HIGH-VOLTAGE SPINEL AND POLYANION CATHODES

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Project ID #: ES051

OVERVIEW

Timeline

- Project start date: June 2010
- Project end date: December 2012
- 100 % complete

Budget

- Total project funding
  - DOE: $672K
- Funding for FY10
  - $260K
- Funding for FY11
  - $260K
- Funding for FY12
  - $152K

Barriers

- Barriers addressed
  - Cost
  - Cycle life
  - Energy and power densities
- Targets
  - Long cycle life high-voltage (4.7 V) spinel cathodes
  - High capacity and high-voltage polyanion cathodes
  - Increased energy and power with spinel and polyanion cathodes

RELEVANCE

Objectives

- To develop high-performance spinel and polyanion cathodes for lithium-ion batteries and a fundamental understanding of their structure-composition-performance relationships

  - To develop high-voltage (4.7 V) spinel oxide compositions with controlled morphology and optimum cationic substitutions that can maximize the tap density, cycle life, energy, and power, while keeping the cost low
  - To develop a fundamental understanding of the factors that control the electrochemical performances of high-voltage spinel manganese oxide cathodes
  - To develop novel low-cost synthesis processes for high-capacity, high energy phosphate and silicate cathodes

MILESTONES

Month/Year	Milestone
September 2011	Development of novel synthesis approaches for high-capacity nanostructured silicate and phosphate cathodes
December 2011	Understanding the role of cation doping, surface modification, and morphology on the electrochemical properties of 4.7 V spinel cathodes

APPROACH / STRATEGY

- Develop a firm understanding of the factors controlling the electrochemical performances of cathode materials and utilize the understanding to develop high-performance cathodes for vehicle batteries

- Cationic substitutions in 4.7 V spinels to stabilize the disordered spinel structure
- Cationic substitutions to realize robust cathode-electrolyte interface in 4.7 V spinel
- Morphological control to increase the tap density of 4.7 V spinel cathodes
- Magnetic measurements to quantify Mn^{3+} content in 4.7 V spinel cathodes
- Novel synthesis approaches for nanostructured polyanion (phosphate and silicate) cathodes that can increase the energy and lower the manufacturing cost

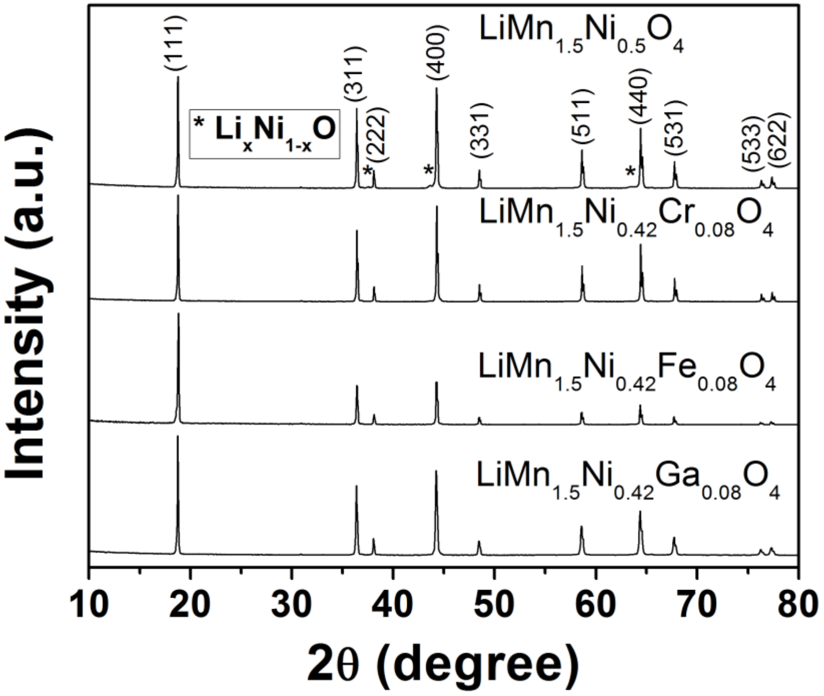
- Solid-state, high-energy ball milling, and solution-based synthesis approaches
- Advanced chemical, structural, and surface characterizations
- In-depth electrochemical evaluation including impedance analysis
- Understanding the structure-property-performance relationships

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

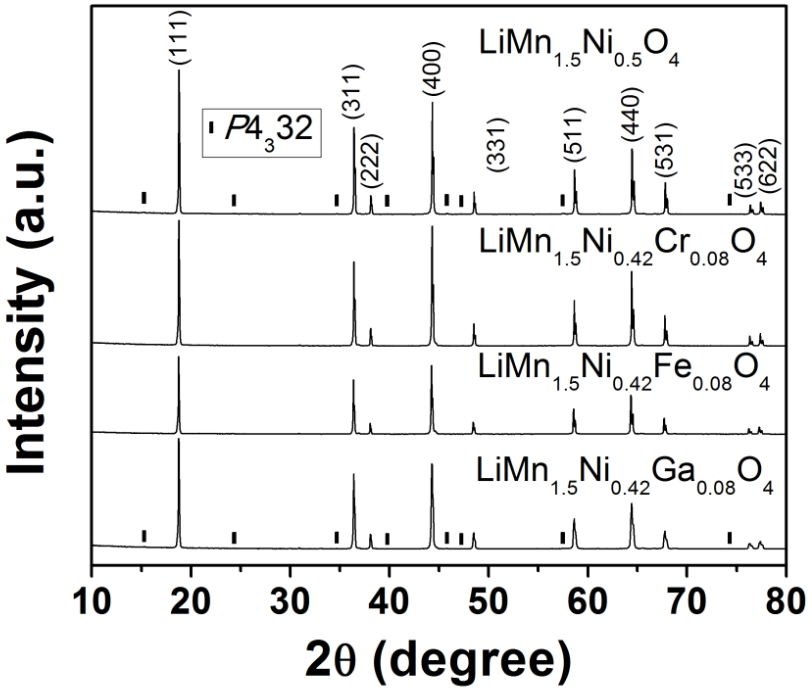
- The solubility of Ni in the high-voltage (4.7 V) spinel $LiMn_{1.5}Ni_{0.5}O_4$ increases with decreasing temperature, eliminating the $Li_xNi_{1-x}O$ impurity on annealing at 700 ^oC
- Cationic substitutions in the 4.7 V spinel $LiMn_{1.5}Ni_{0.42}M_{0.08}O_4$ (M = Cr, Fe, and Ga) eliminate $Li_xNi_{1-x}O$ impurity, stabilize the disordered phase, and offer a stable cathode-electrolyte interface due to the segregation of the M^{n+} ions to the surface
- Cation-substituted $LiMn_{1.5}Ni_{0.42}M_{0.08}O_4$ (M = Cr, Fe, and Ga) spinels exhibit superior cycle life at 55 ^oC with high rate capability compared to $LiMn_{1.5}Ni_{0.5}O_4$
- $LiMn_{1.5}Ni_{0.5}O_4$ synthesized in different morphologies reveals that the electrochemical performance increases with increasing Mn^{3+} content
- A magnetic measurement method has been developed to determine quantitatively the Mn^{3+} content in the $LiMn_{1.5}Ni_{0.5}O_4$ spinel
- Three different polymorphs of $LiVOPO_4$ have been synthesized and characterized by a novel microwave-assisted synthesis approach
- Similar novel approaches are developed to stabilize the Li_2MSiO_4 cathodes

