Development of high-capacity cathode materials with integrated structures

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Overview

Timeline

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

Budget

- Total project funding
  - 100% DOE
- Funding in FY10: $300K
- Funding in FY11: $400K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Sun-Ho Kang
- Collaborators:
  - CSE, Argonne: K. Gallagher, D. Kim, M. M. Thackeray (materials design, synthesis and electrochemical characterization)
  - APS, Argonne: M. Balasubramanian (XAS)
  - MIT: C. Carlton, Y. Shao-Horn (TEM)
- Industrial partners
  - Hanwha Chemical ($LiFePO_4$ olivine)
  - Daejung EM (transition metal precursor)

Objective of this study

Development of cathode materials with ***high-capacity, thermal stability, low-cost, and longevity*** for PHEVs

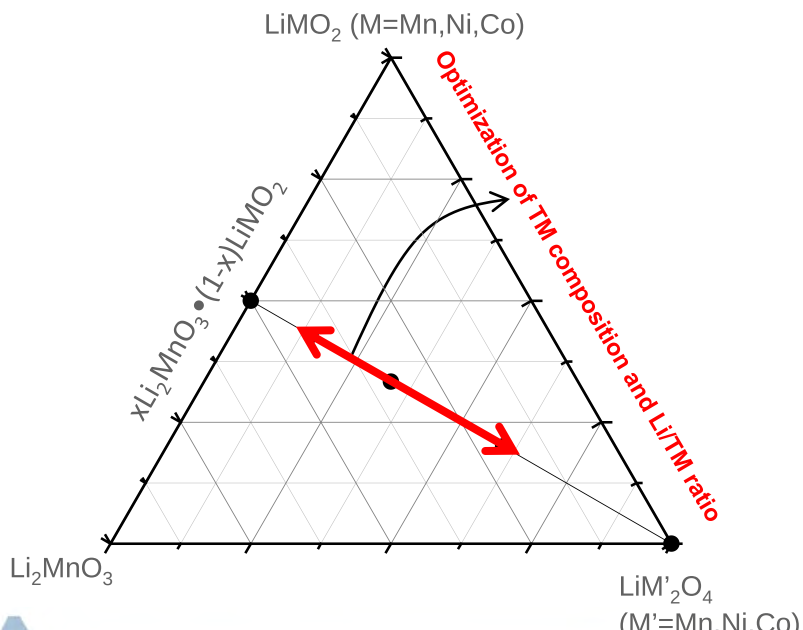
- Design and synthesis of Li- and Mn-rich oxides with integrated structures containing spinel component
  - Performance evaluation and verification of beneficial impact of the spinel component
- Identification and overcoming of performance degradation issues of high-capacity cathode materials with integrated structure
  - Information exchange and close collaboration with diagnostic study team and PHEV cell building team
- Supply of promising high-capacity cathode materials for PHEV cell build

Milestones FY11

- Optimization of chemical composition – *on going*
- Evaluation of high-capacity electrode materials in full Li-ion configuration using various anode materials – on going
- Identification of various issues related with high-capacity cathode materials – initiated
- Investigation of the materials structure after cycling by various analytical techniques – on going
- Study of physical blending of high-capacity cathode and high-power cathode materials – on going
- Study of thermal stability of high-capacity electrode materials – on going

Approach

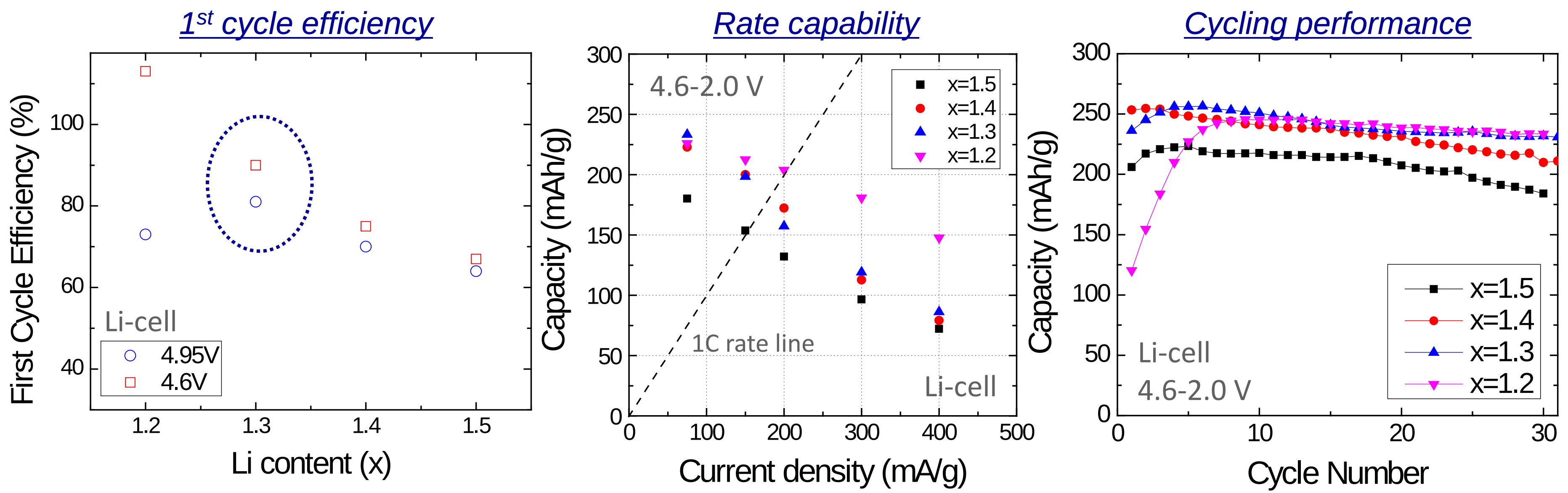
- Embedding spinel component in the 'layered-layered' composite structure
  - *Spinel structure can be created in the composite structure by controlling lithium content*
    - *Lower lithium-to-TM ratio than in $xLi_2MnO_3 \bullet (1-x)LiMO_2$*
  - *First cycle efficiency and rate capability are expected to improve.*



- Identification of challenging issues with high-capacity layered-layered oxide materials (newly added work scope)
  - *This type of electrode materials will be used in the ABR PHEV cell build.*
  - *Voltage profile shape changes (voltage depression) with cycling and Mn dissolution*
    - *Case- and analytic study*
    - *Study results will be implemented into the materials design and development efforts.*
  - *Relatively poor power performance*
    - *Physical blending of layered-layered oxide with other high-power electrode materials (spinel or olivine)*
    - *$LiFePO_4$ was chosen because of its low plateau voltage where the high-capacity electrode shows significantly high impedance.*

