STABILIZED SPINELS AND POLYANION CATHODES

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OVERVIEW

Timeline

- Project start date: June 2009
- Project end date: May 2011
- 50 % complete

Budget

- Total project funding
  - DOE: $520K
- Funding for FY09
  - $260K
- Funding for FY10
  - $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 (e.g., olivine) cathodes
  - Increased energy and power with spinel and polyanion cathodes

RELEVANCE

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

  - To develop low-cost 4 V spinel manganese oxide compositions exhibiting improved capacity retention at elevated temperatures and safety

  - To develop 5 V spinel oxide compositions offering a robust electrode-electrolyte interface and a combination of high energy and power

  - To develop low-cost manufacturing processes for olivine cathodes and novel synthesis approaches for new nanostructured polyanion cathodes

MILESTONES

Month/Year	Milestone
March 2009	Rapid synthesis and characterization of various phospho-olivines with controlled size and nanomorphologies
June 2009	Optimization of stabilized spinel-layered oxide composite cathodes
September 2009	New cathode materials based on polyanions
March 2010	Characterization of surface-modified, stabilized spinel cathodes
September 2010	Polyanion-containing cathodes with controlled nanomorphologies

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
- Cationic substitutions in 5 V spinels to stabilize the disordered spinel structure
- Self-surface segregation of certain cations in 5 V spinels to realize a robust, stable cathode-electrolyte interface with suppressed SEI-layer formation
- Novel synthesis approaches for polyanion-containing cathodes including nano-olivines and silicates that can lower manufacturing cost with improved performance

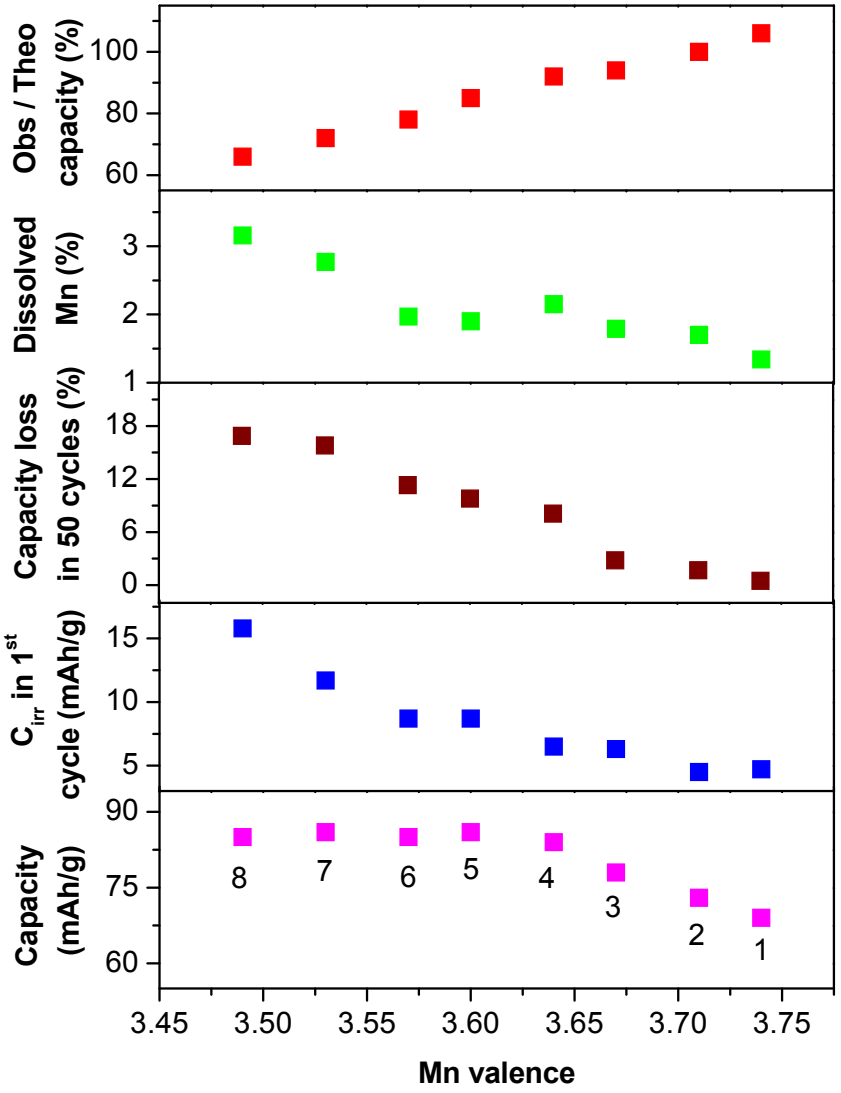
- Solid-state, high-energy ball milling, and solution-based synthesis approaches
- Advanced chemical and structural characterizations
- In-depth electrochemical evaluation including impedance analysis
- Understanding of the structure-property-performance relationships

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- Fundamental understanding of the factors that control the electrochemical performances of cation-substituted 4 V spinels, which can serve as a guide for the design of high-performance 4 V spinel cathodes
- Oxyfluoride spinel cathodes offer better thermal stability than the oxide counterparts
- Segregation of certain cations like Fe^{3+} to the surface during the synthesis of cation-substituted 5 V spinels offers a robust, stable cathode-electrolyte interface, resulting in good cycle life and rate capability despite the high operating voltage and offering a new low-cost approach to develop surface-stabilized, high-voltage cathodes
- The redox energy of the lower-voltage couple increases while that of the higher-voltage couple decreases in olivine solid solutions $LiFe_{1-y}M_yPO_4$ (M = Mn or Co) compared to that in the unsubstituted $LiMPO_4$
- Synthesis of phosphate and silicate cathodes by a novel microwave-assisted solvothermal process
- Synthesis of nano-engineered alloy, carbon-decorated Fe_3O_4 nanowire, and graphene anodes, but only results on the cathodes are given in the next 11 slides

