
STABILIZED SPINEL AND POLYANION CATHODES

ARUMUGAM MANTHIRAM

**Electrochemical Energy Laboratory (ECEL)
Materials Science and Engineering Program
The University of Texas at Austin**

May 10, 2011

Project ID #: ES051

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OVERVIEW

Timeline

- Project start date: June 2010
- Project end date: May 2012
- 75 % complete

Budget

- Total project funding
 - DOE: \$520K
- Funding for FY10
 - \$260K
- Funding for FY11
 - \$260K

Barriers

- Barriers
 - Cost
 - Cycle life
 - Energy and power densities
- Targets
 - Long cycle life for 4 V and 5 V spinel cathodes
 - Low manufacturing cost for polyanion cathodes
 - Increased energy and power with spinel and polyanion cathodes

RELEVANCE

- To develop high-performance spinel and polyanion cathodes for lithium-ion batteries and a fundamental understanding of their structure-composition-performance relationships
 - To develop 5 V spinel oxide compositions with controlled morphology and optimum cationic substitutions that can maximize the tap density and electrochemical performance
 - To develop a fundamental understanding of the factors that control the electrochemical performance and safety of cation- and anion-substituted stabilized 4 V spinel manganese oxide compositions
 - To develop novel low-cost synthesis processes for phosphate and silicate cathodes

MILESTONES

Month/Year	Milestone
September 2010	Polyanion-containing cathodes with controlled nanomorphologies
March 2011	Understanding the self-surface segregation of cations in high-voltage spinel cathodes
September 2011	Development of novel synthesis approaches for high-capacity nanostructured silicate and phosphate cathodes

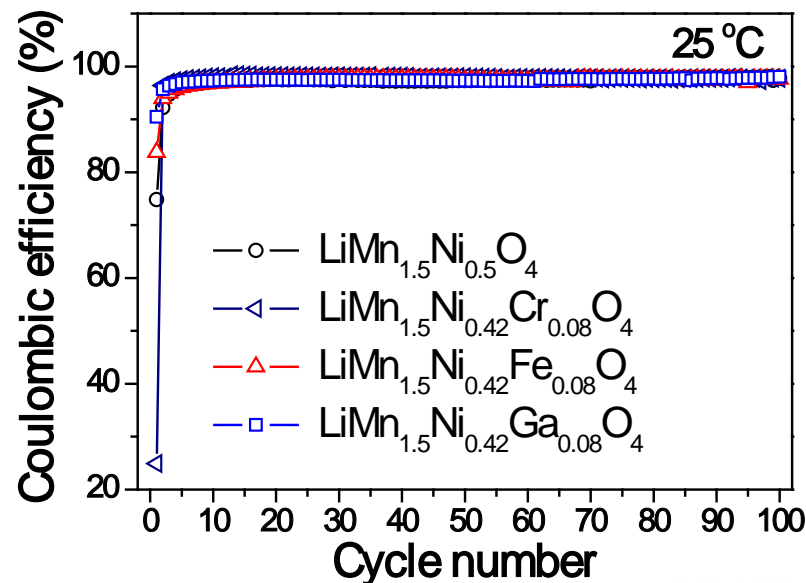
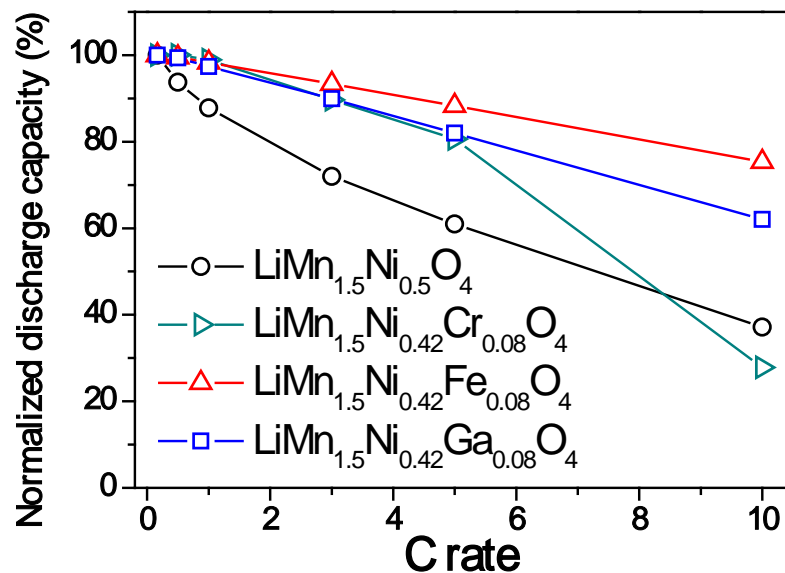
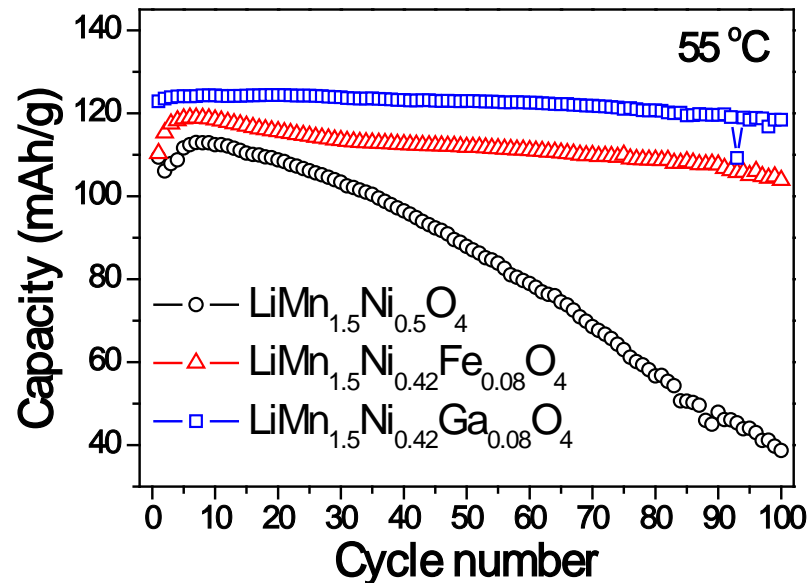
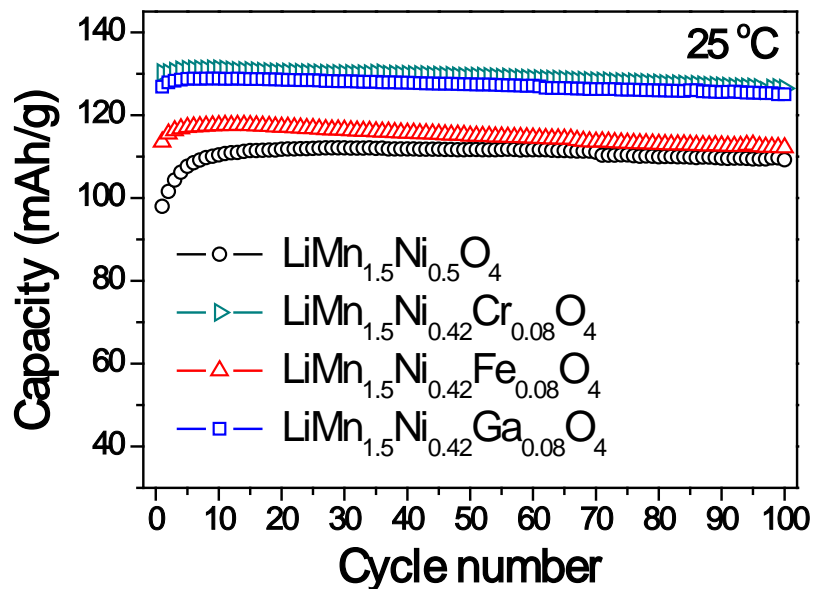
APPROACH / STRATEGY

