Development of high-capacity cathode materials with integrated structures

presented by Sun-Ho Kang
Chemical Sciences and Engineering Division
Argonne National Laboratory

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Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY10: $300K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: S. –H. Kang
- Collaborators:
  - CSE, Argonne: K. Gallagher, D. Kim, C. S. Johnson, M. M. Thackeray (materials design, synthesis and electrochemical characterization)
  - Stony Brook: J. Cabana, C. P. Grey (NMR)
  - APS, Argonne, M. Balasubramanian (XAS)
  - MIT: C. Carlton, Y. Shao-Horn (TEM)
  - Daejung EM (TM precursor)

Objective of this study

Development of ***low-cost and high-energy , and thermally-stable*** cathode materials with integrated structures for PHEVs

- Design Mn-rich cathodes with integrated structures
  - Motivation
    - ✓ Mn-rich: lower cost and enhanced thermal safety
    - ✓ Integrated structure: creation of spinel components in the layered-layered nano-composite structure to improve rate performance
  - Demonstration of improved electrochemical properties
    - ✓ capacity, cycling performance, rate capability, thermal stability
  - Validation of the 'integrated structure including spinel' concept using various analytic techniques (XAS, TEM)

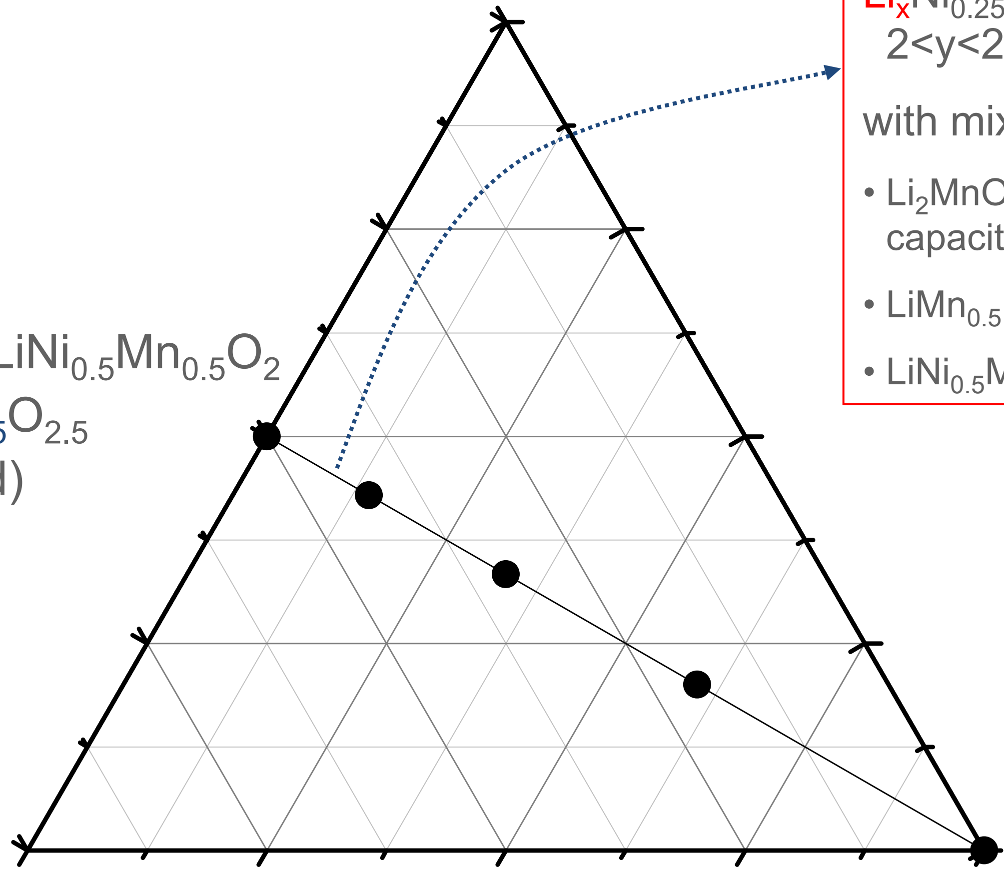
Milestones FY10

- Evaluation of cycling performance and rate capability of baseline material – *done*
- Evaluation of electrode materials with different Li content to find optimum lithium composition – *on going*
- Study of effects of various dopants on the integrated structure and electrochemical properties – *on going*
- Investigation of integrated structure by various analytical techniques – *on going*
- Evaluation of electrochemical properties in full Li-ion cell configuration – *on going*
- Investigation of thermal stability of the electrode materials – *initiated*

Approach

- Li- and Mn-rich oxide electrodes with ‘layered-layered’ composite structure
  - *Shown to deliver high capacity (>200mAh/g)*
    - *Example: $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$ ($\equiv 0.5Li_2MnO_3 \bullet 0.5LiNi_{0.5}Mn_{0.5}O_2$)*
  - *Limitations*
    - Poor rate capability, especially without cobalt, and high first-cycle capacity loss
    - Surface damage from repeated high-voltage cycling
- Embedding spinel component in the ‘layered-layered’ composite structure
  - *Spinel structure can be created in the composite structure by controlling lithium content (e.g., $0.5<x<1.5$ in $Li_xNi_{0.25}Mn_{0.75}O_y$)*
  - *Physical blending of the ‘layered-layered’ material with spinel*
- Oxide particle surface passivation/stabilization
  - *Structurally compatible phase to stabilize the oxide particle surface*
  - *Protection of the surface from detrimental reactions with electrolyte at high voltages and high temperatures*

Approach (Cont'd):
Background of the materials design concept



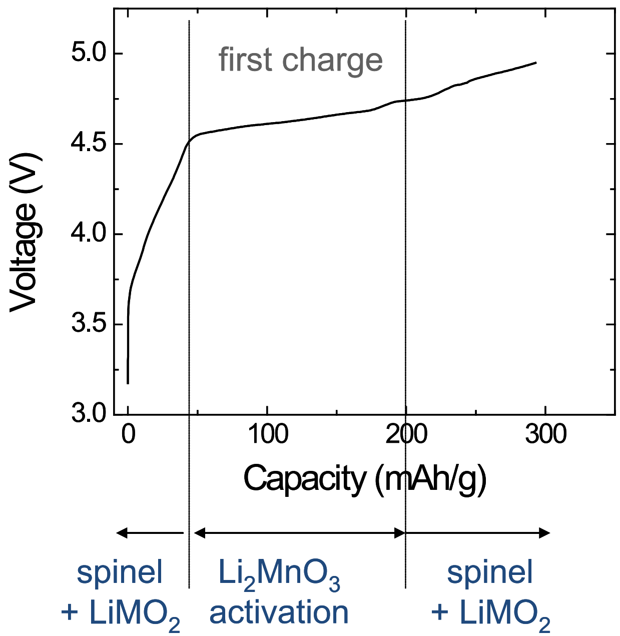
$Li_xNi_{0.25}Mn_{0.75}O_y$ ($0.5<x<1.5$; $2<y<2.5$)

