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Development of high-capacity cathode materials with integrated structures

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Argonne National Laboratory

Annual Merit Review

DOE Vehicle Technologies Program

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Vehicle Technologies Program

Overview

Timeline

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

Budget

- Total project funding
  - 100% DOE
- FY09: $200K

Barriers

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Targets

- Composition optimization

Partners

- Lead PI: S. –H. Kang
- Support PIs: M. M. Thackeray, C. Johnson, D. P. Abraham
- Collaborators:
  - V. Pol, M. Balasubramanian (Argonne)

Objective of This Study

- Design and develop ***low-cost, high-energy, high-power and thermally-stable*** cathode materials with integrated structures for PHEVs
  - *Design Mn-based cathodes with integrated structures*
    - Embed spinel components in the layered structure to improve rate performance
    - Optimize composition (Li- and Mn composition) and synthesis conditions
    - Evaluation of electrochemical properties (capacity, cycling performance and rate capability) of the synthesized cathode materials

Milestones FY09

- Design cathode chemistry with integrated structures – *on going*
- Synthesize nickel-manganese precursors (either Ni-Mn hydroxide or Ni-Mn carbonate) with spherical morphology – *on going*
- Optimize synthesis condition of lithium nickel-manganese oxide – *on going*
- Evaluate basic electrochemical properties (capacity, cycling performance, rate capability) – *on going*
- Investigate various dopants effect – *on going*

Approach

- Li- and Mn-rich oxide electrodes with ‘layered-layered’ composite structure
  - Studied under BATT program and shown to deliver a high capacity (>200mAh/g)
  - *Limitations*
    - rate capability, 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 or may be added as a blend to the ‘layered-layered’ cathode*
  - *Enhanced rate capability ?*
- 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*
- This work will be complementary to, and interactive with, the on-going exploratory research in the BATT program.

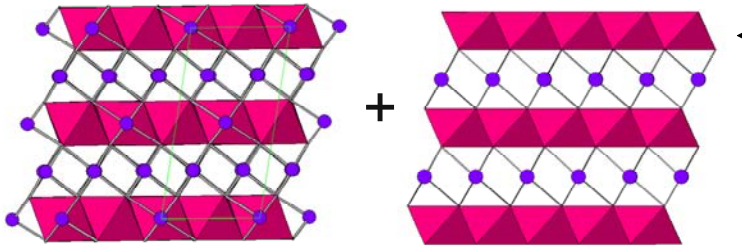
Argonne's Integrated-Structured Materials

- Studied under DOE's Exploratory Battery Research Program (BATT)
- Structural compatibility: common oxygen arrays

layered-layered

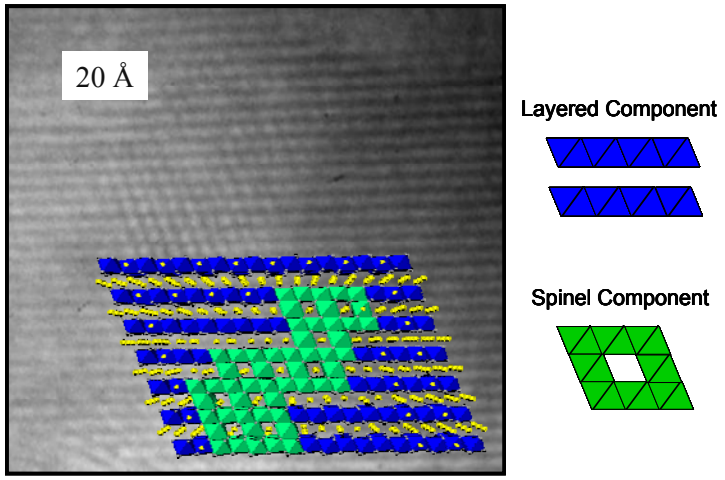
$Li_2Mn^{4+}O_3$ + $LiM^{3+}O_2$

(M^{3+}=Co^{3+}, Ni^{3+}, $Ni^{2+}_{0.5}Mn^{4+}_{0.5}$)



e.g., $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.5}O_2$

layered-spinel



e.g., $0.7Li_2MnO_3 \cdot 0.3Li_4Mn_5O_{12}$

Can we make 3-component (layered-layered-spinel) 'composite' structure?