$Li_xMn_{0.75}Ni_{0.25}O_y$: Basic E-Chem Properties

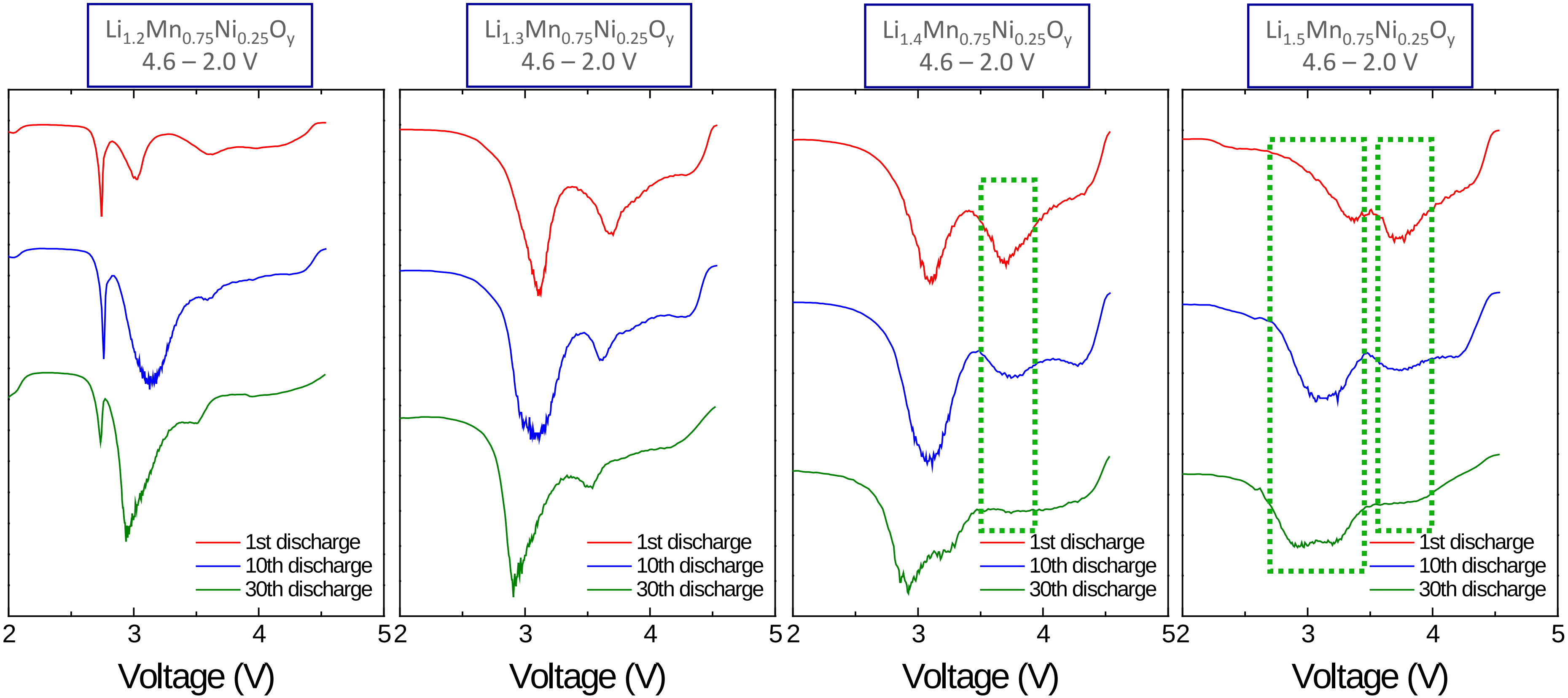
- $Li_xMn_{0.75}Ni_{0.25}O_y$ has the same Mn:Ni ratio (3:1) as $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.5}Ni_{0.5}O_2$ (layered-layered) and $LiMn_{1.5}Ni_{0.5}O_4$ (spinel).
- $Li_xMn_{0.75}Ni_{0.25}O_y$ was synthesized using Li_2CO_3 and $Mn_{0.75}Ni_{0.25}CO_3$* (850 °C, 12 h, air).
- Coexistence of layered (rhombohedral, monoclinic) and spinel was confirmed by X-ray diffraction and HR-TEM (reported last year).
- For all of the cell test, 2325 separator (tri-layer, Celgard), 1.2M $LiPF_6$ in EC:EMC(3:7) were used.



- Improvement in the 1st cycle efficiency was achieved by incorporating spinel phase in the layered-layered matrix. (e.g., 90% for $Li_{1.3}Mn_{0.75}Ni_{0.25}O_y$ when cycled at 4.6-2.0 V)
- Some composition (x=1.2) needs initial break-in cycles to reach high capacity.
- 200 mAh/g at 1C rate was achieved for $Li_{1.2}Mn_{0.75}Ni_{0.25}O_y$.

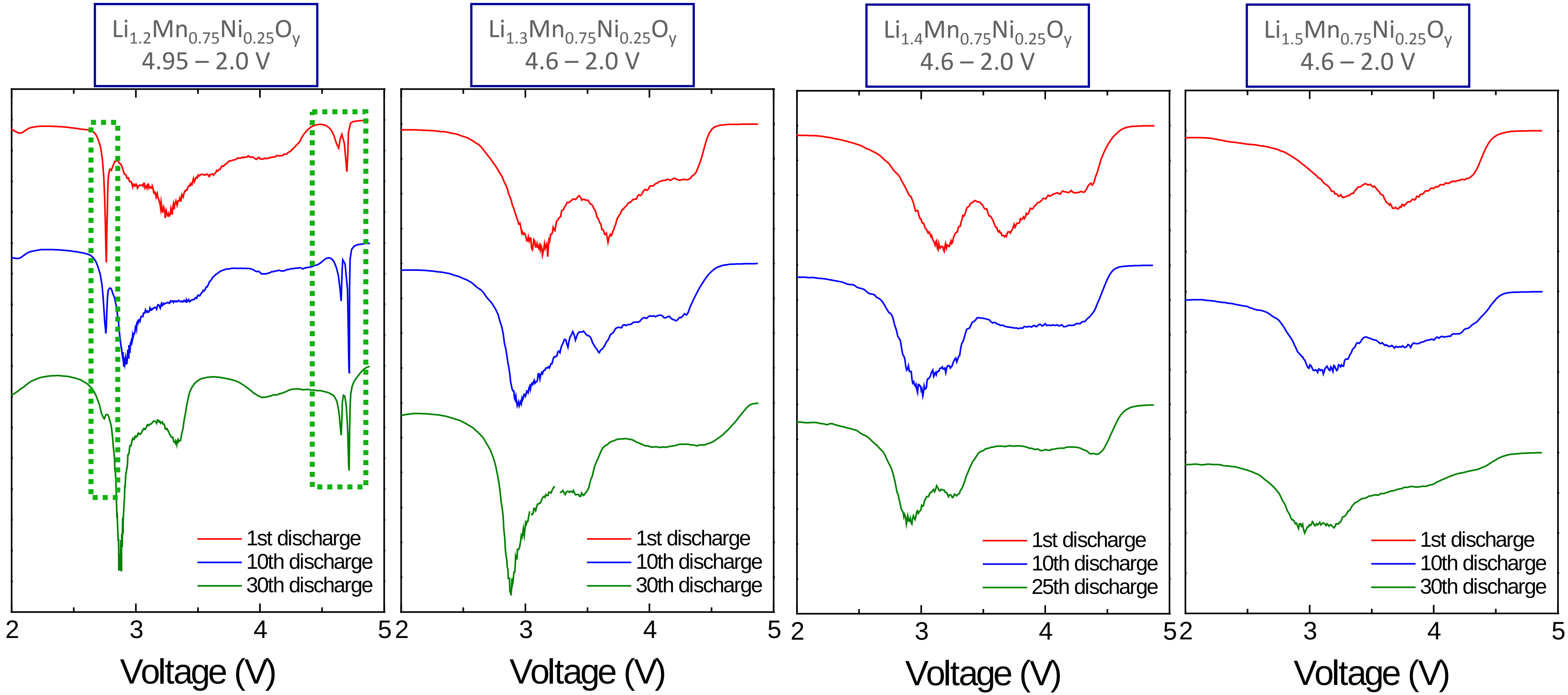
*coprecipitated in-house or provided by industrial partner

$Li_xMn_{0.75}Ni_{0.25}O_y$: differential capacity plot (4.6-2.0 V)



- $Li_{1.5}Mn_{0.75}Ni_{0.25}O_y$ (or alternatively, $0.5Li_2MnO_3$•$0.5LiMn_{0.5}Ni_{0.5}O_2$, i.e., spinel-free composition) shows significant dQ/dV change with cycle (dotted box regions), which corresponds to significant voltage shape change (voltage suppression).
- With decreasing Li content (or increasing spinel content), the less change in the dQ/dV plots is observed, indicating spinel component provides structural stability upon cycling.

$Li_xMn_{0.75}Ni_{0.25}O_y$: differential capacity plot (4.95-2.0 V)

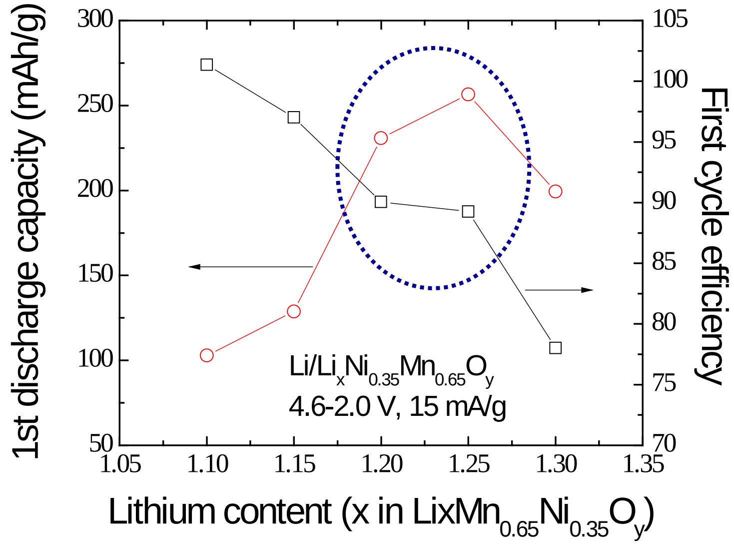


- All of the cells exhibit more significant change in the dQ/dV plots when cycled up to 4.95 V.
- Interestingly, the two dQ/dV peaks at ~4.8 V of $Li_{1.2}Mn_{0.75}Ni_{0.25}O_y$ electrode was practically not affected while the ~2.7 V peak almost disappeared by the high-voltage cycling. Those dQ/dV peaks are signature of '$LiMn_{1.5}Ni_{0.5}O_4$' spinel. ⇒ Needs to be correlated with structural change
- As in the 4.6-2.0 V cycling, **$Li_{1.3}Mn_{0.75}Ni_{0.25}O_y$** material shows the least change.