FACTORS INFLUENCING THE PERFORMANCE OF 4 V SPINELS

Mn content fixed at 1.7

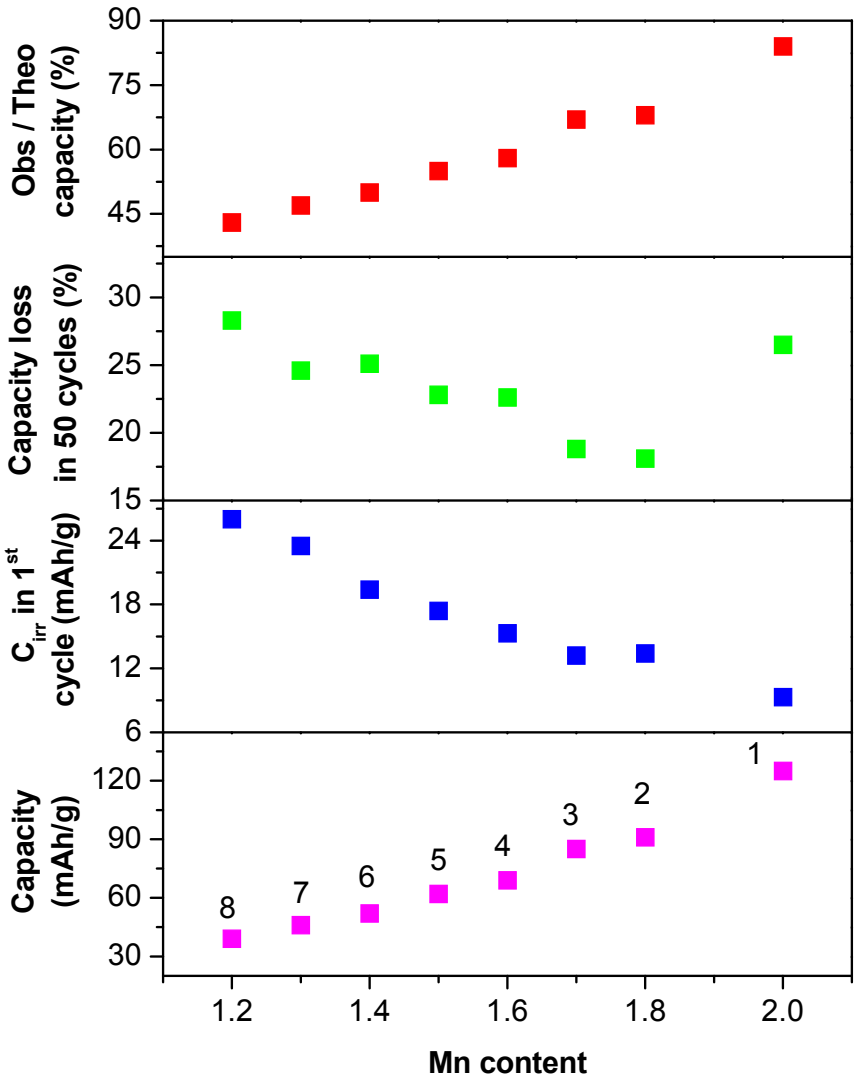


1. $LiMn_{1.7}Ni_{0.28}Ti_{0.02}O_4$
2. $LiMn_{1.7}Ni_{0.25}Ti_{0.05}O_4$
3. $LiMn_{1.7}Ni_{0.22}Ti_{0.08}O_4$
4. $LiMn_{1.7}Ni_{0.19}Ti_{0.11}O_4$
5. $LiMn_{1.7}Ni_{0.16}Ti_{0.14}O_4$
6. $LiMn_{1.7}Ni_{0.13}Ti_{0.17}O_4$
7. $LiMn_{1.7}Ni_{0.10}Ti_{0.20}O_4$
8. $LiMn_{1.7}Ni_{0.07}Ti_{0.23}O_4$

- As the Mn valence increases with a fixed Mn content of 1.7,
  - observed capacity value decreases
  - irreversible capacity (C_{irr}) loss decreases
  - capacity fade decreases
  - Mn dissolution decreases
  - observed/theoretical capacity ratio increases
- A Mn valence of > 3.6+ is desired to get good performance with spinel cathodes, but the capacity value is slightly sacrificed

FACTORS INFLUENCING THE PERFORMANCE OF 4 V SPINELS

Mn valence fixed at 3.5+

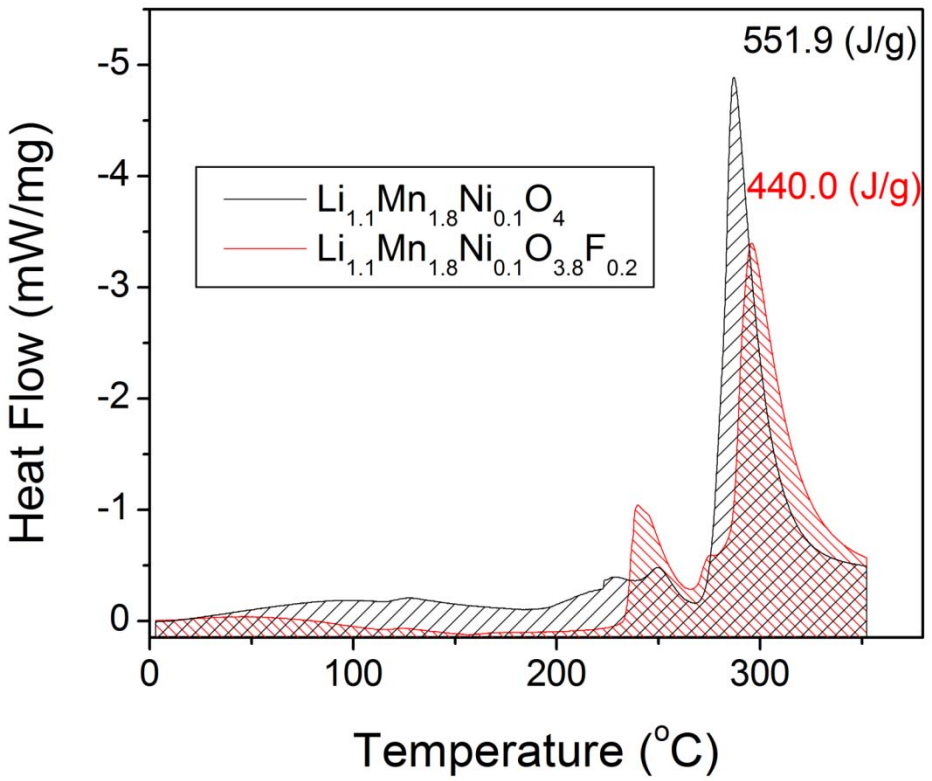


1. $LiMn_2O_4$
2. $LiMn_{1.8}Ni_{0.05}Ti_{0.15}O_4$
3. $LiMn_{1.7}Ni_{0.075}Ti_{0.225}O_4$
4. $LiMn_{1.6}Ni_{0.10}Ti_{0.30}O_4$
5. $LiMn_{1.5}Ni_{0.125}Ti_{0.375}O_4$
6. $LiMn_{1.4}Ni_{0.15}Ti_{0.45}O_4$
7. $LiMn_{1.3}Ni_{0.175}Ti_{0.525}O_4$
8. $LiMn_{1.2}Ni_{0.2}Ti_{0.6}O_4$