- 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 and anionic substitutions to obtain stabilized 4 V spinel cathodes
 - Effect of cationic and anionic substitution on thermal stability of 4 V spinel cathodes
 - Cationic substitutions in 5 V spinels to stabilize the disordered spinel structure
 - Novel synthesis approaches for polyanion-containing cathodes including nano-olivines that can lower manufacturing cost with improved performance
 - Solid-state, high-energy ball milling, and solution-based synthesis approaches
 - Advanced chemical and structural characterizations
 - In-depth electrochemical evaluation including impedance analysis
 - Understanding of the structure-property-performance relationships

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

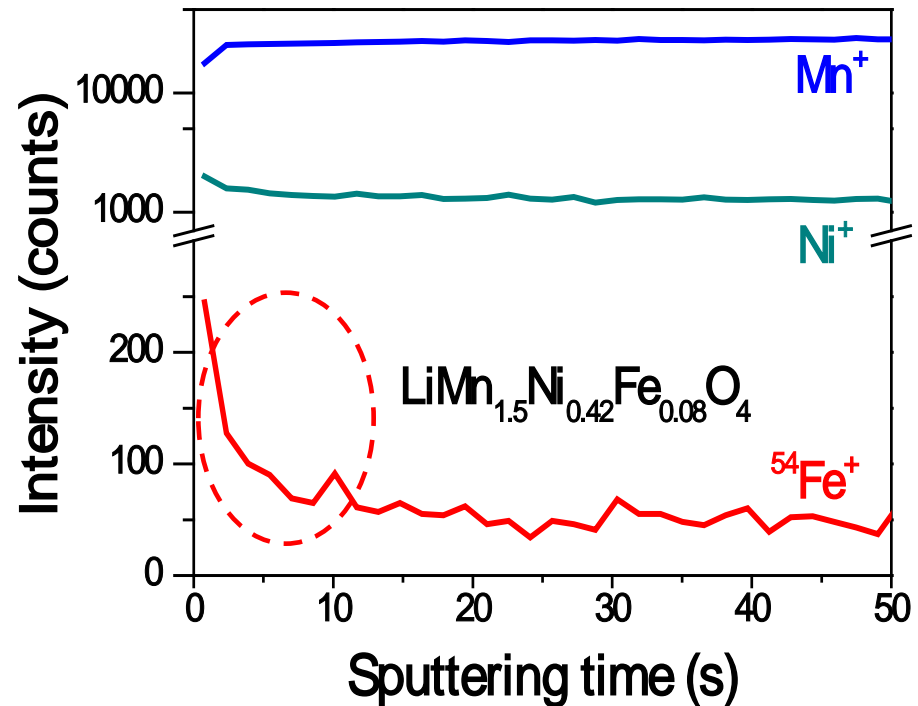
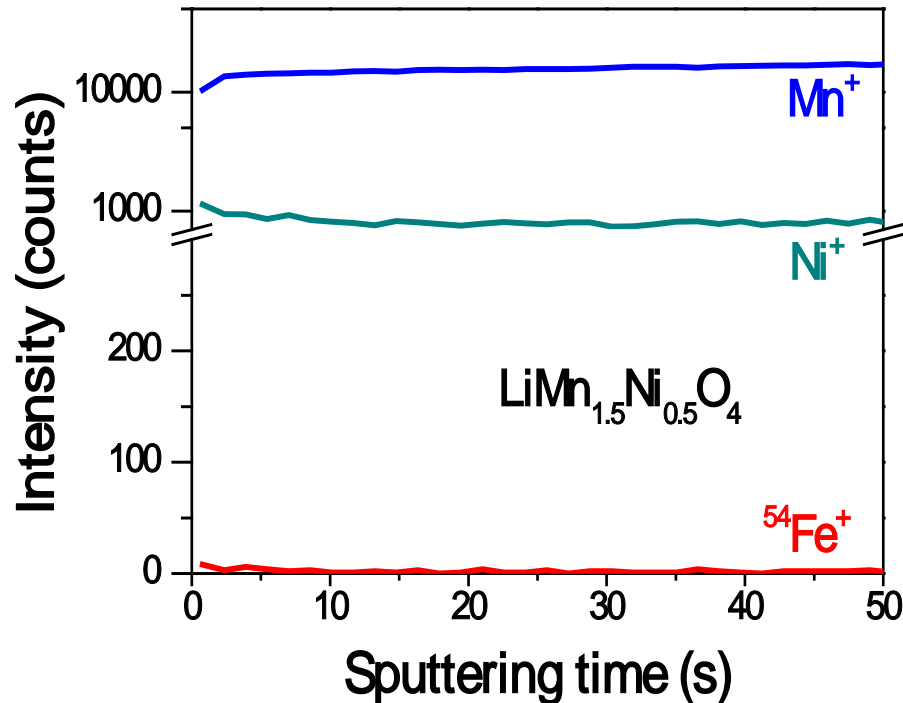
- The influence of cationic substitutions on the bulk and surface structures and electrochemical performances of 5 V spinel cathodes has been identified
 - cationic substitutions stabilize the disordered spinel structure, facilitate segregation of certain cations to the surface, and thereby improve significantly the electrochemical performances (cycle life and rate capability)
- Precursors with unique morphologies have been synthesized by novel synthesis approaches to maximize the tap density and performance of 5 V spinels
- The factors that influence the cycle life and safety of 4 V spinels have been identified; oxyfluorides offer better safety than the oxide counterparts
- Substitution of small amounts of Fe significantly improves the electrochemical performances of both LiMnPO_4 and LiCoPO_4 due to surface segregation
- The substitution of VO for Fe in $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$ has been found to create vacancies in the Fe sites; the $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$ phases formed by the microwave-assisted process are metastable and disproportionate at high temperatures

INFLUENCE OF CATIONIC SUBSTITUTIONS IN 5 V SPINEL



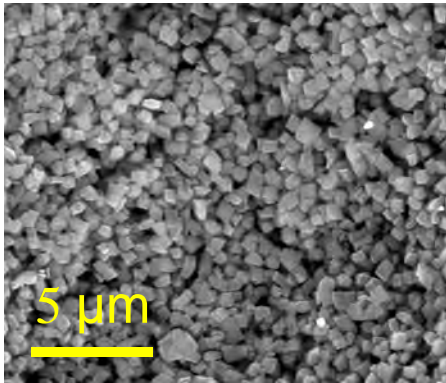
SELF-SURFACE SEGREGATION IN 5 V SPINELS

Time-of-flight – secondary ion mass spectroscopy (TOF-SIMS)

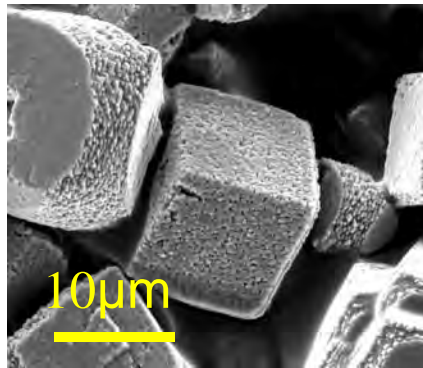


- Fe segregates to the surface during the synthesis and cooling process, which is consistent with our earlier XPS data
- Self-surface segregation is an attractive strategy to develop a robust electrode-electrolyte interface with the high-voltage cathodes

