HIGH-CAPACITY POLYANION CATHODES

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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

RELEVANCE

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

MILESTONES

Month/Year	Milestone
June 2013	Synthesis and characterization of $Li_2MP_2O_7$ (M = Fe, Mn, Co, and Ni) as well as their solid solutions (Complete)
September 2013	Assessment of surface segregation in $Li_2M_{1-x}Fe_xSiO_4$ and $Li_2M_{1-x}Fe_xP_2O_7$ (M = Co, Mn, and Ni) (Complete)
December 2013	Establish whether or not $LiMnPO_4$ and $LiCoPO_4$ could be aliovalently doped with cations like V^{3+} (Complete)
March 2014	Demonstrate > 200 mAh/g capacity with $LiVOPO_4$ prepared by novel synthesis approaches (Complete)

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

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

- 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_2MnSiO_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 $Li_2MP_2O_7$ (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.

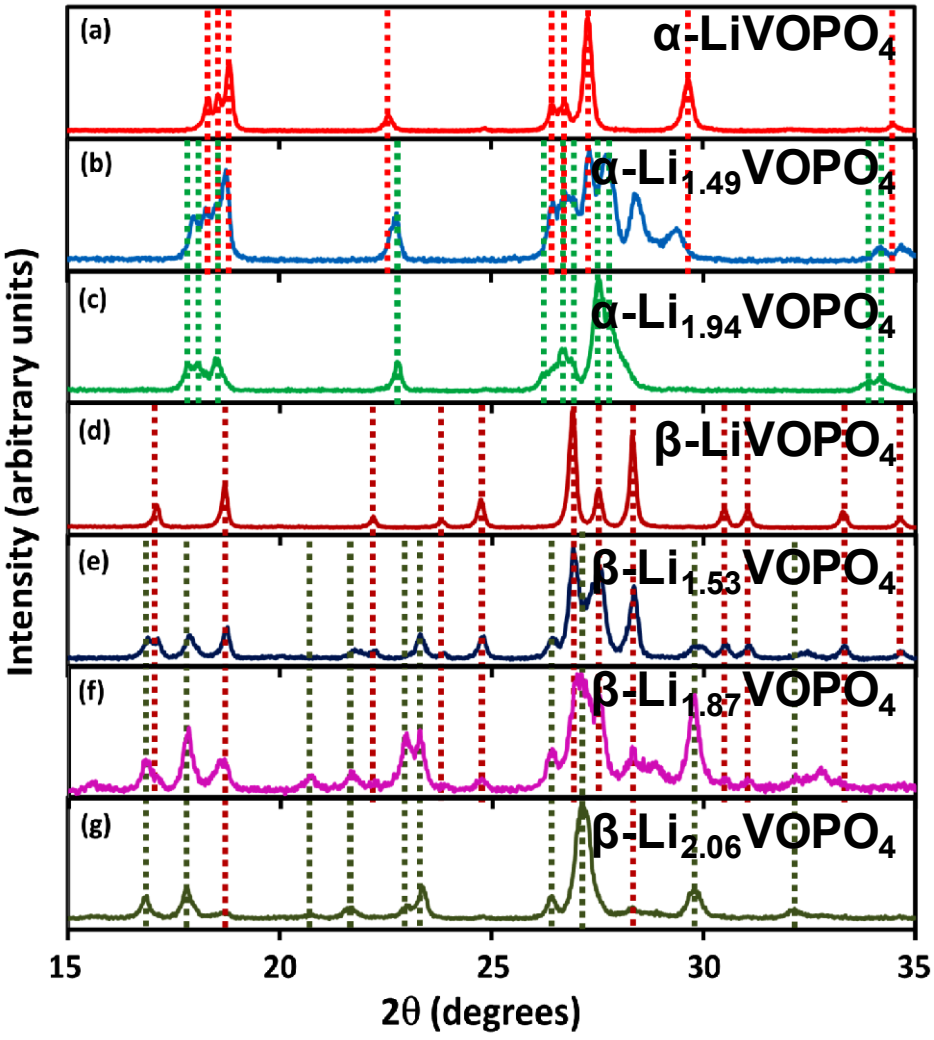
Polyanion cathodes

- A capacity of more than 200 mAh/g was demonstrated with $LiVOPO_4$ and coating with conductive agents like PEDOT enhanced the performance.
- $Li_3V_2(PO_4)_3$-graphene nanocomposite was shown to deliver close to 200 mAh/g.
- Li_2FeSiO_4-graphene nanocomposite exhibited reversible extraction of more than one lithium at 45 ^oC.

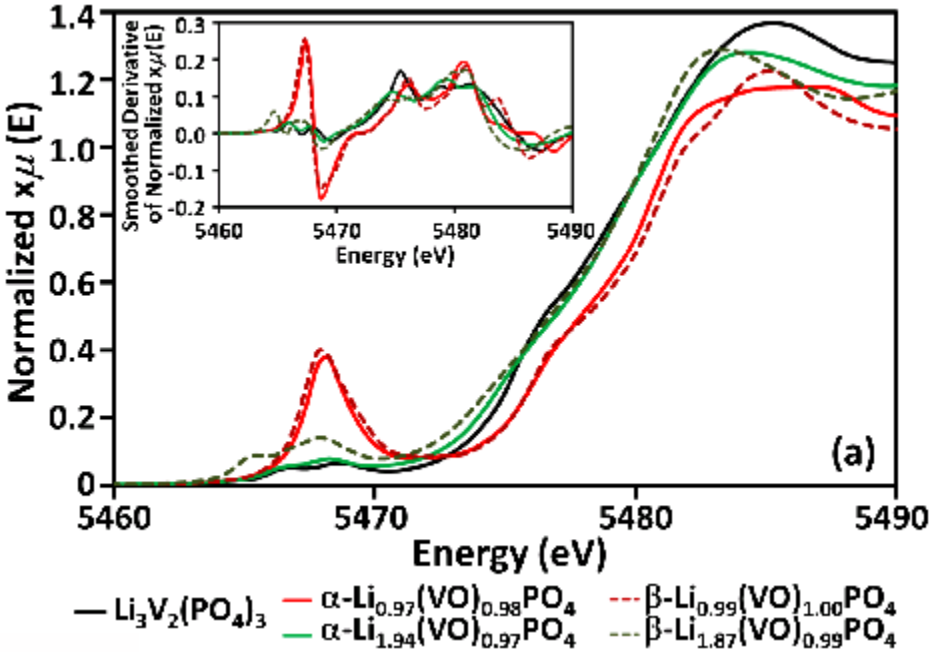
- This year we focus primarily on polyanion cathodes (phosphates and silicates).