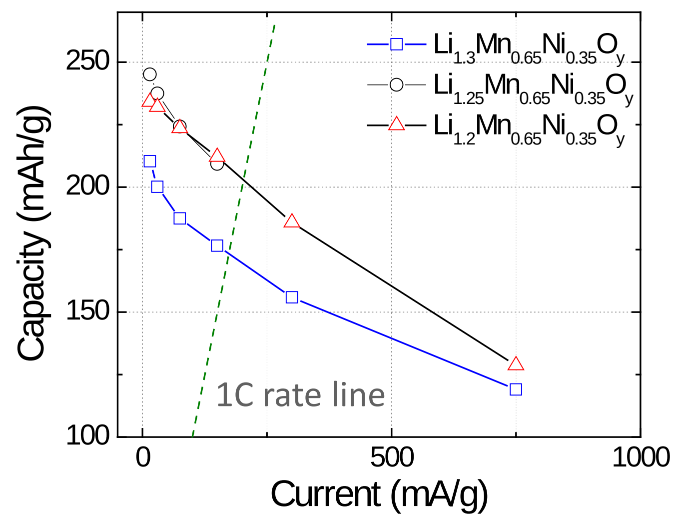
$Li_xMn_{0.65}Ni_{0.35}O_y$: 1st cycle efficiency and rate

- To enhance structural stability during cycling, higher Ni content (Mn:Ni=65:35) has been examined. In this case, $Li_{1.3}Mn_{0.65}Ni_{0.35}O_{2.3}$ is the spinel-free, layered-layered composition ($0.3Li_2MnO_3 \bullet 0.7LiMn_{0.5}Ni_{0.5}O_2$ in two-component notation).
- $Li_xMn_{0.65}Ni_{0.35}O_y$ has been synthesized using Li_2CO_3 and $Mn_{0.65}Ni_{0.35}C_2O_4 \bullet 2H_2O^*$ (850 °C, 12 h, air).

1st cycle efficiency and capacity



Rate capability

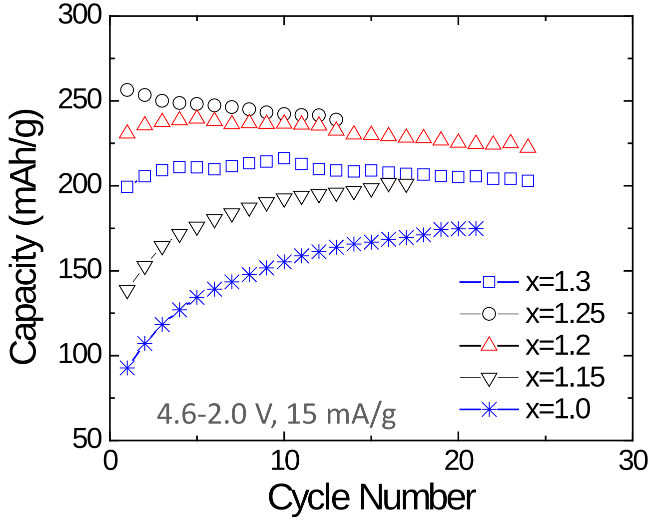


- Similar to the $Li_xMn_{0.75}Ni_{0.25}O_y$ case, the 1st cycle efficiency and rate performance were enhanced by creating spinel component in the layered-layered matrix.
- Based on the 1st cycle efficiency and rate capability, we chose $Li_{1.2}Mn_{0.65}Ni_{0.35}O_y$ and $Li_{1.25}Mn_{0.65}Ni_{0.35}O_y$ for further study.

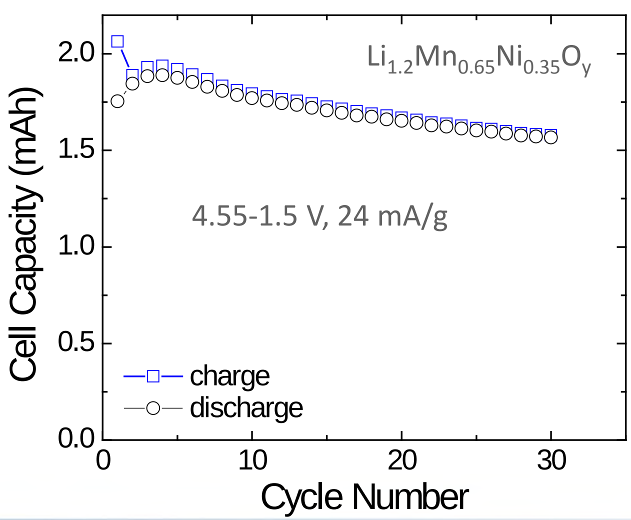
*coprecipitated in-house

$Li_xMn_{0.65}Ni_{0.35}O_y$: Cycling performance

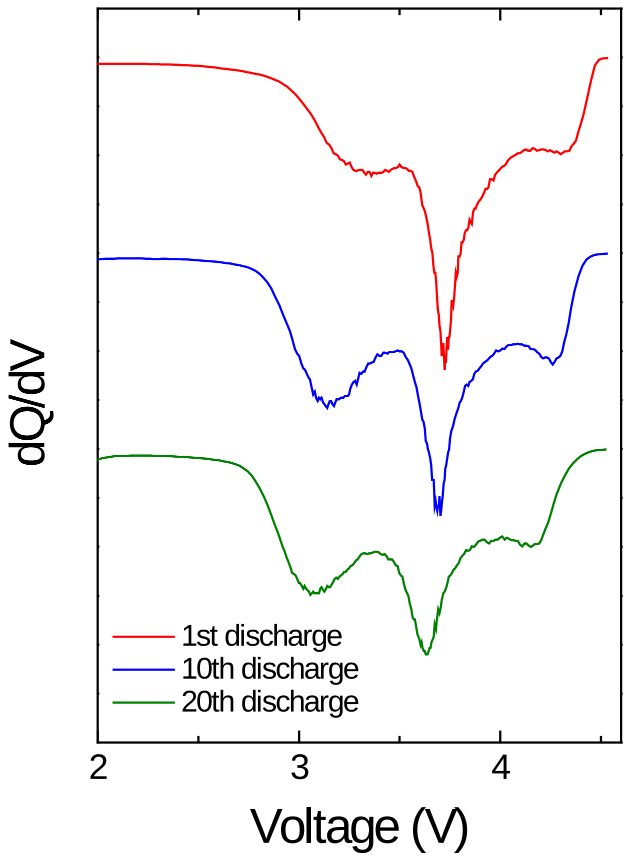
Lithium cells



Li-ion cells (vs. Mag-10 graphite)

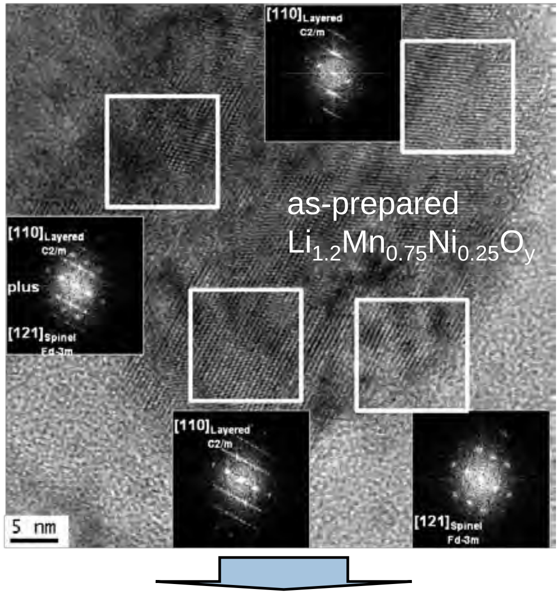


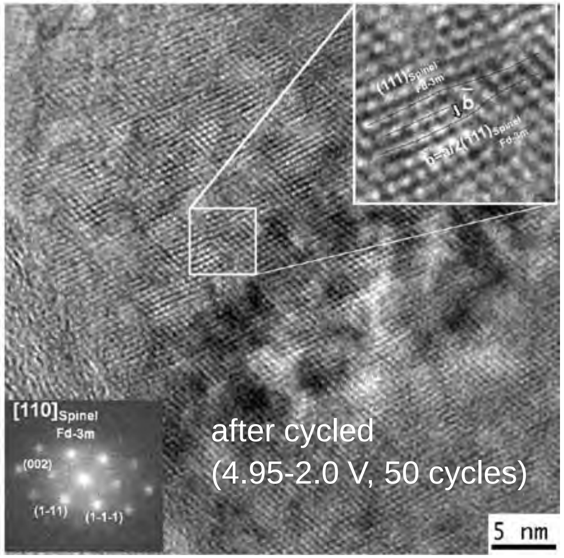
dQ/dV plots of Li/$Li_{1.2}Mn_{0.65}Ni_{0.35}O_y$ cell

