HIGH-VOLTAGE, HIGH-CAPACITY POLYANION CATHODES

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Project ID #: ES051

OVERVIEW

Timeline

- Project start date: January 2012
- Project end date: December 2015
- 75 % complete

Budget

- Total project funding
  - DOE: $1,120K
- Funding for FY14
  - $280K
- Funding for FY15
  - $280K

Barriers

- Barriers
  - Cost
  - Cycle life
  - Energy and power densities
- Targets
  - High-capacity, high-voltage polyanion cathodes

Partners

- None officially

RELEVANCE

Project Objectives

- To develop high-voltage, high-capacity 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 polyanion cathodes that can undergo **multi-electron redox process**

  - To develop novel synthesis approaches and doping strategies to obtain nanostructured phosphate cathodes with optimized microstructures to enhance ionic and electronic transport

  - To develop a fundamental understanding of the factors that influence the electrochemical performances of polyanion cathodes, employing both electrochemical and chemical lithiation/delithiation processes

MILESTONES

Month/Year	Milestone
June 2014	Demonstrate > 150 mAh/g capacity with $Li_9V_3(P_2O_7)_3(PO_4)_3$ prepared by novel synthesis approaches (Complete)
September 2014	Demonstrate > 150 mAh/g capacity with $Li_3M(CO_3)(PO_4)$ prepared by microwave-assisted synthesis (Complete)
December 2014	Demonstrate the synthesis of $LiVOPO_4$ nanoparticles with > 200 mAh/g capacity by employing ordered macroporous carbon as a hard-template (Complete)
March 2015	Demonstrate aliovalent doping with Ti^{4+} in $LiM_{1-2x}Ti_x\square_xPO_4$ with enhanced electrochemical properties by the microwave-assisted solvothermal synthesis (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

  - Develop novel synthesis approaches to obtain all three polymorphs (triclinic, orthorhombic, and tetragonal) of $LiVOPO_4$ that has the potential to insert/extract two lithium ions per formula unit (**multi-electron redox process**)

  - Analyze the electrochemically/chemically lithiated/delithiated $LiVOPO_4$ cathodes to understand the structural evolution and evaluate the possibility for multiple lithium-ion insertion/extraction

  - Explore aliovalent doping in $LiCoPO_4$ (substitution of V^{3+} for Co^{2+}) by low-temperature synthesis approaches to enhance the electrochemical performance

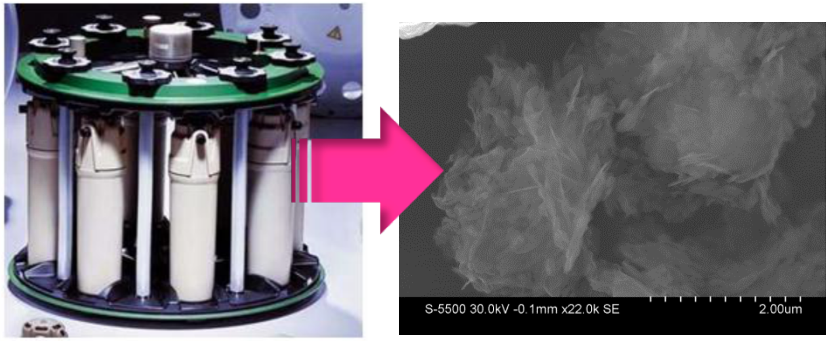
  - Solid-state, template, and microwave-assisted synthesis approaches
  - Advanced chemical, structural, and surface characterizations
  - In-depth electrochemical characterization and evaluation
  - Understanding the structure-property-performance relationships

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

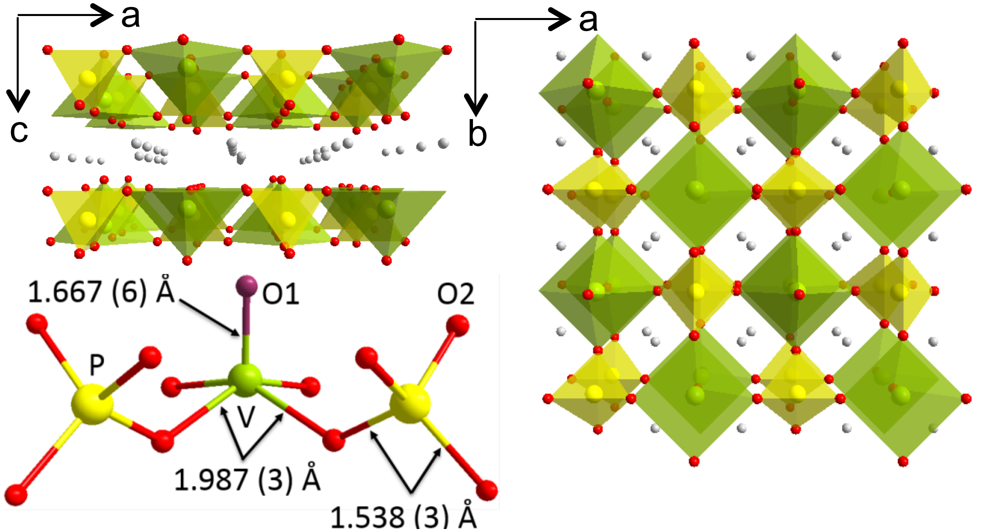
- The tetragonal $LiVOPO_4$ synthesized by a low-temperature microwave-assisted solvothermal synthesis process has been systematically studied
  - An additional lithium ion could be inserted into the structure either by electrochemical or chemical lithiation process, consistent with the findings with the other two forms of $LiVOPO_4$ (triclinic and orthorhombic)
  - Lithium diffusion is slower in triclinic $LiVOPO_4$ as evidenced by chemical delithiation experiments with the three polymorphs of $LiVOPO_4$
  - A new form of $VOPO_4$ with a layer structure has been obtained by delithiating the tetragonal $LiVOPO_4$
- A novel synthesis of triclinic $LiVOPO_4$ nanoparticles with conductive polymer coating offers reversible insertion of more than one lithium ion
- $Na_3MCO_3PO_4$ with M = Mn, Co, Ni, and Cu have been synthesized by the microwave approach at 220 ^{o}C, but good cell performance could not be obtained due to the lack of compatible electrolyte
- Aliovalent substitution of V^{3+} for Co^{2+} in $LiCoPO_4$ increases the capacity to ~ 100 mAh/g, reduces the polarization, and enhances cyclability