CHEMICAL INSERTION OF AN ADDITIONAL Li INTO $LiVOPO_4$

X-ray diffraction (XRD) of chemically lithiated $LiVOPO_4$

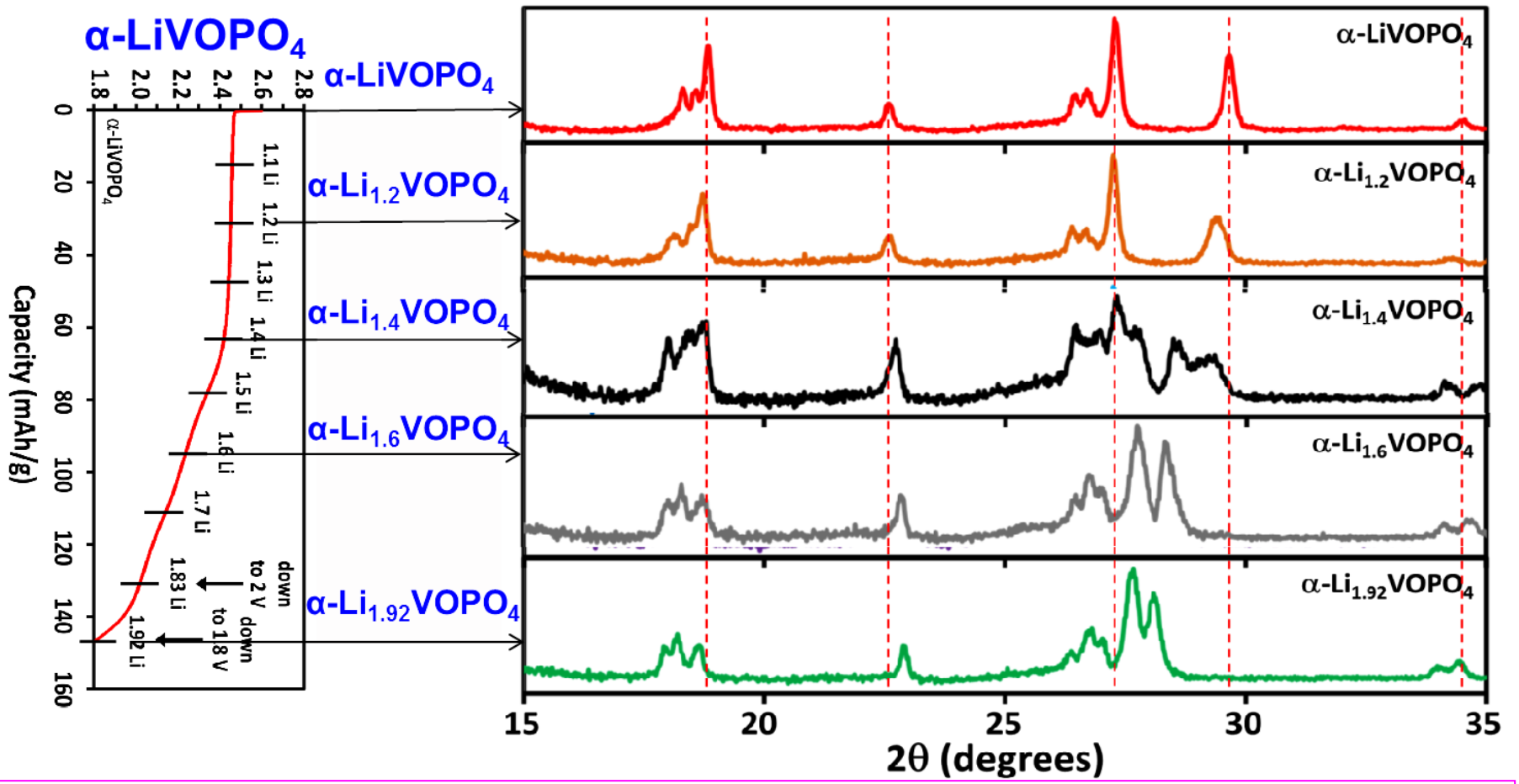


XANES of $LiVOPO_4$ before and after chemical lithiation



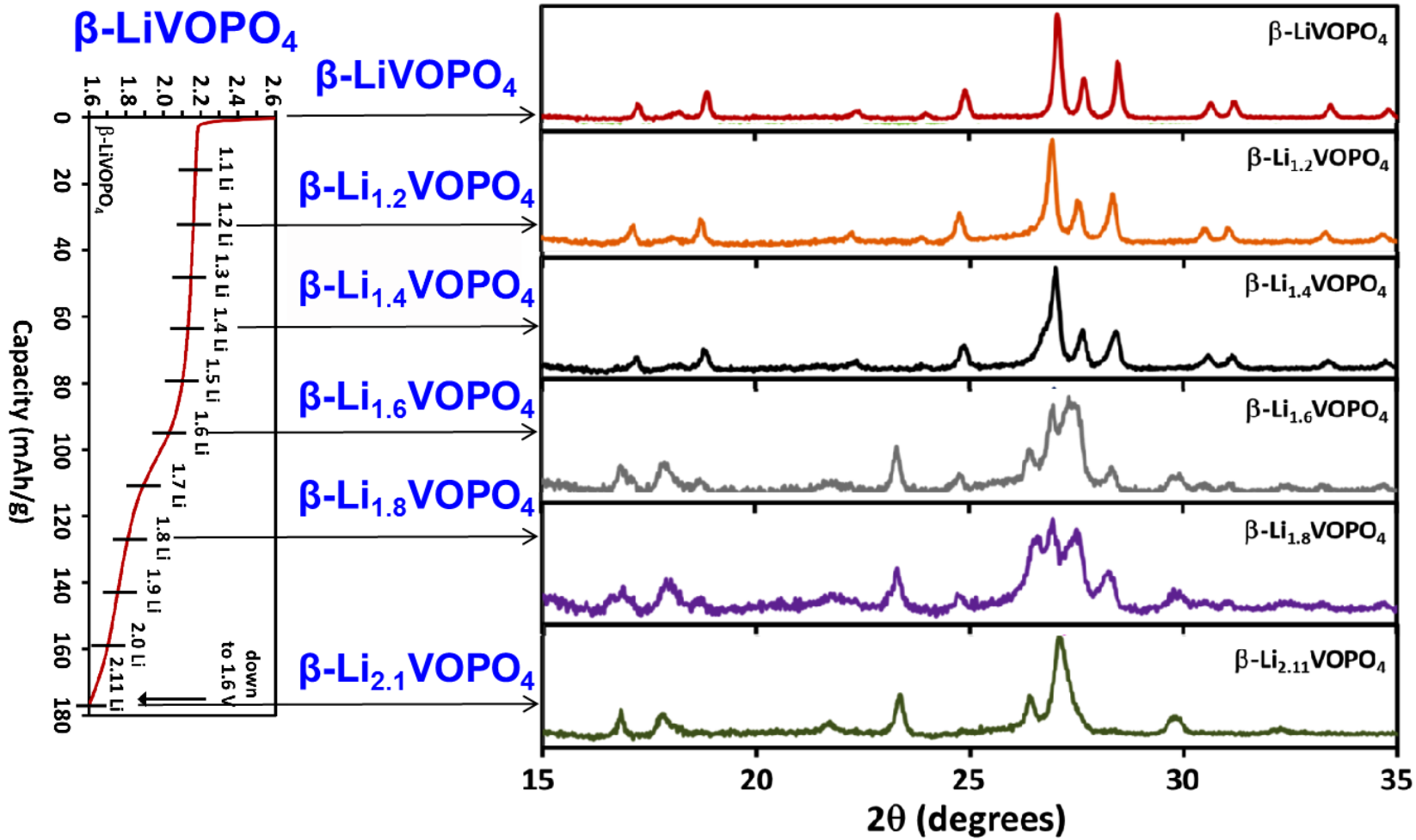
- Chemical analysis, structural changes, and decrease in the oxidation state of V (XANES data) confirm that an additional lithium can be inserted into α and β forms (triclinic and orthorhombic) of $LiVOPO_4$ to give Li_2VOPO_4.