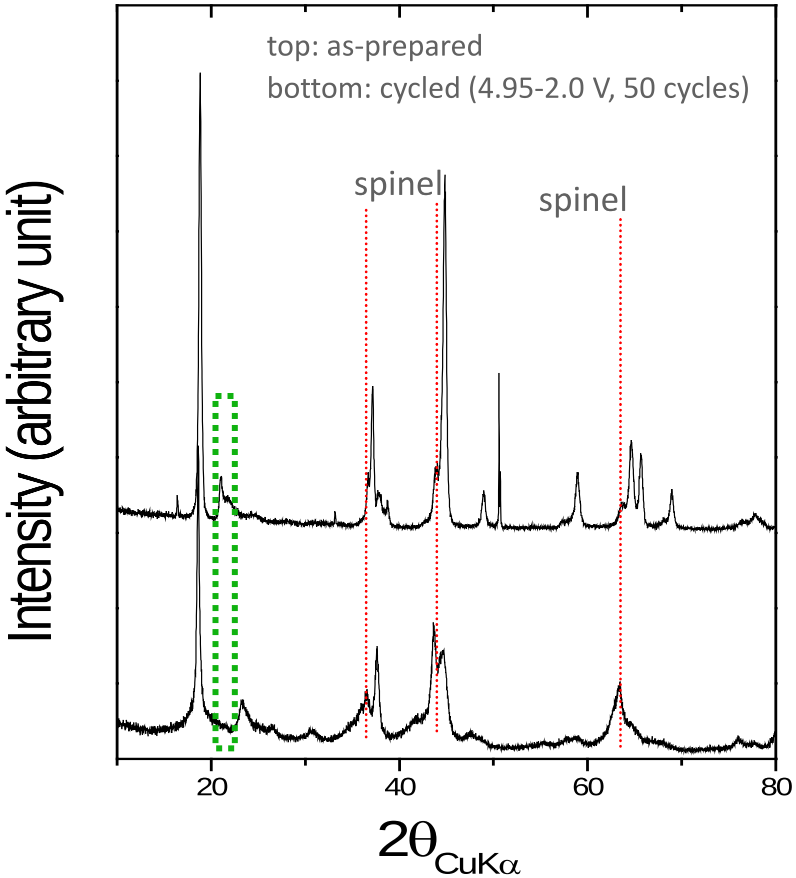


- Cycling performance evaluation is on going.
  - — Various anode materials will be coupled.
- dQ/dV plot seems to be relatively stable behavior.

Structural Study – TEM and XRD



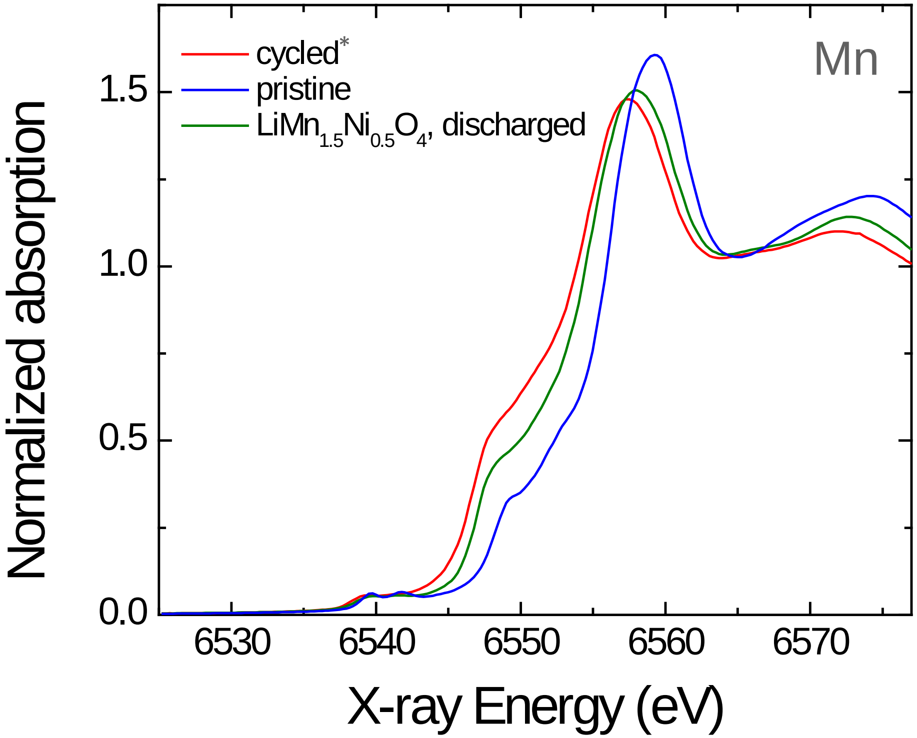




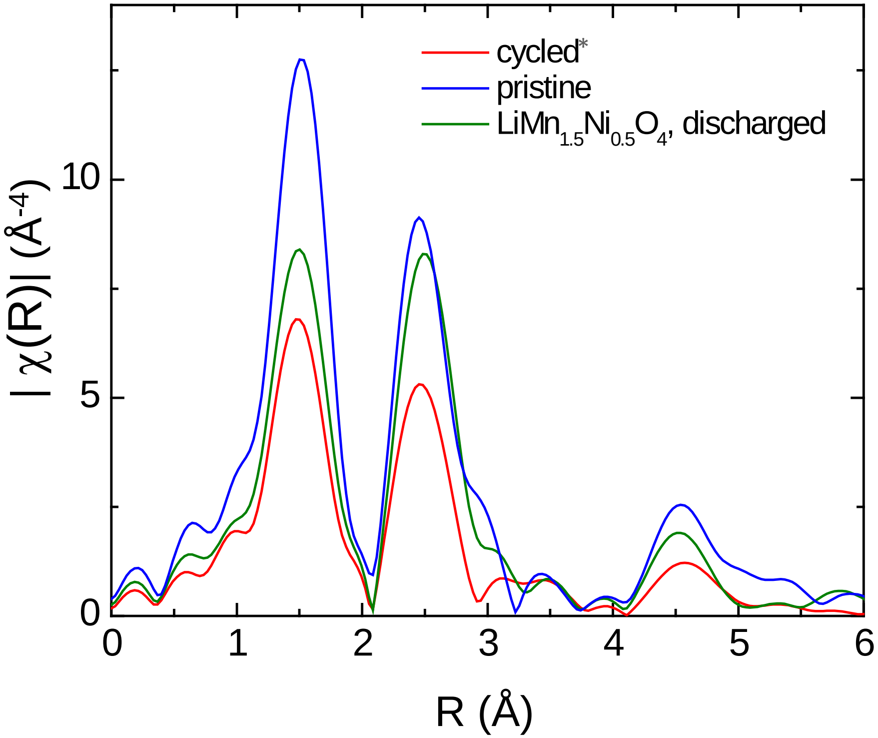
- Significant increase of spinel content in the cycled electrode
- Disappearance of cation ordering peak at ~22 °θ (Li_2MnO_3 activation)
- Dislocations and disordered structure observed from the cycled material