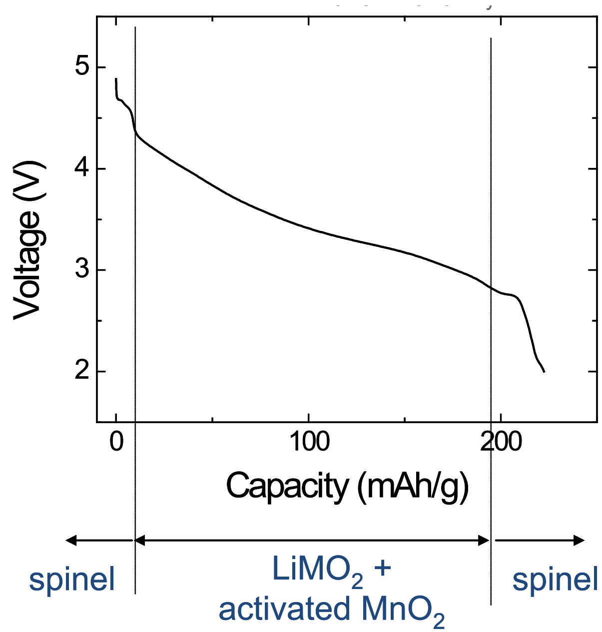
with mixed characters of

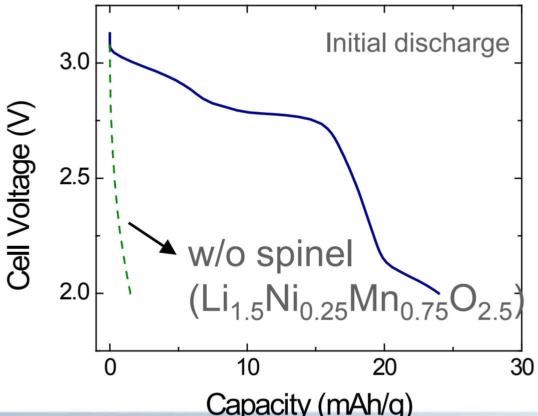
- Li_2MnO_3 (structure stabilization and capacity after activation)
- $LiMn_{0.5}Mn_{0.5}O_2$ (capacity)
- $LiNi_{0.5}Mn_{1.5}O_4$ (rate)

Voltage profiles demonstrate the presence of spinel component in the integrated structure

$Li/Li_{1.2}(Ni_{0.25}Mn_{0.75})O_y$



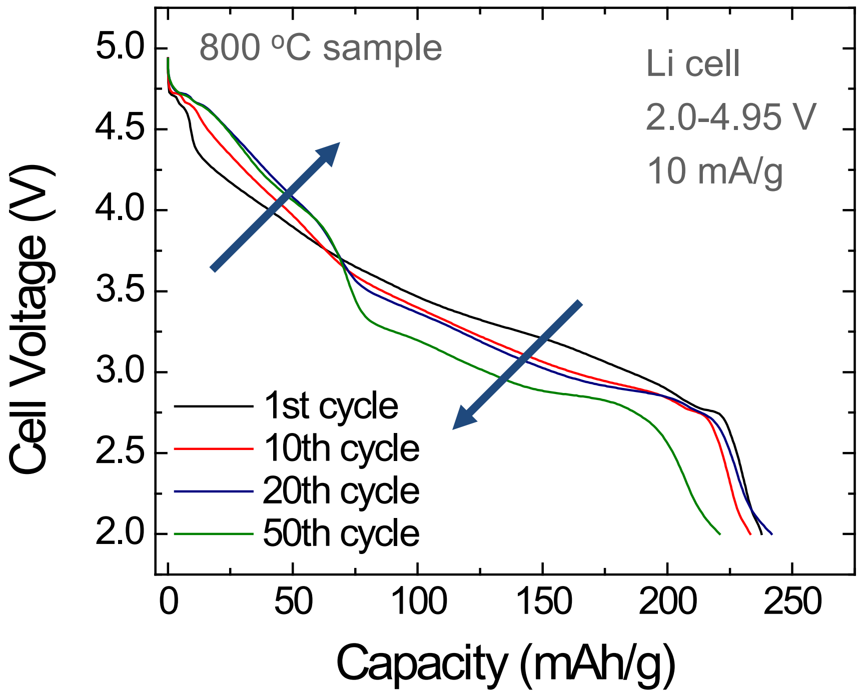


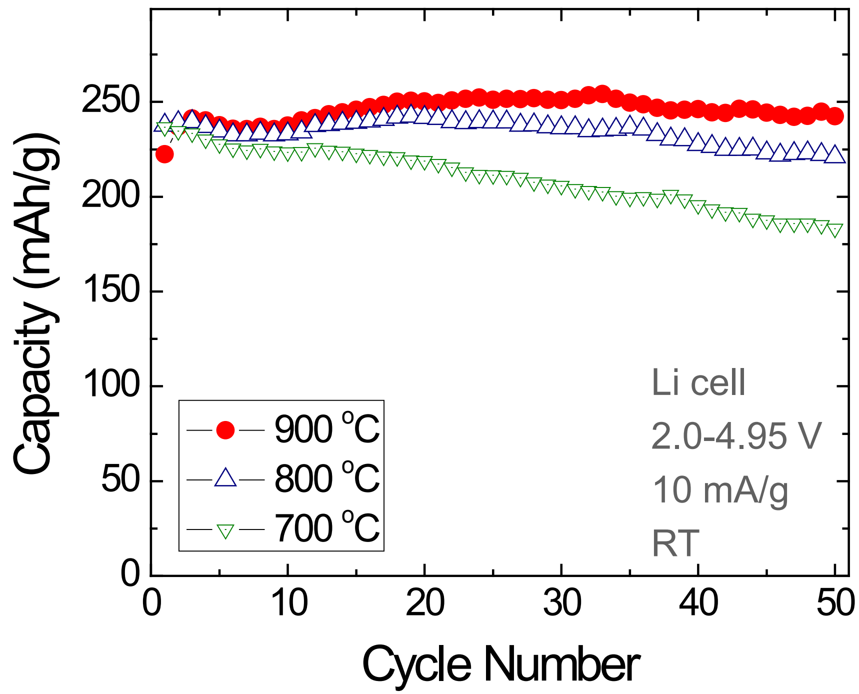


- The voltage profiles indicate the presence of $LiMO_2$, Li_2MnO_3, and LiM'_2O_4 components.
- $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y \equiv$ $0.18LiNi_{0.5}Mn_{1.5}O_4 \bullet 0.41Li_2MnO_3 \bullet 0.41LiNi_{0.5}Mn_{0.5}O_2$ (calculated)