ELECTROCHEMICAL LITHIATION OF α-$LiVOPO_4$ (TRICLINIC)



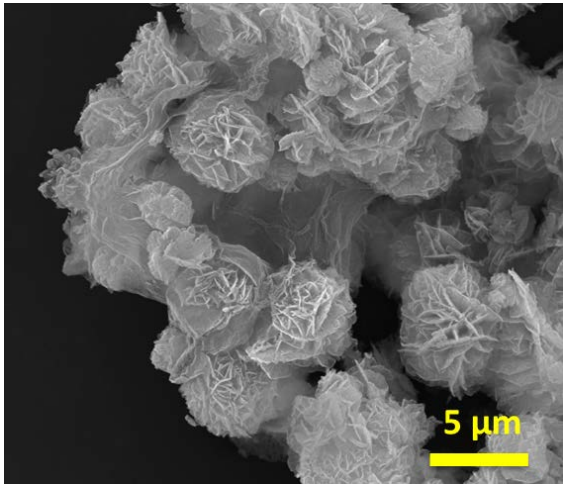
- XRD patterns at different depths of discharge demonstrate the insertion of an additional lithium at ~ 2.5 – 1.9 V into α-$LiVOPO_4$ with a capacity of ~ 140 mAh/g.
- Considering a capacity of ~ 100 mAh/g in the 4 V region, $LiVOPO_4$ exhibits a total capacity of > 200 mAh/g at ~ 4 – 2 V.

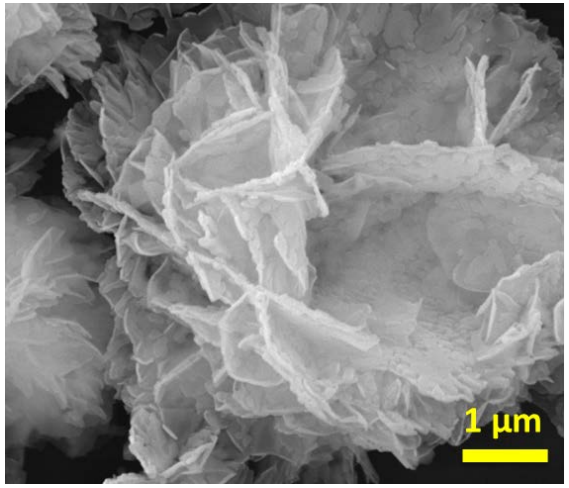
ELECTROCHEMICAL LITHIATION OF β-LiVOPO$_4$ (ORTHORHOMBIC)