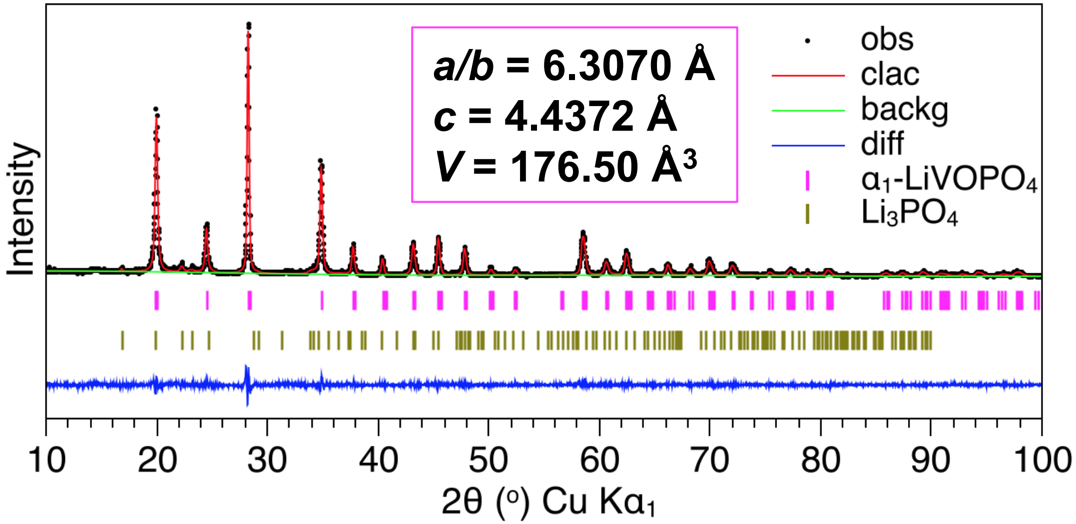
MICROWAVE SYNTHESIS OF METASTABLE α_1-$LiVOPO_4$

microwave synthesis of nanostructured α_1-$LiVOPO_4$



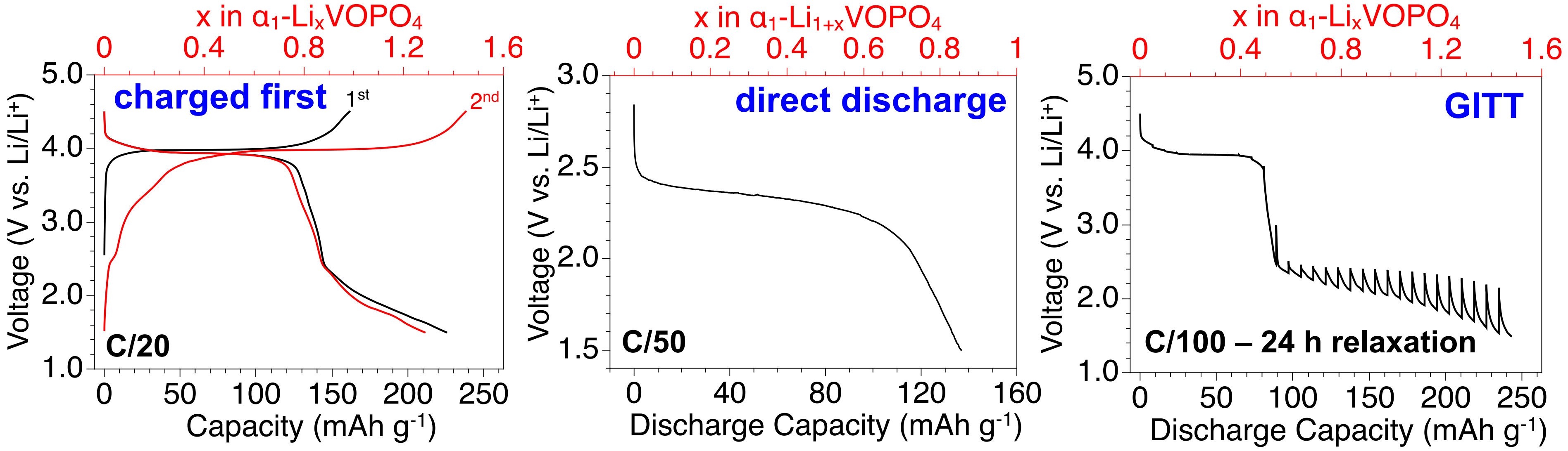
tetragonal (*P4/nmm*) with a layered structure



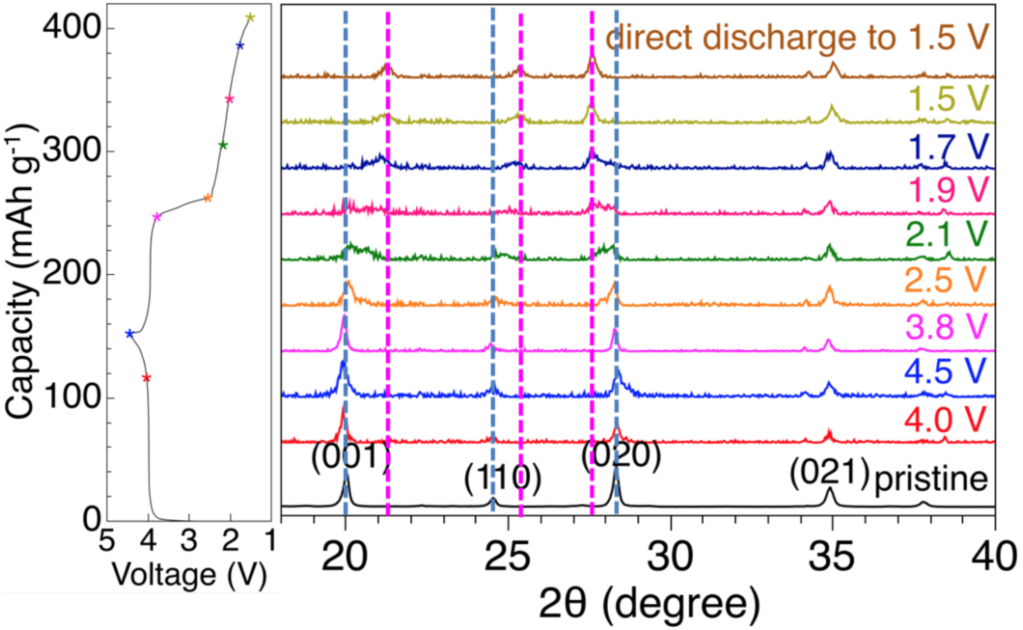


- Metastable α_1-$LiVOPO_4$ and α_1-$LiVOPO_4$/graphene have been synthesized by the microwave-assisted solvothermal (MW-ST) method
- Tetragonal α_1-$LiVOPO_4$ has a layered structure with lithium ions occupying ¼ of the *8j* sites between the $VOPO_4$ layers

