HIGH-CAPACITY POLYANION CATHODES

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

June 17, 2014

Project ID #: ES051

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

### Timeline
- Project start date: January 2012
- Project end date: December 2015
- 50% complete

### Budget
- **Total project funding**
  - DOE: $1,120K
- **Funding for FY12**
  - $280K
- **Funding for FY13**
  - $280K
- **Funding for FY14**
  - $280K

### Barriers
- **Barriers**
  - Cost
  - Cycle life
  - Energy and power densities

### Targets
- High-capacity and high-voltage polyanion cathodes

### Partners
- None officially
Project Objectives

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

- To develop low-cost, thermally stable, high-energy density phosphate and silicate cathodes that offer multi-electron redox process with the insertion/extraction of more than one lithium per transition-metal ion

- To develop novel, low-temperature synthesis processes and doping strategies to obtain nanostructured phosphate and silicate cathodes as well as their nanocomposites with graphene to overcome the limitations of poor ionic and electronic conductivity

- To develop a fundamental understanding of the factors that control the electrochemical performances of polyanion cathodes
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2013</td>
<td>Synthesis and characterization of Li$_2$MP$_2$O$_7$ ($M = \text{Fe, Mn, Co, and Ni}$) as well as their solid solutions (Complete)</td>
</tr>
<tr>
<td>September 2013</td>
<td>Assessment of surface segregation in Li$<em>2$M$</em>{1-x}$Fe$_x$SiO$_4$ and Li$<em>2$M$</em>{1-x}$Fe$_x$P$_2$O$_7$ ($M = \text{Co, Mn, and Ni}$) (Complete)</td>
</tr>
<tr>
<td>December 2013</td>
<td>Establish whether or not LiMnPO$_4$ and LiCoPO$_4$ could be aliovalently doped with cations like V$^{3+}$ (Complete)</td>
</tr>
<tr>
<td>March 2014</td>
<td>Demonstrate &gt; 200 mAh/g capacity with LiVOPO$_4$ prepared by novel synthesis approaches (Complete)</td>
</tr>
</tbody>
</table>
APPROACH / STRATEGY

• Develop a firm understanding of the factors controlling the electrochemical performances of polyanion cathodes and utilize the understanding to develop high-performance cathodes for vehicle batteries
  
  - Novel synthesis approaches to obtain the three polymorphs (triclinic, orthorhombic, and tetragonal) of LiVOPO$_4$ that have the potential to insert/extract two lithium ions per formula unit (multi-electron redox process)

  - Integrate the nanostructured phosphate and silicate cathodes with graphene or conductive carbon to overcome the limitations of ionic and electronic transport

  - Aliovalently dope LiMnPO$_4$ (substitution of V$^{3+}$ for Mn$^{2+}$) by low-temperature synthesis approaches to enhance the electrochemical performances

  - Solid-state, template, and microwave-assisted synthesis approaches

  - Advanced chemical, structural, and surface characterizations

  - In-depth electrochemical characterization and evaluation

  - Understanding the structure-property-performance relationships
• The tetragonal form of LiVOPO$_4$ has been synthesized without any impurity phase by a microwave-assisted solvothermal synthesis process.

• Reversible insertion of more than one lithium into the three forms (triclinic, orthorhombic, and tetragonal) of LiVOPO$_4$ with a capacity of ~ 220 mAh/g has been demonstrated through systematic chemical and electrochemical lithiation processes and structural and chemical analyses of the lithiated phases at various stages.

• Aliovalent substitution of V$^{3+}$ for Mn$^{2+}$ in LiMnPO$_4$ has been found to drastically increase the capacity to 155 mAh/g and the samples have been characterized by soft X-ray absorption spectroscopy.

• Nanostructured Li$_2$MnSiO$_4$/C cathodes with periodic macroporosity synthesized with a hard-template approach exhibit stable cycling at high rates (1C rate).

• A reversible capacity of only ~ 100 mAh/g could be achieved with Li$_2$MP$_2$O$_7$ (M = Mn and Co) due to larger particle size.
**REVIEW OF THE LAST-YEAR WORK**

**High-voltage spinel LiMn_{1.5}Ni_{0.5}O_{4} cathodes**

- Particle morphology and surface facets were found to play a dominant role compared to other factors such as cation ordering in controlling the electrochemical properties of the high-voltage spinel cathodes.
- Two new methods (magnetic and discharge profile behavior below 3 V) were developed to determine the relative degree of cation ordering.