Baseline Chemistry $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

Cycling performance (2.0-4.95 V)



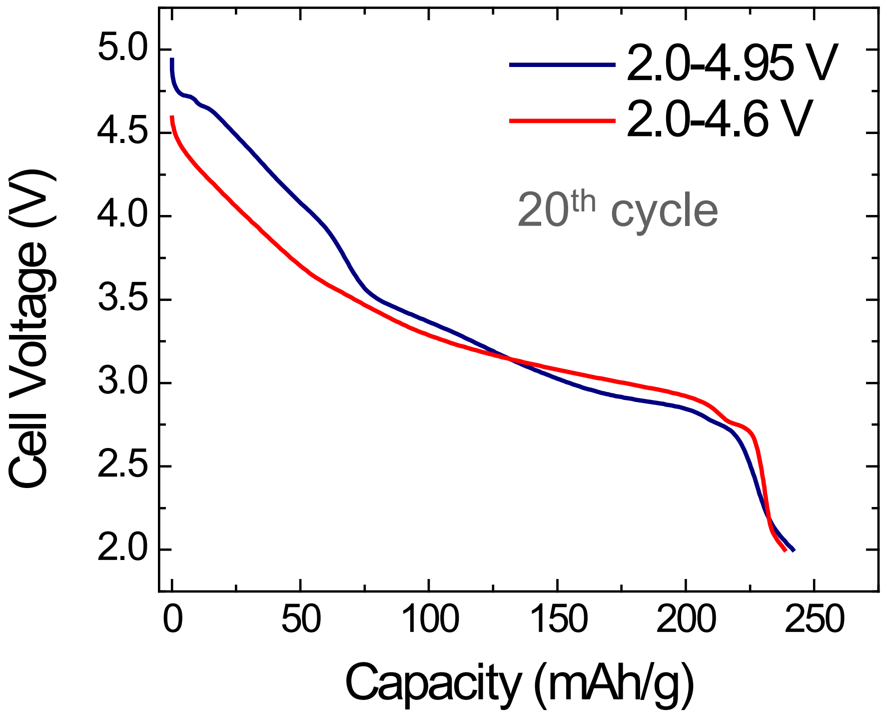


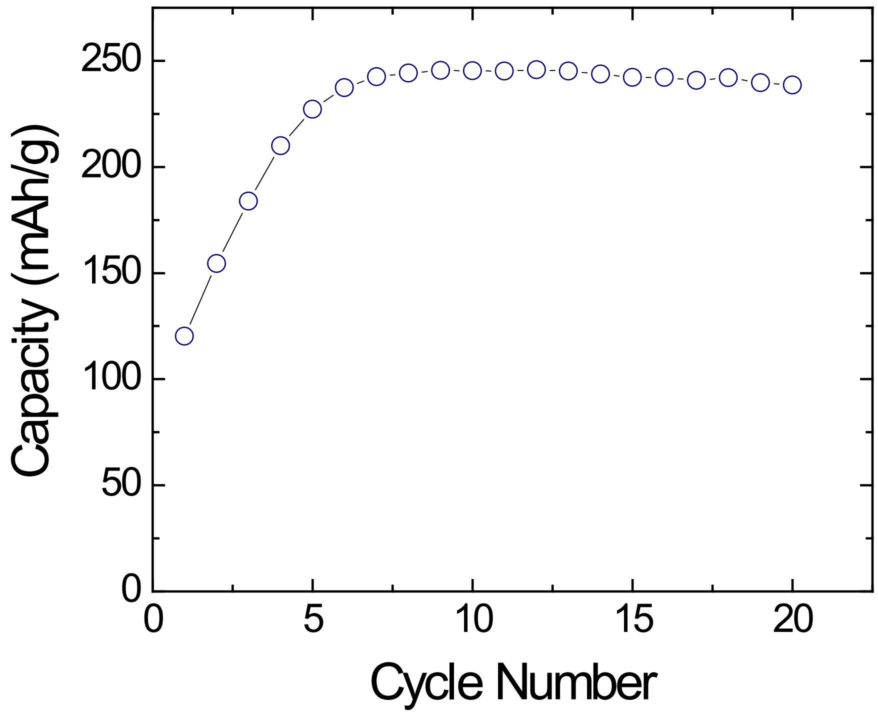
- Excellent cycling performance (800, 900 °C samples)
- However, too severe shape change of voltage profiles was observed.

* Electrolyte: 1.2 M $LiPF_6$ in EC:EMC(3:7)

Baseline Chemistry $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

Cycling performance (2.0-4.6 V: upper cut-off voltage lowered)