Structural Study – X-ray absorption spectroscopy

Mn XANES



Mn EXAFS

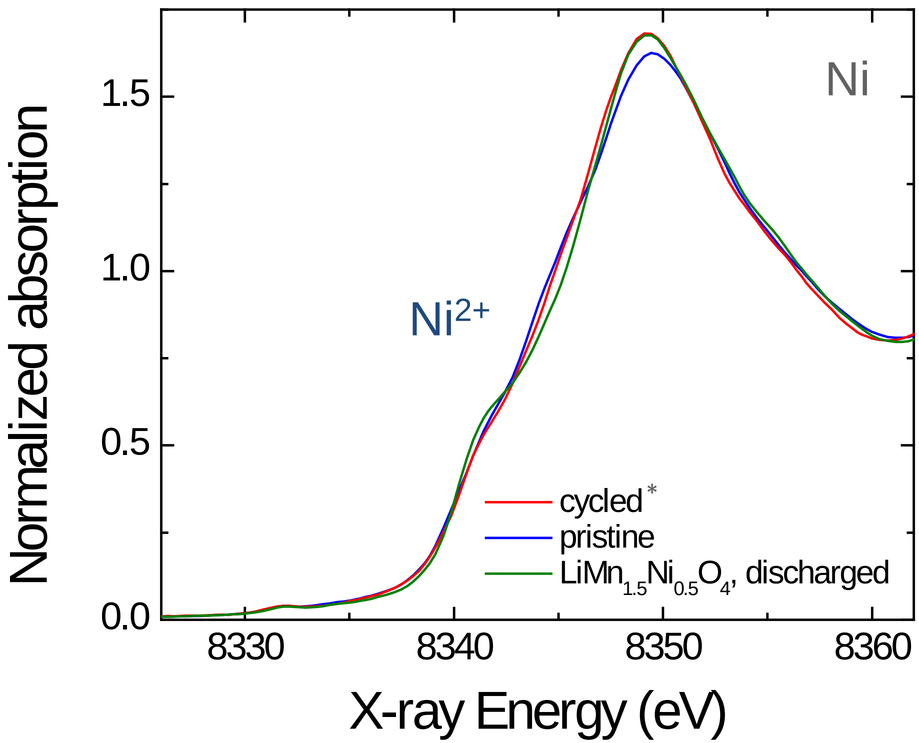


❖ Mn shows large reduction (close to Mn^{3+}) after 50 cycles in the fully discharged state. The cycled (and discharged) material is similar to the discharged spinel sample.

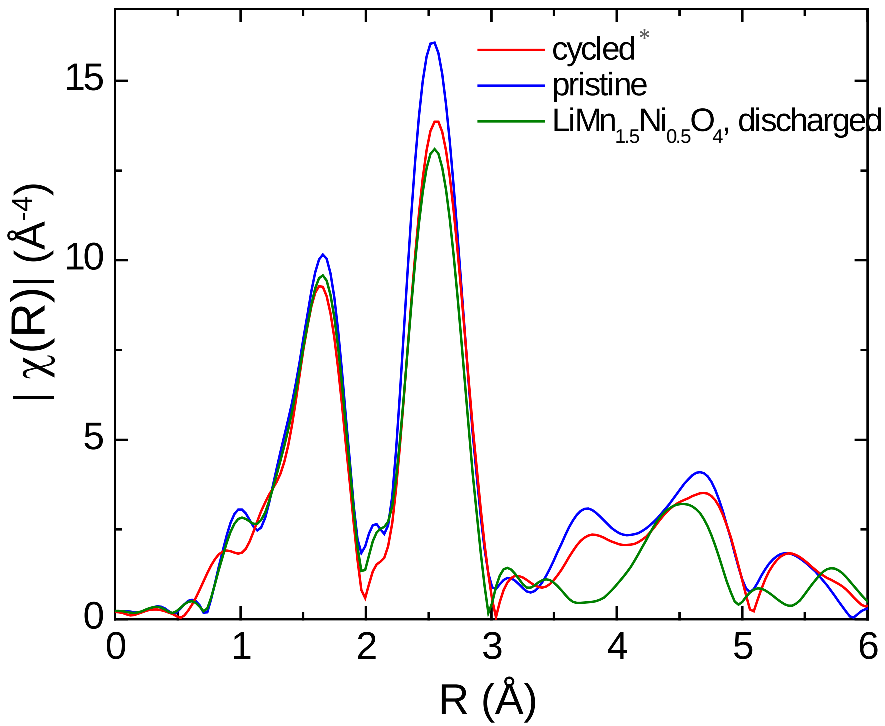
** cycled at 4.95-2.0 V, 50 cycles*

Structural Study – X-ray absorption spectroscopy

Ni XANES



Ni EXAFS

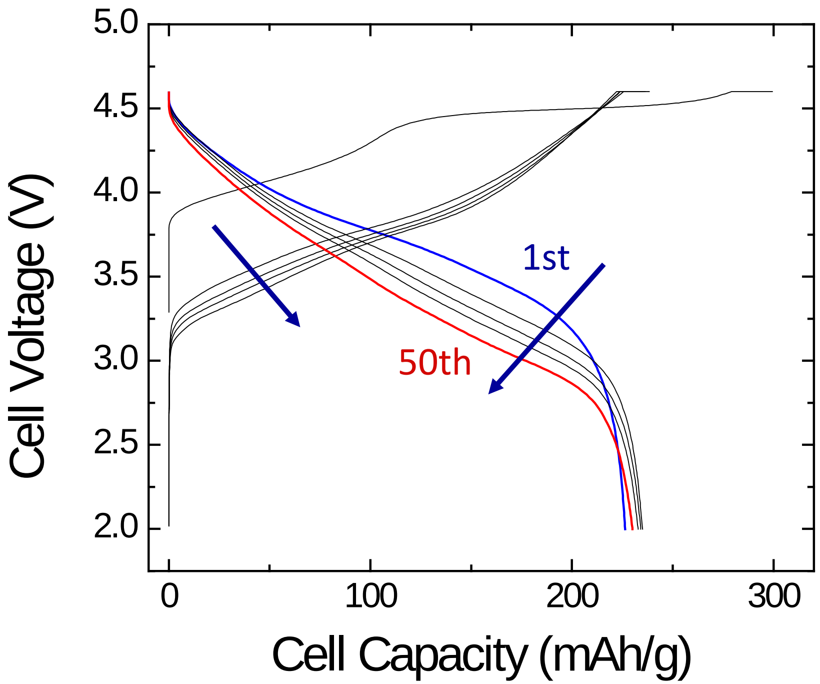


- ❖ Ni environment shows little change with cycling, consistent with the little change in ~4.8 V dQ/dV peaks with cycling (shown in slide p.8)
- ❖ Ni is predominantly Ni^{2+}, and remains fully reduced after 50 cycles. When compared to the lithiated spinel, the local structure is very different, consistent with the large local Ni-O-Ni rocksalt-like correlations present in the sample.

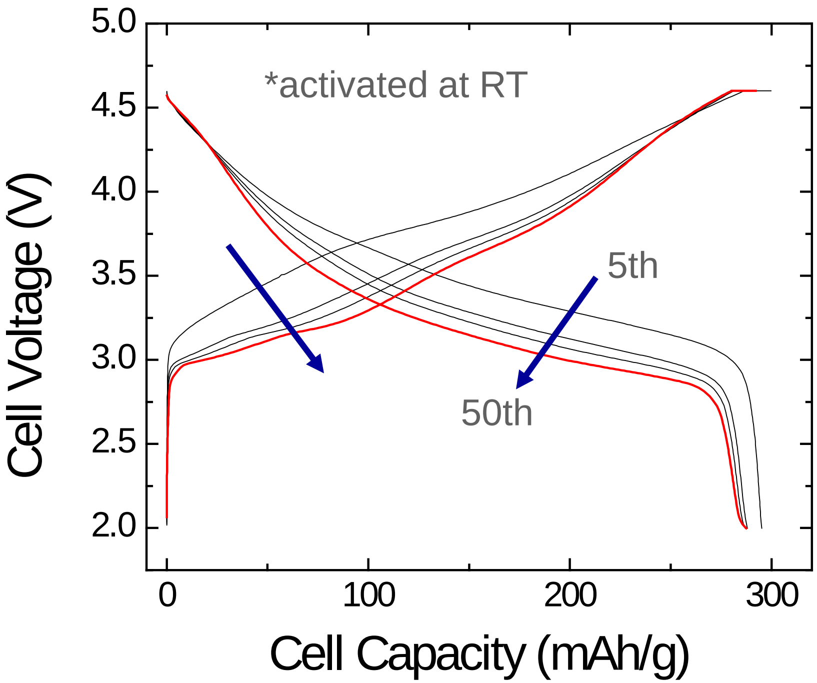
** cycled at 4.95-2.0 V, 50 cycles*

Issues with High-Capacity Layered-Layered Cathode Materials: Voltage shape change