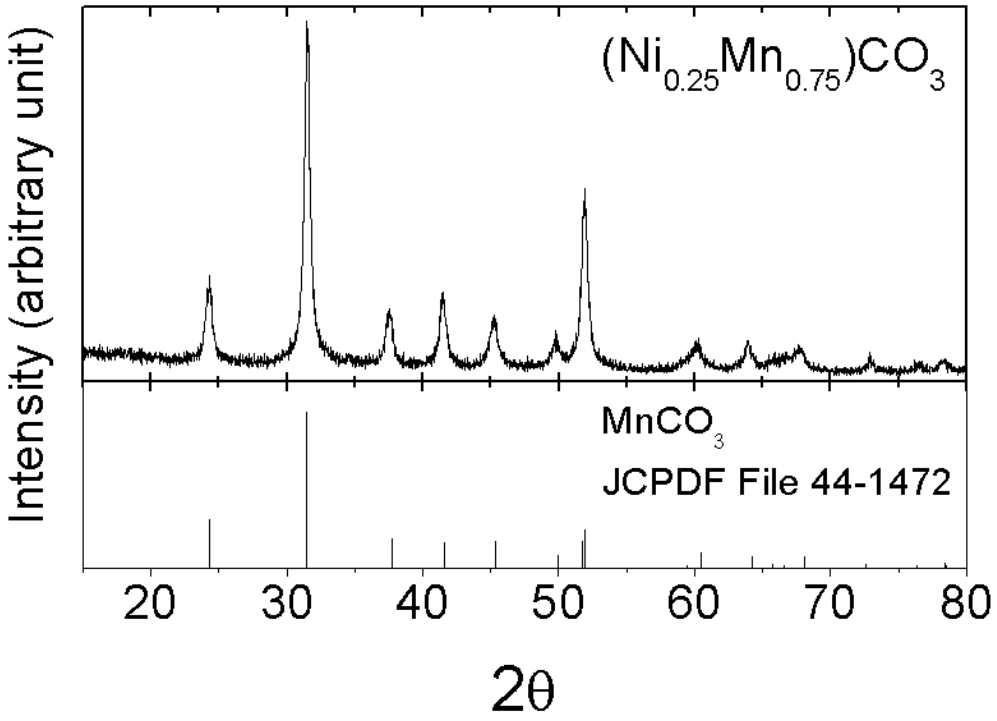
Materials Design Strategy

	$Li(Ni_{0.5}Mn_{1.5})O_4$ or $Li_{0.5}Ni_{0.25}Mn_{0.75}O_2$	$Li_xNi_{0.25}Mn_{0.75}O_y$	$0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.5}O_2$ or $Li_{1.5}Ni_{0.25}Mn_{0.75}O_{2.5}$
Ni:Mn	1:3	1:3	1:3
Li/M	0.5	x (0.5<x<1.5)	1.5
Note	Spinel structure - High voltage (~4.8 V) - High rate (3D Li path) - Low capacity (148 mAh/g theoretical)	?	Layered-layered structure - High capacity (>200 mAh/g practical) - Wide voltage range (2-4.8 V) - Inferior rate capability

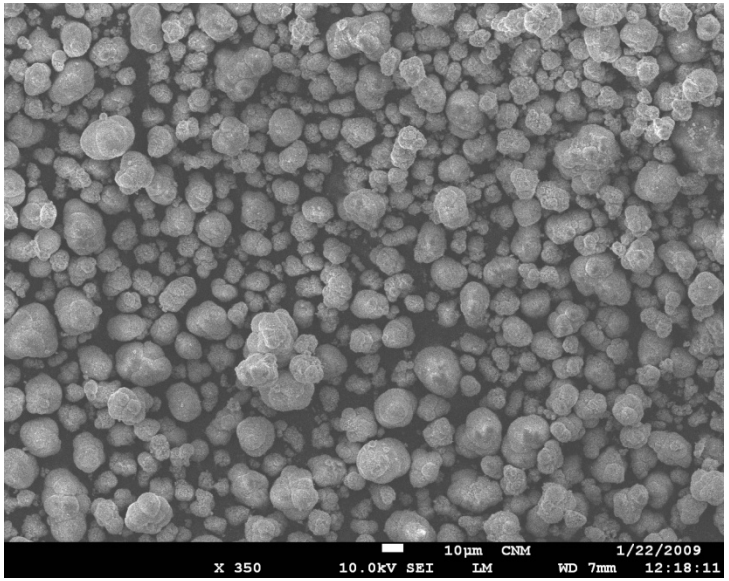
- Resulting oxides (0.5<x<1.5) structure and electrochemical properties?
  - Integrated spinel (LiM_2O_4)-layered (Li_2MnO_3)-layered ($LiMO_2$) structures?
  - Synergetic effect in electrochemical properties (high rate, high capacity and wide stability window)?