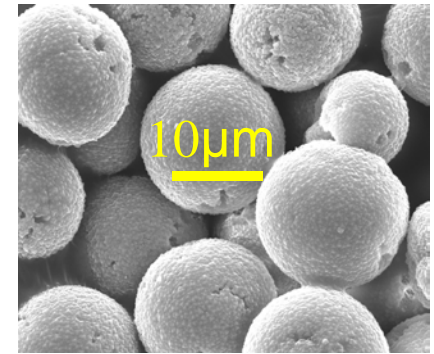
MORPHOLOGY CONTROL OF 5 V SPINEL CATHODES



oxalate, AOT,
polyhedral

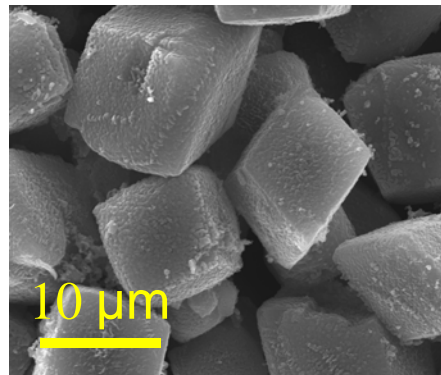
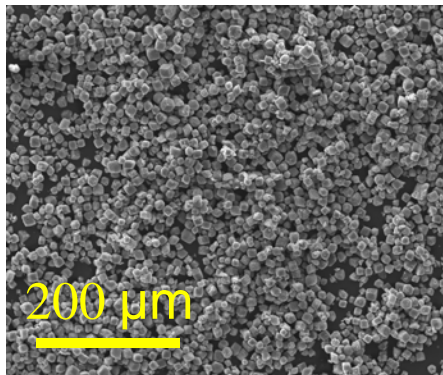


carbonate, CTAB
cubic



carbonate, $(\text{NH}_4)_2\text{SO}_4$
spherical

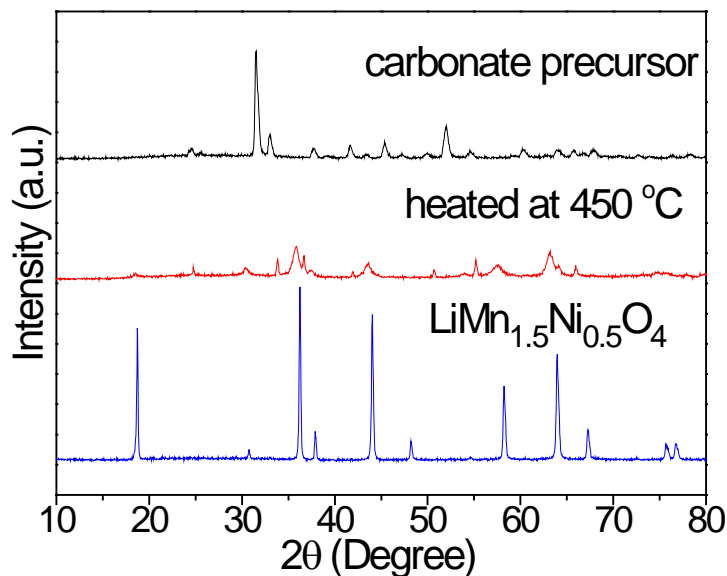
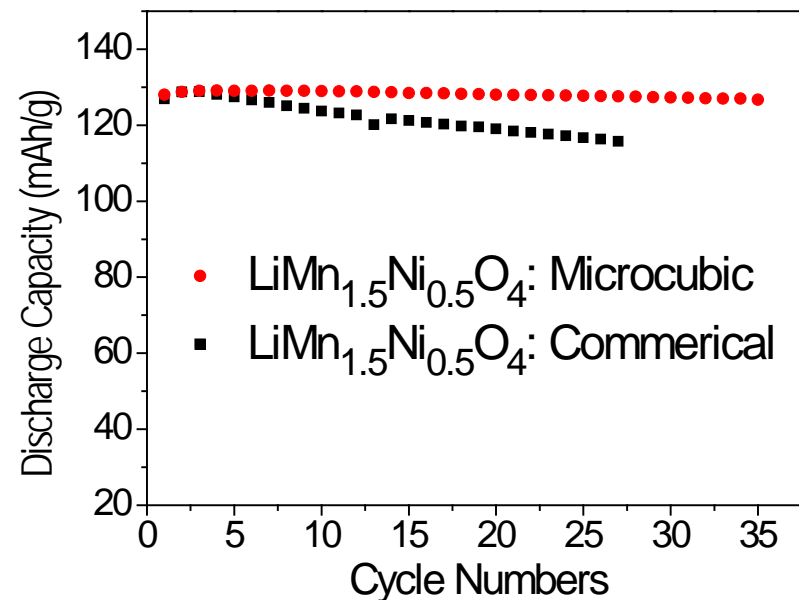
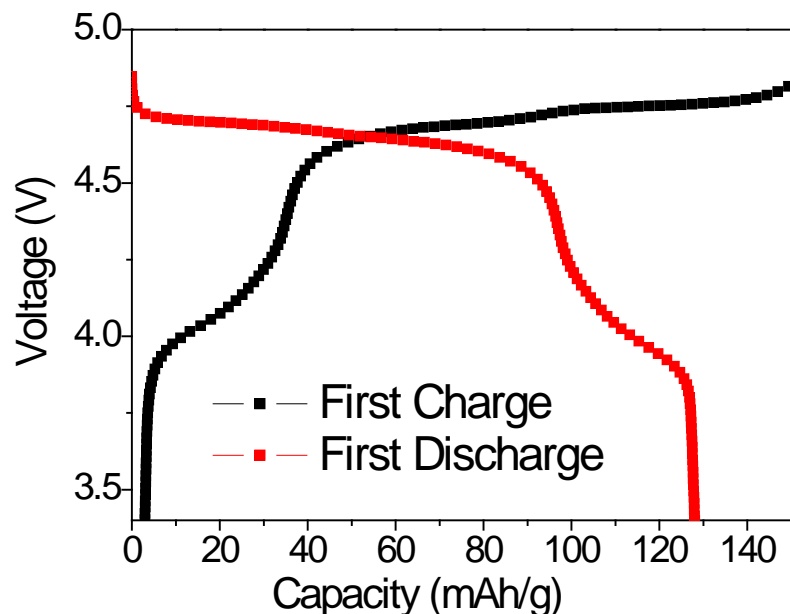
- Morphology could be controlled with different precipitating agents and additives such as AOT, CTAB, or $(\text{NH}_4)_2\text{SO}_4$



$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel

- Microcubic precursor is preheated at 450 °C, followed by mixing with LiOH and firing at 900 °C for 12 h
- Precursor morphology is retained in the final spinel sample
- High tap density: 2.0 g/cm³

5 V SPINEL WITH MICRO-CUBIC MORPHOLOGY

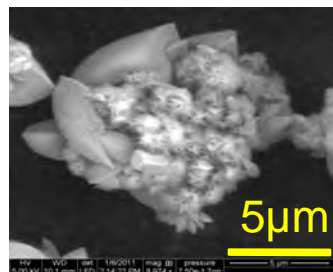


- The 5 V spinel was obtained from the single-phase micro-cubic carbonate precursor
- The 5 V spinel exhibits excellent cyclability without any capacity fade compared to a commercial 5 V spinel sample