**Polyanion cathodes**

- A capacity of more than 200 mAh/g was demonstrated with LiVOPO_{4} and coating with conductive agents like PEDOT enhanced the performance.
- Li_{3}V_{2}(PO_{4})_{3}-graphene nanocomposite was shown to deliver close to 200 mAh/g.
- Li_{2}FeSiO_{4}-graphene nanocomposite exhibited reversible extraction of more than one lithium at 45 °C.

- This year we focus primarily on polyanion cathodes (phosphates and silicates).
Chemical analysis, structural changes, and decrease in the oxidation state of V (XANES data) confirm that an additional lithium can be inserted into α and β forms (triclinic and orthorhombic) of LiVOPO₄ to give Li₂VOPO₄.
ELECTROCHEMICAL LITHIATION OF α-LiVOPO₄ (TRICLINIC)

- XRD patterns at different depths of discharge demonstrate the insertion of an additional lithium at ~ 2.5 – 1.9 V into α-LiVOPO₄ with a capacity of ~ 140 mAh/g.
- Considering a capacity of ~ 100 mAh/g in the 4 V region, LiVOPO₄ exhibits a total capacity of > 200 mAh/g at ~ 4 – 2 V.
An additional lithium is inserted at a lower voltage of 2.2 – 1.6 V into \( \beta\)-LiVOPO\(_4\) compared to that in \( \alpha\)-LiVOPO\(_4\), exhibiting a total capacity of > 200 mAh/g at 4.0 – 1.6 V.
A third polymorph of LiVOPO$_4$ ($\alpha_1$ form; tetragonal) has been synthesized in phase-pure form by a microwave-assisted solvothermal (MW-ST) process. $\alpha_1$-LiVOPO$_4$/graphene nanocomposite obtained by the MW-ST process improves the electrical conductivity and offers a capacity of ~ 220 mAh/g at C/20 rate with the insertion of 1.4 Li per vanadium. The voltage profile corresponding to the insertion of the second lithium is more sloping compared to those in the other two LiVOPO$_4$ polymorphs (triclinic and orthorhombic) shown in the previous slides.
MICROWAVE SYNTHESIS OF ALIOVALENTLY DOPED LiMnPO₄

Table 2. ICP data for undoped and V-doped LiMnPO₄ prepared according to LiMn₁₋₃ₓ/₂Vₓ/₂PO₄

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li/Pᵃ</th>
<th>Mn/Pᵃ</th>
<th>V/Pᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMnPO₄</td>
<td>1.00</td>
<td>0.97</td>
<td>0.00</td>
</tr>
<tr>
<td>LiMn₀.₉₂₅V₀.₀₅PO₄</td>
<td>1.03</td>
<td>0.91</td>
<td>0.06</td>
</tr>
<tr>
<td>LiMn₀.₈₅V₀.₁₀PO₄</td>
<td>0.98</td>
<td>0.82</td>
<td>0.11</td>
</tr>
<tr>
<td>LiMn₀.₇₇₅V₀.₁₅PO₄</td>
<td>1.02</td>
<td>0.74</td>
<td>0.15</td>
</tr>
<tr>
<td>LiMn₀.₇₀V₀.₂₀PO₄</td>
<td>1.00</td>
<td>0.67</td>
<td>0.17</td>
</tr>
</tbody>
</table>

ᵃErrors in ICP ratios are estimated to be around 2 – 3 %.

- Chemical analysis and XRD confirm the substitution of significant amount of V³⁺ in LiMn₁₋₃ₓ/₂Vₓ/₂PO₄ (0 ≤ x ≤ 0.20) by a low-temperature microwave-assisted synthesis.
- Vanadium is distributed homogeneously in the nanorod (20 – 200 nm in length) morphology of LiMn₁₋₃ₓ/₂Vₓ/₂PO₄.
CHARACTERIZATION OF ALIOVALENTLY DOPED LiMnPO$_4$

- X-ray absorption near edge spectroscopy (XANES) reveals V$^{3+}$ and Mn$^{2+}$.
- Pre-edge feature indicates that the VO$_6$ octahedra are less distorted than in LiVOPO$_4$ but more distorted than in Li$_3$V$_2$(PO$_4$)$_3$.
- The V-doped samples disproportionate to give LiMnPO$_4$ and other vanadium-containing phases on heating to 575 ºC, demonstrating the necessity of the low-temperature microwave-assisted synthesis to realize aliovalent doping.
EFFECT OF ALIOVALENT DOPING ON PERFORMANCE

As-prepared at < 300 °C in 30 min

- Discharge capacity in the 4.1 V region increases with V content.
- A capacity of 155 mAh/g (close to theoretical value) could be obtained in the post-annealed x = 0.2 sample without any carbon coating!
ORIGIN OF IMPROVED PERFORMANCE WITH V DOPING

- Mn L-edge match that in MnF$_2$, evidencing that the oxidation state of Mn is unaffected by vanadium doping.
- Mn-O hybridization improves with V-doping in delithiated samples, which is the origin of the increased capacity with vanadium doping.
Li$_2$MnSiO$_4$ exhibits the potential for the extraction of two lithium, but hampered by extremely low electronic ($10^{-16}$ S/cm) and ionic conductivities.