Mixed Ni-Mn Carbonate Precursor

X-ray diffraction patterns



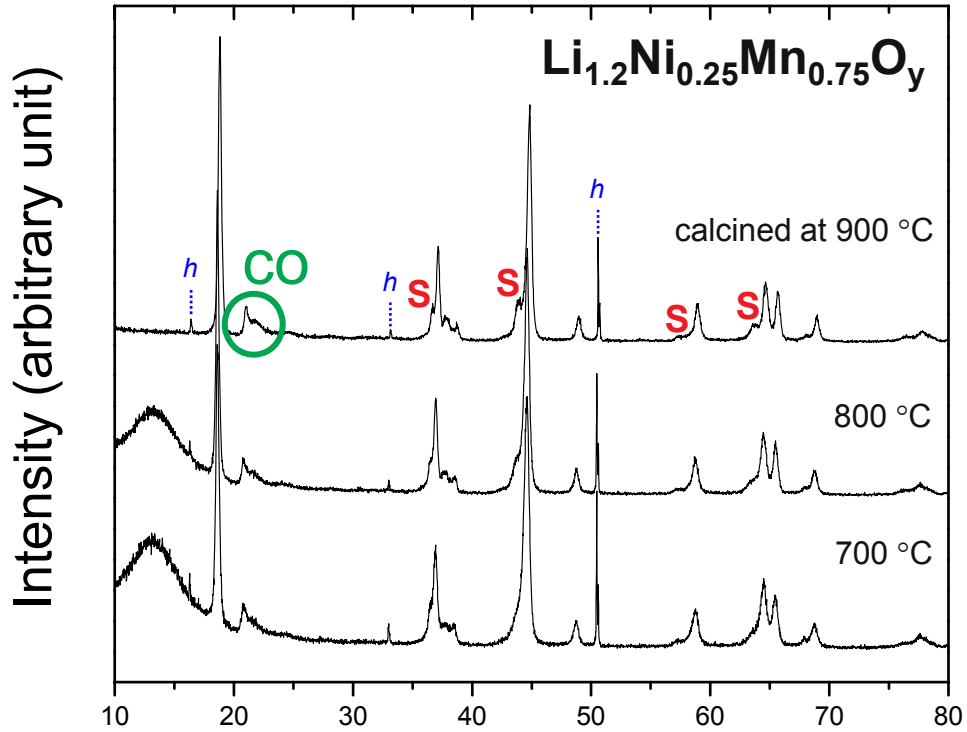
SEM



- $(Ni_{0.25}Mn_{0.75})CO_3$ precursor was prepared by coprecipitation.
- Single phase (R-3c) with spherical morphology was obtained.
- Lithium content, x=1.2 was chosen. $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ was synthesized using Li_2CO_3 and $(Ni_{0.25}Mn_{0.75})CO_3$ at 700-900 °C.