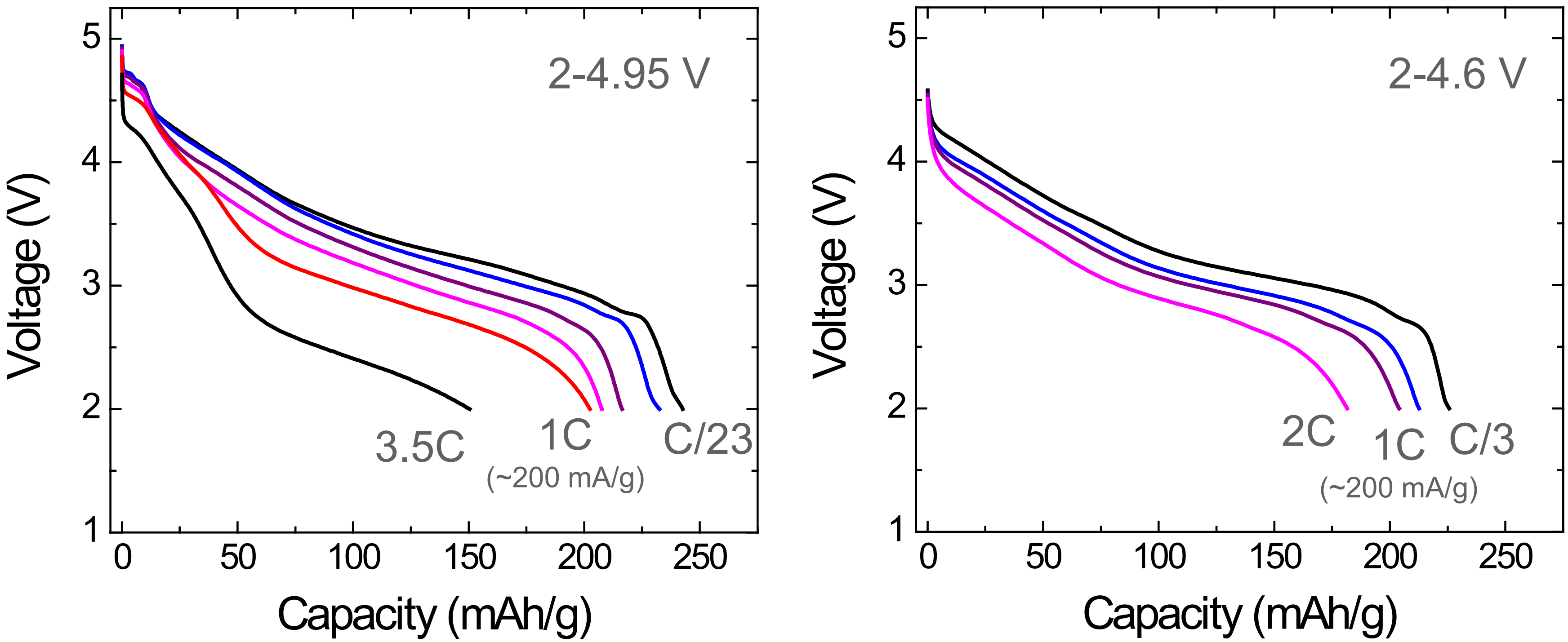




- When the upper cut-off voltage was limited to 4.6 V, the discharge voltage profiles showed significantly suppressed shape change while the high capacity was maintained.
- However, the capacity gradually increased during initial 5-10 cycles. Optimum ‘formation cycling’ condition should be established.

Baseline Chemistry $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

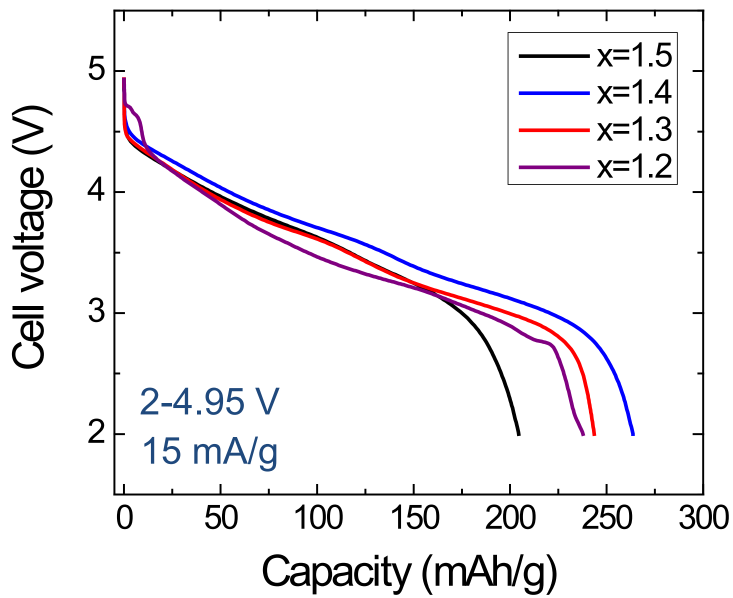
Rate performance



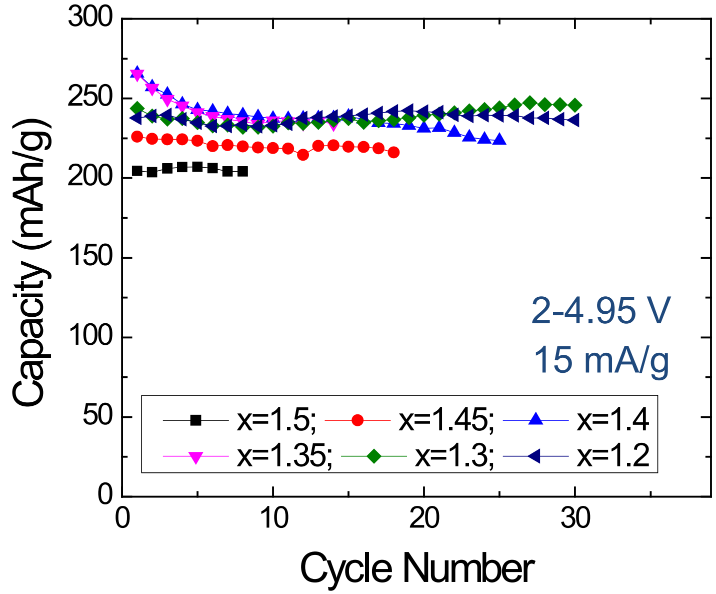
- Beneficial impact of the spinel component in the structure
  - Excellent rate capability: ~200 mAh/g at 1C rate (in spite of the absence of cobalt!)
  - After enough break-in cycles, the outstanding rate performance was also observed in 2.0-4.6 V range.

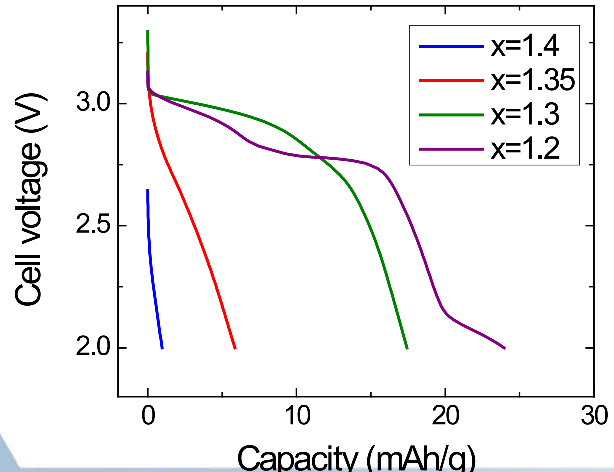
Different Li content, $Li_xNi_{0.25}Mn_{0.75}O_y$