ELECTROCHEMICAL LITHIATION OF α_1-LiVOPO$_4$

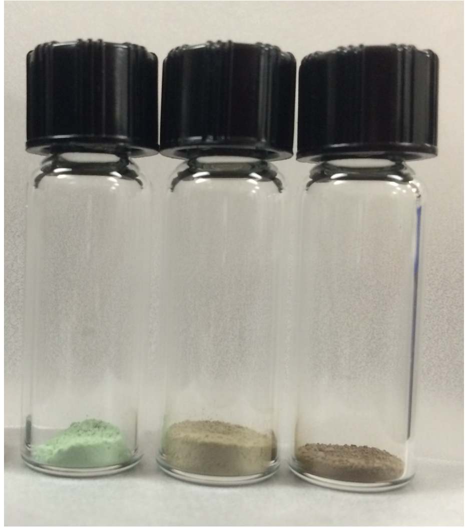


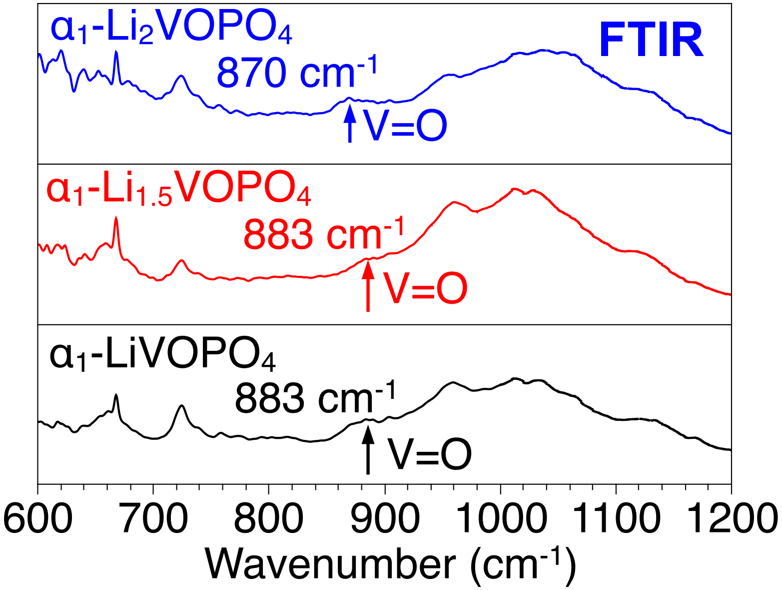
ex-situ XRD

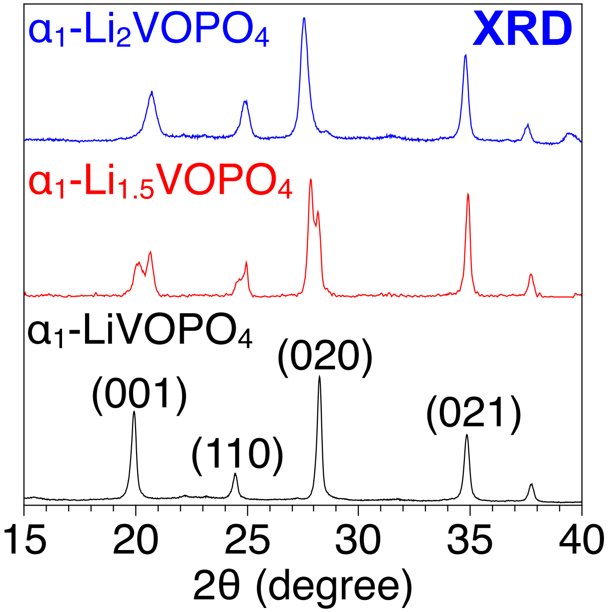


- 0.55 and 0.85 additional lithium could be inserted into α_1-LiVOPO$_4$, respectively, at C/20 and C/50 rates
- *Ex-situ* XRD patterns indicate a two-phase reaction for the insertion of the additional lithium ion. The sloping profile at low potentials is likely to be a result of slow kinetics of lithium insertion

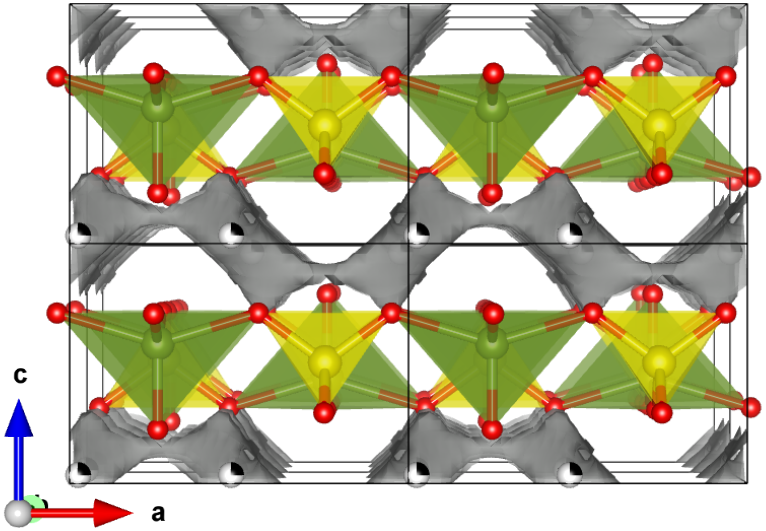
CHEMICAL LITHIATION OF α_1-$LiVOPO_4$ WITH n-BUTYLLITHIUM