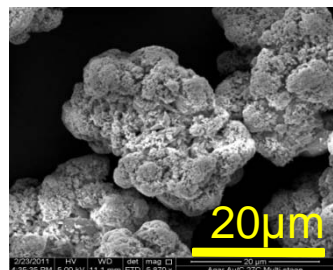
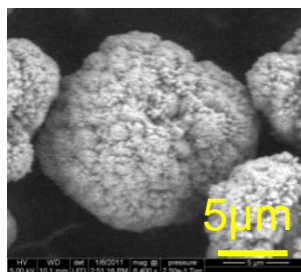
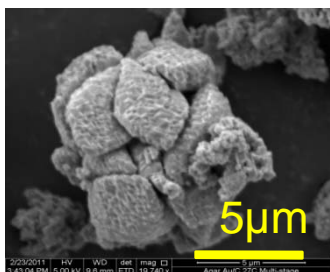
EFFECTS OF REACTION TIME AND CATIONIC SUBSTITUTIONS



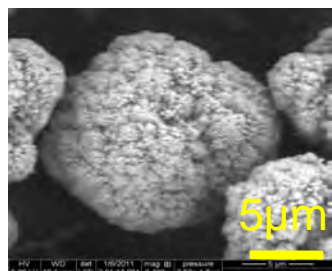
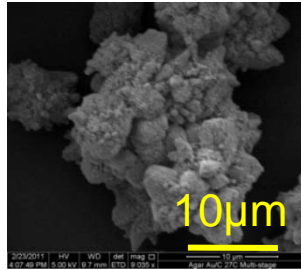
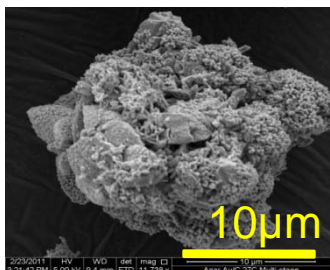
$\text{Mn}_{0.75}\text{Ni}_{0.25-z}\text{Fe}_z\text{CO}_3$
12 hours, pH 7.9 +/- 0.05



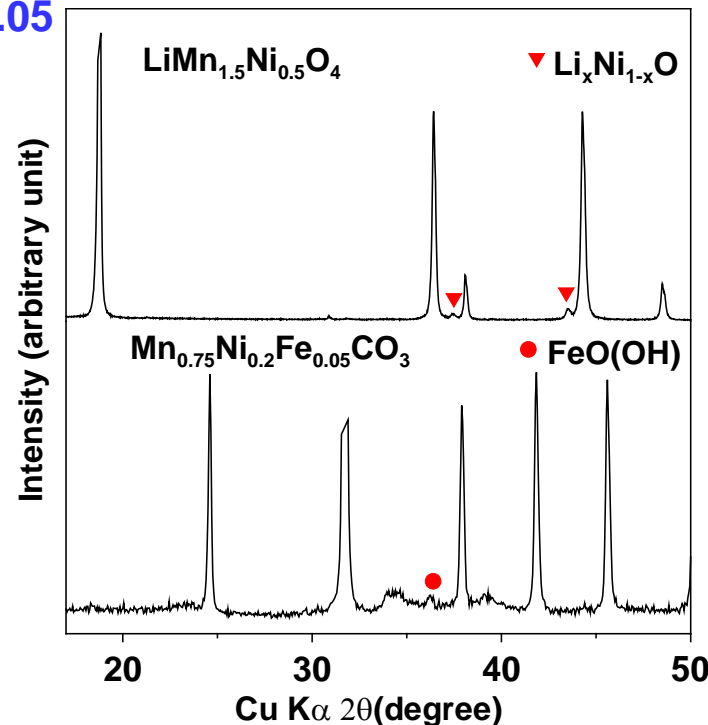
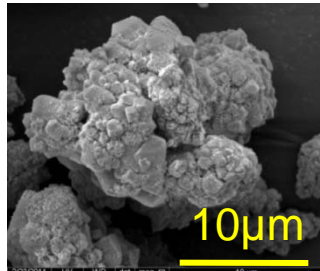
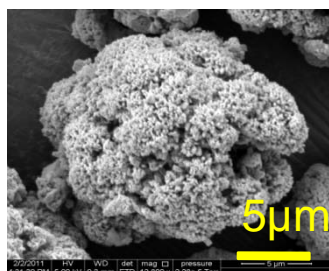
3 hour reaction time



6 hour reaction time

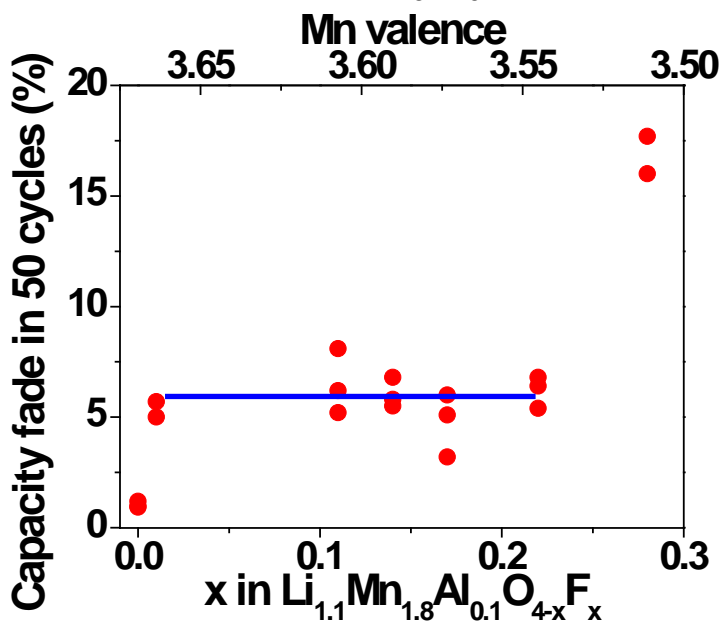
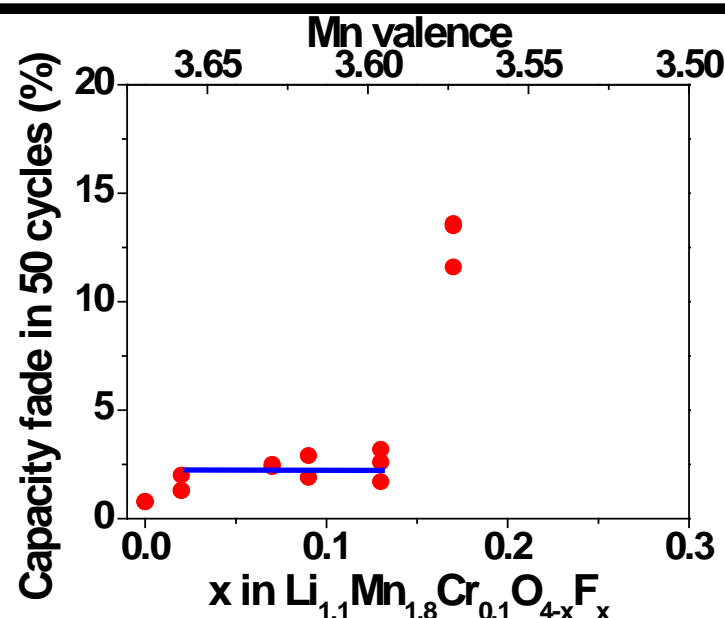
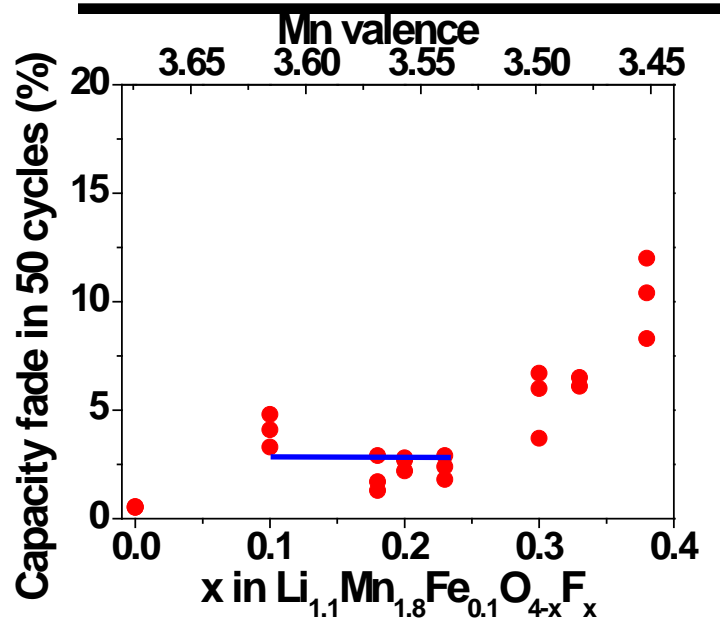