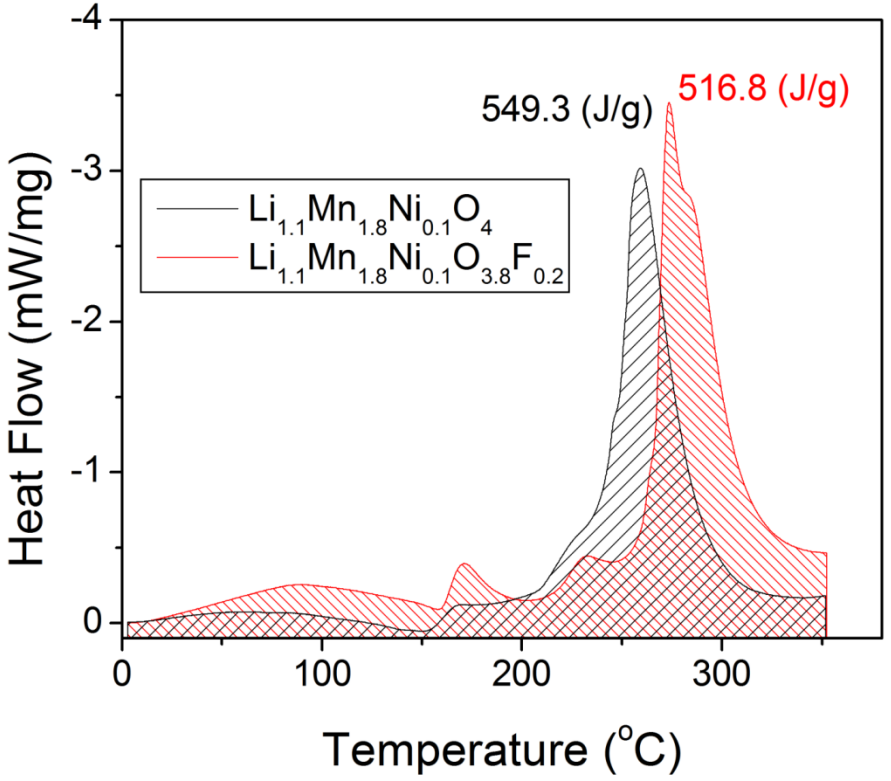
- As the Mn content decreases from 2 with a fixed Mn valence of 3.5+,
  - observed capacity value decreases
  - irreversible capacity (C_{irr}) loss increases
  - capacity fade increases
  - observed/theoretical capacity ratio decreases
- $LiMn_2O_4$ deviates from the capacity fade trend due to unperturbed Mn-Mn interaction and high Mn dissolution

THERMAL STABILITY OF 4 V OXYFLUORIDE SPINELS

DSC Plots in the discharge state



DSC Plots in the charged state

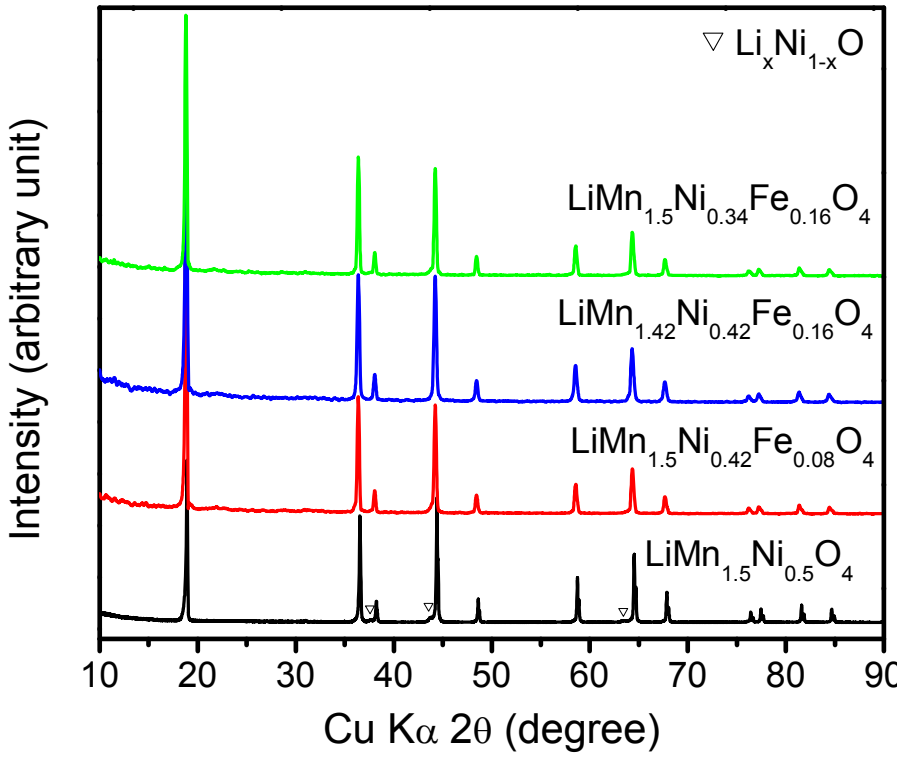


- Substitution of fluorine for oxygen increases the thermal stability in the charged and discharged states as indicated by the increase in DSC peak temperature and decrease in ΔH
- The spinel oxyfluoride cathodes offer the combination of higher capacity and better thermal stability compared to the oxide counterparts