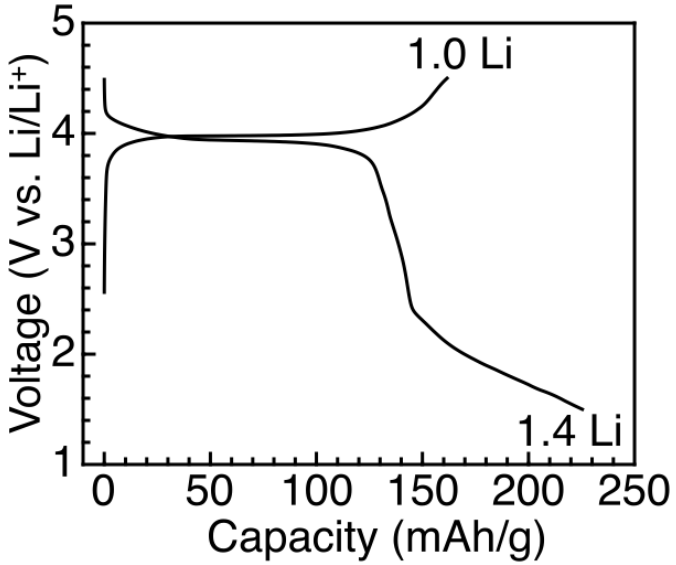


- An additional lithium is inserted at a lower voltage of 2.2 – 1.6 V into β-LiVOPO$_4$ compared to that in α-LiVOPO$_4$, exhibiting a total capacity of > 200 mAh/g at 4.0 – 1.6 V.

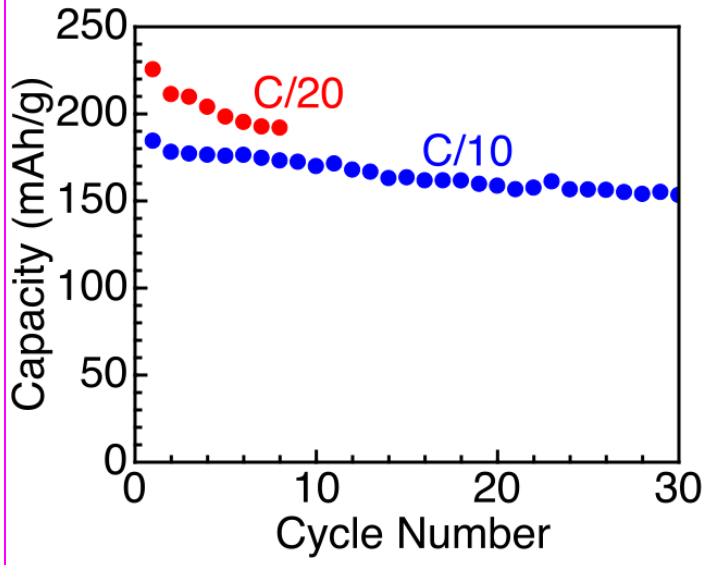
MICROWAVE-SYNTHESIS OF α_1-LiVOPO$_4$ (TETRAGONAL)



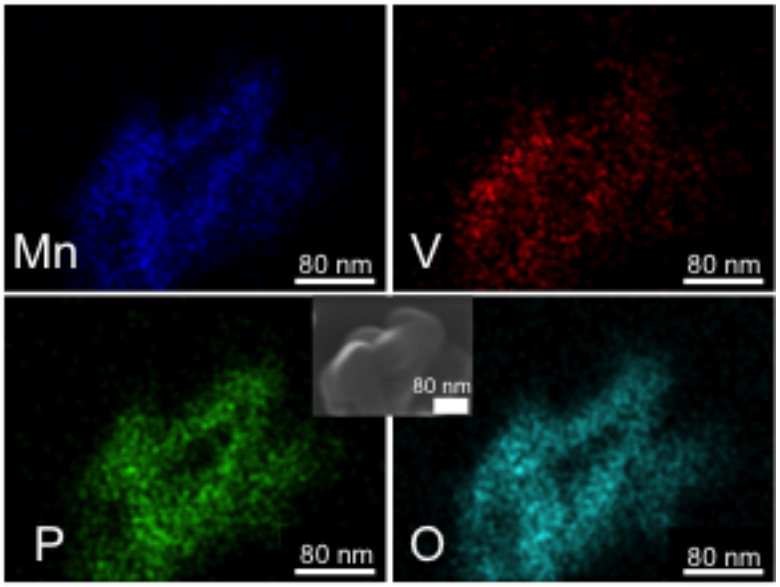




- A third polymorph of LiVOPO$_4$ (α_1 form; tetragonal) has been synthesized in phase-pure form by a microwave-assisted solvothermal (MW-ST) process.
- α_1-LiVOPO$_4$/graphene nanocomposite obtained by the MW-ST process improves the electrical conductivity and offers a capacity of ~ 220 mAh/g at C/20 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 $LiMnPO_4$