Structural Feature of $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

X-ray diffraction patterns



h: X-ray sample holder

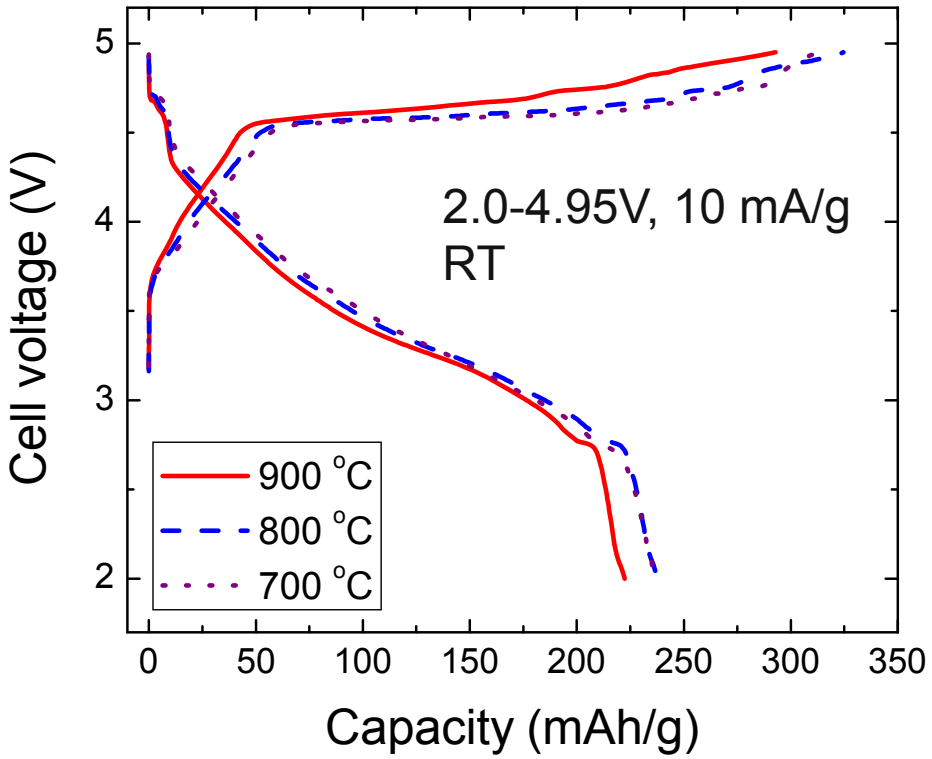
co, cation ordering; **s**, spinel

$LiMO_2$
(layered)
+
Li_2MnO_3
(layered with cation ordering)
+
LiM'_2O_4
(spinel)

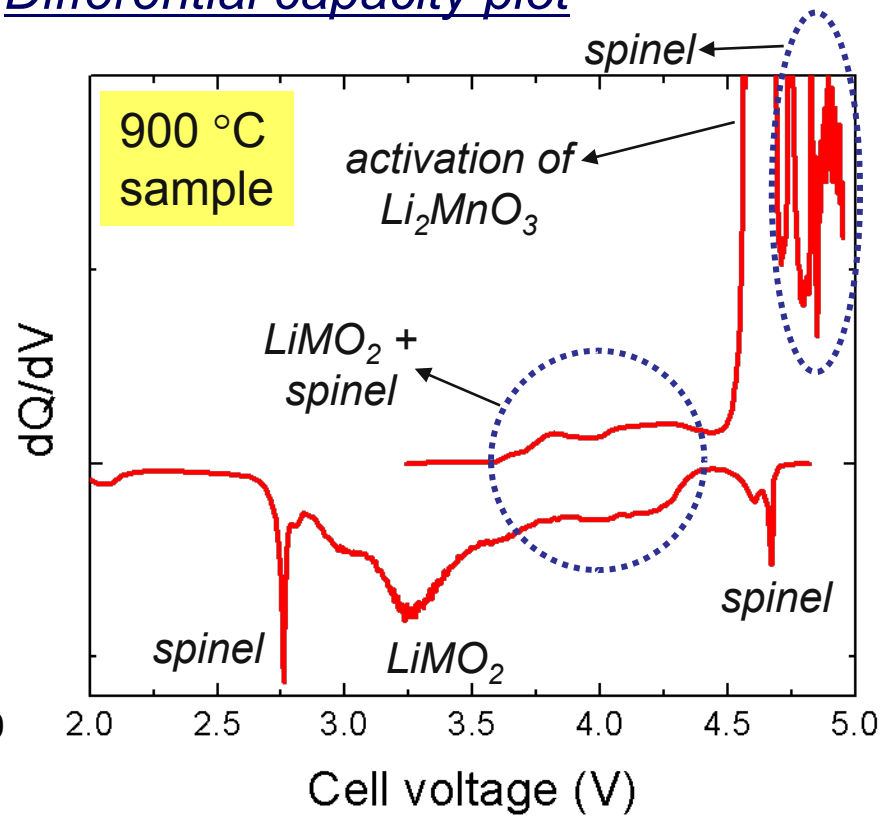
- Li-Ni-Mn oxides with integrated spinel, Li_2MnO_3 and $LiMO_2$ structures have been successfully synthesized.

Electrochemical Feature of $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