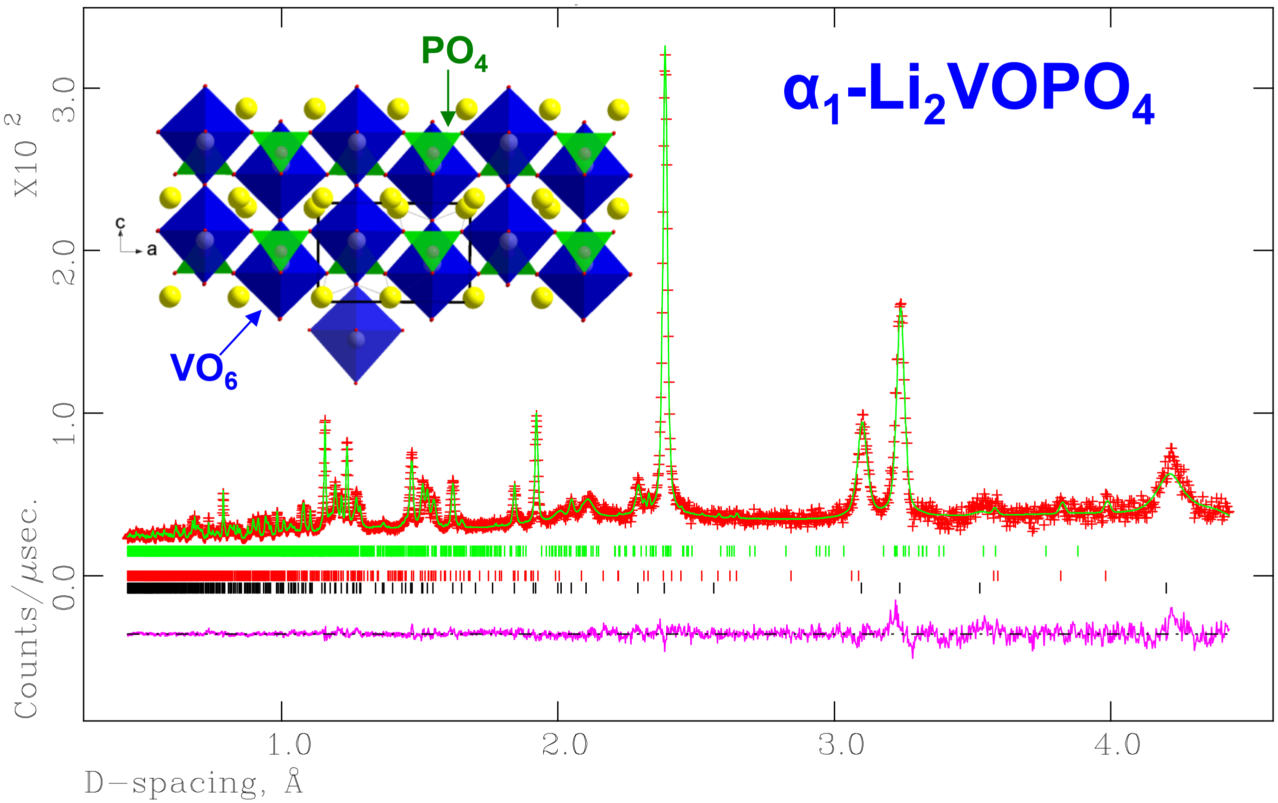


bond valence sum map



- The chemically lithiated α_1-$LiVOPO_4$ samples show color changes similar to that observed with the chemical lithiation of α- and β-$LiVOPO_4$
- Both FTIR and XRD confirm the structural change upon the lithiation of α_1-$LiVOPO_4$
- Bond valence sum map suggests that the additional lithium ion possibly takes the available *8j* sites as the original lithium ion

NEUTRON SCATTERING OF CHEMICALLY LITHIATED α_1-Li_2VOPO_4

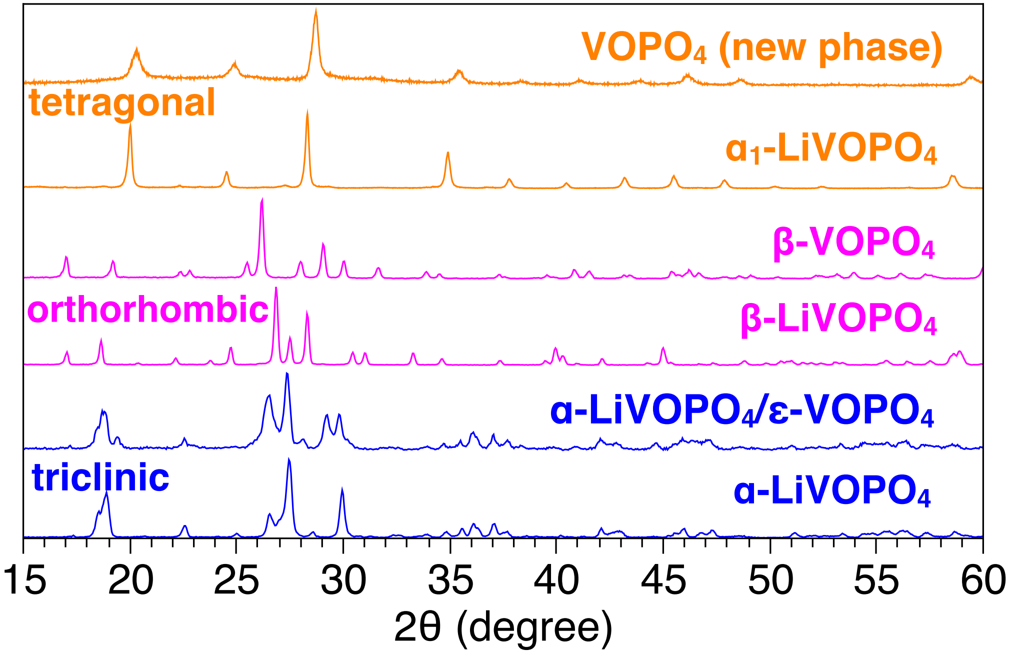


- Each VO_6 octahedron is connected to 2 other VO_6 by corner sharing to form chains
- The 2D layered structure of α_1-$LiVOPO_4$ is changed to a 3D structure in α_1-Li_2VOPO_4
- Volume change is < 0.5% on inserting the second lithium ion

