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**

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
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<tbody>
<tr>
<td>March 2009</td>
<td>Rapid synthesis and characterization of various phospho-olivines with controlled size and nanomorphologies</td>
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<tr>
<td>June 2009</td>
<td>Optimization of stabilized spinel-layered oxide composite cathodes</td>
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<tr>
<td>September 2009</td>
<td>New cathode materials based on polyanions</td>
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<tr>
<td>March 2010</td>
<td>Characterization of surface-modified, stabilized spinel cathodes</td>
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<tr>
<td>September 2010</td>
<td>Polyanion-containing cathodes with controlled nanomorphologies</td>
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• 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\textsubscript{1.7}Ni\textsubscript{0.28}Ti\textsubscript{0.02}O\textsubscript{4}
2. LiMn\textsubscript{1.7}Ni\textsubscript{0.25}Ti\textsubscript{0.05}O\textsubscript{4}
3. LiMn\textsubscript{1.7}Ni\textsubscript{0.22}Ti\textsubscript{0.08}O\textsubscript{4}
4. LiMn\textsubscript{1.7}Ni\textsubscript{0.19}Ti\textsubscript{0.11}O\textsubscript{4}
5. LiMn\textsubscript{1.7}Ni\textsubscript{0.16}Ti\textsubscript{0.14}O\textsubscript{4}
6. LiMn\textsubscript{1.7}Ni\textsubscript{0.13}Ti\textsubscript{0.17}O\textsubscript{4}
7. LiMn\textsubscript{1.7}Ni\textsubscript{0.10}Ti\textsubscript{0.20}O\textsubscript{4}
8. LiMn\textsubscript{1.7}Ni\textsubscript{0.07}Ti\textsubscript{0.23}O\textsubscript{4}

- As the Mn valence increases with a fixed Mn content of 1.7,
  - observed capacity value decreases
  - irreversible capacity (C\textsubscript{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+

- 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$_2$O$_4$ deviates from the capacity fade trend due to unperturbed Mn-Mn interaction and high Mn dissolution

1. LiMn$_2$O$_4$
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$_4$
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.
• LiMn$_{1.5}$Ni$_{0.5}$O$_4$ encounters the formation of NiO impurity and adopts the undesired, ordered P4$_3$32 structure
• Fe substitution eliminates NiO impurity and stabilizes the desirable disordered Fd3m structure as indicated by the FTIR data with an Fe-enriched surface (see later)
• LiMn$_{1.5}$Ni$_{0.42}$Fe$_{0.08}$O$_4$ offers excellent cyclability 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 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$_{0.5-x}$Fe$_x$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$_x$O$_4$ – XPS analysis

<table>
<thead>
<tr>
<th>Quantity</th>
<th>LiMn$<em>{1.5}$Ni$</em>{0.5}$O$_4$</th>
<th>LiMn$<em>{1.5}$Ni$</em>{0.42}$Fe$_{0.08}$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Nominal percentage</td>
<td>75</td>
</tr>
<tr>
<td>Ni</td>
<td>Surface percentage</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Bulk percentage</td>
<td>75</td>
</tr>
</tbody>
</table>

- 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

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$_{y}$PO$_4$

- The redox potential (open-circuit voltage) of a given M$^{2+/3+}$ couple in the LiM$_{1-y}$M$_{y}$PO$_4$ 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$_{y}$PO$_4$ 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$_2$FeSiO$_4$/C NANOSPHERES

**X-ray diffraction**

- Li$_2$MnSiO$_4$/C heated to 700 °C
- Li$_2$FeSiO$_4$/C heated to 700 °C
- as-synthesized Li$_2$FeSiO$_4$

**Electrochemical Performance of Li$_2$FeSiO$_4$/C**

- Voltage (V)
- Capacity (mAh/g)
- Cycle number

**SEM of Li$_2$FeSiO$_4$/C nanospheres**

- Li$_2$MSiO$_4$ (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$_2$MSiO$_4$ are synthesized by the microwave-assisted solvothermal (MW-ST) process we developed before for LiMPO$_4$ (M = Mn, Fe, Co, and Ni).

- However, Li$_2$FeSiO$_4$ needs post-annealing at 700 °C in argon to obtain a highly crystalline, pure sample.

- Li$_2$FeSiO$_4$/C gives 150 mAh/g with stable cycle life.
MW-ST SYNTHESIS OF LiFe$_{1-x}$(VO)$_{x}$PO$_4$ SOLID SOLUTIONS

- LiFe$_{1-x}$(VO)$_{x}$PO$_4$ ($x = 0$ 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$_4$.

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**X-ray Diffraction Patterns**

**First Charge-Discharge Curves**
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 Li₂MSiO₄ (M = Mn, Fe, Co, and Ni) and LiₓM₂(PO₄)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$_y$PO$_4$ (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$_2$FeSiO$_4$ 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.