INFLUENCE OF SYNTHESIS CONDITIONS: XRD

Synthesized at 900 °C

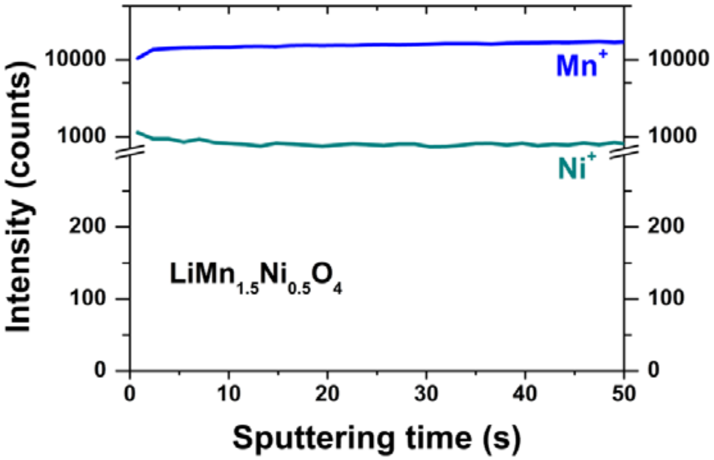


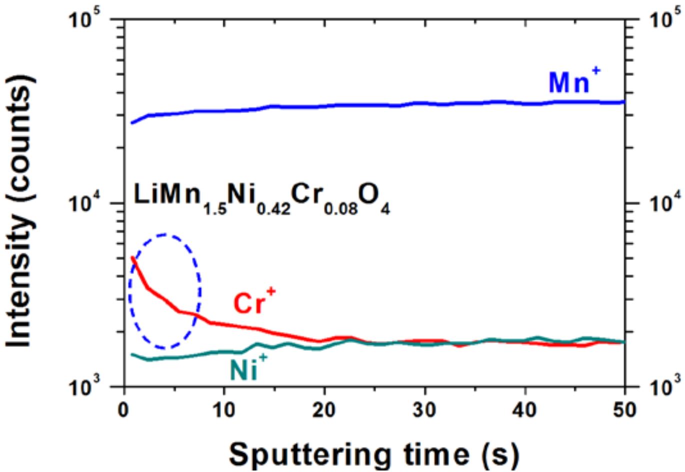
After annealing at 700 °C

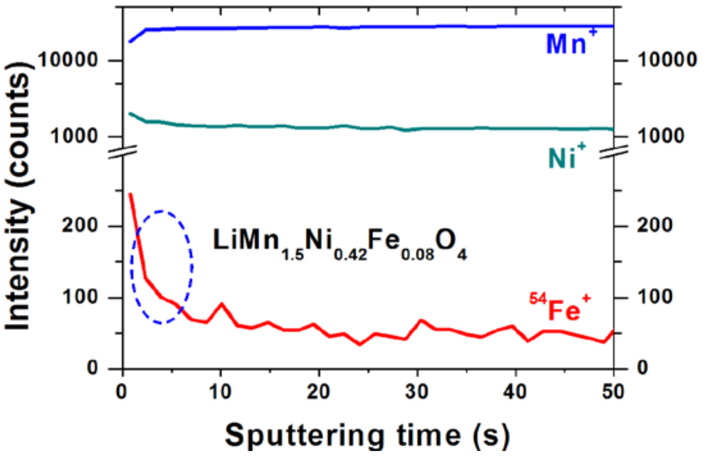


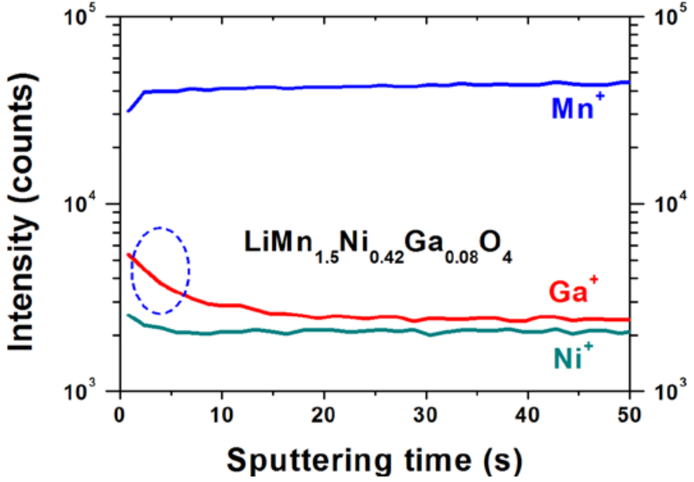
- Substitution of Cr, Fe, and Ga eliminates the $Li_xNi_{1-x}O$ impurity phase and stabilizes the disordered spinel phase
- Annealing at 700 °C eliminates $Li_xNi_{1-x}O$ impurity (Ni solubility increases at low T) and increases the cation ordering in undoped and Ga-doped samples
- Similar conclusions were obtained with FTIR data as well