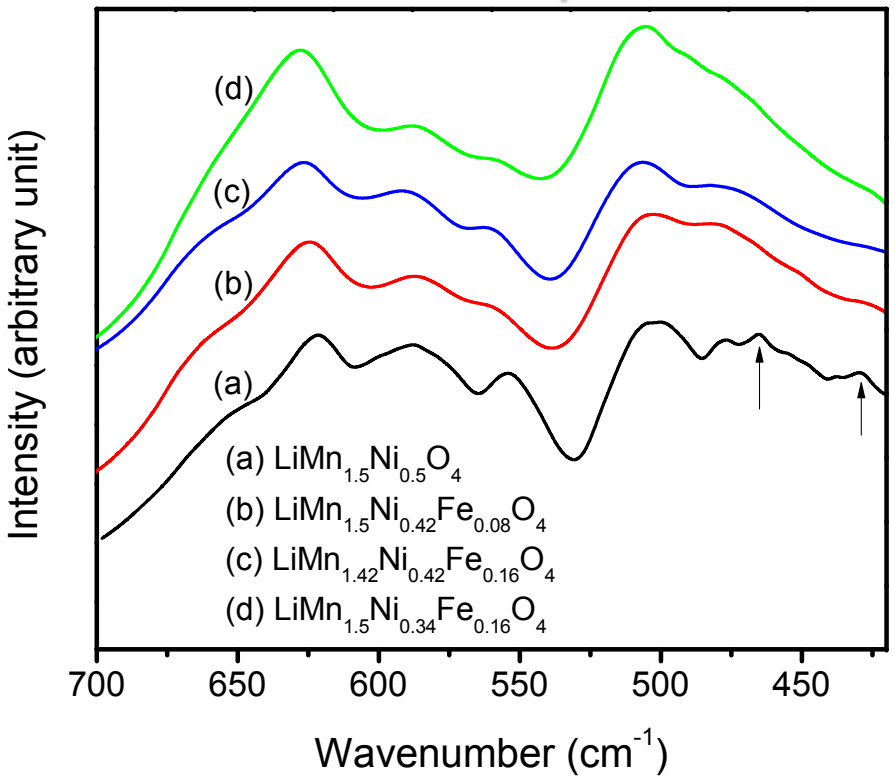
SELF-SURFACE SEGREGATED 5 V SPINELS

$Li[Mn_{1.5}Ni_{0.5-x}Fe_x]O_4$

X-ray Diffraction Patterns

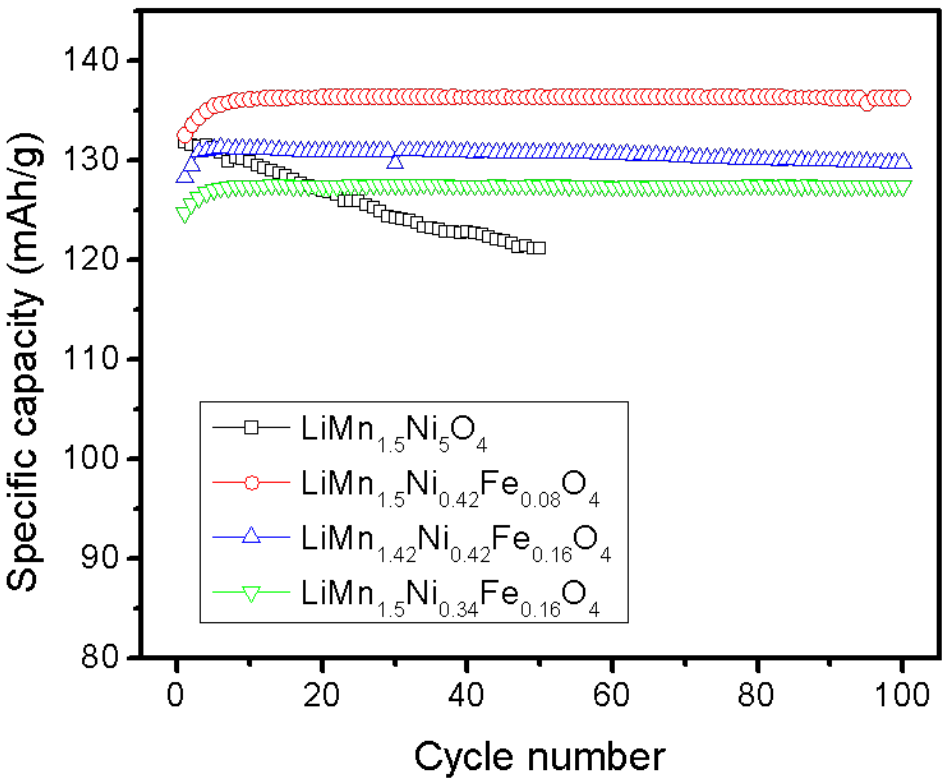


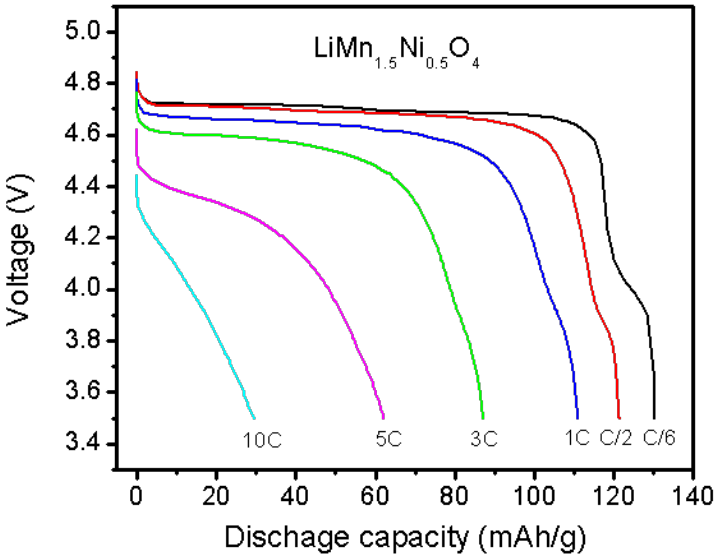
FTIR Spectra

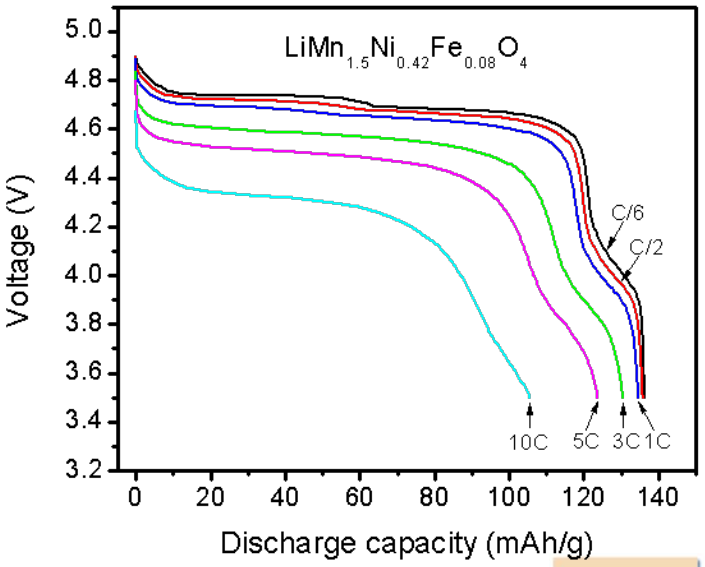


- $LiMn_{1.5}Ni_{0.5}O_4$ encounters the formation of NiO impurity and adopts the undesired, ordered $P4_332$ structure
- Fe substitution eliminates NiO impurity and stabilizes the desirable disordered Fd3m structure as indicated by the FTIR data with an Fe-enriched surface (see later)