Li/ANL-NMC†, 4.6-2.0 V, RT



Li/ANL-NMC, 4.6-2.0 V, 55 ℃

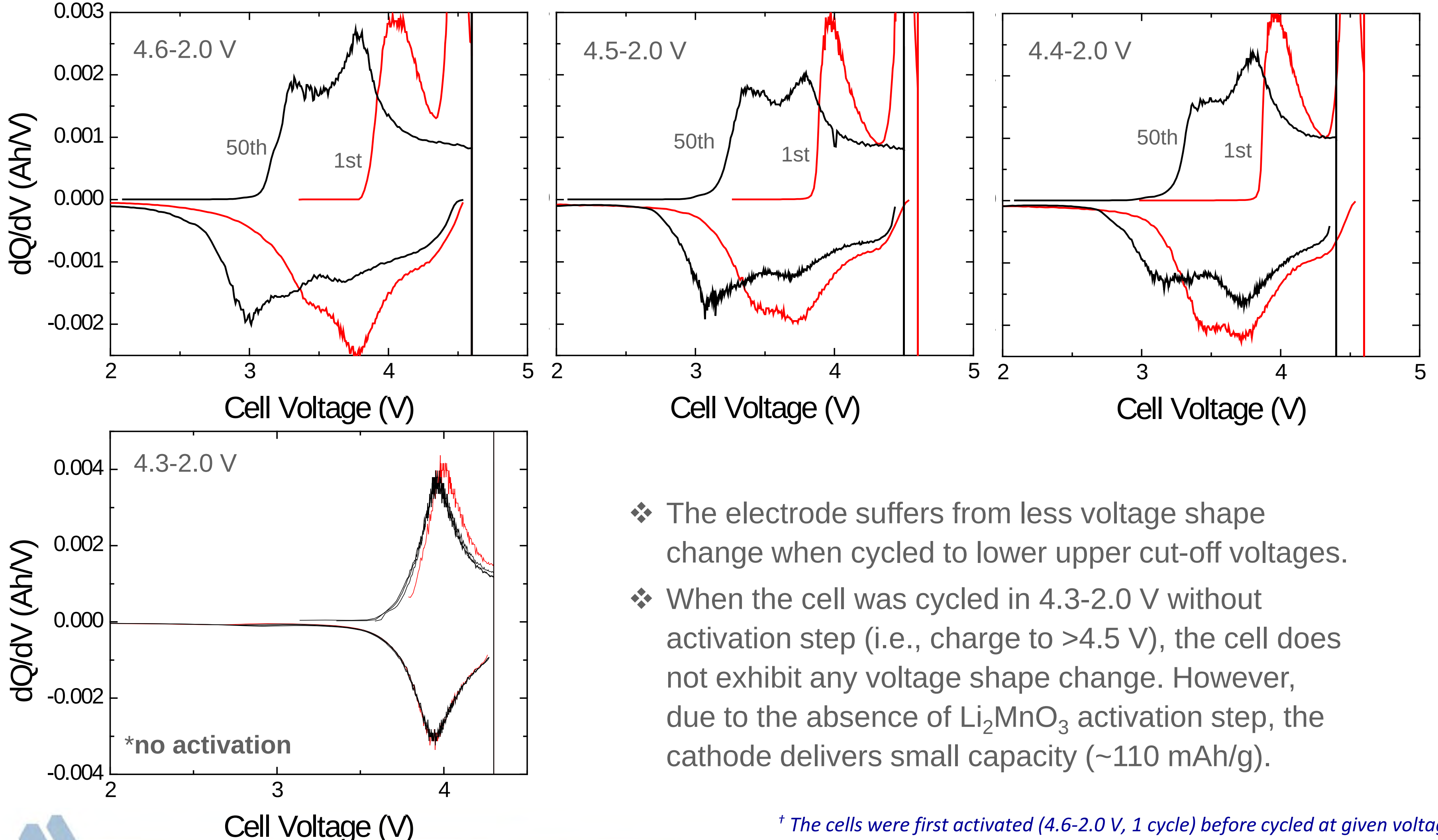


- The layered-layered cathode material exhibits **good capacity retention** but a **significant voltage suppression** with cycling, which is more severe during high-temperature cycling.
- This is not just **energy density** issue, but also **battery management** issue.

†ANL-NMC: $0.5Li_2MnO_3 \bullet 0.5LiMn_{0.31}Co_{0.25}Ni_{0.44}O_2$ (mildly fluorinated)

Issues with High-Capacity Layered-Layered Cathode Materials: Voltage shape change

dQ/dV plots of Li/ANL-NMC cells cycled in various voltage windows†

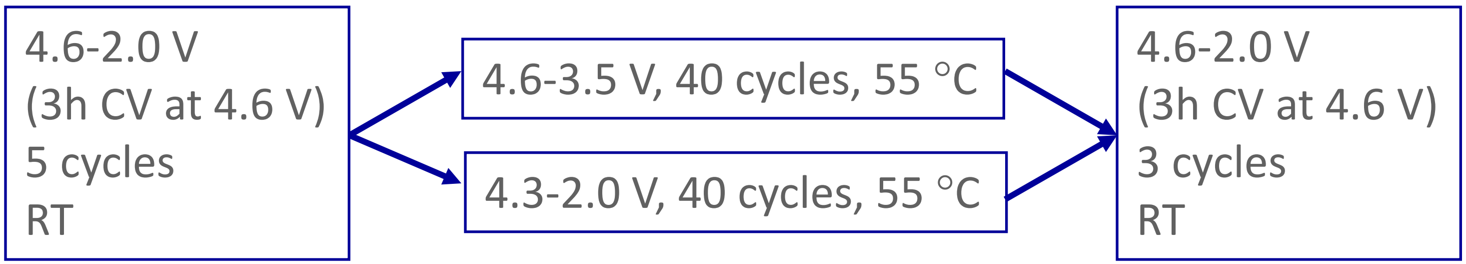


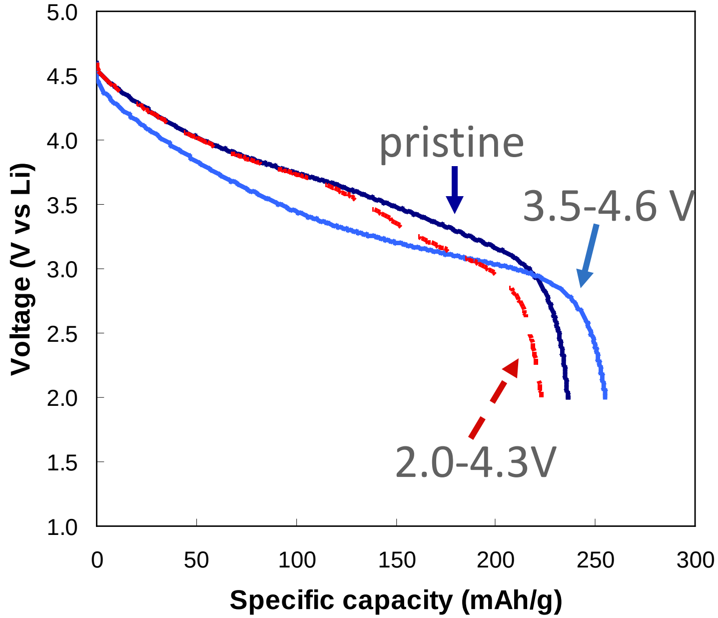
- ❖ The electrode suffers from less voltage shape change when cycled to lower upper cut-off voltages.
- ❖ When the cell was cycled in 4.3-2.0 V without activation step (i.e., charge to >4.5 V), the cell does not exhibit any voltage shape change. However, due to the absence of Li_2MnO_3 activation step, the cathode delivers small capacity (~110 mAh/g).

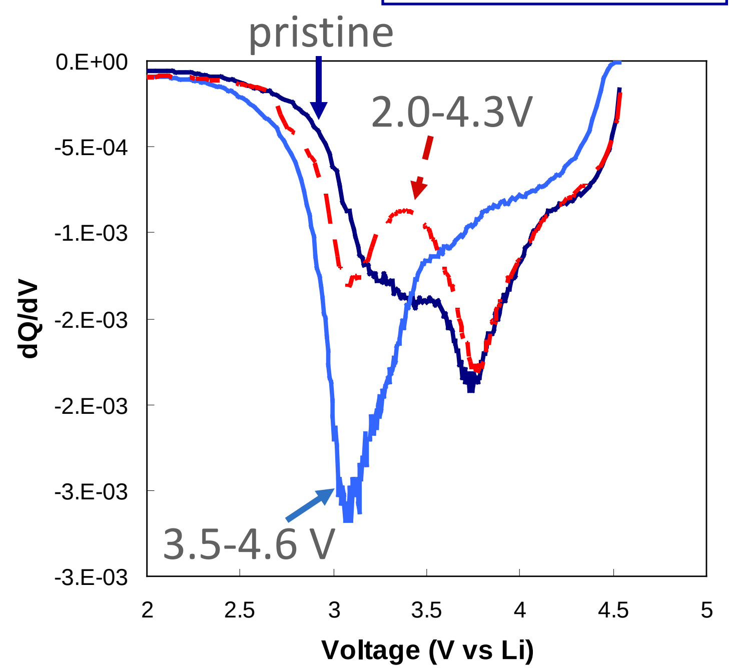
† *The cells were first activated (4.6-2.0 V, 1 cycle) before cycled at given voltages.*

Issues with High-Capacity Layered-Layered Cathode Materials: Voltage shape change