First-cycle profiles



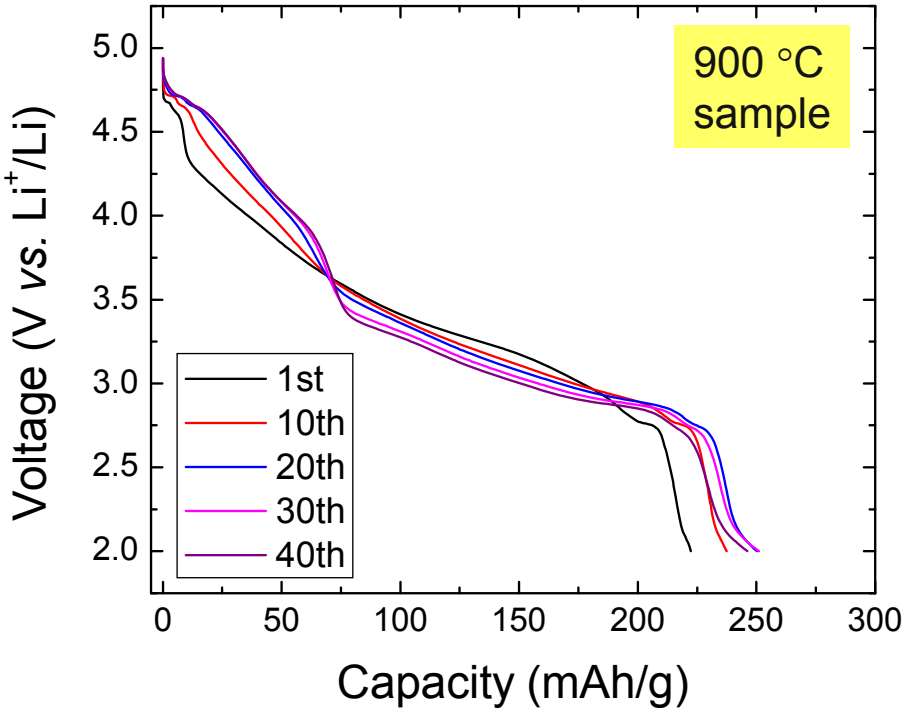
Differential capacity plot



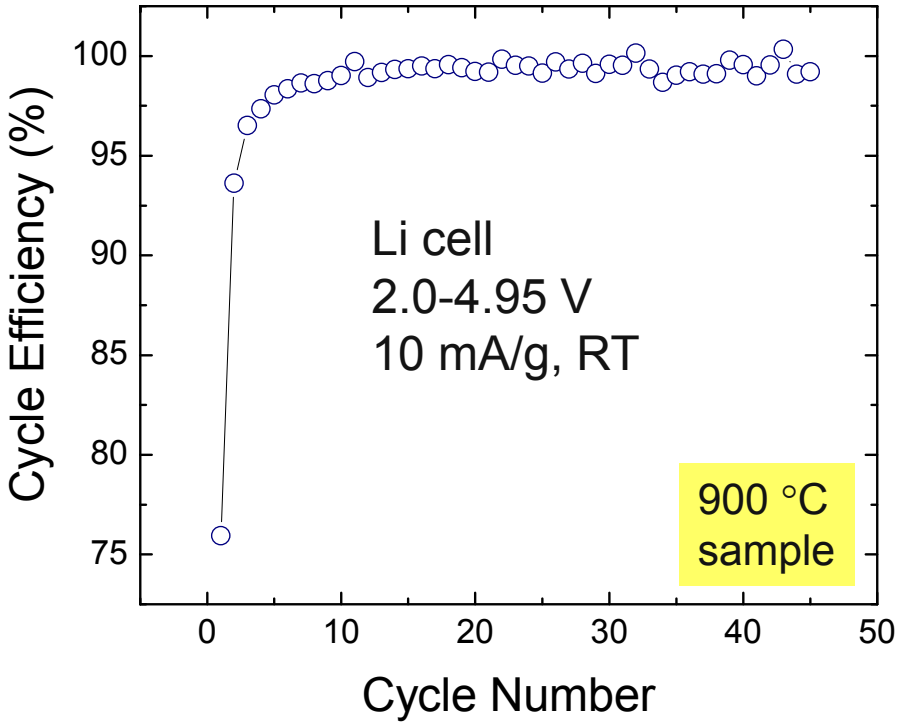
- More than 200 mAh/g of initial discharge capacity
- Electrochemical signatures from 5V spinel, Li_2MnO_3 activation and layered $LiMO_2$, in agreement with XRD patterns