initial discharge



cycling performance

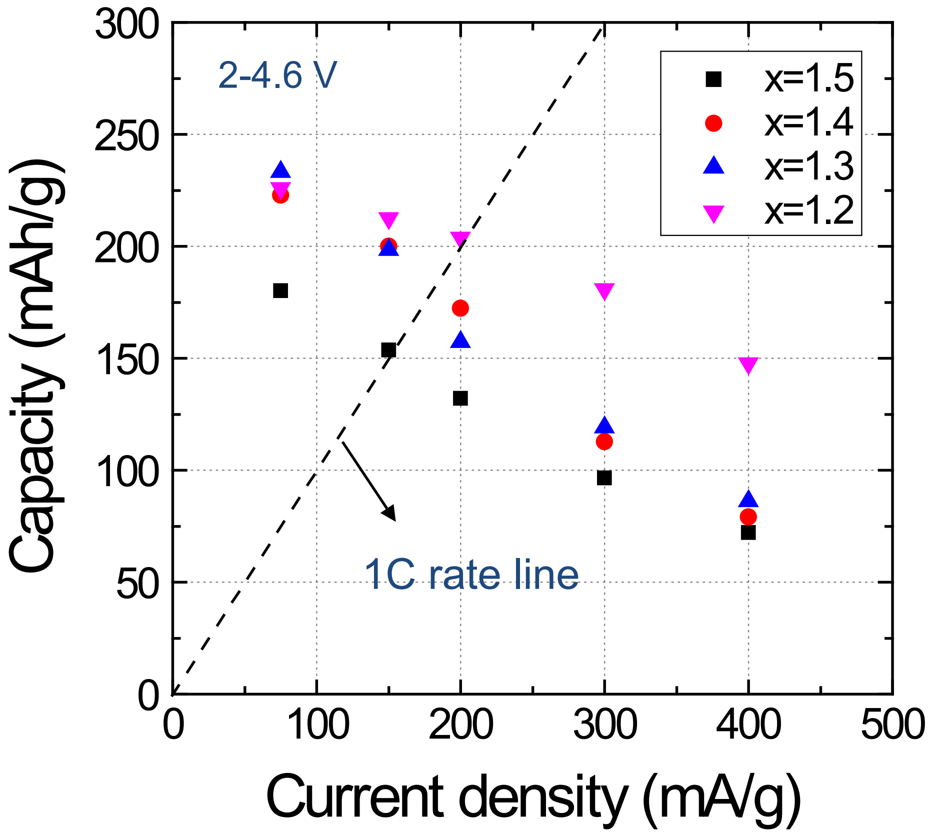




- With decreasing Li content:
  - spinel content increased
    - Increase of capacity during the initial discharge from OCV
  - electrochemical properties improved

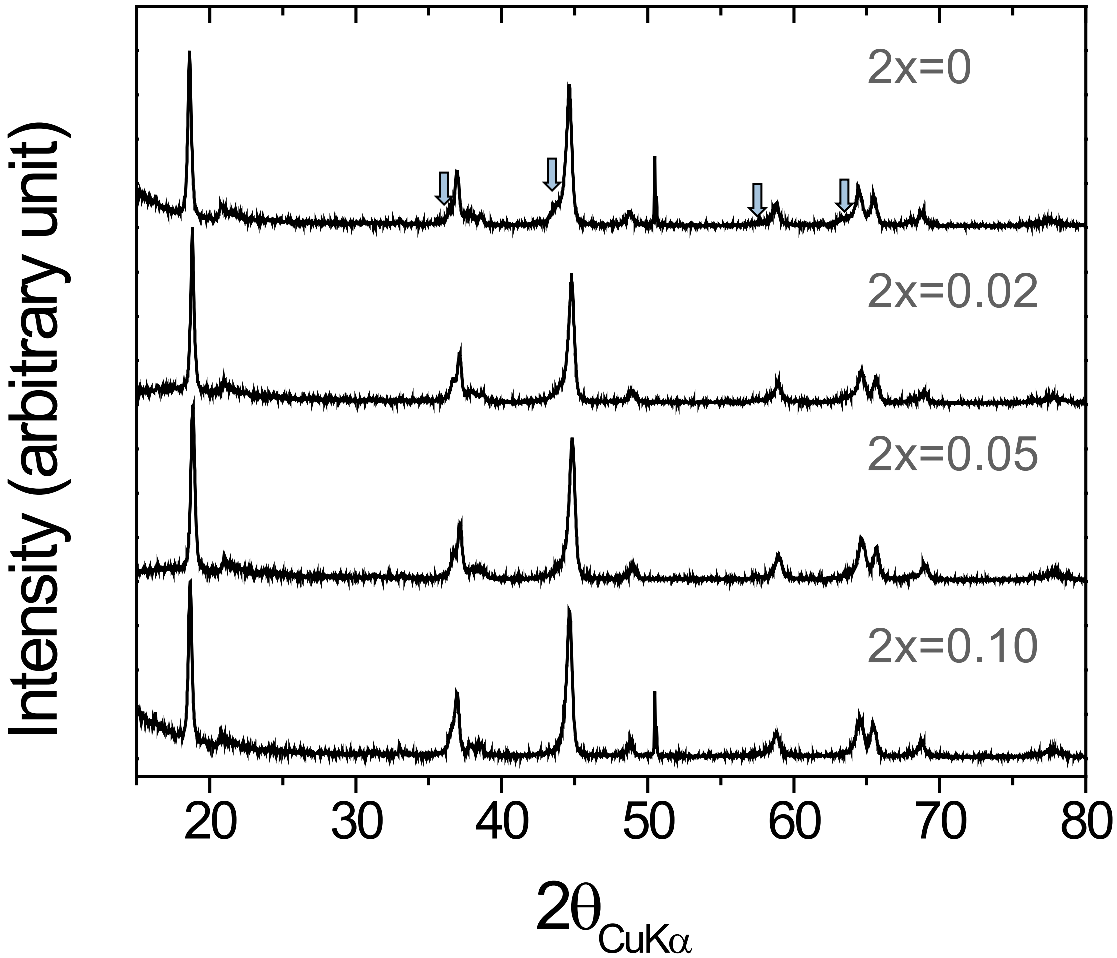
Different Li content, $Li_xNi_{0.25}Mn_{0.75}O_y$