TOF-SIMS DEPTH PROFILES OF 5 V SPINELS





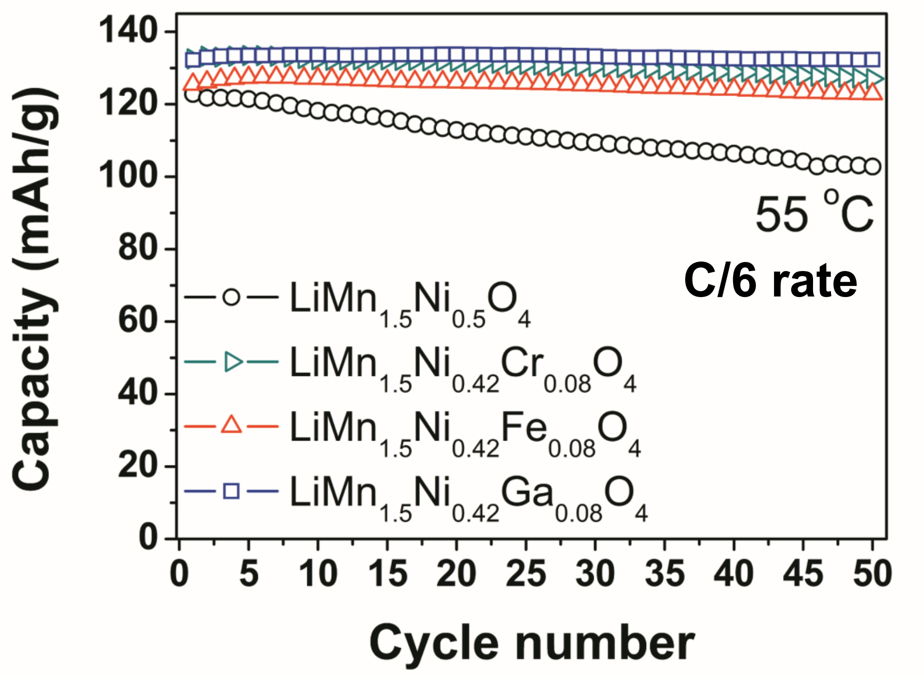




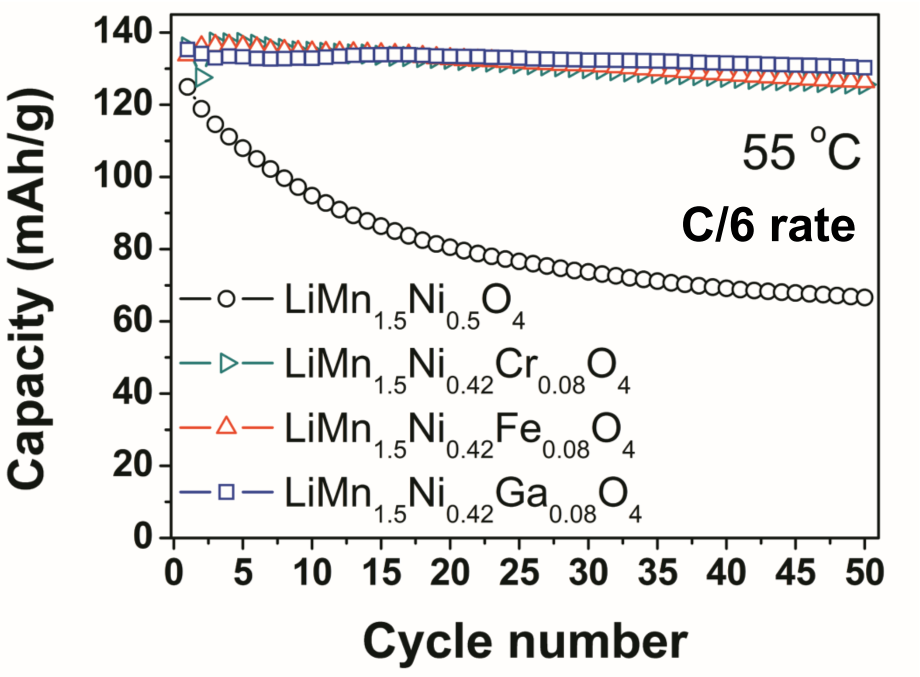
- The depth profiles show higher concentration of Cr, Fe, and Ga on the surface
- The surface segregation does not change after annealing at 700 °C

CYCLABILITY OF 5 V SPINELS AT 55 °C

Synthesized at 900 °C



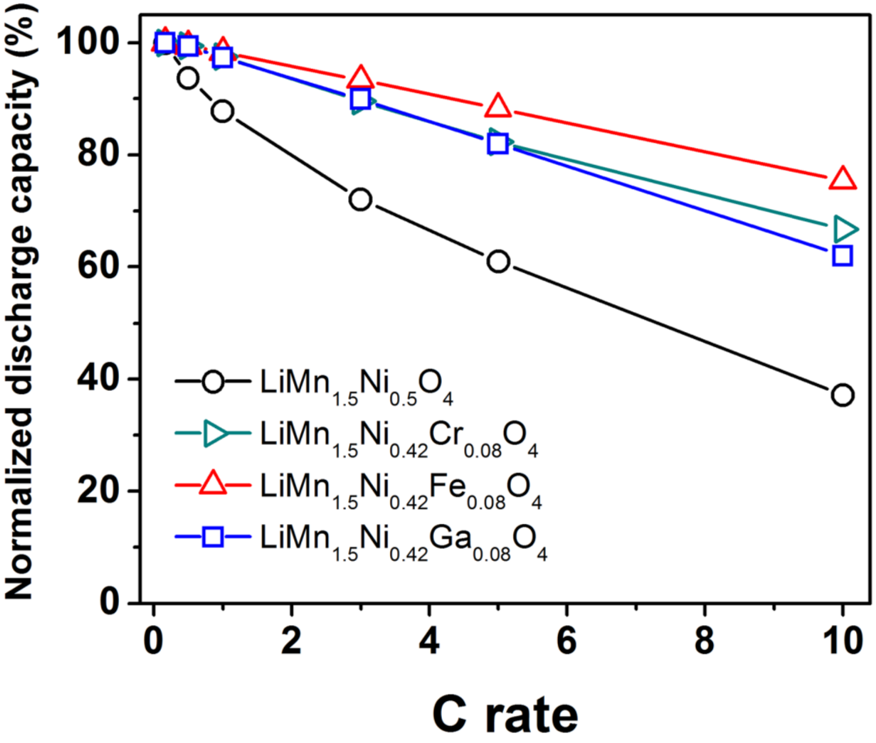
After annealing at 700 °C



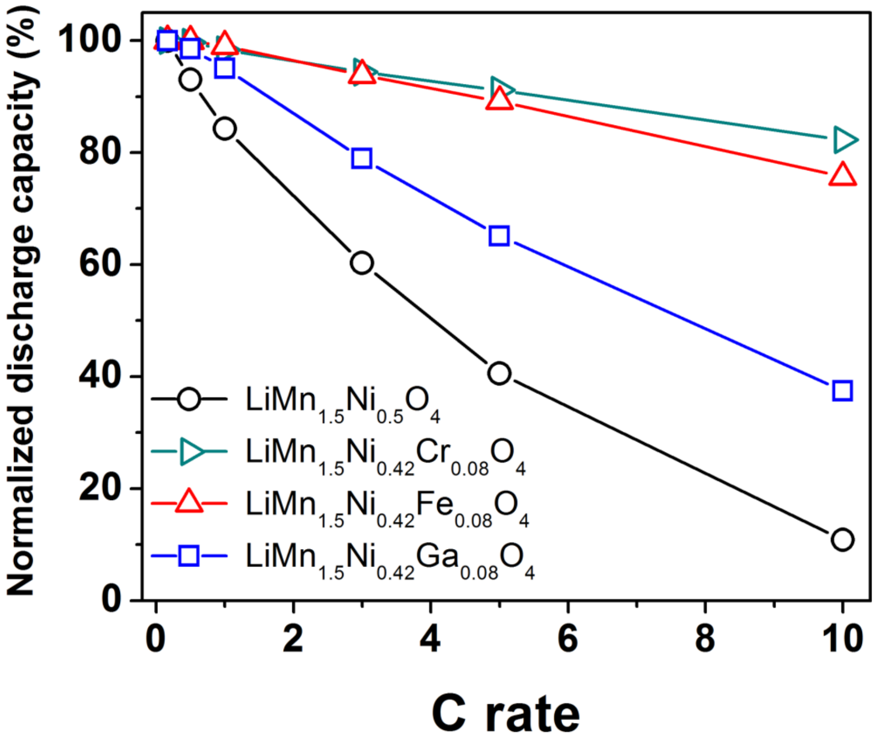
- Cr, Fe, and Ga doped samples offer improved cyclability at 55 °C as the surface segregated ions provide stable cathode-electrolyte interface
- Doped samples maintain good cyclability even after annealing at 700 °C irrespective of degree of cation ordering due to surface segregation
- Difference in cyclability between the doped and undoped samples is larger after annealing at 700 °C due to an increase in cation ordering

