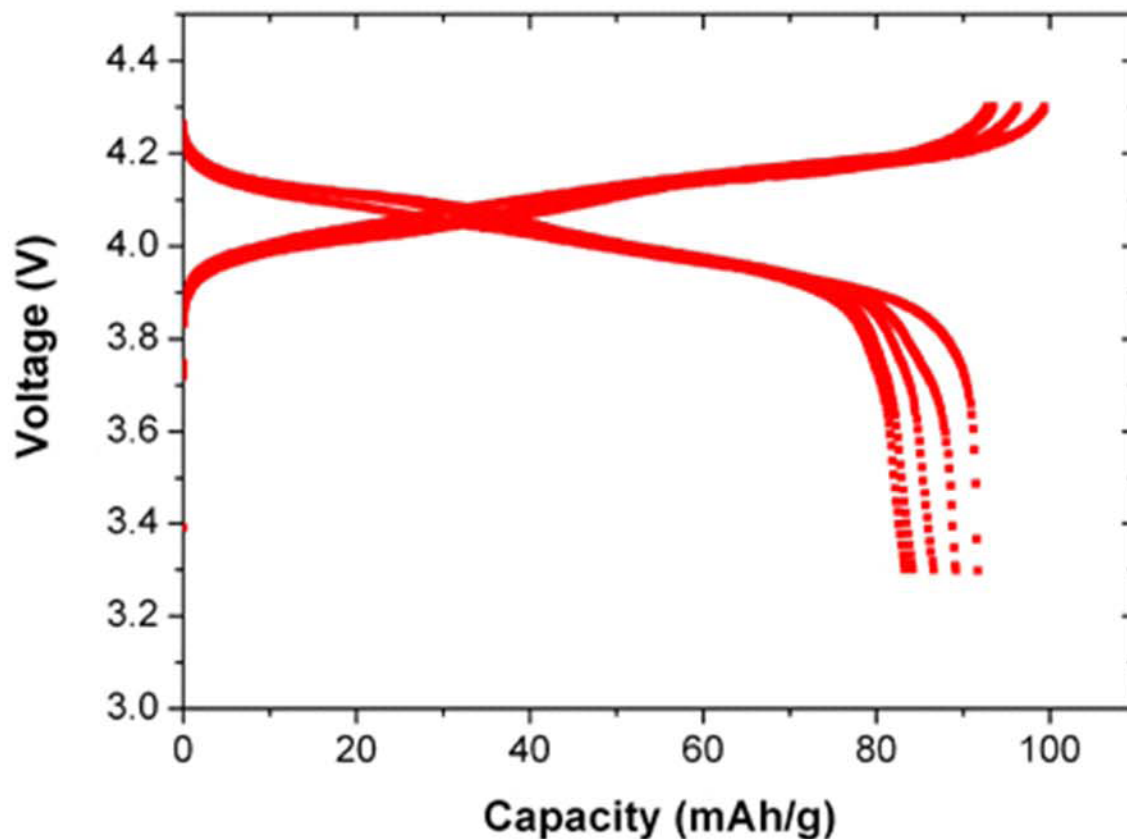
No	Electrolyte	t_{Li^+}	t_{x^-}
1	0.6 M TPFPB-0.6 M LiF-EC:DMC (1:1)	0.65	0.35
2	0.6 M TPFPB-0.6 M LiF-PC:DMC (1:1)	0.71	0.29
3	0.6 M THFPB-0.6 M LiF-EC:DMC (1:1)	0.58	0.42
4	0.6 M THFPB-0.6 M LiF-PC:DMC (1:1)	0.46	0.54
5	1M LiClO ₄ , PC-DMC(1:1)	0.34	0.66

Conductivity comparison of different electrolytes at several temperatures (mS/cm).

No	Electrolyte	-40 °C	-20 °C	0 °C	20 °C	60 °C
a	0.6 M TPFPB-0.6 M LiF-EC:DMC	0.003	0.15	1.5	2.6	4.4
b	0.6 M TPFPB-0.6 M LiF-PC:DMC	0.71	1.2	2.0	3.2	5.8
c	0.6 M THFPB-0.6 M LiF-EC:DMC	/	/	0.51	0.68	1.6
d	0.6 M THFPB-0.6 M LiF-PC:DMC	0.34	0.80	2.4	3.3	6.0
e	1M LiBF ₄ -PC-DMC (1:1)	0.62	1.8	3.2	4.9	7.9

For LiF-TPFPB based electrolytes, the conductivities are good and Li⁺ transfer numbers are almost doubled comparing with conventional electrolytes.