CYCLABILITY AND RATE CAPABILITY OF $LiMn_{1.5}Ni_{0.5-x}Fe_xO_4$



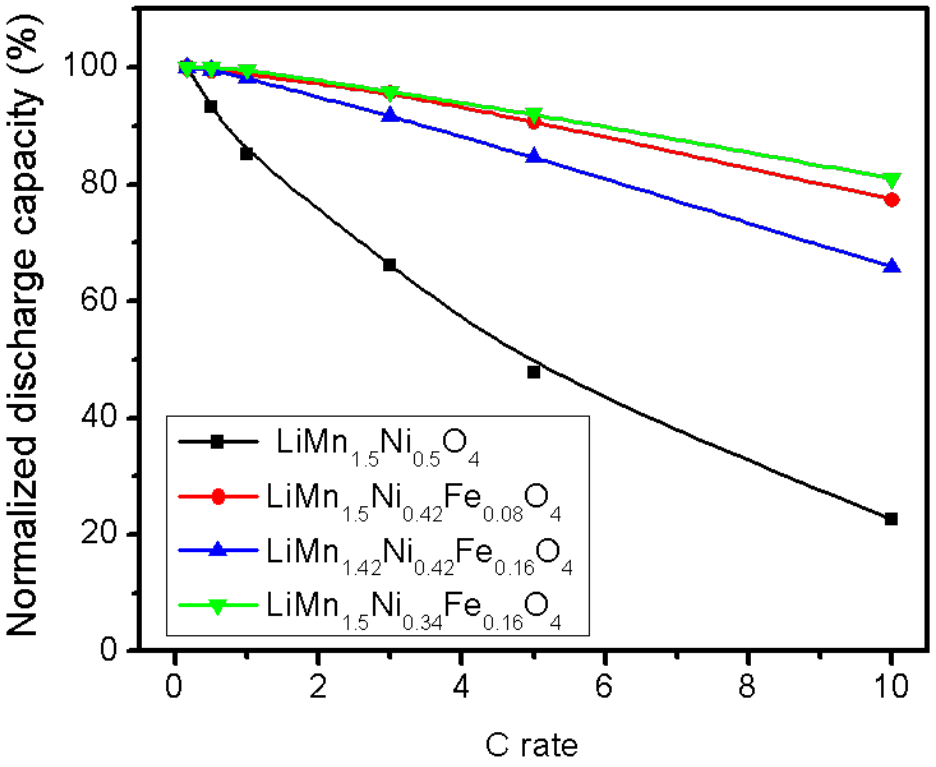




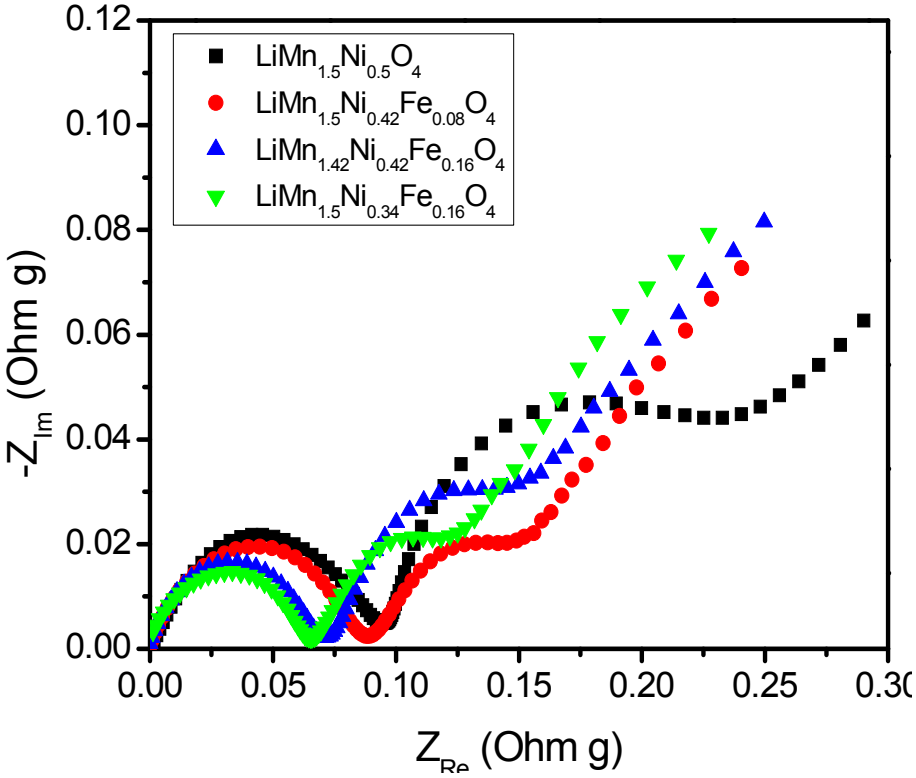
- $LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$ offers excellent cylability and rate capability without any external surface modification even though the operating voltage is high (4.8 V)
- Capacity value decreases for Fe content > 0.08
- With a higher capacity & voltage, it offers higher energy & power than 4 V spinel, making it attractive for vehicles

RATE CAPABILITY RETENTION AND EIS DATA OF $LiMn_{1.5}Ni_{0.5-x}Fe_xO_4$

Rate capability retention



Electrochemical impedance spectra (EIS)



- Rate capability retention was obtained by dividing the capacity obtained at various C rates after 50 cycles by the capacity obtained at the corresponding C rates after 3 cycles
- Fe-substituted samples exhibit remarkably higher rate capability retention than $LiMn_{1.5}Ni_{0.5}O_4$, *i.e.* the Fe-substituted samples retain the high rate capability as they are cycled
- The better rate capabilities of the Fe-substituted samples are due to lower impedance

ORIGIN OF BETTER CYCLABILITY AND RATE CAPABILITY

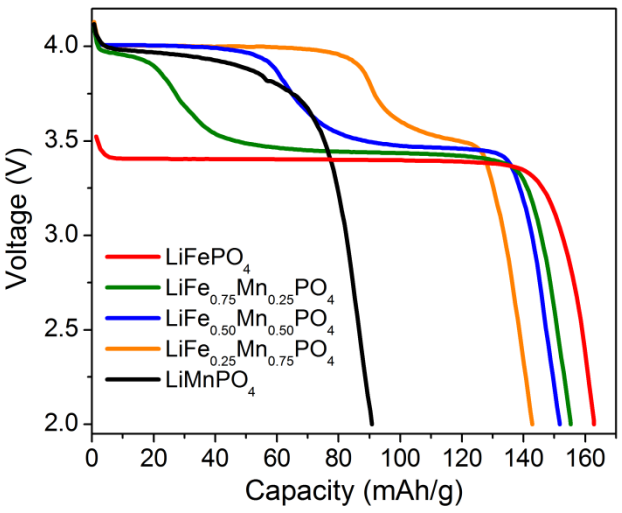
Concentrations of various ions on the surface of $LiMn_{1.5}Ni_{0.5-x}Fe_xO_4$ – XPS analysis

Quantity	$LiMn_{1.5}Ni_{0.5}O_4$		$LiMn_{1.5}Ni_{0.42}Fe_{0.08}O_4$		
	Mn	Ni	Mn	Ni	Fe
Nominal percentage	75	25	75	21	4
Surface percentage	77.8	22.2	73.5	16.4	10.1
Bulk percentage	75.2	24.8	74.9	20.9	4.2