rate study



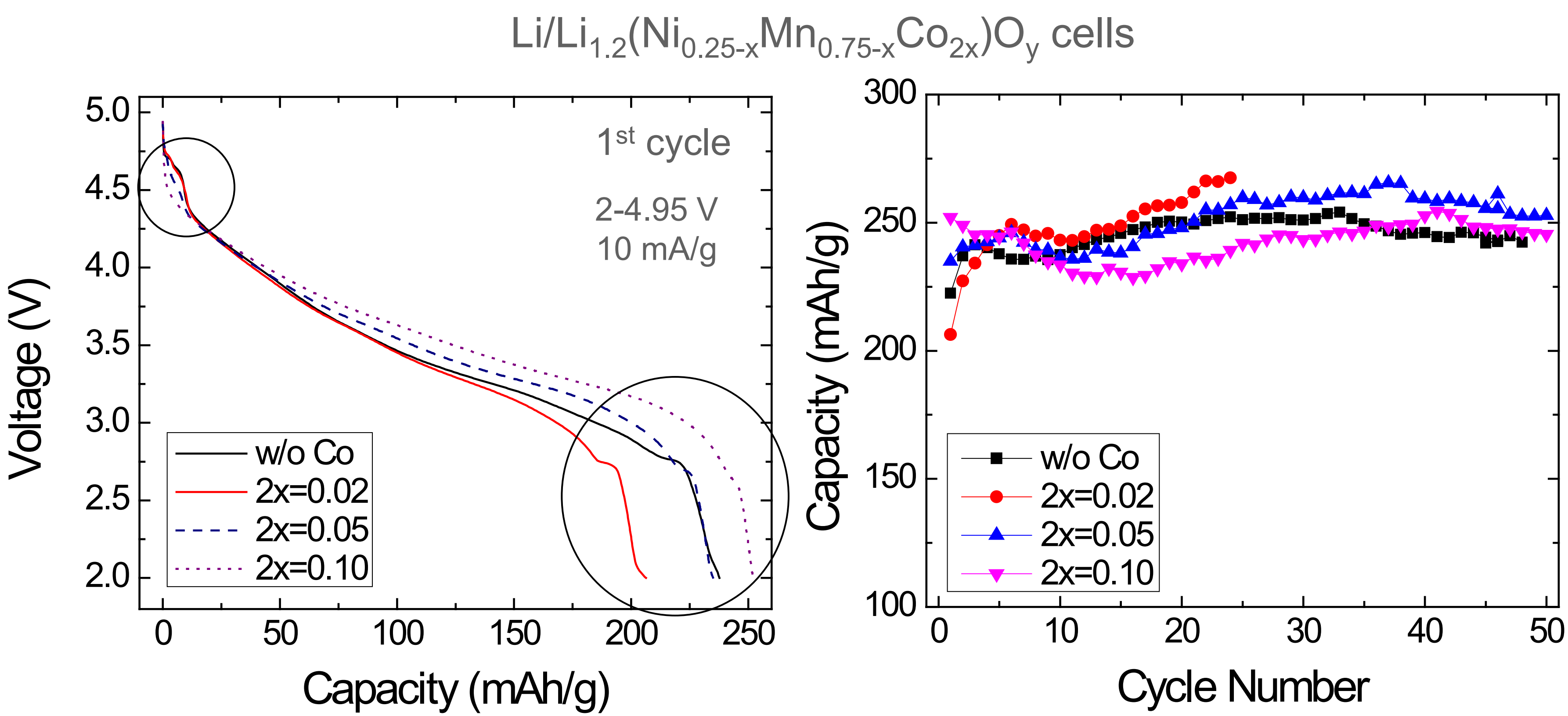
- With decreasing Li content, rate capability was improved.
- Further characterization is in progress to determine the optimum lithium content.

Effect of Co, $Li_{1.2}Ni_{0.25-x}Mn_{0.75-x}Co_{2x}O_y$



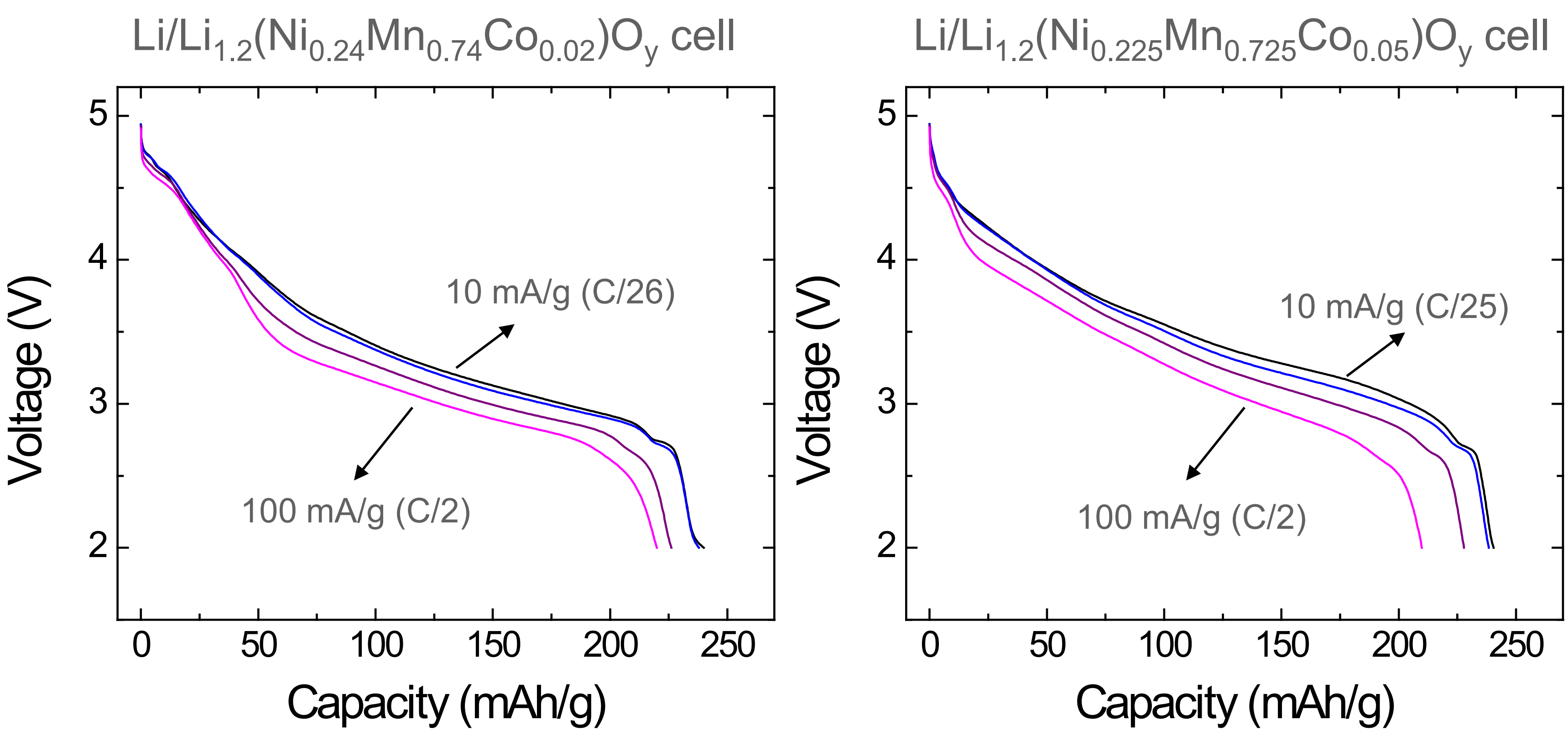
- With increasing Co content, the spinel signature becomes less prominent.