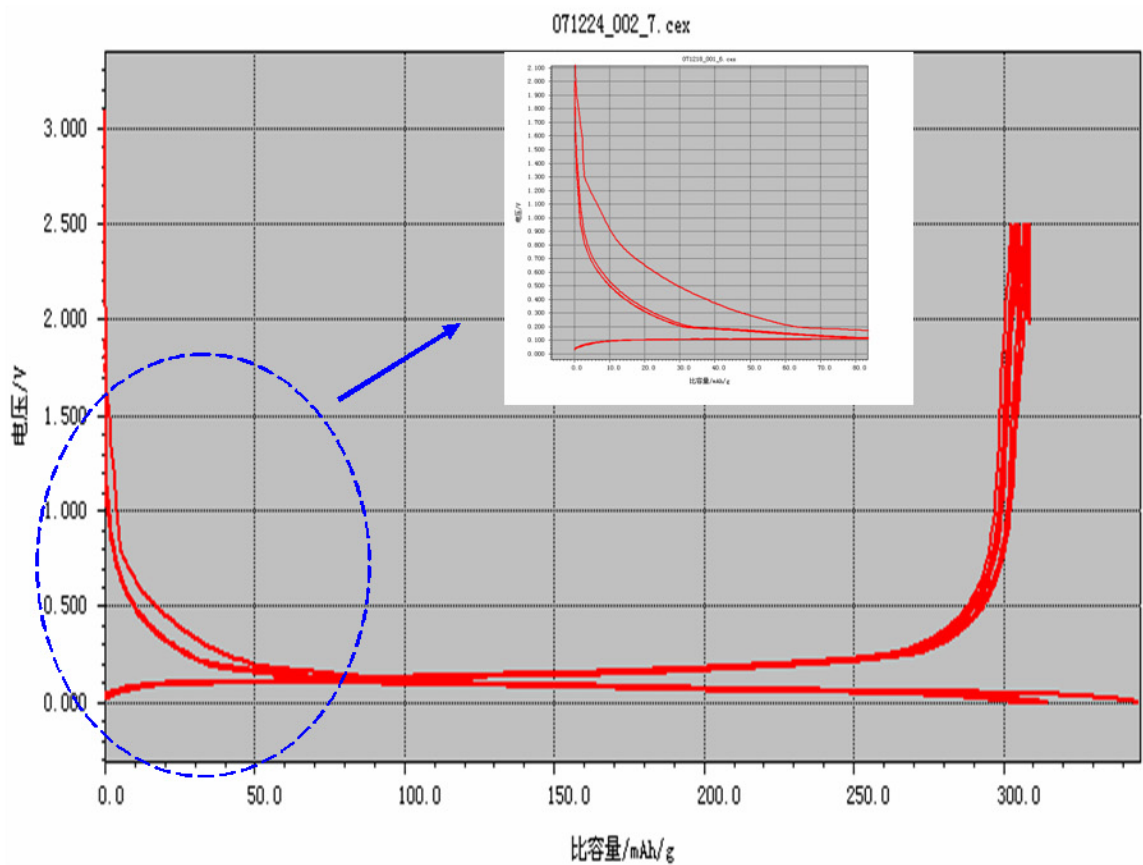
LiF-TPFPB based electrolytes



Charge-discharge curves for Li/LiMn₂O₄ cells with composite electrolytes containing 0.6 M TPFPB and 0.6 M LiF in PC/DMC (1:1, v/v).

The LiF-TPFPB electrolyte is compatible with surface coated LiMn₂O₄.

Improved SEI layer formation by adding LiBOB in LiF-TPFPB based electrolytes



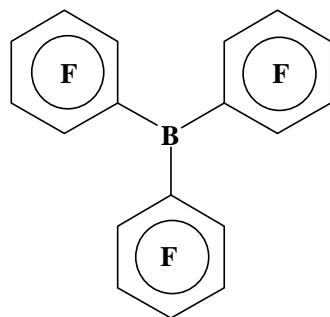
1 st	89.3%
2 nd	97.3%
3 rd	98.0%
4 th	98.4%
5 th	98.7%

MCMB anode, 0.05M LiBOB-0.5M TPFPB-0.5M LiF in PC/DMC
0.06C rate, the first 5 cycles

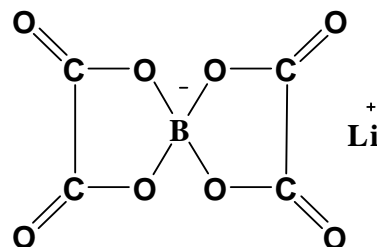
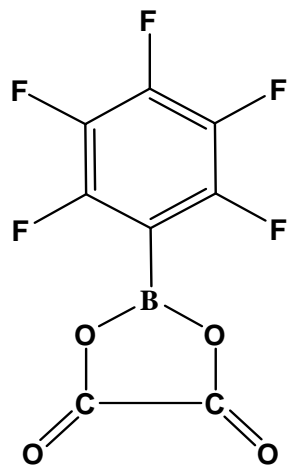
When 0.05M LiBOB was used as additives, both the 1.7V and 0.8V plateaus were suppressed, indicating a stable SEI layer was formed on the surface of MCMB anode.