RATE CAPABILITY OF 5 V SPINELS

Synthesized at 900 ^{o}C

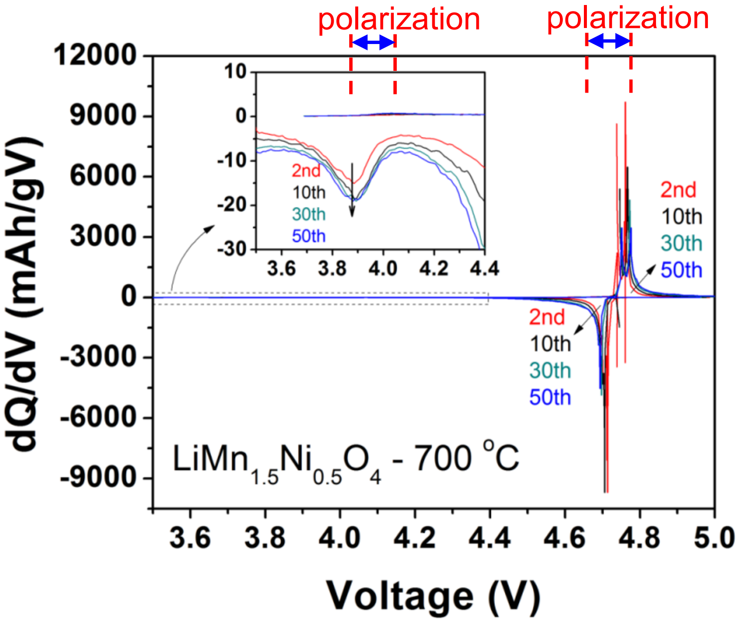


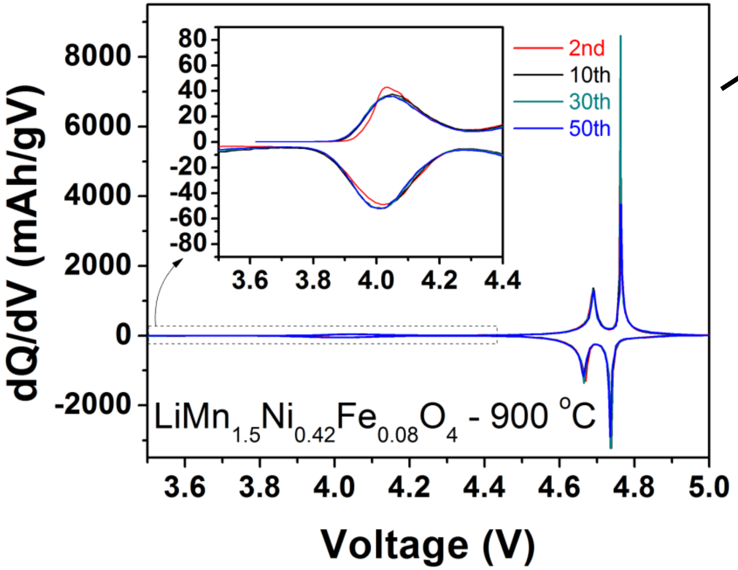
After annealing at 700 ^{o}C

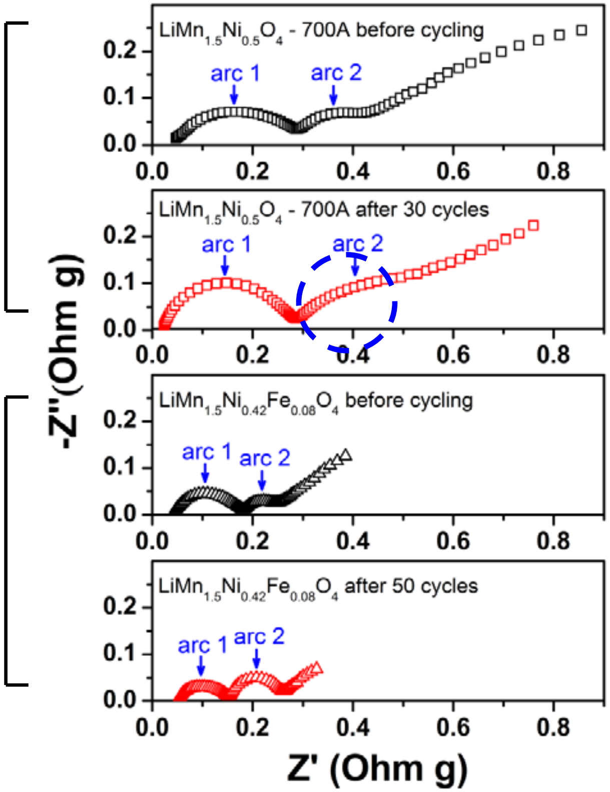


- Doped samples have higher rate capability due to lower cation ordering and suppressed SEI layer formation by surface segregation
- Rate capabilities of the undoped and Ga-substituted samples decrease after annealing at 700 ^{o}C due to an increase in cation ordering

ORDRED VS. DISORDERED 5 V SPINELS

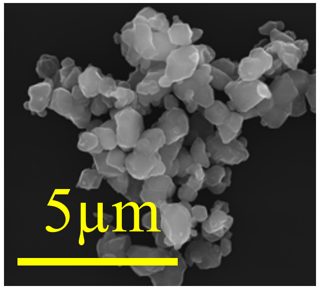




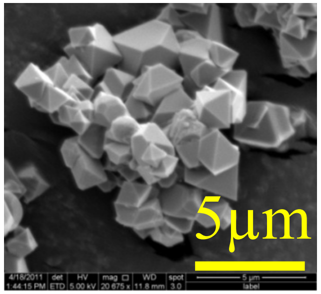


- Higher cation ordering induces an increase in polarization corresponding to an increase in charge transfer resistance
- The ordered spinel exhibits an asymmetry in the charge/discharge capacities in the 4 V region, which increases on cycling − Mn dissolution on cycling?

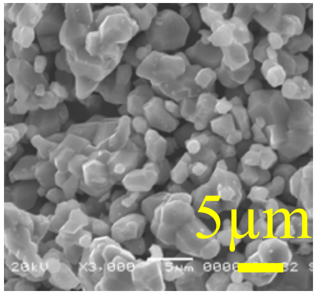
UNDOPED $LiMn_{1.5}Ni_{0.5}O_4$ WITH DIFFERENT MORPHOLOGIES



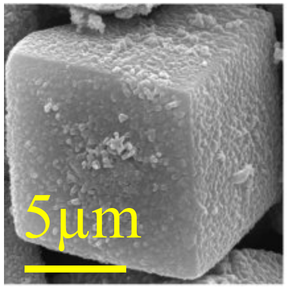
Commercial
NEI Corp.



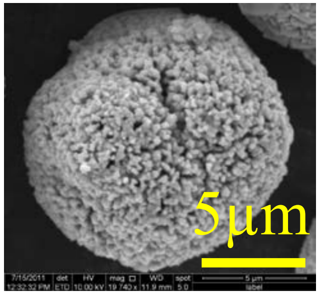
Polyhedral 1
Tank reactor



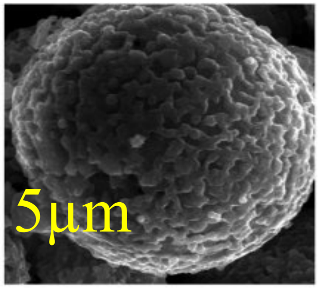
Polyhedral 2
Burette



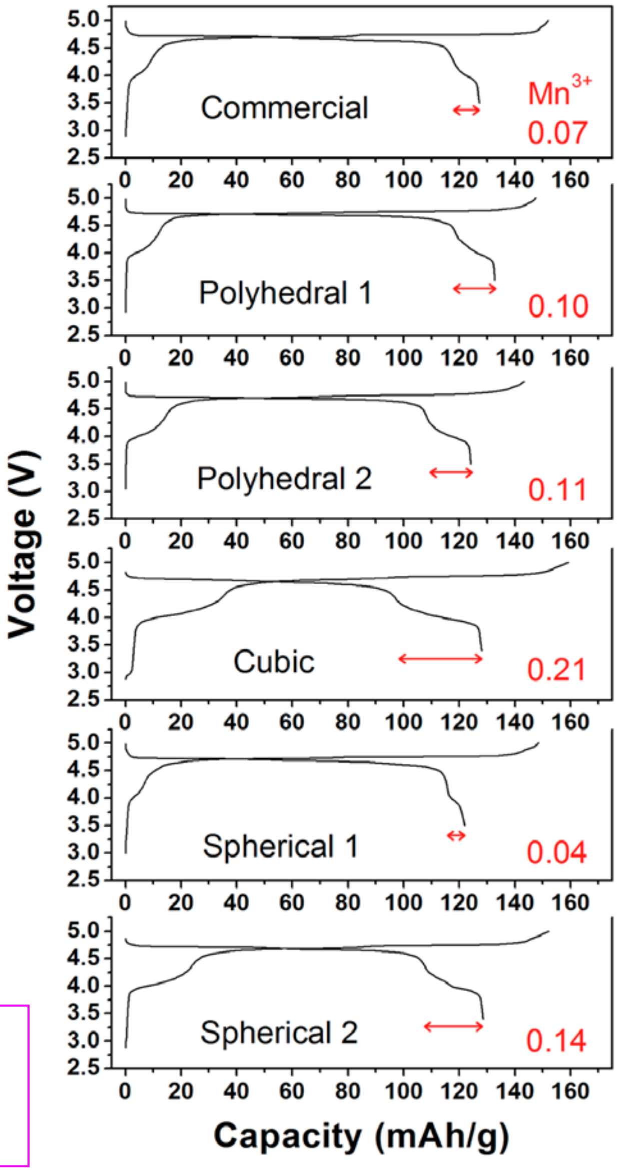
Cubic
Hydrothermal
(chloride)