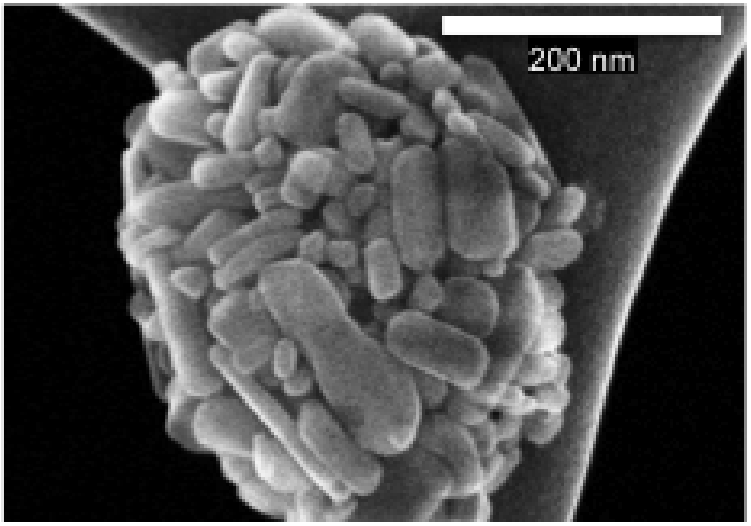


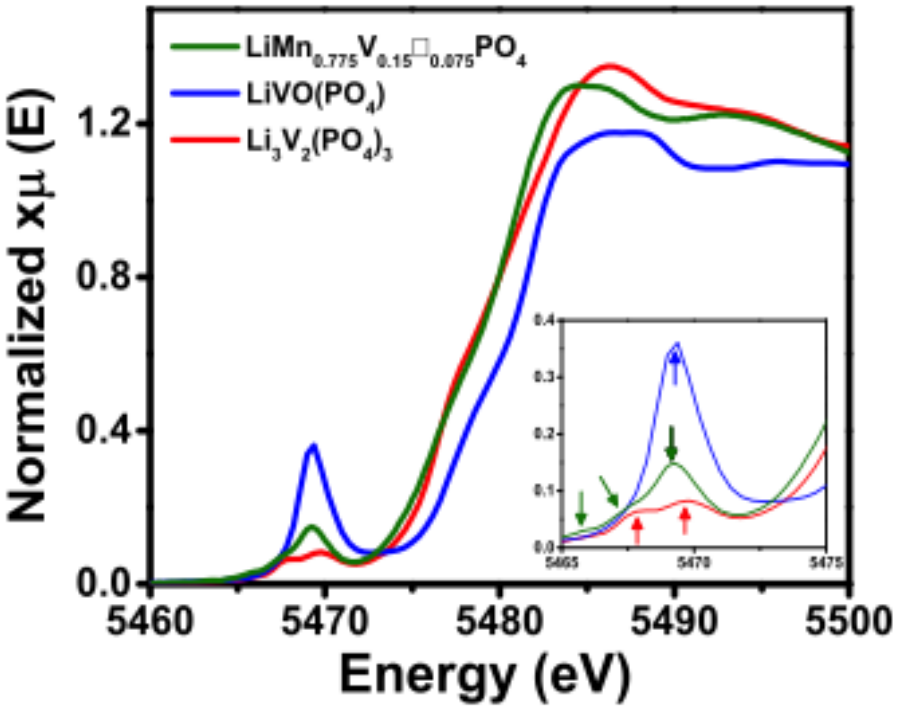
Table 2. ICP data for undoped and V-doped $LiMnPO_4$ prepared according to $LiMn_{1-3x/2}V_x\square_{x/2}PO_4$

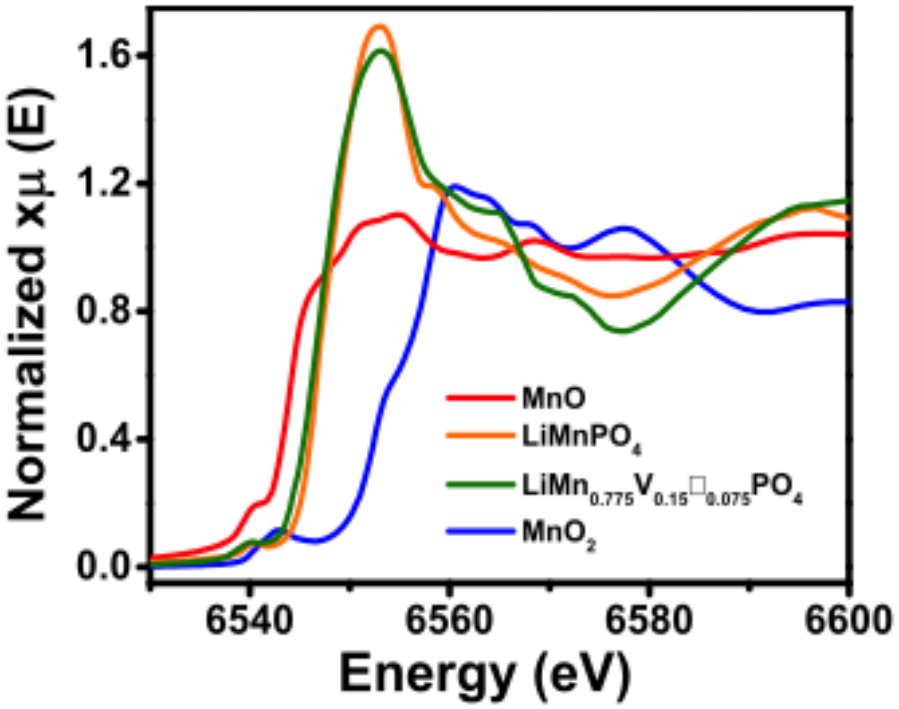
Sample	Li/P[a]	Mn/P[a]	V/P[a]
$LiMnPO_4$	1.00	0.97	0.00
$LiMn_{0.925}V_{0.05}PO_4$	1.03	0.91	0.06
$LiMn_{0.85}V_{0.10}PO_4$	0.98	0.82	0.11
$LiMn_{0.775}V_{0.15}PO_4$	1.02	0.74	0.15
$LiMn_{0.70}V_{0.20}PO_4$	1.00	0.67	0.17

[a]Errors in ICP ratios are estimated to be around 2 – 3 %.

- Chemical analysis and XRD confirm the substitution of significant amount of V^{3+} in $LiMn_{1-3x/2}V_x\square_{x/2}PO_4$ ($0 \le x \le 0.20$) by a low-temperature microwave-assisted synthesis.
- Vanadium is distributed homogeneously in the nanorod (20 – 200 nm in length) morphology of $LiMn_{1-3x/2}V_x\square_{x/2}PO_4$.