New Additives and new salts being developed at BNL

Example of New Additives

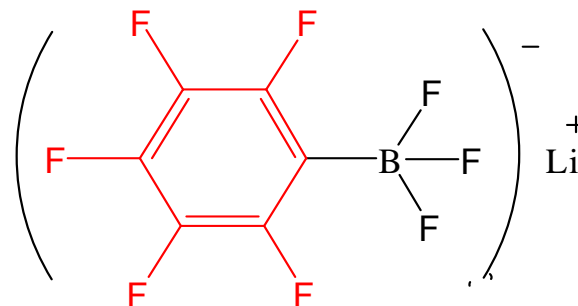


tris(pentafluorophenyl) borane (TPFPB)
An anion receptor



Lithium bisoxalatoborate (LiBOB)
An lithium salt

Example of New salts



Examples of low temperature electrolytes using BNL synthesized new boron based salts for MER Corp.

<u>Sample #</u>	<u>Electrolyte Composition</u>
19-60-1	1.0 M LiPF ₆ in EC/N-Methyl-oxazolidinone (1:10)
19-60-2	1.0 M LiPF ₆ in EC/N-Methyl-oxazolidinone (1:15).
19-60-3	0.6M $\left(\text{F-C}_6\text{H}_4 \right)_2 \text{B} \left(\text{O-CF}_3 \right)_2 \text{Li}$ with Et ₂ O in EC/EMC (1:10)
19-60-4	0.6M $\left(\text{F-C}_6\text{H}_4 \right)_2 \text{B} \left(\text{O-CF}_3 \right)_2 \text{Li}$ in EC/EMC (1:10)
19-60-5	0.6M $\left(\text{F-C}_6\text{H}_4 \right)_2 \text{B} \left(\text{O-CF}_3 \right)_2 \text{Li}$ with Et ₂ O in EC/EMC (1:10)
19-60-6	0.6M $\left(\text{F-C}_6\text{H}_4 \right)_3 \text{B} \left(\text{O-CF}_3 \right)_2 \text{Li}$ with Et ₂ O in EC/EMC (1:10)
19-60-7	0.6M $\left(\text{F-C}_6\text{H}_4 \right) \text{BF}_3 \text{Li}$ in EC/EMC (1:10)
19-60-8	0.6M LiBF ₄ in EC/EMC (1:10)
20-14-1	1.0 M LiPF ₆ in EC/ N-Methyl-oxazolidinone (1:20, v/v)

Planned work for FY 2009 and FY2010

- Complete the *in situ* XRD studies in collaboration with Argonne national Lab. on the thermal stability of layer structured Gen2 and Gen3 cathode materials.
(milestone for Sep/09)
- Design, synthesize and test new boron based anion receptors (BBAR) as additives and new boron based lithium salts for high voltage Li-ion battery electrolytes. Study the solubility, conductivity and Li⁺ transference number studies using BBAR-LiF and BBAR-Li₂O/Li₂O₂ electrolytes.
- Design, synthesize and test new organic solvent for high voltage Li-ion battery electrolytes, develop new electrolytes using PC to replace EC.
- Further development of *in situ* XAS technique for thermal stability studies. Apply this new technique to various electrode materials to probe the structural changes at the surface and in the bulk simultaneously. Co-relate these changes to understand the fundamental aspects of the safety related thermal run away of lithium-ion cells.
- Expand the collaborative research with US and International academic research institutions and US industrial partners.
- Provide technical support to the development of setting up Li-ion battery manufacturing in the US.

Summary

- In collaboration with LG Chemical, the structural changes of the composite cathode made by mixing spinel LiMn_2O_4 and layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in both Li-half and Li-full cells during charge/discharge are studied by in situ XRD. The results give us valuable information for designing and optimizing the composite cathode
- Using time-resolved X-ray diffraction (TR-XRD) and X-ray absorption spectroscopy (XAS) techniques during heating, new findings of the unique phase transition behaviors of the charged $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (Gen3) cathode during thermal decomposition have been studied in comparison with $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (Gen2) cathode materials. These results demonstrated the structural stabilization role of Mn in Gen3 for improving the thermal abuse tolerance.
- New boron based lithium salts have been designed and synthesized. The application of using these salts for low temperature electrolytes have been studied in collaboration with MER Corp.
- New boron based additives with capability to dissolve LiF and Li_2O in organic solvents as well as stable SEI layer formation have been synthesized and studied. These new electrolytes have high potential to be used in high energy density Li-ion and lithium metal batteries (two patent applications are being prepared). Some new organic solvents with low flammability are being developed.
- In situ XRD and XAS techniques developed at NSLS are being used by Li-ion battery developer (Duracell and Yaderney) and end users (Lockheed Martin Space System).