Spherical 1
Tank reactor
(carbonate)

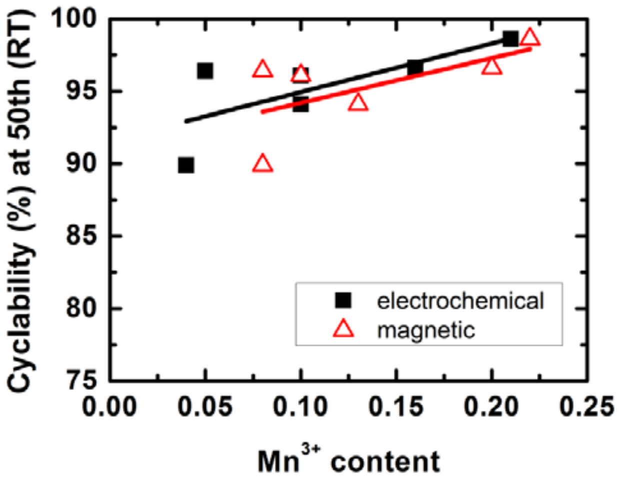


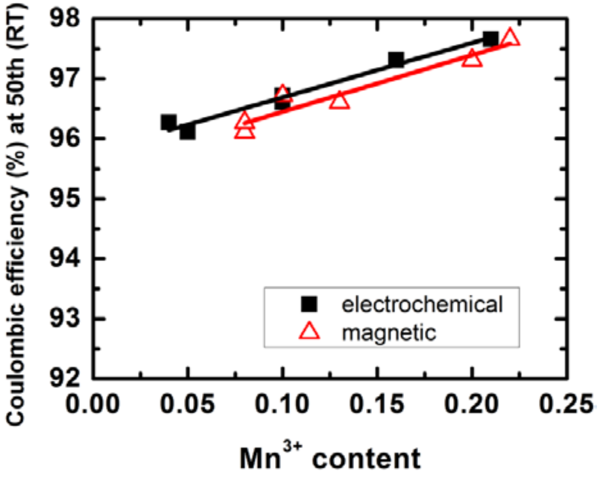
Spherical 2
Hydrothermal
(sulfate)



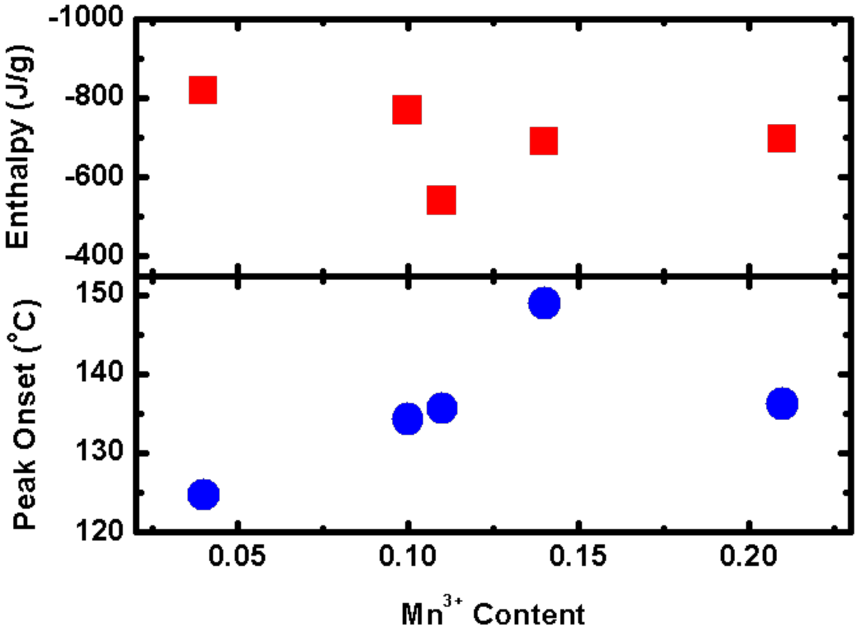
- Morphological control to obtain samples with tap density up to 2.0 g/cm^3

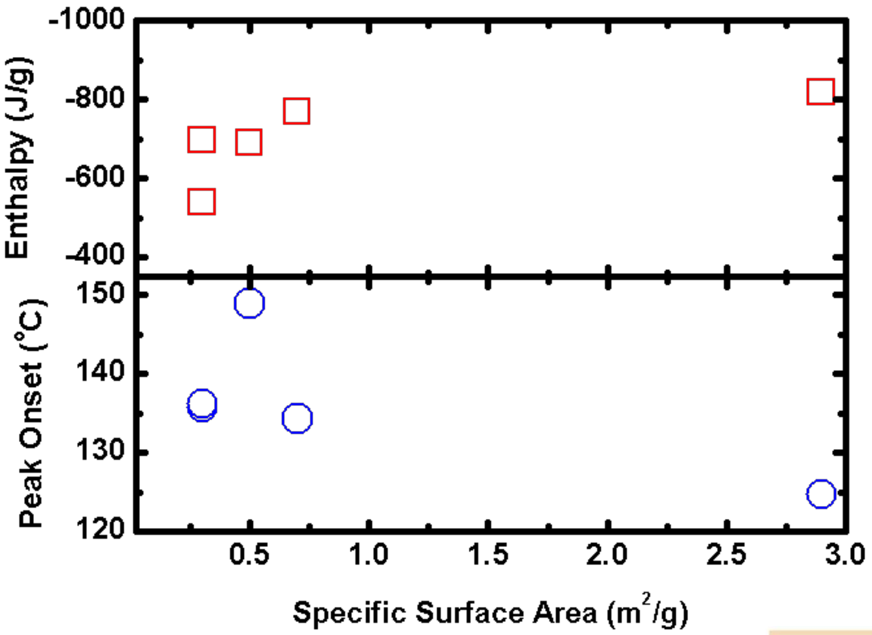
Mn^{3+} CONTENT vs. CYCLABILITY & THERMAL STABILITY