CHARACTERIZATION OF ALIOVALENTLY DOPED $LiMnPO_4$

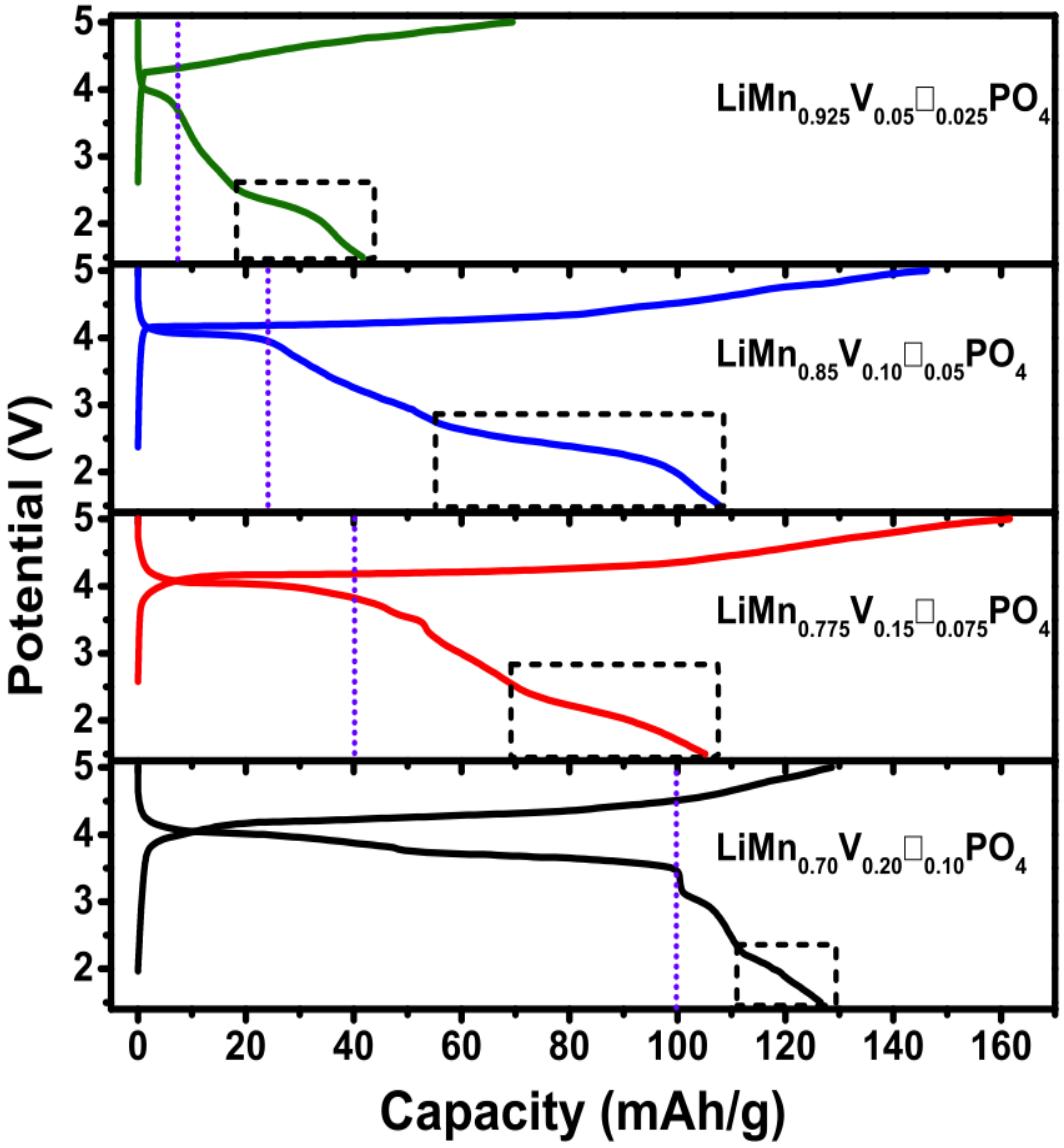




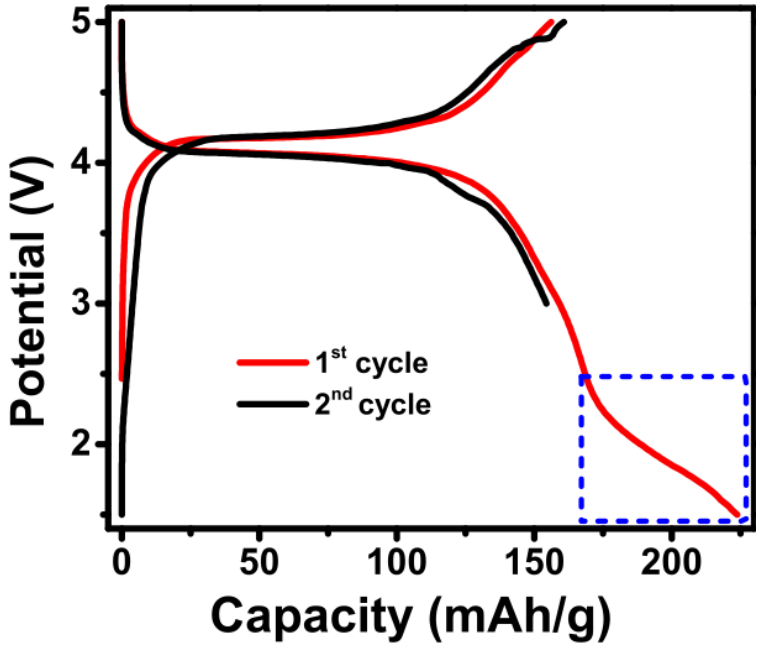
- X-ray absorption near edge spectroscopy (XANES) reveals V^{3+} and Mn^{2+}.
- Pre-edge feature indicates that the VO_6 octahedra are less distorted than in $LiVOPO_4$ but more distorted than in $Li_3V_2(PO_4)_3$.
- The V-doped samples disproportionate to give $LiMnPO_4$ and other vanadium-containing 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