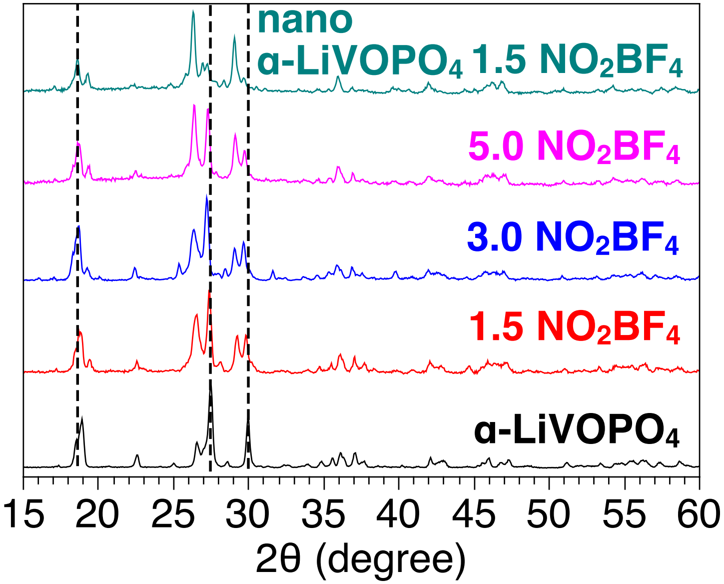
	space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å³)
α_1-$LiVOPO_4$	*P4/nmm*	6.3070(1)	6.3070(1)	4.4372(2)	176.50(1)
α_1-Li_2VOPO_4	*P4/nmm*	6.4796(2)	6.4796(2)	4.2135(2)	176.91(2)
Li_3PO_4: < 3%, α-$LiVOPO_4$: < 0.5%					

DELITHIATION OF THE THREE POLYMORPHS OF $LiVOPO_4$

XRD of delithiated $LiVOPO_4$ polymorphs



α-$LiVOPO_4$: effect of NO_2BF_4



- Complete delithiation is achieved with both α_1- and β-$LiVOPO_4$
- A new layered $VOPO_4$ phase is obtained on delithiating the α_1-$LiVOPO_4$
- Complete delithiation of α-$LiVOPO_4$ (triclinic) was not possible, indicating the difficulty of lithium diffusion in the structure

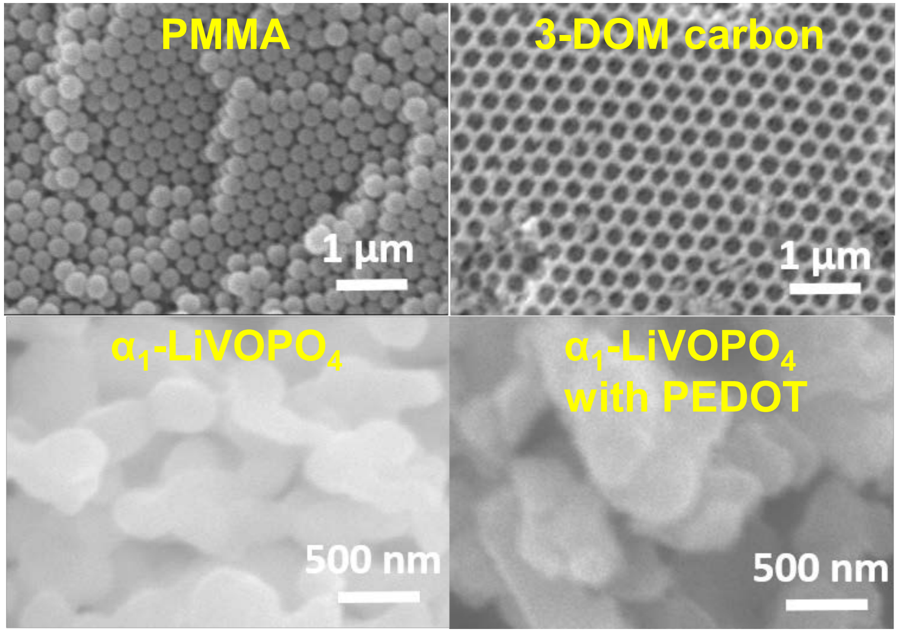
ICP results

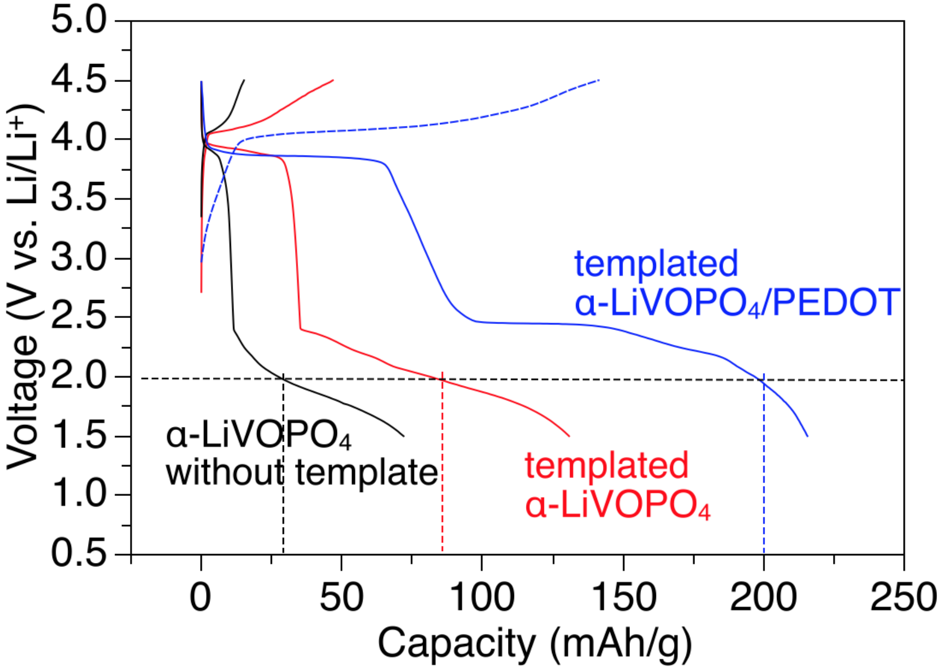
sample	NO_2BF_4	Li:P
nano α-$LiVOPO_4$	1.5	0.44:1
α-$LiVOPO_4$	5.0	0.49:1
α-$LiVOPO_4$	3.0	0.72:1
α-$LiVOPO_4$	1.5	0.81:1
β-$LiVOPO_4$	1.5	0.03:1
α_1-$LiVOPO_4$	1.5	0.03:1

TEMPLATED α-$LiVOPO_4$ WITH CONDUCTIVE POLYMER COATING

- α-$LiVOPO_4$ is not stable either during high speed ball-milling with carbon or under pyrolysis carbon-coating at 400 °C
- Nanosized α-$LiVOPO_4$/PEDOT was synthesized with a hard-template, followed by *in-situ* polymerization of EDOT
- Electrochemical results show a high capacity of ~ 220 mAh/g at C/20 rate with this optimized cathode, highlighting the significant influence of both particle size and conductive coating