12 hour reaction time



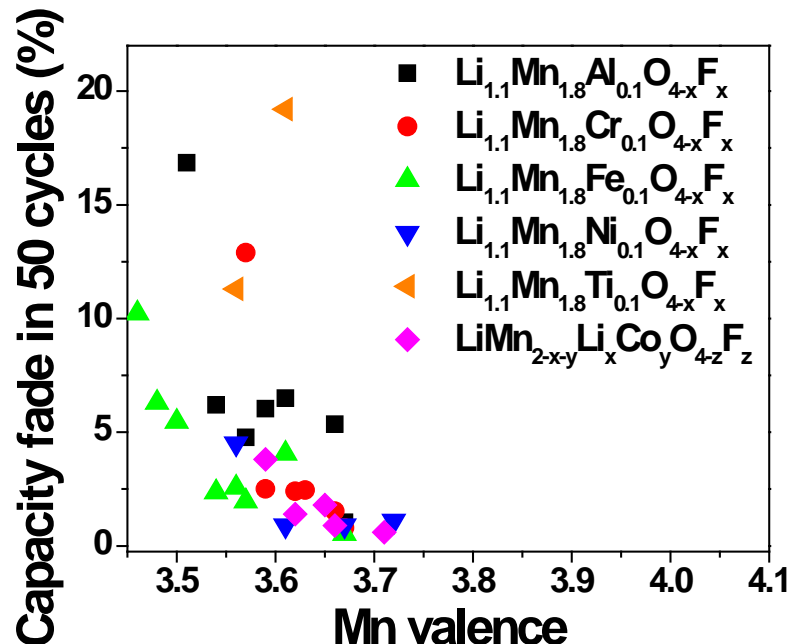
- Morphology changes with reaction time; 12 h gives spherical morphology
- $\text{Fe}(\text{OH})_2$ formed due to hydrolysis with Fe substitution, which becomes FeOOH at 120 °C

CYCLABILITY OF CATION-SUBSTITUTED 4 V OXYFLUORIDE SPINELS

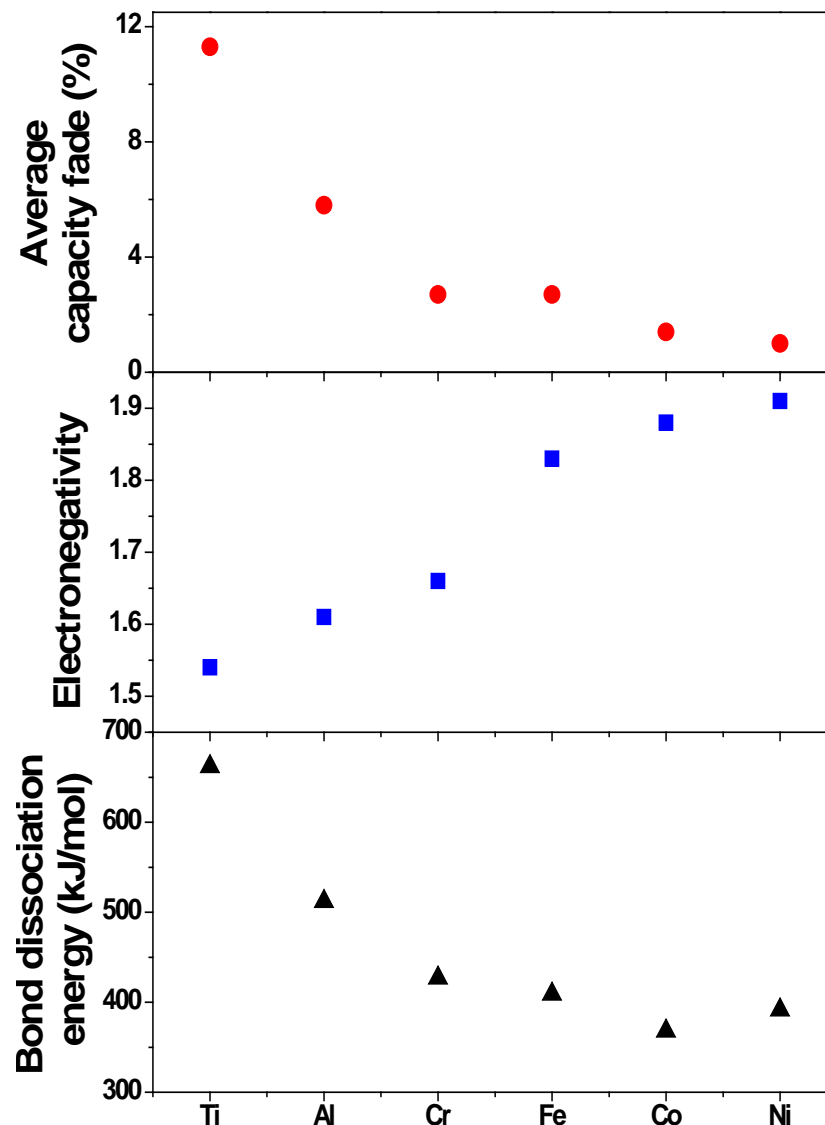


- Capacity fade increases drastically above a fluorine content of 0.2 or below a Mn valence of $\sim 3.55+$
- This is due to an increasing amount of Mn^{3+} and the consequent Mn dissolution and dynamic Jahn-Teller distortion
- The initial Mn valence should be maintained above $\sim 3.6+$ to realize acceptable performance