Voltage windows responsible for the shape change



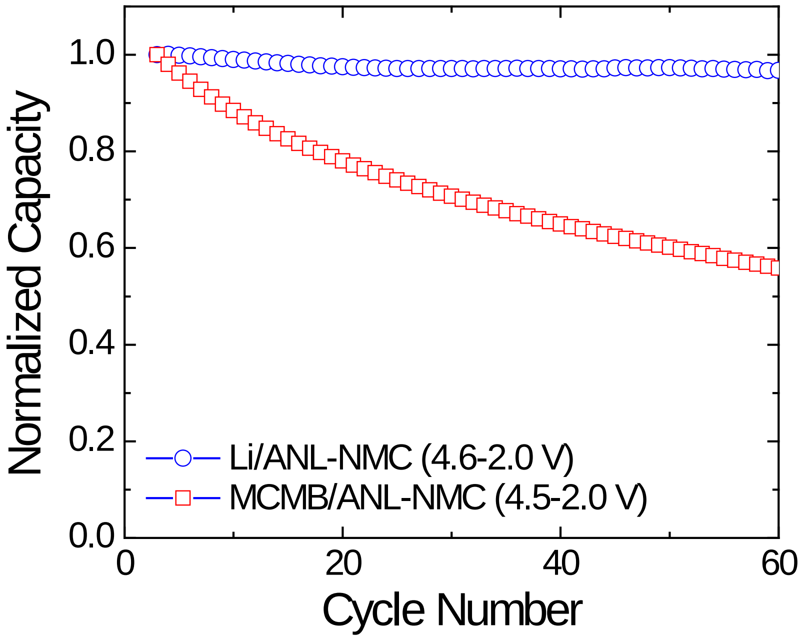




❖ Cycling at higher potential window has a bigger impact on the growth of 3-V peak and disappearance of 3.7-V peak.

Issues with High-Capacity Layered-Layered Cathode Materials: Mn dissolution

High-temperature (55 °) cycling



good high-temp cycling from half cell

poor high-temp cycling from full cell

cell disassembled, anode harvested and analyzed by ICP

µg_cation detected on MCMB surface / g_cathode

Mn	Co	Ni
804	65	241

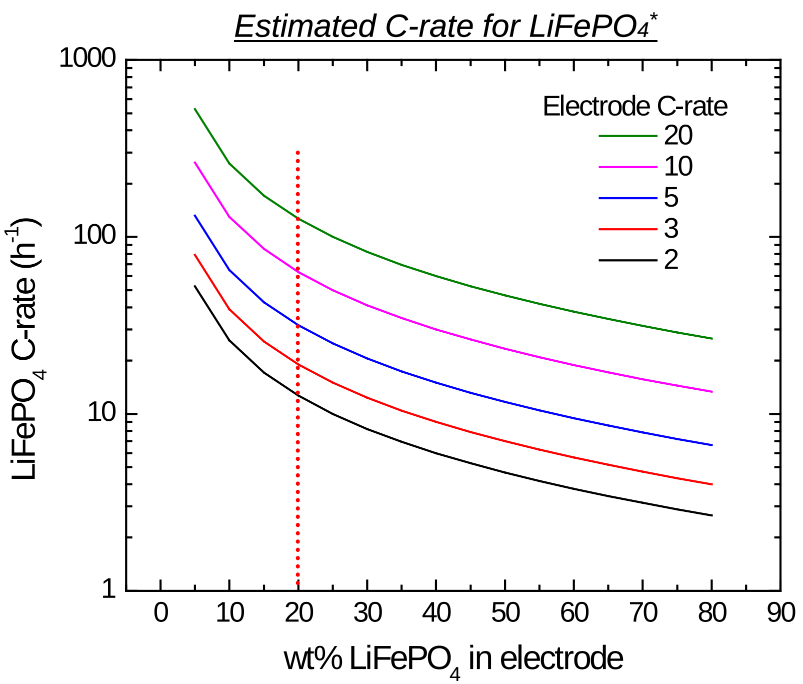
❖Possible mechanism of full cell capacity fading (similar to Mn-spinel)

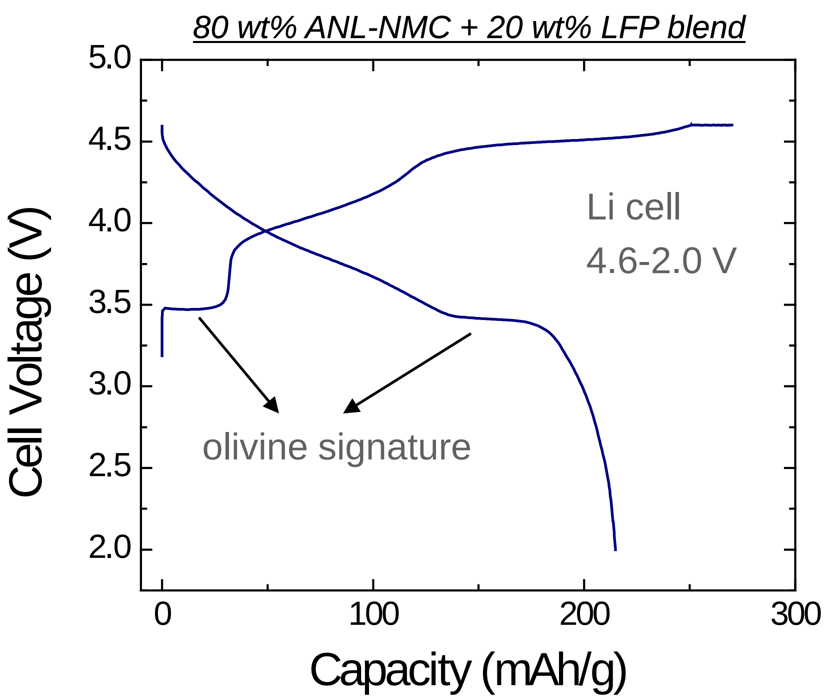
- Dissolution of TM ions from ANL-NMC into the electrolyte → reduction of TM on the graphite surface → side reaction on the graphite surface consuming lithium ions (most likely caused by Mn) → reduction of cycleable lithium in the cell

❖Surface protection and/or electrolyte additives might suppress TM dissolution and/or side reaction on the graphite surface.

Improving Pulse Power Performance of High-Capacity Layered-Layered Cathode Materials

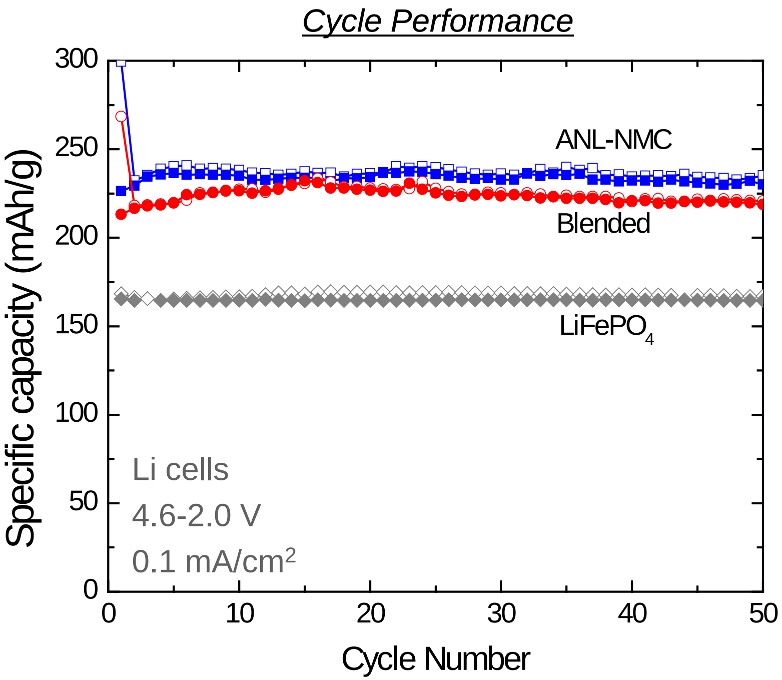
- One of the important requirement of a PHEV cathode is reasonable power performance at charge-sustaining mode (low SOC). Layered-layered materials suffer from poor power performance especially at low SOC.
- To improve the pulse power performance at low SOC, the ANL-NMC was blended with $LiFePO_4$. Active voltage window for $LiFePO_4$ (≤3.5 V) is where the ANL-NMC exhibits quite poor impedance characteristics.