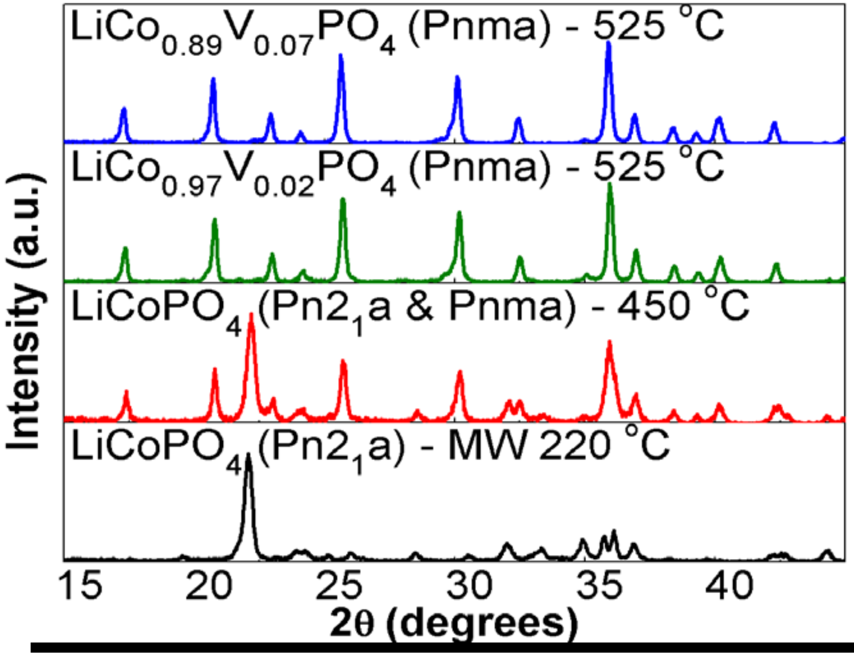
nanostructured α-$LiVOPO_4$/PEDOT

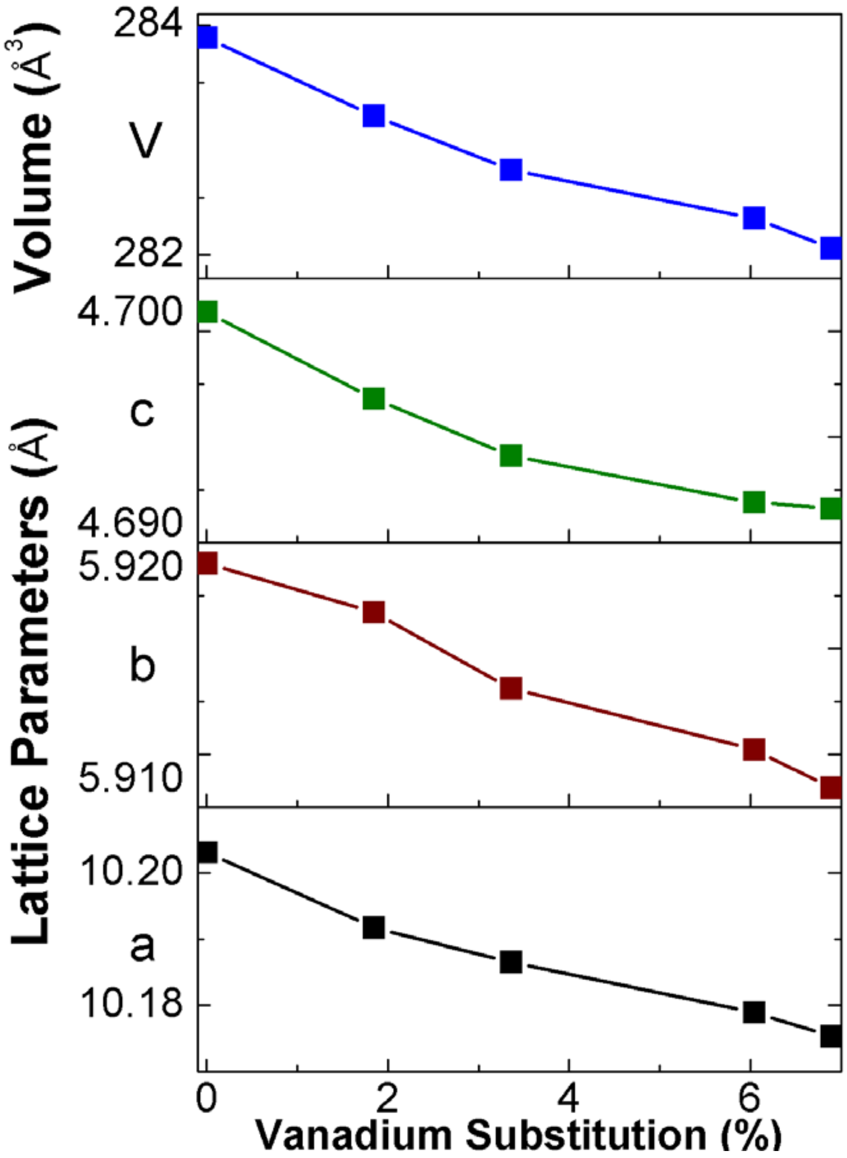




SYNTHESIS OF ALIOVALENTLY-DOPED $LiCo_{1-3x/2}V_x\square_{x/2}PO_4$

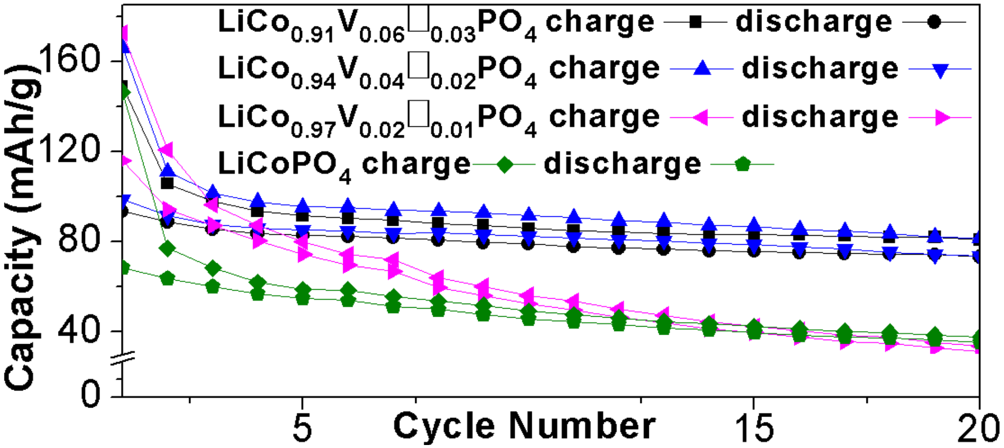
- Co^{2+} was aliovalently substituted with V^{3+} to obtain $LiCo_{1-3x/2}V_x\square_{x/2}PO_4$ with x ~ 0.07
- $LiCo_{1-3x/2}V_x\square_{x/2}PO_4$ ($Pn2_1a$) was made by microwave-assisted solvothermal synthesis, and subsequently converted to (*Pnma*) by calcining in argon at 525 °C
- Lattice parameters and unit cell volume decrease with increasing x due to the substitution of smaller V^{3+} for Co^{2+}