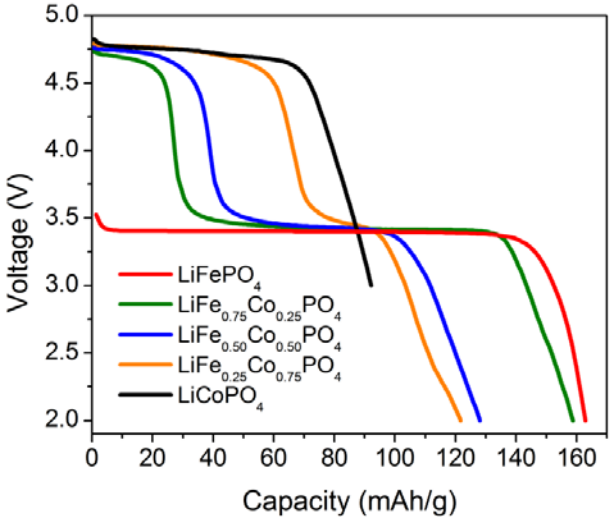
- Fe^{3+} segregates to the surface as Fe^{3+} prefers a lower coordination number (tetrahedral)
- Fe^{3+} enrichment on the surface suppresses SEI layer formation due to a decrease in the catalytic decomposition of the electrolyte at the high operating voltage of 4.8 V, which is consistent with the lower charge-transfer resistance found in the impedance data
- The finding offers a new strategy to overcome the instability of the cathode surface in contact with the electrolyte at high operating voltages
- The self-surface segregation during synthesis offers a low-cost manufacturing approach without requiring external, surface modification by solution-based methods

FACILE SYNTHESIS OF CARBON-COATED NANO-OLIVINES

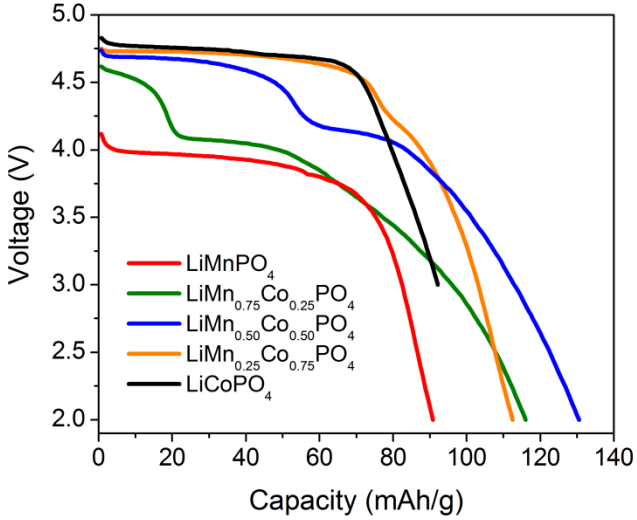
$LiFe_{1-y}Mn_yPO_4$ solid solution



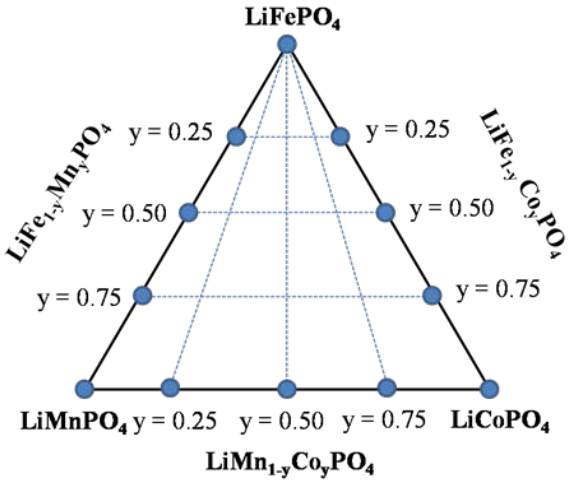
$LiFe_{1-y}Co_yPO_4$ solid solution



$LiMn_{1-y}Co_yPO_4$ solid solution



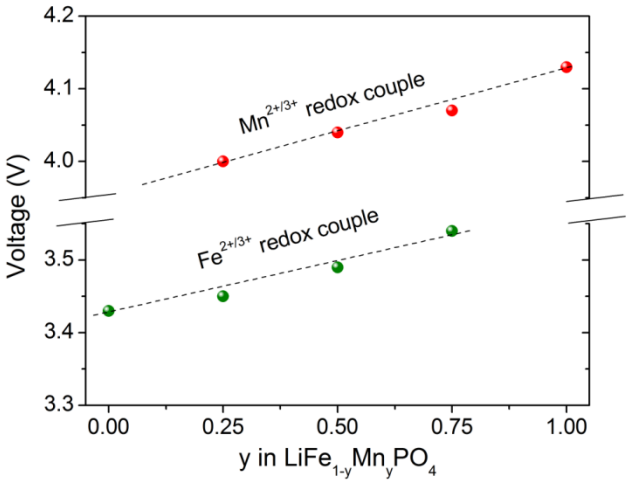
Compositions Investigated



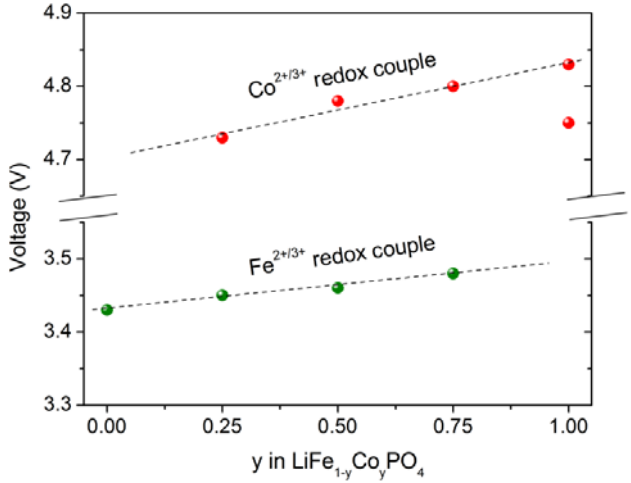
- Carbon-coated $LiM_{1-y}M_yPO_4$ synthesized by high-energy mechanical milling (HEMM) of the transition metal oxalates, Li_2CO_3, $NH_4H_2PO_4$, and super-p carbon for 10 h, followed by heating in argon at 550 °C for a short time of 6 h
- $LiM_{1-y}M_yPO_4$: C ratio is 80 : 20
- Represents an easy, low-cost synthesis approach
- Steps in the voltage profiles are characteristic of the different redox couples involved