Effect of Co, $Li_{1.2}Ni_{0.25-x}Mn_{0.75-x}Co_{2x}O_y$



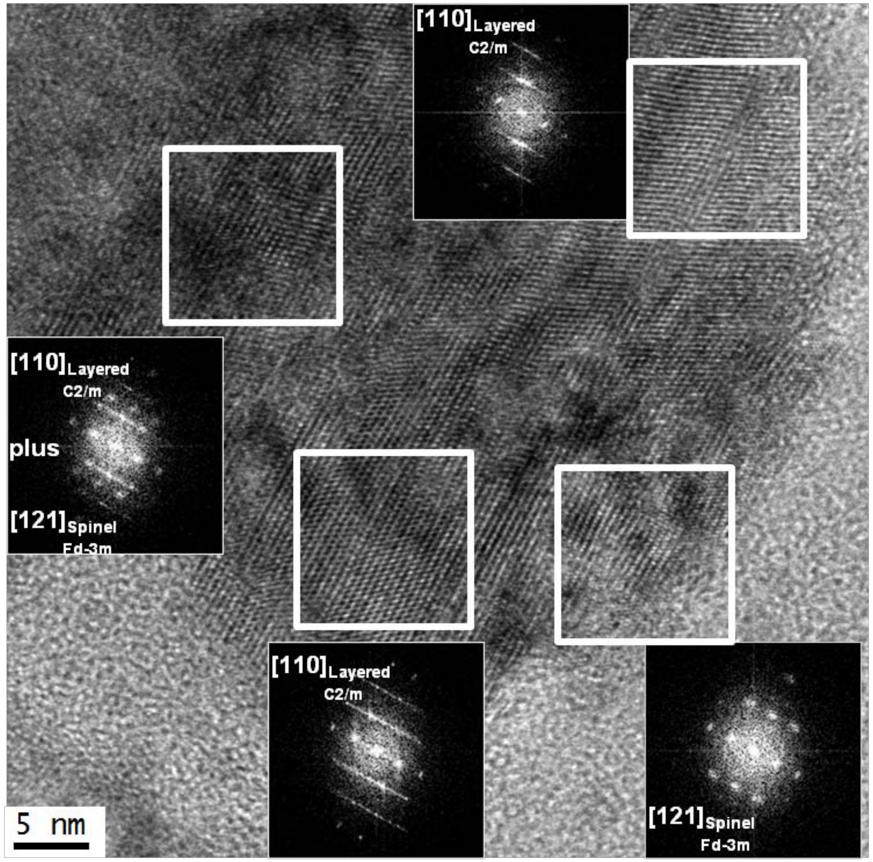
- With increasing Co content, the spinel signatures in the voltage profiles become less prominent, in agreement with the XRD patterns.
- All the cells exhibited excellent cycling performance.

Effect of Co, $Li_{1.2}Ni_{0.25-x}Mn_{0.75-x}Co_{2x}O_y$



- The 2x=0.02 material exhibits better rate performance than undoped material. Further characterization is underway.
- The 2x=0.10 material showed the least prominent spinel signature and worst rate performance (not shown).

Structural Study – Transmission Electron Microscopy*

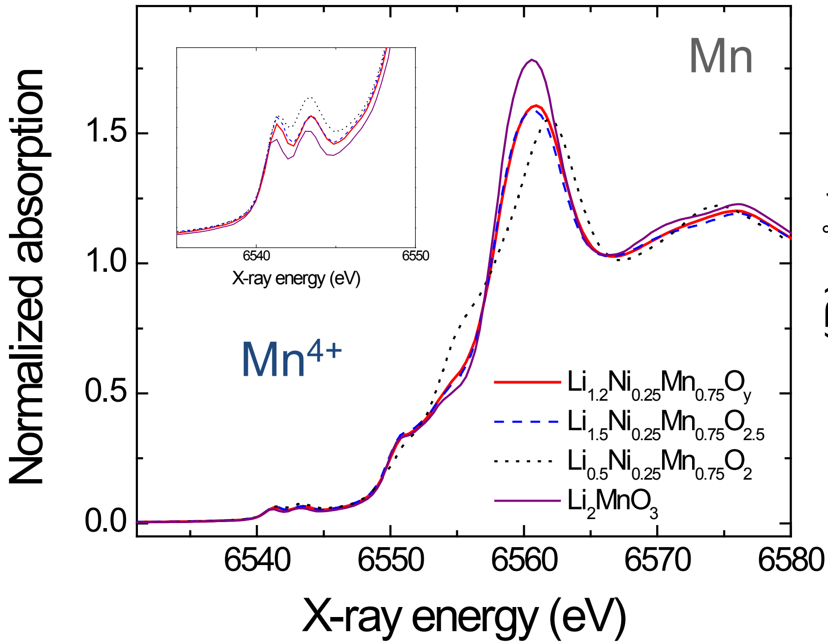


❖ This high-resolution TEM image clearly shows presence and integration of layered and spinel components in nano scale.