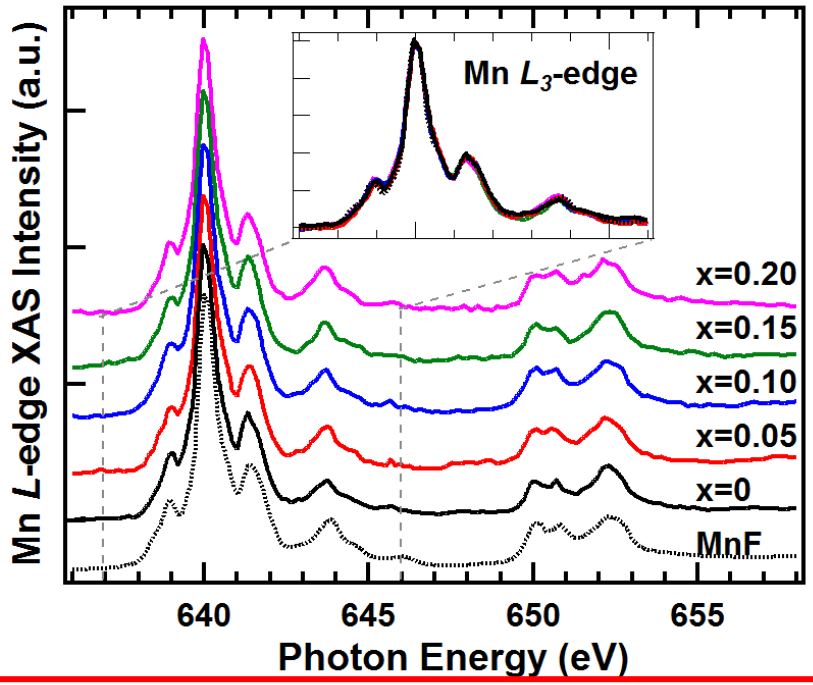


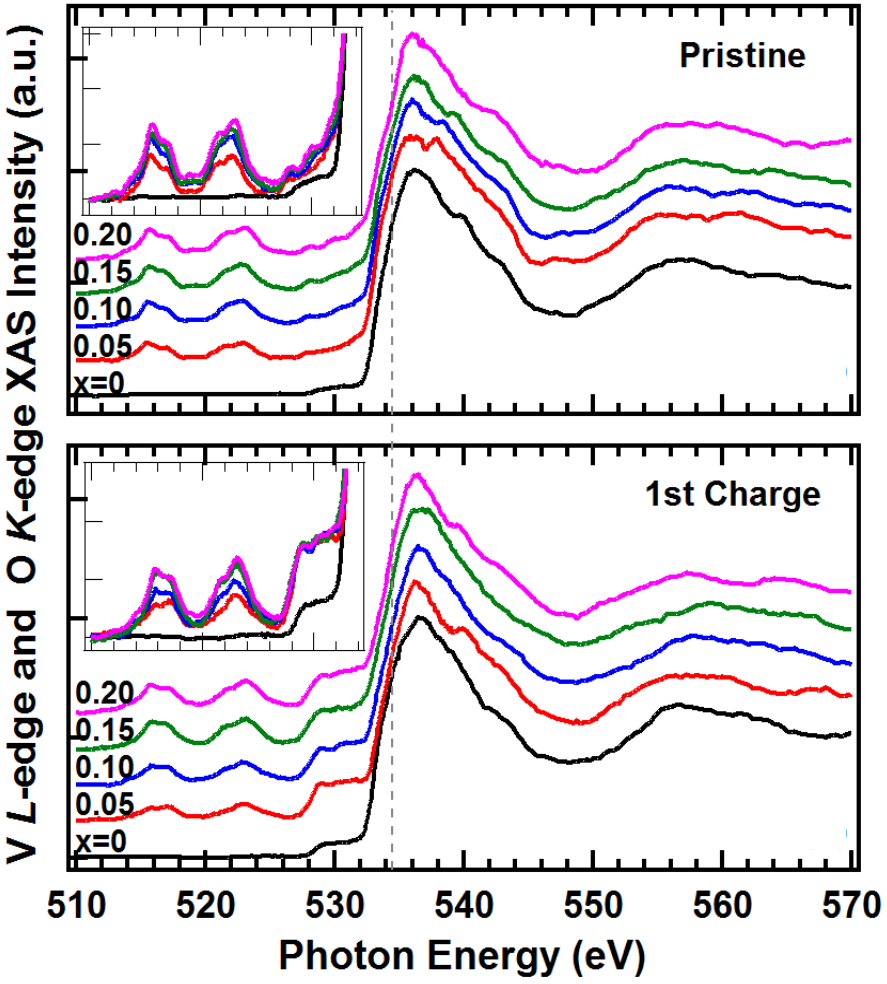
Post-heated to 525 °C



- 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!

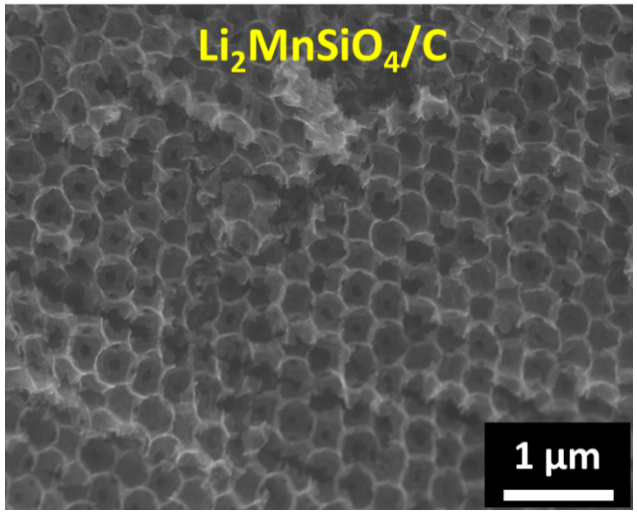
ORIGIN OF IMPROVED PERFORMANCE WITH V DOPING