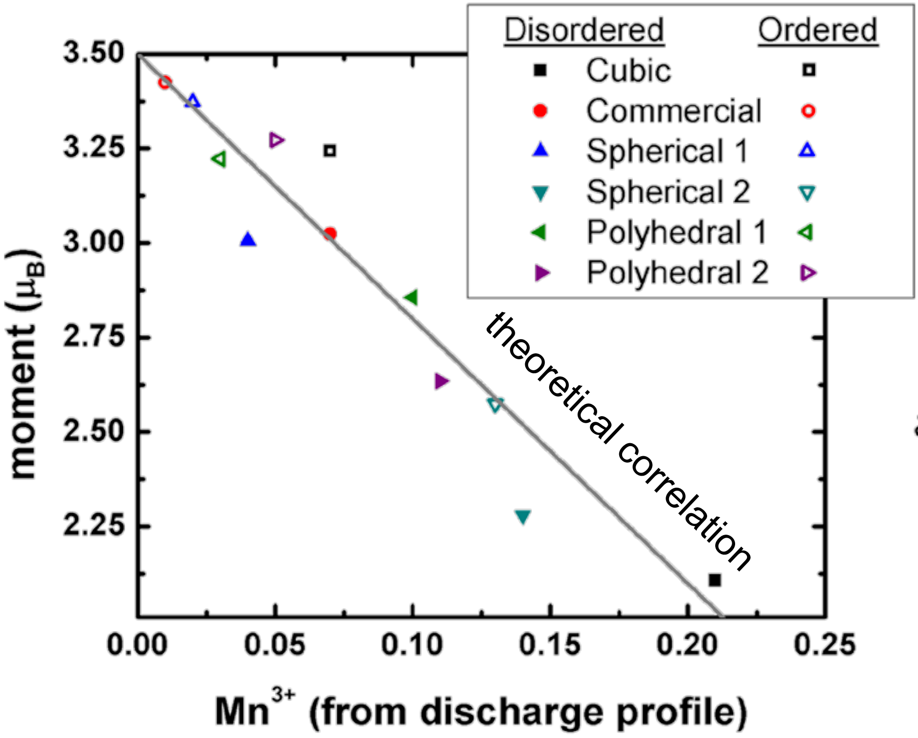


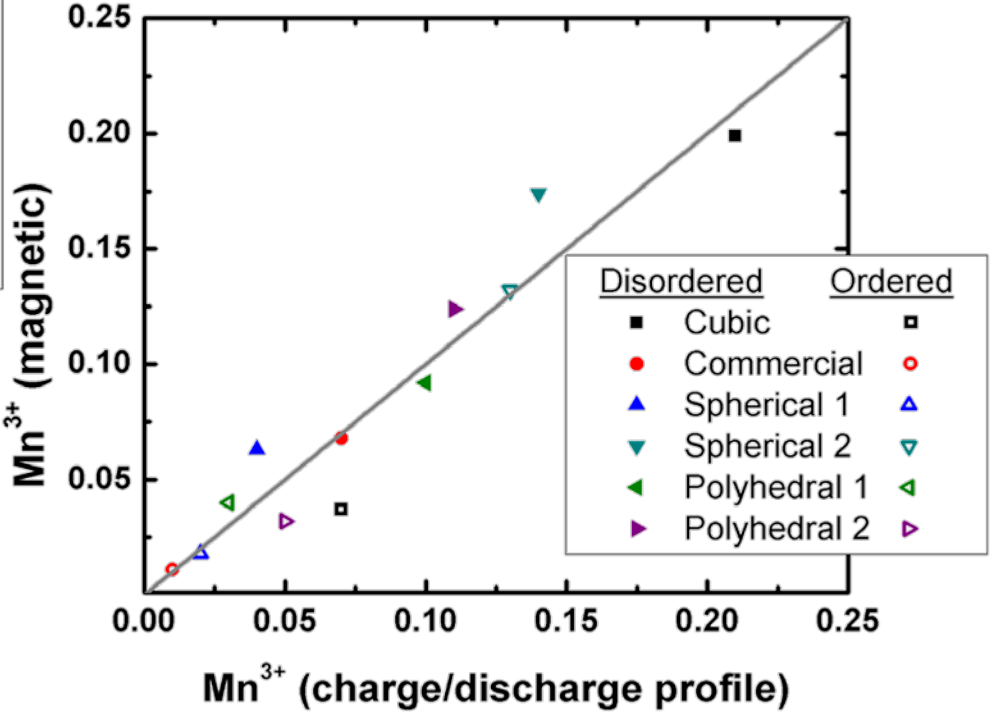
- Cyclability, coulombic efficiency, and thermal stability increase with Mn^{3+} content
- Larger surface area leads to poor thermal stability





QUANTIFICATION OF Mn^{3+} CONTENT BY MAGNETIC DATA



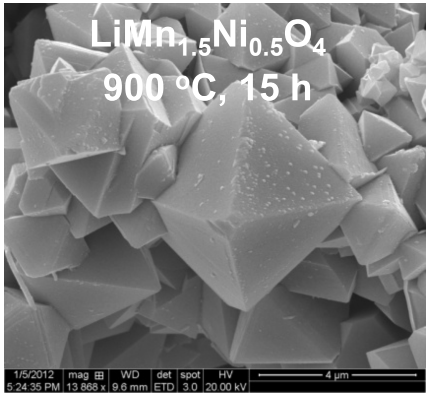


- Ferrimagnetic ordering below Curie temperature
- Mn^{3+} and Ni^{2+} spin moments are parallel to each other and antiparallel to Mn^{4+}
- Saturated moment at 0 K gives Mn^{3+}

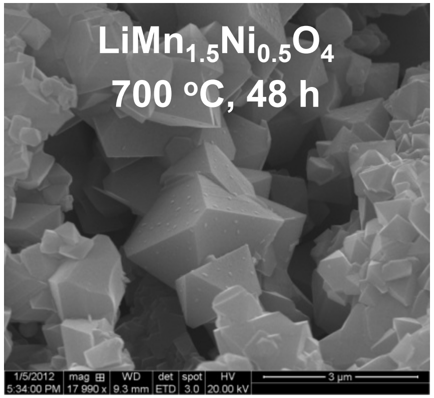
$$\frac{\mu_B}{FW} = g_e S_{Mn^{4+}} N_{Mn^{4+}} - g_e S_{Ni^{2+}} N_{Ni^{2+}} - g_e S_{Mn^{3+}} N_{Mn^{3+}}$$

μ_B: measured moment/formula
FW: formula weight
g_e: gyromagnetic factor for an electron = 2
S: the total net spin of the electron in each ion
N: the number of ions per formula unit

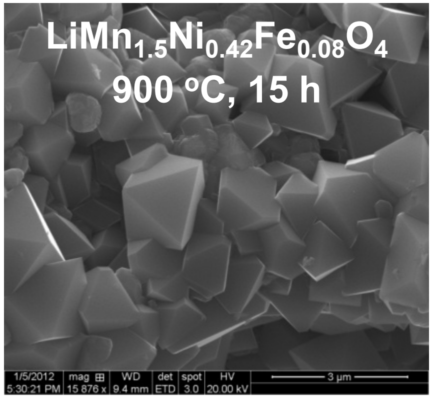
ROLE OF CATION ORDERING ON RATE CAPABILITY