SHIFTS IN THE REDOX POTENTIALS OF $LiM_{1-y}M_yPO_4$

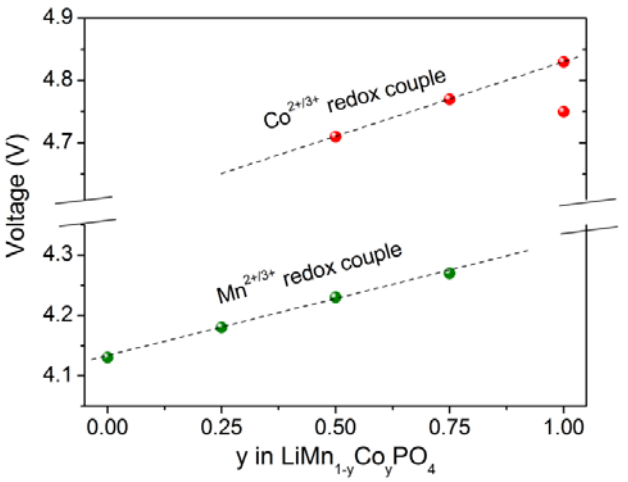
$LiFe_{1-y}Mn_yPO_4$ Solid solution



$LiFe_{1-y}Co_yPO_4$ Solid solution



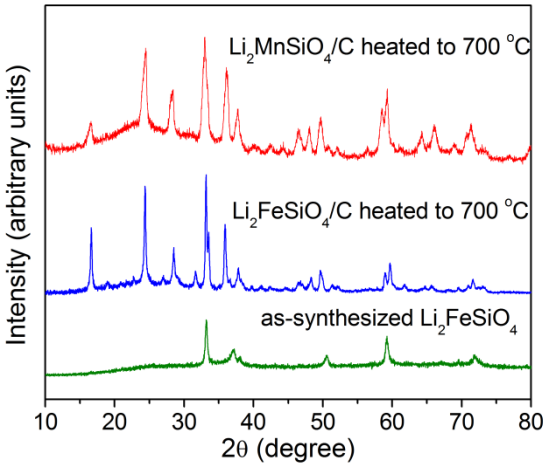
$LiMn_{1-y}Co_yPO_4$ Solid solution



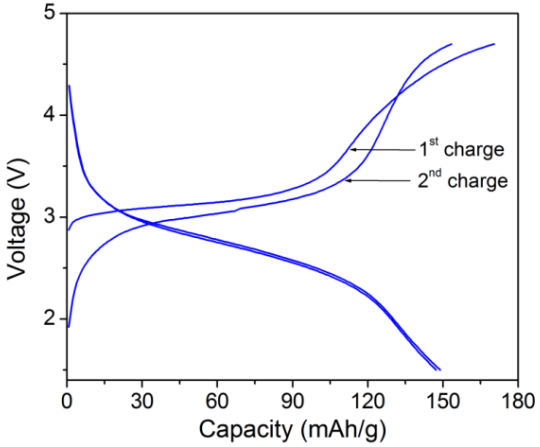
- The redox potential (open-circuit voltage) of a given $M^{2+/3+}$ couple in the $LiM_{1-y}M_yPO_4$ solid solution shifts systematically compared to that in the pristine $LiMPO_4$
- The potential of the lower-voltage couple increases while the potential of the higher-voltage couple decreases in the $LiM_{1-y}M_yPO_4$ solid solution compared to that in the pristine $LiMPO_4$
- Changes in the M-O covalence (inductive effect) play a role in shifting the redox potentials
- Substitution of less electropositive Co^{2+} for Fe^{2+} or Mn^{2+} decreases the Fe-O or Mn-O covalence and thereby lowers the $Fe^{2+/3+}$ or $Mn^{2+/3+}$ redox energy and increases the voltages of $Fe^{2+/3+}$ and $Mn^{2+/3+}$, while the substitution of more electropositive Fe^{2+} or Mn^{2+} for Co^{2+} increases the Co-O covalence and thereby raises the $Co^{2+/3+}$ redox energy and decreases the voltage of $Co^{2+/3+}$

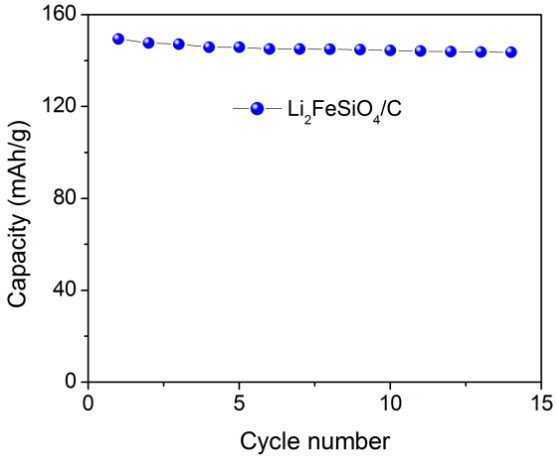
NOVEL MW-ST SYNTHESIS OF Li_2FeSiO_4/C NANOSPHERES