UNDERSTANDING THE CAPACITY FADE IN 4 V OXYFLUORIDE SPINELS

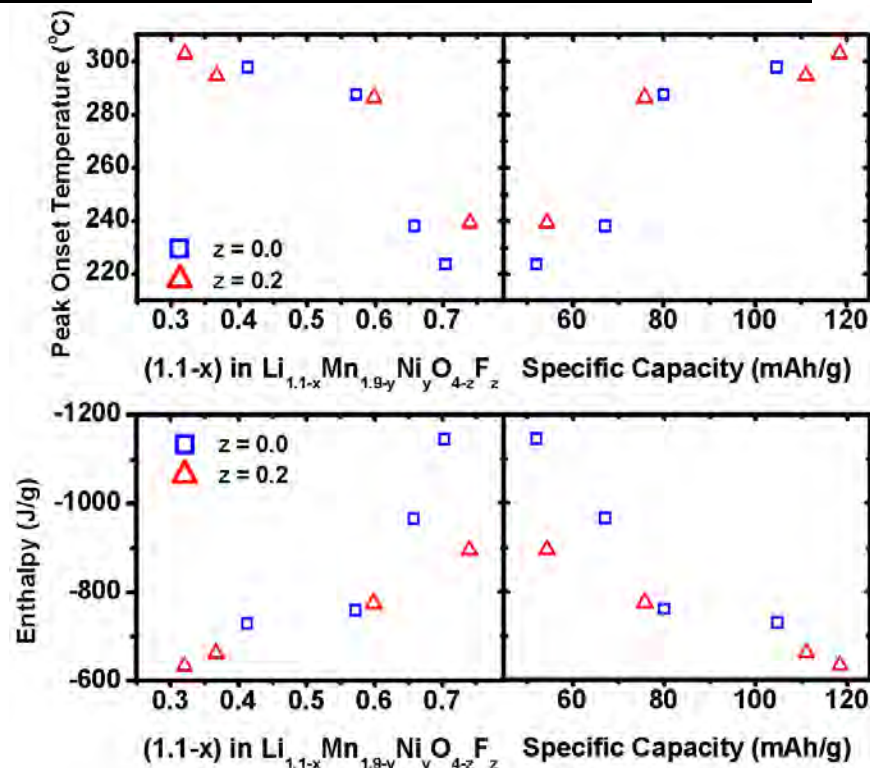
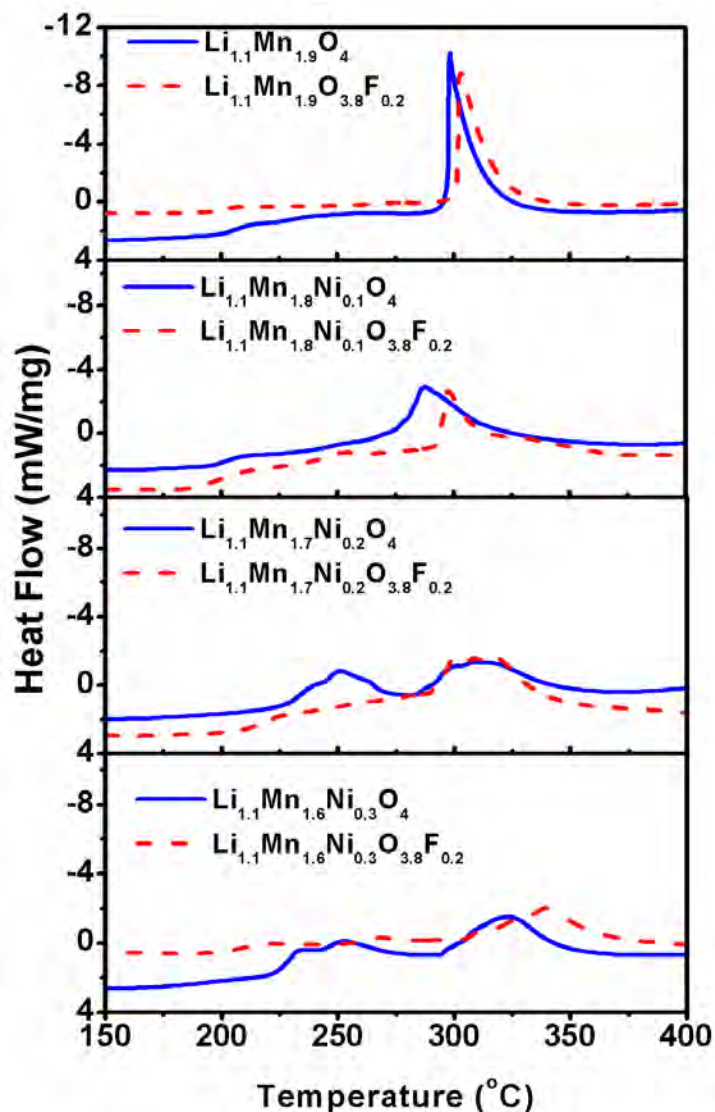


- The capacity fade in 4 V oxyfluoride spinels
 - increases with decreasing Mn valence below ~ 3.6+
 - decreases with increasing electronegativity of the substituted cations M from Ti to Ni
 - decreases with decreasing M-O bond dissociation energy



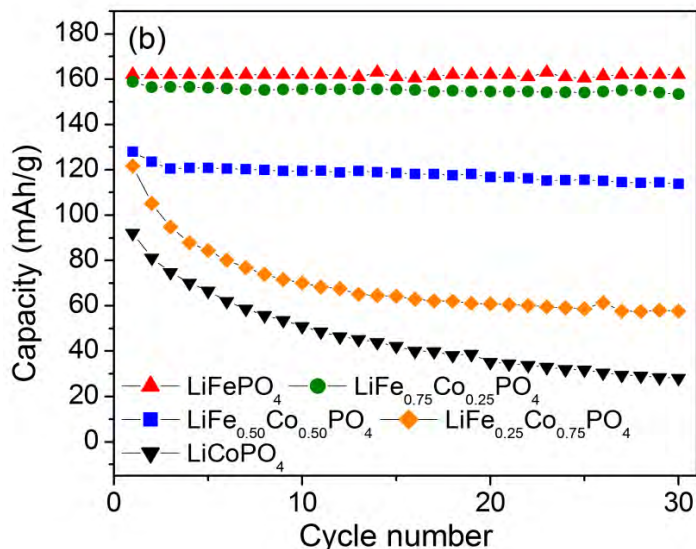
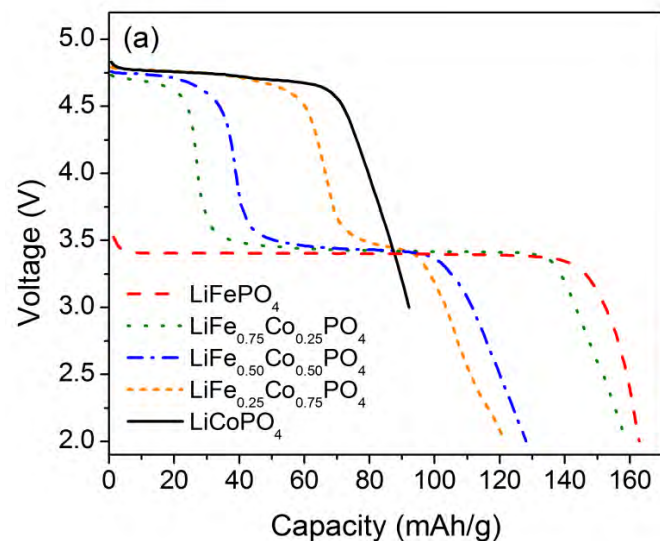
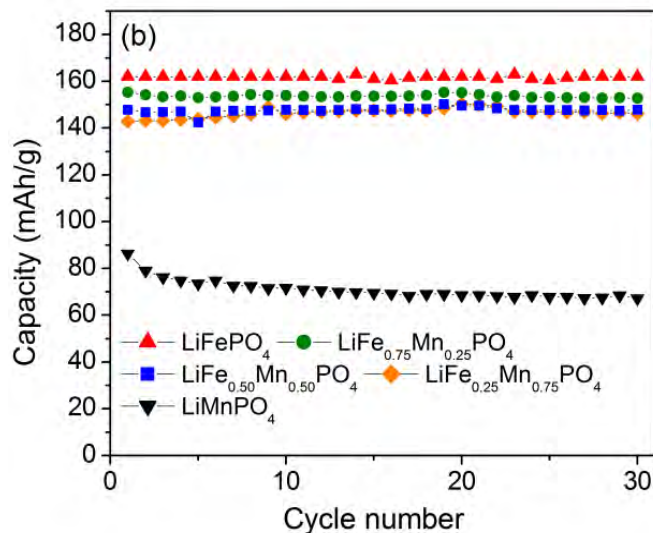
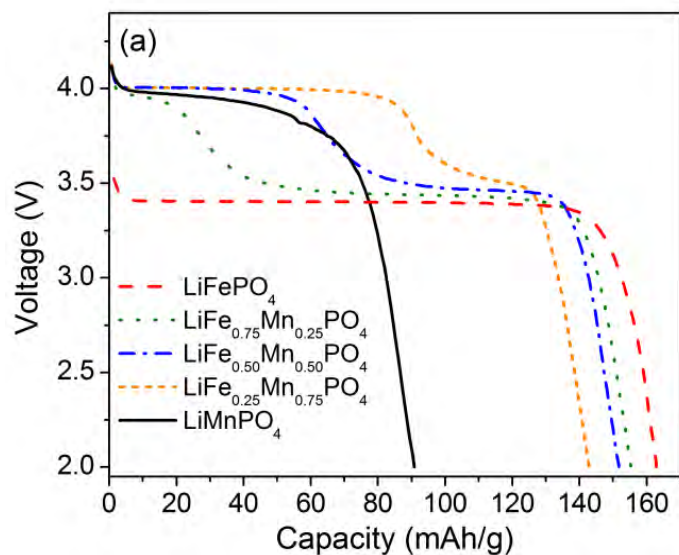
THERMAL STABILITY OF 4 V SPINEL CATHODES