Cycling Stability of $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$

Discharge profiles



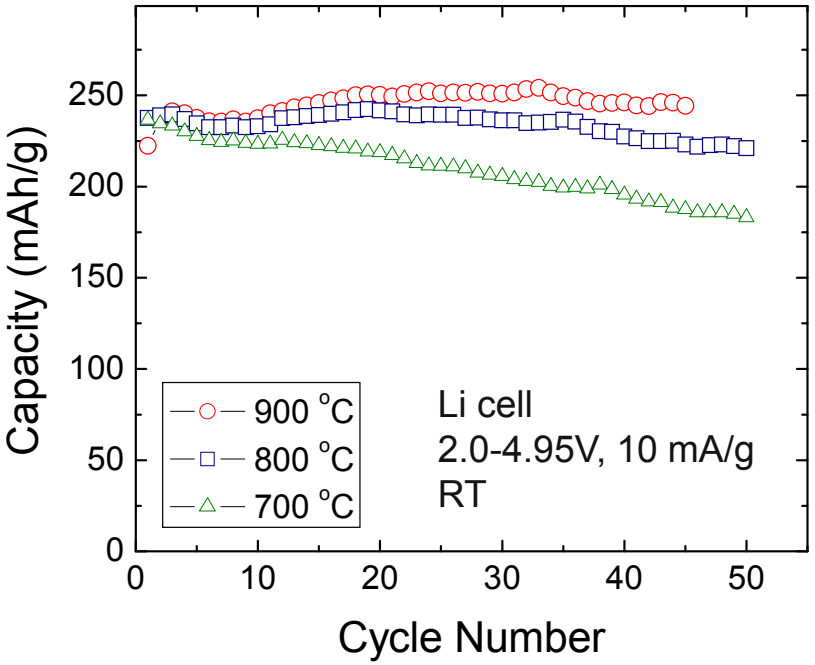
Cycling efficiency



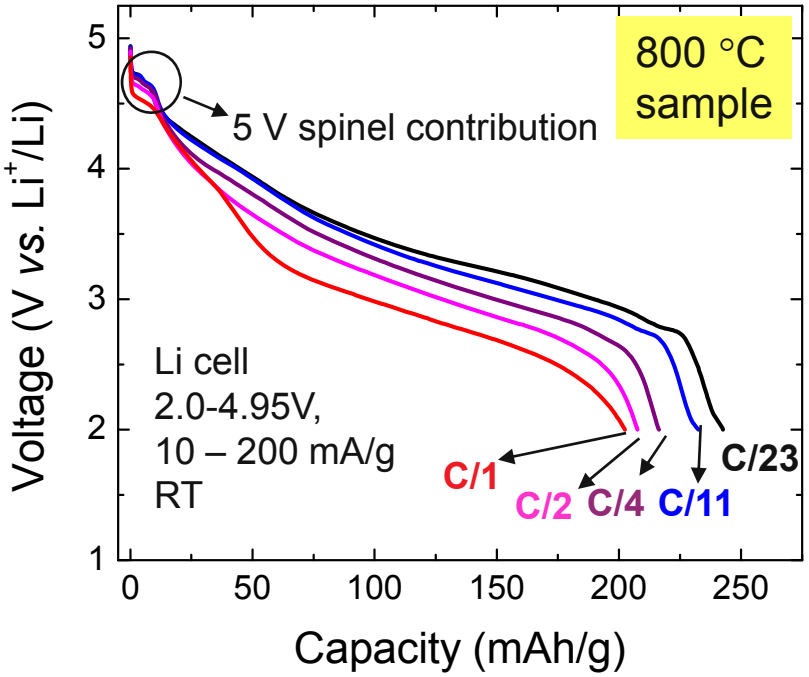
- Excellent cycling stability in spite of the very high charge voltage (4.95 V)
- >99% cycle efficiency after 10 cycles ⇒ minimal electrolyte decomposition at high voltages

Capacity Retention and Rate Capability

Capacity retention



Rate capability



- Excellent capacity retention (800, 900 °C samples) during 50 cycles.
- Good rate capability: 210 mAh/g at C/2 rate and 200 mAh/g at C/1 rate
- Little change in plateau voltage and length at 4.8 V (circled, contribution from spinel) regardless of current rate – beneficial impact of integrated spinel phase (high-rate tolerance)

Future Work – FY09, FY10

- Continue to study to optimize the cathode materials properties
  - lithium content of $Li_xNi_{0.25}Mn_{0.75}O_y$
  - various dopants (e.g., Co, F)
  - synthesis route to improve powder characteristics (morphology, tap density, etc.)
- Evaluate the cathode materials in full Li-ion configuration
- Study the thermal safety characteristics
- Detailed structural study by X-ray absorption spectroscopy

Summary

- Cathode materials with three-component 'composite' structures have been successfully designed and synthesized.
- $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ showed electrochemical features from the three integrated components (spinel, Li_2MnO_3, $LiMO_2$) and exhibited very high initial capacity (>225 mAh/g, ~C/23 rate).
- $Li_{1.2}Ni_{0.25}Mn_{0.75}O_y$ showed excellent cycling efficiency and stability in wide voltage windows (2.0-4.95 V) and good rate performance (200 mAh/g at C/1 rate).

Acknowledgment

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