X-ray diffraction

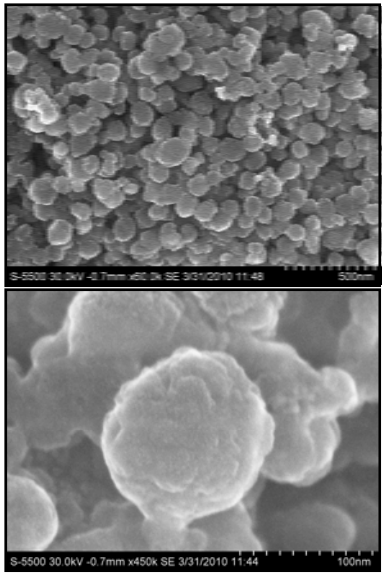


Electrochemical Performance of Li_2FeSiO_4/C





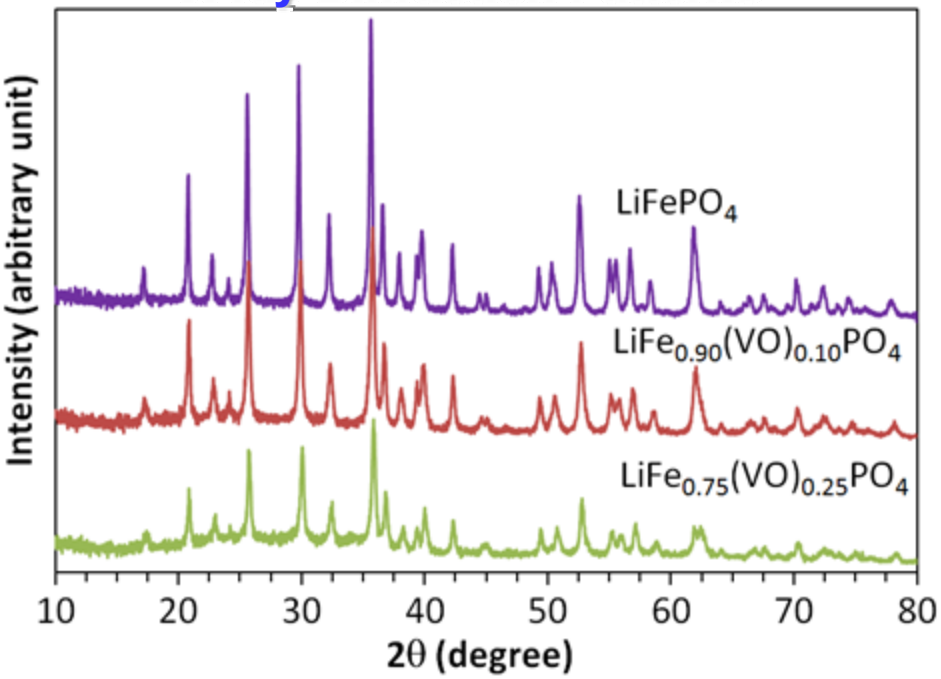
SEM of Li_2FeSiO_4/C nanospheres



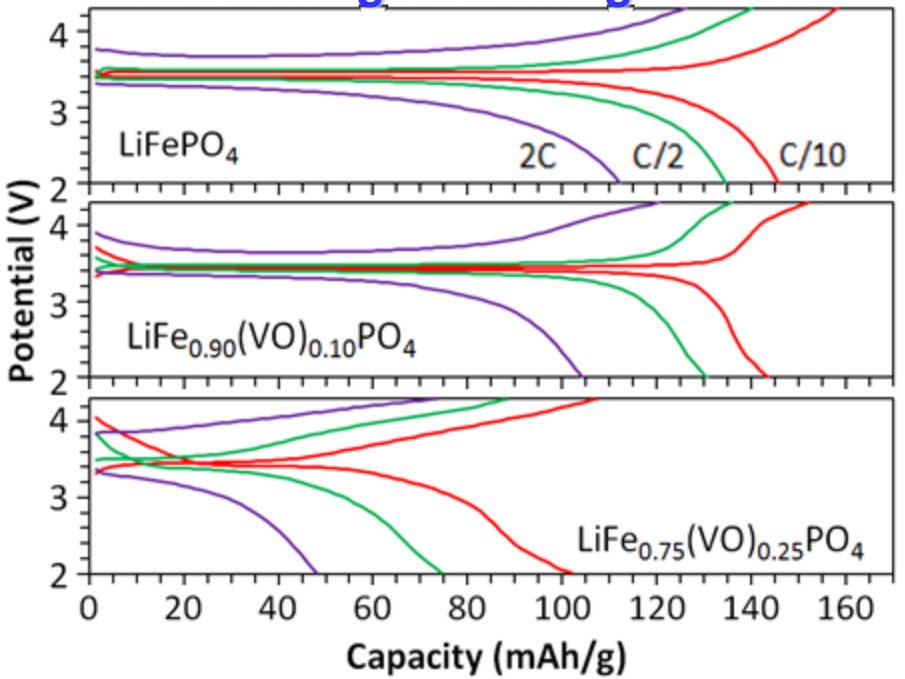
- Li_2MSiO_4 (M = Fe and Mn) offers two times higher theoretical capacity than $LiMPO_4$ due to the possibility of extracting/inserting two Li per formula unit
- Li_2MSiO_4 are synthesized by the microwave-assisted solvothermal (MW-ST) process we developed before for $LiMPO_4$ (M = Mn, Fe, Co, and Ni)
- However, Li_2FeSiO_4 needs post-annealing at 700 ^oC in argon to obtain a highly crystalline, pure sample
- Li_2FeSiO_4/C gives150 mAh/g with stable cycle life

MW-ST SYNTHESIS OF $LiFe_{1-x}(VO)_xPO_4$ SOLID SOLUTIONS

X-ray Diffraction Patterns



First Charge-Discharge Curves



- $LiFe_{1-x}(VO)_xPO_4$ (x = 0 to 0.25) were synthesized by a microwave-assisted solvothermal process (MW-ST) within a short reaction time of 10 min at < 300 °C without requiring post annealing at elevated temperatures in reducing gas atmospheres
- Change in lattice parameters confirm the formation of solid solutions
- The large sloping voltage profile of $LiFe_{0.75}(VO)_{0.25}PO_4$ suggests suppression of the two-phase behavior found in $LiFePO_4$

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Brookhaven National Laboratory – Dr. Kyung-Wan Nam
  - *In-situ* X-ray diffraction and X-ray absorption spectroscopy

- Stanford Linear Accelerator Center (SLAC) – Drs. Sumohan Misra & Michael Toney
  - *In-situ* diffraction experiments

- University of Texas at Austin – Professor John B. Goodenough
  - Discussion of experimental results

PROPOSED FUTURE WORK

- Continue to develop a fundamental understanding of the factors influencing the electrochemical performances of spinel cathodes and utilize the understanding to develop optimized spinel cathode compositions
- Identify the cations that self-segregate to the surface during synthesis process by examining the samples by XPS and high-resolution TEM, and utilize the information to develop 5 V cathodes that can offer a robust cathode-electrolyte interface
- Investigate systematically how the SEI layer (formation, thickness, and composition) changes with different surface-segregated cations in 5 V spinel cathodes
- Investigate systematically the thermal stability of oxyfluoride cathodes by DSC and establish whether fluorine substitution can be utilized to improve the safety
- Utilize the microwave-assisted solvothermal approaches to synthesize new polyanion cathodes such as Li_2MSiO_4 (M = Mn, Fe, Co, and Ni) and $Li_xM_2(PO_4)_3$ and assess the defect chemistry of the phases formed (kinetically stabilized phases)
- Develop a one-pot microwave-assisted solvothermal synthesis approach to obtain olivine-graphene or silicate-graphene nanocomposite cathodes

SUMMARY

- Mn valence and Mn content are found to play a critical role in determining the capacity value, capacity fade, Mn dissolution, and irreversible capacity loss in 4 V spinel cathodes; samples with Mn valence > 3.6+ offer superior performances
- Substitution of fluorine for oxygen improves the safety of spinel cathodes
- Certain cations like Fe^{3+} segregate to the surface during synthesis due to their preference for tetrahedral coordination, which leads to a more stable cathode-electrolyte interface with high-voltage cathodes like 5 V spinel, offering a viable, low-cost approach to develop high-voltage cathodes
- The redox energies of the couples are shifted in olivine solid solutions $LiFe_{1-y}M_yPO_4$ (M = Mn or Co) compared to that in their $LiMPO_4$ counterparts – lower-voltage couple potential increases and the higher-voltage couple potential decreases
- Li_2FeSiO_4 cathodes have been synthesized by a novel microwave-assisted solvothermal process
- Building on the fundamental understanding gained, our future work will continue focusing on developing high-performance spinel and polyanion cathodes