DSC Plots of Ni-substituted cathodes in the charged state, wetted with electrolyte



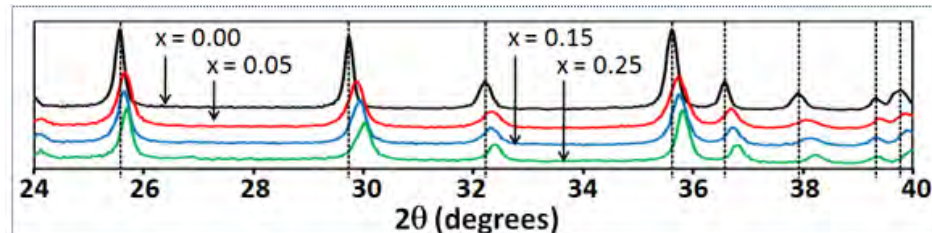
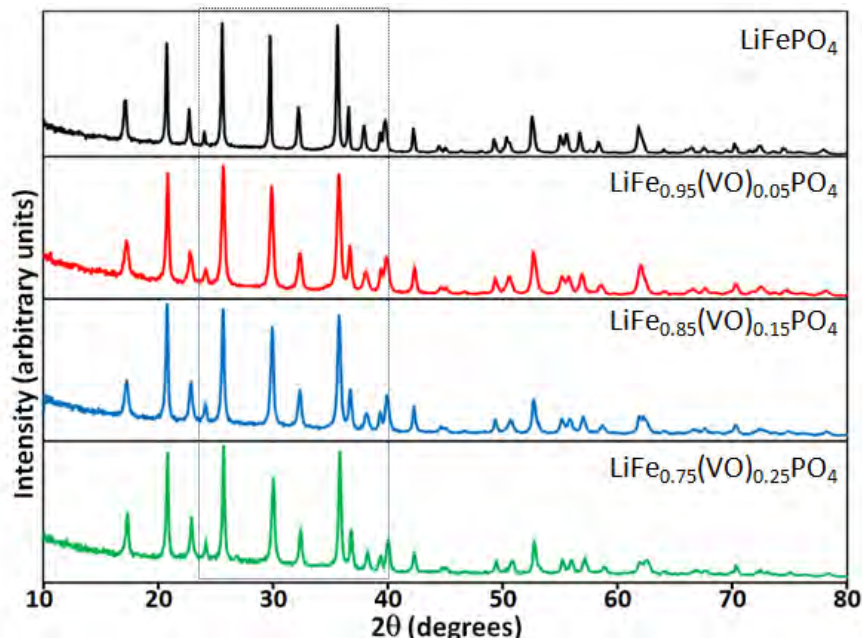
- Samples with lower lithium content in the charged state show better thermal stability
- Metal-oxygen bond strength affects the thermal stability significantly
- Similar results were obtained for Al- and Li-doped samples

OLIVINE SOLID SOLUTIONS



- Substitution of Fe for Mn or Co improves the electrochemical activity

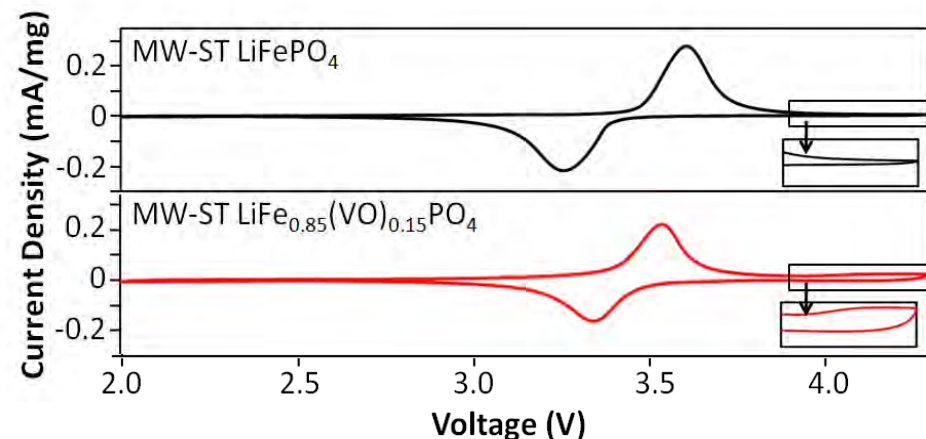
MICROWAVE-SOLVOTHERMAL (MW-ST) SYNTHESIS OF $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$