Li$_2$MnSiO$_4$/C nanocomposite with periodic macropores obtained by using PMMA (polymethylmethacrylate) as a sacrificial hard-template exhibits ~ 100 mAh/g at a high rate of 1C rate and 45 °C.
FY 2013 REVIEWERS’ COMMENTS AND RESPONSE

• The overall comments by the reviewers were positive. The reviewers appreciated the overall approach, accomplishments, focus of the project on the technical barriers (cost, cycle life, and energy/power density), and collaboration with other institutions.

• Some of the comments including the electrolyte stability were focused towards the high-voltage spinel cathode since we presented last year some results on the high-voltage spinel. Our current work and the future work are focused mainly on polyanion cathodes that operate below 4.3 V, so electrolyte stability is not an issue.

• One reviewer asked whether all lithium is incorporated into the structure during synthesis and whether the samples are phase-pure. The lithium content values presented are based on our actual chemical analysis of the samples. Similarly, the X-ray diffraction data confirm that the samples are phase-pure without impurity phases.

• Another reviewer asked the timeline for prioritizing or ruling out. This is an exploratory research and we prioritize and rule out materials systems based on our results.
COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

• Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL) – Dr. Wanli Yang
  - Understanding of the variations in the characteristics of LiMnPO$_4$ cathodes by soft X-ray techniques on aliovalently doping with vanadium

• Brookhaven National Laboratory (BNL) – Dr. Feng Wang
  - Determination of the oxidation state of vanadium and manganese doped LiMnPO$_4$ by X-ray absorption near edge spectroscopy (XANES)

• Oak Ridge National Laboratory – Dr. Craig Bridges
  - Investigation of the crystal structure of lithiated LiVOPO$_4$ by spallation neutron source and synchrotron X-ray diffraction
PROPOSED FUTURE WORK

• Develop a comprehensive understanding of the structure-composition-performance relationships for the three polymorphs (triclinic, orthorhombic, and tetragonal) of LiVOPO$_4$ and determine which polymorph is the most promising to achieve the highest capacity with acceptable cyclability

• Synthesize LiVOPO$_4$/graphene nanocomposites with the three polymorphs by a single-step microwave-assisted solvothermal process involving the \textit{in situ} reduction of graphene oxide to overcome the low electronic and ionic conductivities and thereby realize a practical capacity of $\sim$ 250 mAh/g

• Based on our results on aliovalently doped LiFePO$_4$ and LiMnPO$_4$ with a substitution of V$^{3+}$ for Mn$^{2+}$, explore whether or not LiFePO$_4$ and LiMnPO$_4$ could be aliovalently doped with other cations such as tetravalent Ti$^{4+}$

• Explore the synthesis of nanocomposites consisting of aliovalently doped LiMPO$_4$ and graphene by a single-step microwave-assisted process

• Explore the aliovalent doping with other olivine cathodes like LiCoPO$_4$ as well as Li$_2$MSiO$_4$ and Li$_2$MP$_2$O$_7$ (M = Mn, Fe, Co, and Ni)
SUMMARY

• Systematic structural, chemical, spectroscopic, and electrochemical characterization of the chemically and electrochemically lithiated LiVOPO₄ cathodes demonstrate the reversible insertion of more than one lithium ion with a capacity of > 200 mAh/g with the three forms of LiVOPO₄.

• Significant amount of aliovalent V³⁺ has been substituted for Mn²⁺ in LiMn₁₋₃x/₂Vₓ/₂PO₄ (0 ≤ x ≤ 0.20) by a microwave-assisted synthesis process at < 300 °C, but the samples disproportionate to LiMnPO₄ on heating to 575 °C, demonstrating the necessity of the low-temperature method.

• Vanadium-doping in LiMnPO₄ drastically increases the capacity close to the theoretical value of 155 mAh/g due to enhanced Mn-O hybridization as revealed by soft X-ray spectroscopy.

• Li₂MnSiO₄/C nanocomposite with hierarchical macroporosity exhibits ~ 100 mAh/g at a high rate (1C rate).

• Li₂MP₂O₇ (M = Mn and Co) exhibits only ~ 100 mAh/g due to larger particle size, and the surface segregation in Li₂M₁₋ₓFeₓP₂O₇ (M = Mn and Co) could not be assessed as Fe could not be substituted.