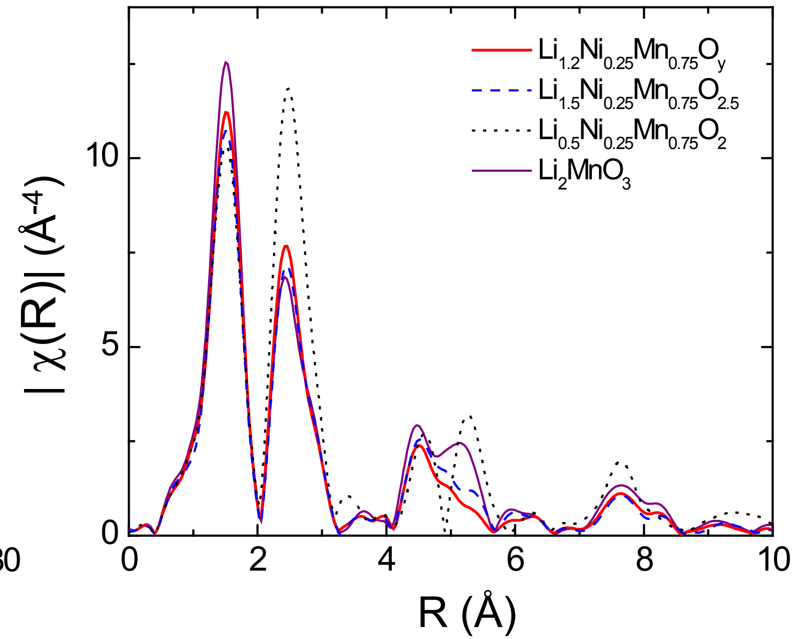
* C. Carlton and Y. Shao-Horn, MIT

Structural Study – X-ray absorption spectroscopy*

Mn XANES



Mn EXAFS

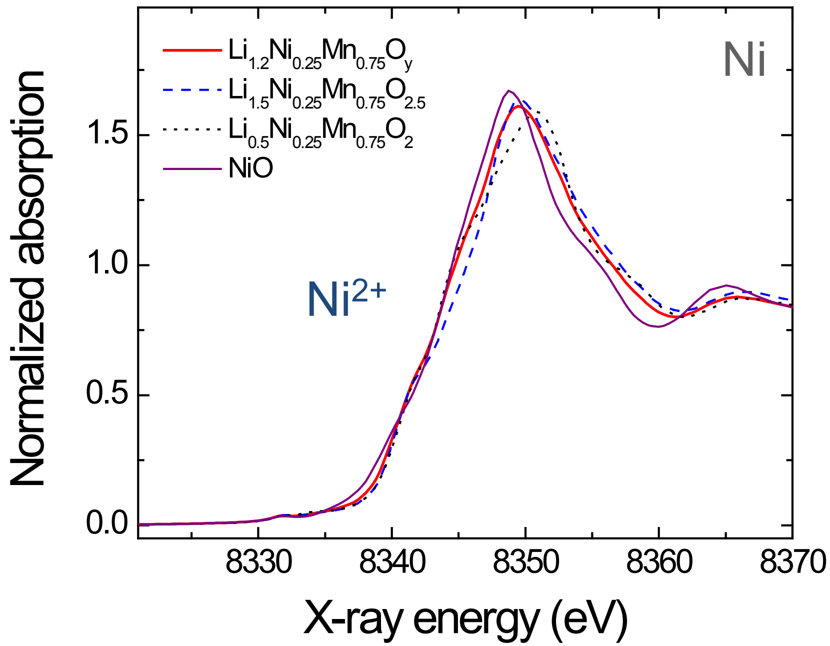


- Oxidation state of Mn is close to +4.
- Lithium ions in TM layer are clustered preferentially around Mn ions, similar to $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$ (layered-layered).
- The presence of spinel like environments in $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ is estimated to be ~ 10% (maximum).

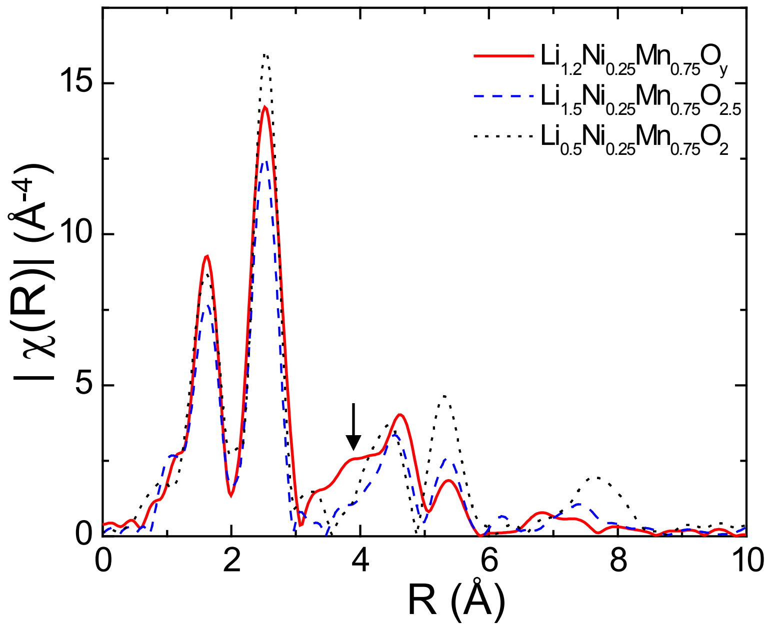
* M. Balasubramanian, APS, Argonne

Structural Study – X-ray absorption spectroscopy

Ni XANES



Ni EXAFS



- Oxidation state of Ni is close to +2.
- Much higher Ni-O-Ni 180 degree correlation (arrow in EXAFS spectrum) is observed than $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$. This is present in rocksalt NiO and if Ni occupies Li layers in layered compounds. Further analysis is under way for better understanding the local structure.

Future work

- Identification of optimum chemistry
  - Lithium-to-TM ratio, Co content
  - Close collaboration with industrial partner (good TM precursor)
- Investigation of thermal safety characteristics
- Further structural study
  - Detailed analysis of the XAS and TEM results of as-prepared powders and cycled electrodes to understand the structural features
- Physical blending of spinel and layered materials
- Full cell study
  - Carbonaceous anode
  - Advanced anode materials through collaboration with other ABRT or BATT team

Summary

- Initial cycling performance and rate capability study of baseline chemistry ($Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$) at 2.0-4.95 V have been completed.
  - Good cycling performance and rate capability (~200 mAh/g at 1C rate)
  - But severe voltage shape change was observed during extended cycling.
- High capacity (~250 mAh/g) and outstanding rate capability (>200 mAh/g at 1C rate) was also observed at 2.0-4.6 V.
  - However, 5-10 break-in cycles were required. Initial formation cycle condition needs to be optimized.
- Various Li- and Co contents have been studied; further characterization is under way to establish optimum chemistry.
- X-ray absorption and high-resolution transmission electron microscopy (HR TEM) were conducted for structural study. HR TEM image clearly showed integrated structure between spinel and layered structure in nano scale.

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged - David Howell