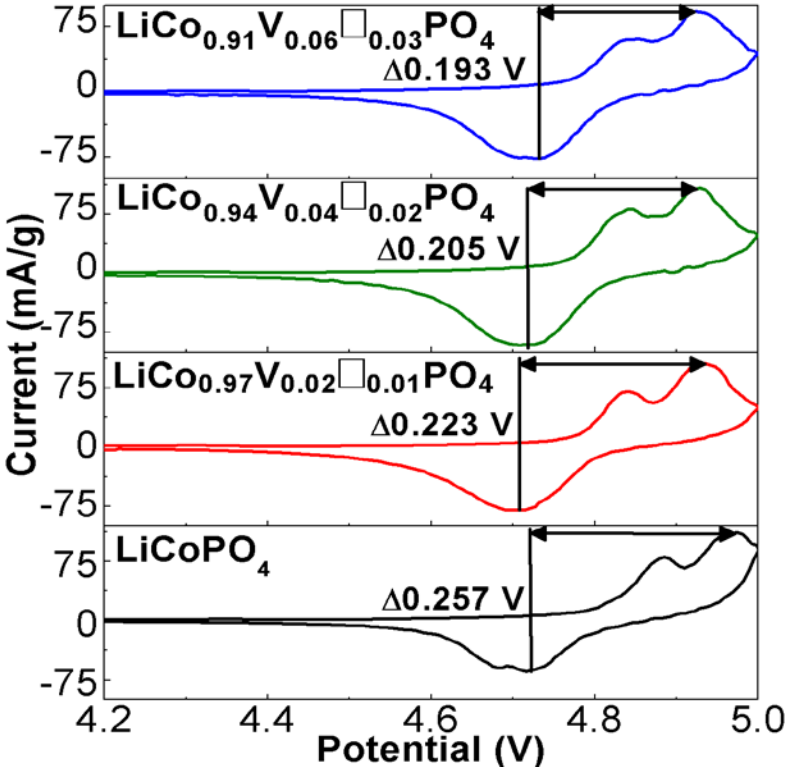


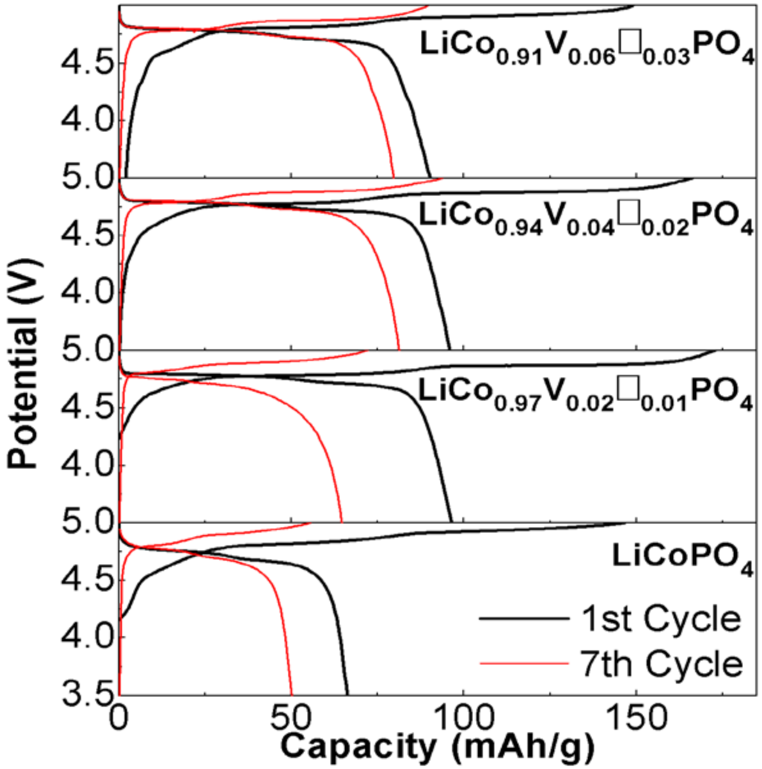


EFFECT OF V^{3+} SUBSTITUTION ON PERFORMANCE

- Aliovalent substitution of V^{3+} for Co^{2+} decreases polarization and increases the initial capacity
- The samples were not coated with carbon