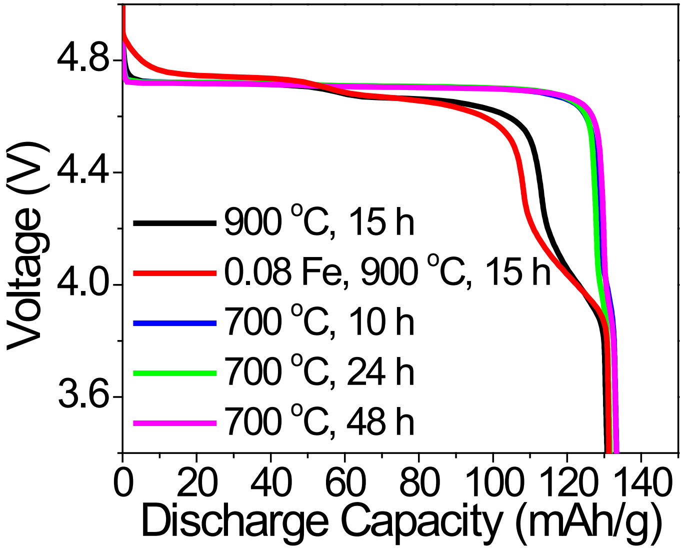
$LiMn_{1.5}Ni_{0.5}O_4$
900 °C, 15 h

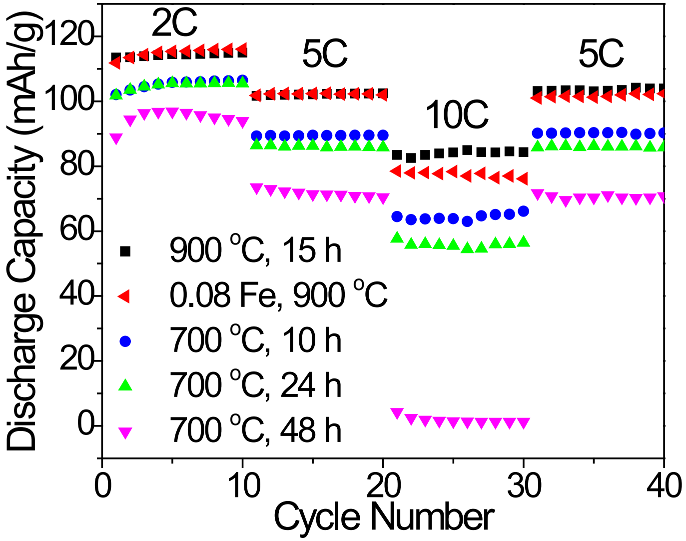


$LiMn_{1.5}Ni_{0.5}O_4$
700 °C, 48 h



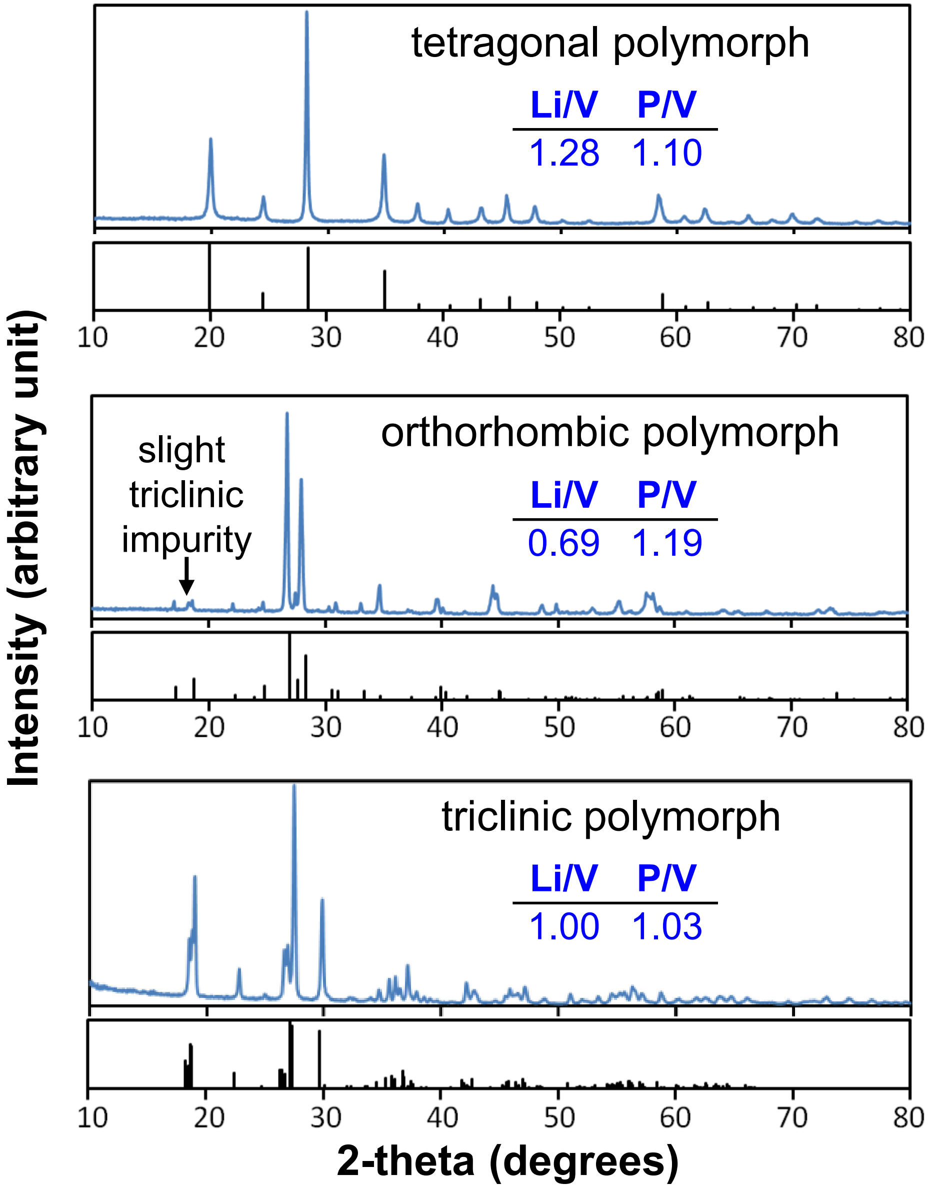
$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$
900 °C, 15 h





- Post-annealing at 700 °C and Fe doping do not affect the morphology of the spinel prepared by a sol-gel method
- Post-annealing at 700 °C reduces the Mn^{3+} content
- As the annealing time increases, the rate capability decreases due to an increase in cation ordering although the Mn^{3+} content is similar among the annealed samples