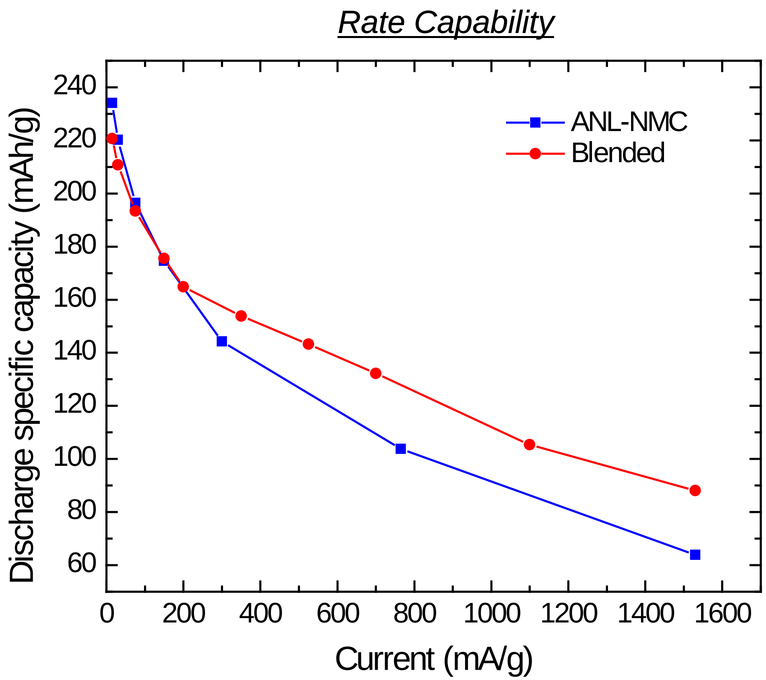




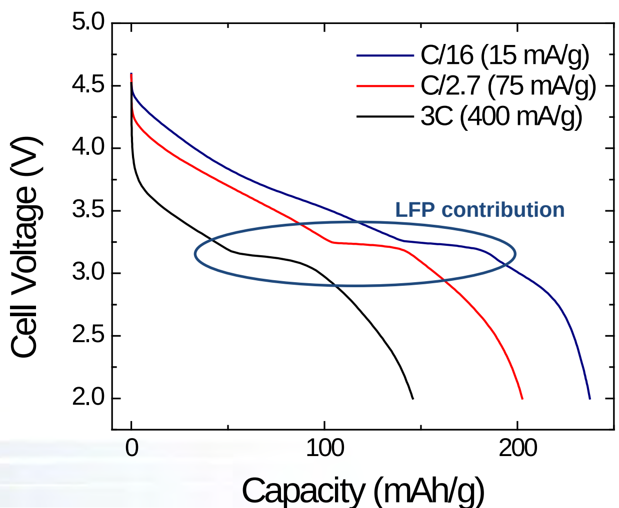
*Assumption: All of the current is carried by LFP during a pulse.

Improving Pulse Power Performance of High-Capacity Layered-Layered Cathode Materials

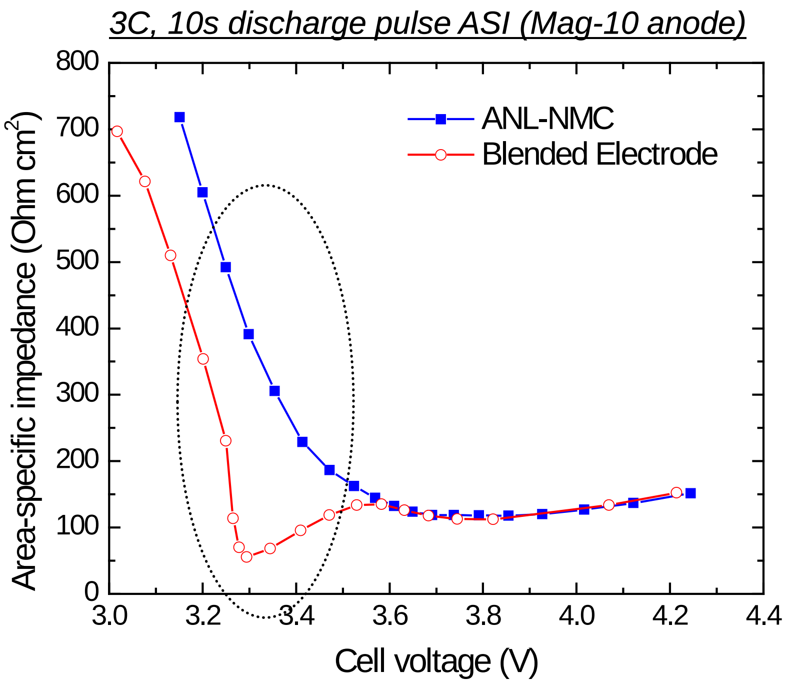


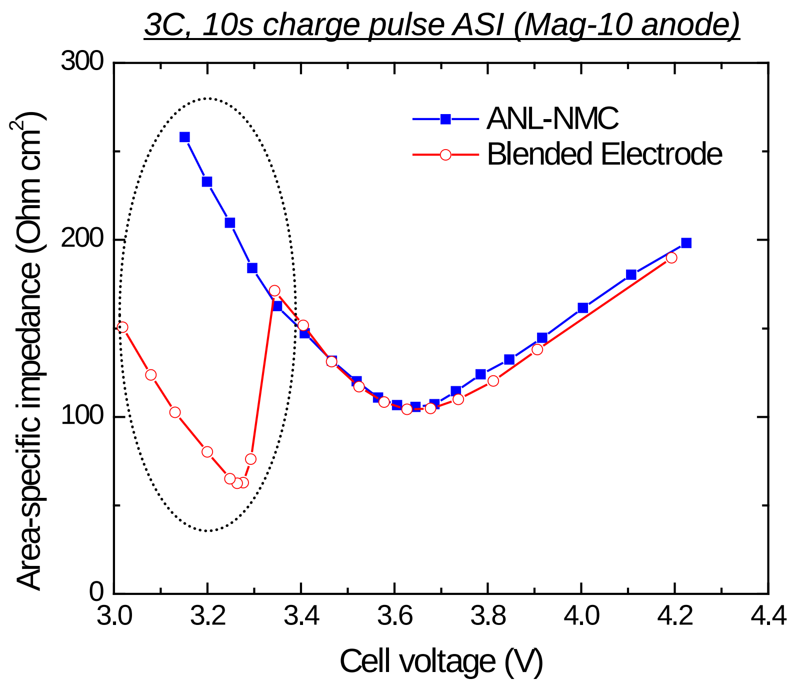


- All half cells (with ANL-NMC, $LiFePO_4$, or blended electrode) show good cycling performance.
- The blended electrode shows smaller capacity than ANL-NMC electrode at low current due to lower ANL-NMC content in the electrode (by 20 wt%), but at high current (≥100 mA/g) the blended electrode delivers higher capacity (by LFP contribution).



Improving Pulse Power Performance of High-Capacity Layered-Layered Cathode Materials





- Impedance characteristic of the ANL-NMC needs to be improved.
- Blending with $LiFePO_4$ results in significant improvement of ASI measured by 3C, 10s pulse at low cell voltage.
  - A good way to enhance power performance at the charge-sustaining mode for PHEV cell with a high-capacity layered-layered cathode material

Future work

- Composition optimization
  - Improvement of cycling performance
  - Close collaboration with other ABR participants as well as with industrial partners (good TM precursor)
  - Selection of two most promising chemistries and focusing on the battery performance (and its improvement) of the selected cathode materials
- Identification and evaluation of various electrochemical couples
  - Carbonaceous anodes
  - Advanced anode materials through collaboration with other ABR or BATT team
  - Full cell performance characterization
- Evaluation of thermal safety characteristics
- Further optimization and characterization of blended electrode of energy-providing material (e.g., layered-layered) and power-supplying material (e.g., $LiFePO_4$)

Summary

- The objective of this work is to develop cathode materials with high-capacity, thermal stability, low cost, and longevity. The cathode chemistry is based on Li- and Mn-rich oxide with integrated structures.
- Our approach to achieve the objective and technical accomplishments are:
  - Creating integrated spinel component in layered-layered matrix
    - The first cycle efficiency of ~90 %
    - Good rate capability (>200 mAh/g at 1C rate)
    - Excellent structural analysis utilizing TEM and XAS
  - Identifying and understanding voltage depression and Mn dissolution issues for layered-layered composite cathode materials
  - Physical blending of high-capacity material (layered-layered oxide) with high-power material ($LiFePO_4$ olivine)
    - Significant improved pulse power characteristics at low SOC without compromising the high capacity
- In FY12, two most promising composition will be selected and focused study will be carried out. At the same time, industrial partner will be identified as a high-quality TM precursor supplier for scale-up purpose (enough to deliver to ABR cell building group).

Acknowledgment

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

- David Howell
- Peter Faguy