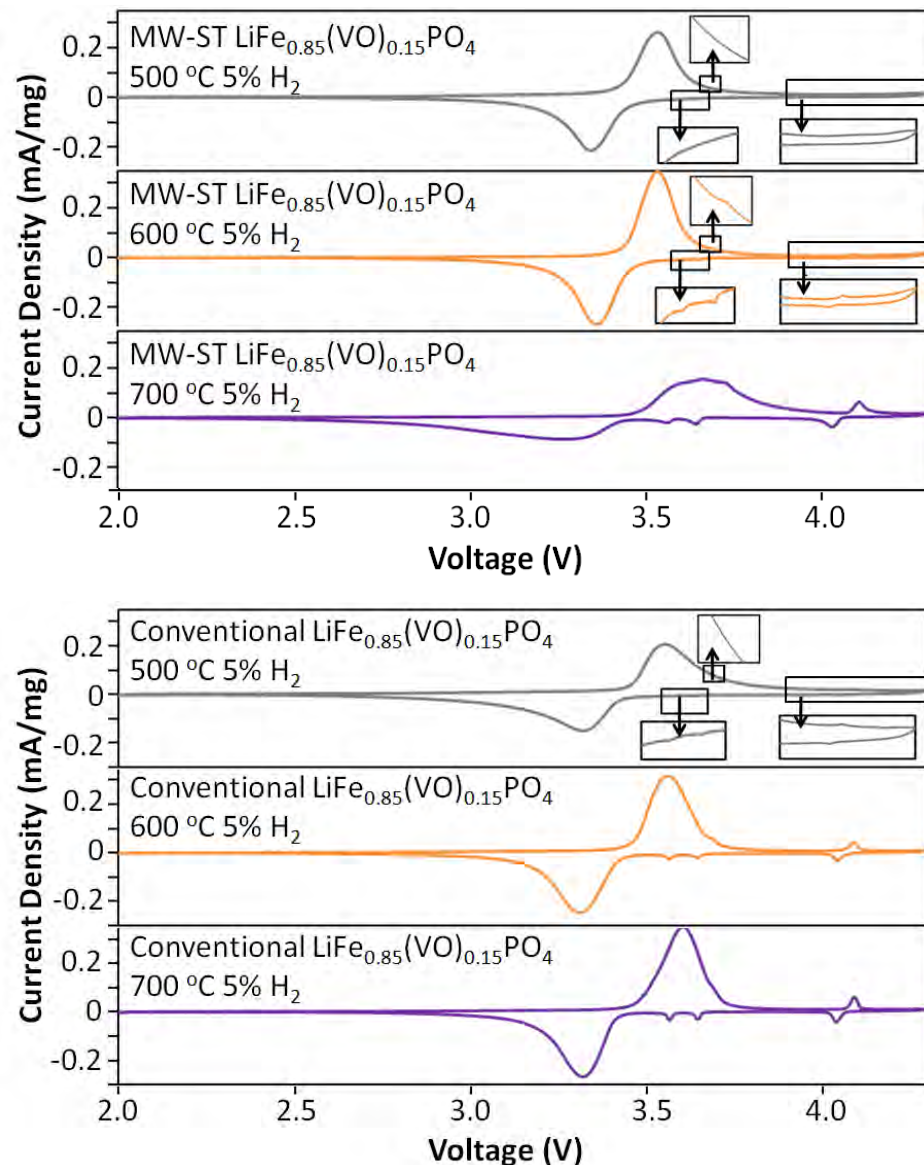
Compound	V (\AA^3)	Li/P	V/P	Fe/P
LiFePO_4	289.85	1.00	-----	0.99
$\text{LiFe}_{0.95}(\text{VO})_{0.05}\text{PO}_4$	287.82	0.99	0.05	0.96
$\text{LiFe}_{0.90}(\text{VO})_{0.10}\text{PO}_4$	287.29	0.97	0.10	0.86
$\text{LiFe}_{0.85}(\text{VO})_{0.15}\text{PO}_4$	286.40	1.02	0.16	0.77
$\text{LiFe}_{0.75}(\text{VO})_{0.25}\text{PO}_4$	285.21	0.99	0.24	0.70

- Substitution of a larger $(\text{VO})^{2+}$ for a smaller Fe^{2+} should increase the unit cell volume, but exactly the opposite is found due to the formation of Fe vacancies as indicated by a lower Fe/P ratio in the sample in the ICP analysis and Fe_3O_4 impurity that could be removed with a magnetic bar
- Fe vacancies are formed to accommodate the larger $(\text{VO})^{2+}$ ions
- Formation of Fe vacancies and the corresponding oxidation of Fe^{2+} to Fe^{3+} decrease the unit cell volume

THERMAL STABILITY OF $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$



- The MW-ST $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$ samples are metastable and cannot not be made by conventional high-temperature methods
 - With increasing heating temperature in 5 % H_2 – 95 % Ar, the vanadium activity changes from that of $(\text{VO})^{2+/3+}$ in LiVOPO_4 to that of $\text{V}^{3+/4+/5+}$ in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$
 - $\text{LiFe}_{0.85}(\text{VO})_{0.15}\text{PO}_4$ synthesized by conventional heating shows only $\text{V}^{3+/4+/5+}$ activity without any $(\text{VO})^{2+/3+}$ activity, indicating the instability of $\text{LiFe}_{0.85}(\text{VO})_{0.15}\text{PO}_4$



COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- National Renewable Energy Laboratory – Dr. Anne Dillon
 - *ALD coating of Al_2O_3 on 5 V spinel cathodes*
- University of Rhode Island – Professor Brett Lucht
 - *Investigation of SEI layer formation with stabilized 5 V spinel cathodes*
- Pacific Northwest National Laboratory – Dr. Jiguang (Jason) Zhang
 - *Discussion and coordination of results on 5 V spinel cathodes*
- Lawrence Berkeley National Laboratory – Dr. Jordi Cabana Jiménez
 - *Discussion and coordination of results on 5 V spinel cathodes*

PROPOSED FUTURE WORK

- Continue to identify the factors that influence the electrochemical performances of the 5 V spinel cathodes, *e.g.*, role of ordered vs. disordered spinel structure, segregation of cations to the surface, synthesis temperature, and morphology
- Extend the morphological-control synthesis approach pursued for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel to other cation-substituted $\text{LiMn}_{1.5}\text{Ni}_{0.5-y}\text{M}_y\text{O}_4$ ($\text{M} = \text{Cr}, \text{Fe}, \text{and Ga}$)
- Recognizing that the substitution of a small amount of Fe improves the performances of LiMnPO_4 and LiCoPO_4 , explore whether surface segregation of Fe plays a role in improving the performance of $\text{LiM}_{1-x}\text{Fe}_x\text{PO}_4$ ($\text{M} = \text{Mn and Co}$)
- Following our earlier work, explore the microwave-assisted solvothermal synthesis approaches to obtain $\text{Li}_2\text{Fe}_{1-x}\text{M}_x\text{SiO}_4$ ($\text{M} = \text{Mn}, \text{Co}, \text{and Ni}$) silicate that have the potential to reversibly insert/extract two lithium per transition metal ion
- Explore the microwave-assisted solvothermal synthesis approach to obtain nanostructured NASICON-related $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_9\text{V}_3(\text{P}_2\text{O}_7)_3(\text{PO}_4)_2$ cathodes that has the potential to extract more than one lithium per transition metal ion

SUMMARY

5 V Spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$

- Cationic substitutions stabilize the disordered spinel structure, eliminate the $\text{Ni}_{1-x}\text{Li}_x\text{O}$ impurity, and improve significantly the electrochemical performance
- Certain cations like Fe^{3+} segregate to the surface during the synthesis process of $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{Fe}_x\text{O}_4$ and provide a robust interface with the electrolyte
- Controlled synthesis with unique morphologies offer high tap density

4 V Spinel $\text{LiMn}_{2-y}\text{M}_y\text{O}_{4-z}\text{F}_z$

- The Mn valence has to be above $\sim 3.6+$ to offer acceptable cycle life
- Electronegativity of M and M-O bond energies play a role in the capacity fade
- The oxyfluoride spinels offer better safety than the oxide counterparts

Polyanion cathodes

- Substitution of Fe improves the performances of LiMnPO_4 and LiCoPO_4
- The substitution of VO for Fe in $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$ is accompanied by the formation Fe vacancies and oxidation of Fe^{2+} to Fe^{3+}
- The $\text{LiFe}_{1-x}(\text{VO})_x\text{PO}_4$ phases are metastable and decompose at high temps.