MICROWAVE-SOLVOTHERMAL (MW-ST) SYNTHESIS OF $LiVOPO_4$

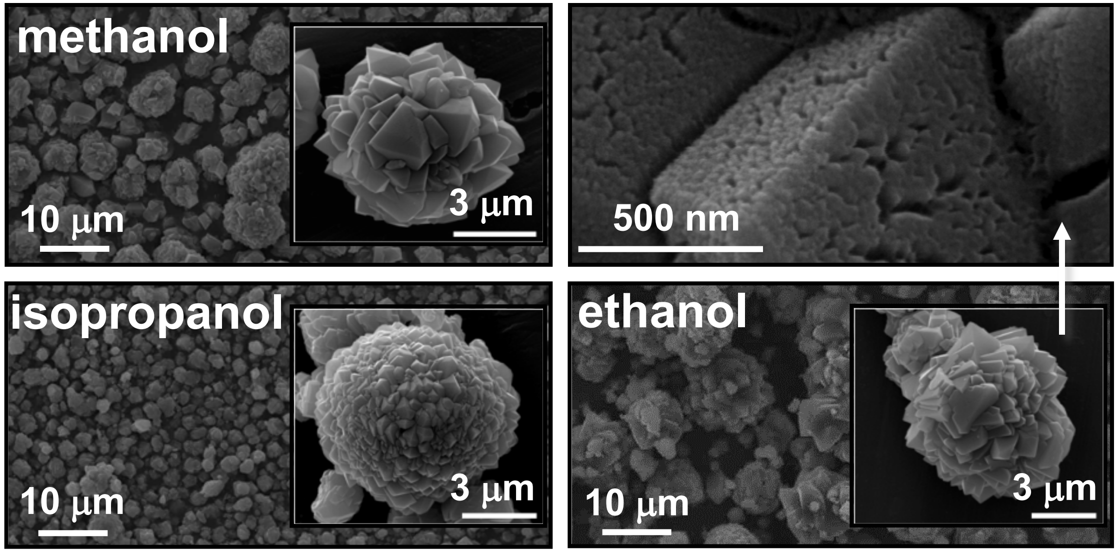


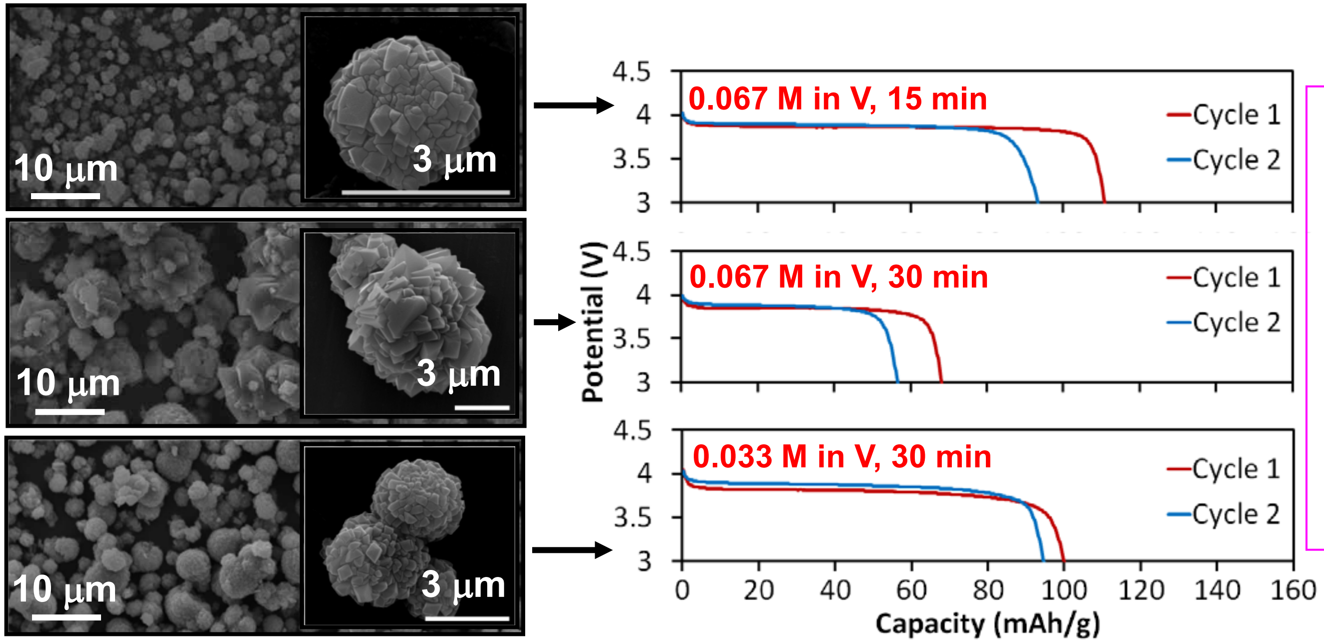
- $LiVOPO_4$ exists in orthorhombic, tetragonal, and triclinic polymorphs
- All three polymorphs have been synthesized by the MW-ST method by varying solvent and precursor ratios
- The triclinic polymorph shows stoichiometric elemental ratios while the tetragonal and orthorhombic polymorphs show nonstoichiometric elemental ratios, which could be related to defects or an amorphous impurity

polymorph	water: ethanol	Li:V:P
tetragonal	1:1	1.8:1:1
orthorhombic	1:3	1:1:4
triclinic	3:1	5:1:5

MORPHOLOGY AND PERFORMANCE OF TRICLINIC LiVOPO$_4$

- Triclinic LiVOPO$_4$ can be made in water mixed with a variety of alcohols (water : alcohol = 3:1)
- A microflower-like morphology forms for all alcohols
- Each microflower is composed of nanoparticle agglomerates





- Smaller particles yield better electrochemical performance
- Size is controlled by decreasing reaction time or precursor concentration

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- University of Rhode Island – Professor Brett Lucht
  - *Investigation of SEI layer formation with stabilized 4.7 V spinel cathodes*

- Pacific Northwest National Laboratory – Dr. Jiguang (Jason) Zhang
  - *Discussion and coordination of results on 4.7 V spinel cathodes*
  - *Investigation of the 4.7 V spinel cathodes by solid state NMR*

- Lawrence Berkeley National Laboratory – Dr. Jordi Cabana Jiménez
  - *Discussion and coordination of results on 4.7 V spinel cathodes*
  - *Investigation of the 4.7 V spinel cathodes by X-ray absorption spectroscopy*

- Oak Ridge National Laboratory – Dr. Craig Bridges
  - *Investigation of the phosphate and 4.7 V spinel cathodes by spallation neutron source and high resolution transmission electron microscopy*

- DuPont – Dr. George Kodokian
  - *Evaluation of the 4.7 V spinel cathodes with DuPont's new electrolytes*

PROPOSED FUTURE WORK

- Continue to develop a firm understanding of the various factors that influence the electrochemical performances of the 4.7 V spinel cathodes (*e.g.*, role of degree of cation ordering, segregation of cations to the surface, Mn^{3+} content, morphology, and synthesis/processing methods/conditions), and use the understanding to develop high-performance, high-power spinel cathodes for vehicle applications

- Recognizing that segregation of certain cations to the surface provides a unique advantage to enhance the electrochemical properties of high-voltage spinels, investigate by surface characterization techniques such as XPS and TOF-SIMS whether such surface segregations also play a role in enhancing the electrochemical properties of $LiMn_{1-x}Fe_xPO_4$ and $LiCo_{1-x}Fe_xPO_4$

- Pursue novel solution-based synthesis approaches such as microwave-assisted solvothermal and hydrothermal methods to access the high-capacity nanostructured Li_2MSiO_4 (M = Mn, Fe, Co, and Ni) and thereby improve their capacity

SUMMARY

5 V Spinel $LiMn_{1.5}Ni_{0.5}O_4$

- The solubility of Ni in $LiMn_{1.5}Ni_{0.5}O_4$ is dependent on temperature and it increases on annealing at 700 °C, eliminating the $Li_xNi_{1-x}O$ impurity
- Cationic substitutions in $LiMn_{1.5}Ni_{0.42}M_{0.08}O_4$ (M = Cr, Fe, and Ga) eliminate the $Li_xNi_{1-x}O$ impurity even at the high synthesis temperature of 900 °C, increase the degree of cation disorder between Mn^{4+} and Ni^{2+}, and offer a more stable cathode-electrolyte interface due to the decoration of the surface by the dopant ions, resulting in superior cyclability at 55 °C and high rate capability
- Doping with small amounts of cations is the way to employ them in practical cells
- The performance of the undoped $LiMn_{1.5}Ni_{0.5}O_4$ spinel is influenced by the Mn^{3+} content; a magnetic method has been developed, for the first time, to determine quantitatively the Mn^{3+} content that agrees closely with the electrochemical data

Polyanion cathodes

- A microwave-assisted solvothermal method has been developed to access the three polymorphs (tetragonal, orthorhombic, and triclinic) of $LiVOPO_4$
- Similar approaches are being developed for the high capacity Li_2MSiO_4 cathodes