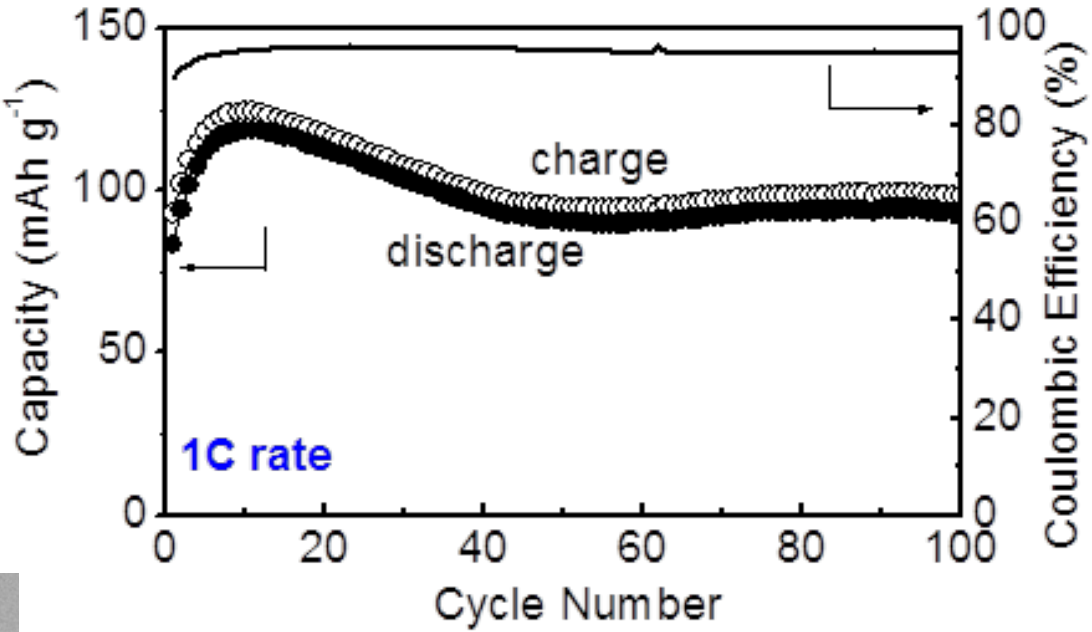


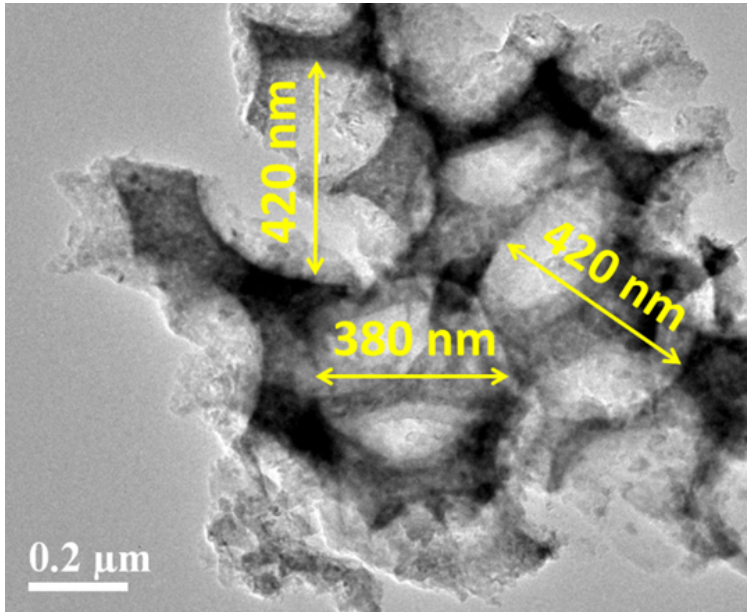


- Mn L-edge match that in MnF_2, evidencing that the oxidation state of Mn is unaffected by vanadium doping.
- Mn-O hybridization improves with V-doping in delithiated samples, which is the origin of the increased capacity with vanadium doping.

MACROPOROUS Li_2MnSiO_4/C NANOCOMPOSITE CATHODE







- Li_2MnSiO_4 exhibits the potential for the extraction of two lithium, but hampered by extremely low electronic (10^{-16} S/cm) and ionic conductivities.
- Li_2MnSiO_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 ºC.

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 *in situ* reduction of graphene oxide to overcome the low electronic and ionic conductivities and thereby realize a practical capacity of ~ 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_2MSiO_4 and $Li_2MP_2O_7$ (M = Mn, Fe, Co, and Ni)

SUMMARY

- Systematic structural, chemical, spectroscopic, and electrochemical characterization of the chemically and electrochemically lithiated $LiVOPO_4$ cathodes demonstrate the reversible insertion of more than one lithium ion with a capacity of > 200 mAh/g with the three forms of $LiVOPO_4$.
- Significant amount of aliovalent V^{3+} has been substituted for Mn^{2+} in $LiMn_{1-3x/2}V_x\square_{x/2}PO_4$ ($0 \le x \le 0.20$) by a microwave-assisted synthesis process at < 300 ^oC, but the samples disproportionate to $LiMnPO_4$ on heating to 575 ^oC, demonstrating the necessity of the low-temperature method.
- Vanadium-doping in $LiMnPO_4$ 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.
- Li_2MnSiO_4/C nanocomposite with hierarchical macroporosity exhibits ~ 100 mAh/g at a high rate (1C rate).
- $Li_2MP_2O_7$ (M = Mn and Co) exhibits only ~ 100 mAh/g due to larger particle size, and the surface segregation in $Li_2M_{1-x}Fe_xP_2O_7$ (M = Mn and Co) could not be assessed as Fe could not be substituted.