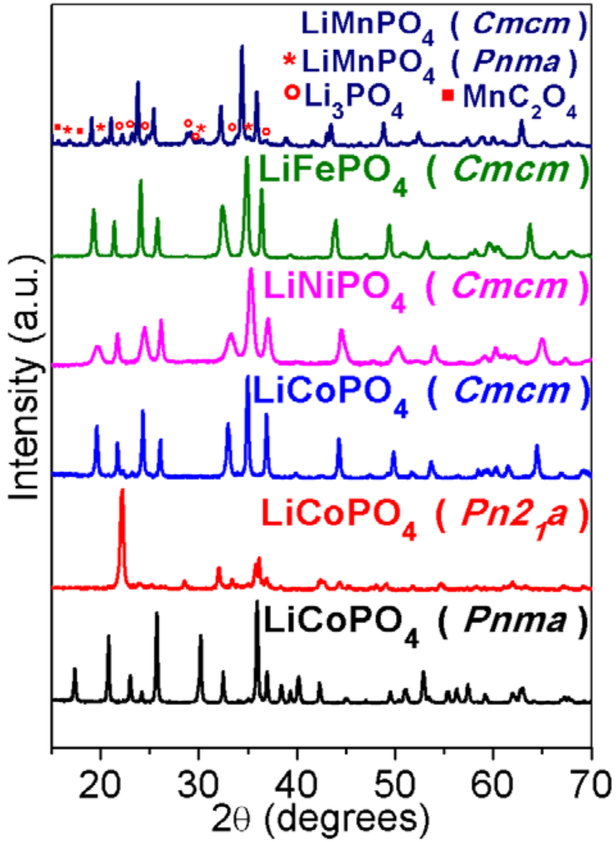


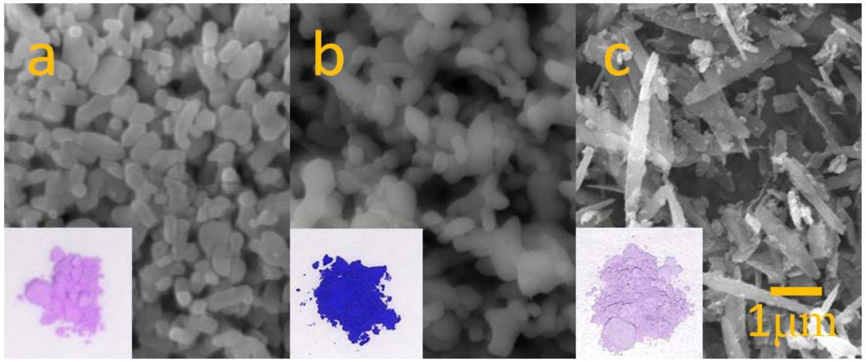


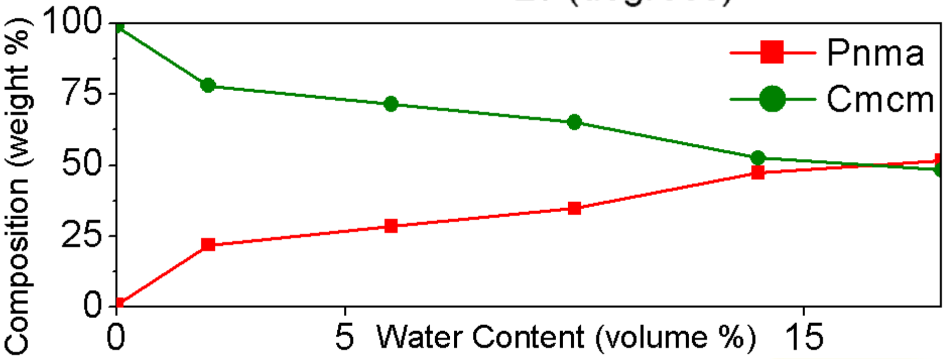


SYNTHESIS OF NON-OLIVINE $LiMPO_4$ (M = Fe, Mn, Co, Ni)

- Three polymorphs of $LiCoPO_4$, belonging to the space groups *Cmcm*, *Pn*2$_1$*a*, and *Pnma* have been synthesized by a facile microwave method in TEG
- $LiCoPO_4$ (*Cmcm*) and $LiNiPO_4$ (*Cmcm*) have been previously obtained only at high pressures (15 Mpa)
- $LiMnPO_4$ (*Cmcm*) is reported here for the first time
- $LiCoPO_4$ (*Cmcm*) shows irreversible removal of Li at ~ 4.3 V
- Polyglycols are hygroscopic and the water content influences the type of phase formed with $LiCoPO_4$, $LiFePO_4$, and possibly other $LiMPO_4$







FY 2014 REVIEWERS' COMMENTS AND RESPONSES

Comment: "the insertion of Li into $LiVOPO_4$ has caused a significant potential reduction to the level that it becomes not practically useful"

Response: It is an intrinsic problem for most of the redox couples undergoing multi-electron process, except for the $Ni^{2+/3+}$ and $Ni^{3+/4+}$ couples. Compared to other cathodes, $LiVOPO_4$ is still one of the most promising candidates with high capacity and energy density.

Comment: "suggested that the PI should investigate how to improve the cyclability and charge/discharge rate of $LiVOPO_4$"

Response: The reversible insertion/extraction of two lithium at a practical rate is still challenging due to the low ionic and electrical conductivities, as observed with many other polyanion cathodes. However, we have developed some efficient strategies for structural/electrode optimization to improve the performance of these cathodes.

Comment: "to explore new cathode materials that can intercalate multiple Li-ions and or provide higher capacity"

Response: We agree. We have been actively exploring new cathodes capable of inserting multiple Li^+ ions, *e.g.*, we have developed approaches to obtain non-olivine $LiMPO_4$ (M = Fe, Mn, Co, and Ni) and a new form of $VOPO_4$ by delithiating the tetragonal $LiVOPO_4$ that might exhibit interesting electrochemical performances.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Oak Ridge National Laboratory – Dr. Craig Bridges
  - *Investigation of the crystal structure of the lithiated $LiVOPO_4$ with spallation neutron source and X-ray diffraction*

REMAINING CHALLENGES AND BARRIERS

- The primary challenge to achieving the insertion/extraction of two lithium with the $LiVOPO_4$ cathode is the low electronic and ionic conductivities. Thus, preparation of nanoparticles with desired conductive coating is still the primary task for this material. Previous work on the tetragonal form of $LiVOPO_4$ indicates that *in-situ* incorporation of graphene is an efficient way to enhance the electrical conductivity. It will be extended to the other two forms of $LiVOPO_4$ in the future. In parallel, optimization of the microwave synthesis will be pursued to obtain smaller $LiVOPO_4$ particles.

- Structural variation is another factor that needs to be considered for the multi-electron process in $LiVOPO_4$, especially for the insertion of a second lithium. A firm understanding of the structure-performance correlation of $VOPO_4$-$LiVOPO_4$-Li_2VOPO_4 in the future will help determine which form of $LiVOPO_4$ is the most promising and worthy of further studies.

PROPOSED FUTURE WORK

- Develop further understanding on the structures of the three polymorphs (triclinic, orthorhombic, and tetragonal) of $LiVOPO_4$ and determine which polymorph is the most promising to achieve fast ionic and electronic transport with the extraction of two-lithium per vanadium

- Develop $LiVOPO_4$ electrodes with controlled particle size and conductive coating to overcome the low electronic and ionic conductivities and thereby realize a practical capacity of ~ 250 mAh/g

- Explore the preparation and electrochemical properties of various $VOPO_4$ that potentially insert two lithium ions per formula, as well as sodium ions

- Explore the synthesis of the non-olivine phases of $LiMPO_4$ (M = Mn, Fe, Co, and Ni) and their electrochemical properties

SUMMARY

- Systematic structural and chemical/electrochemical characterizations demonstrate reversible insertion of more than one lithium ion with a capacity of > 200 mAh/g with all the three forms of $LiVOPO_4$.

	Symmetry	**Lithiation**	**Delithiation**
α-$LiVOPO_4$	triclinic	✔ α-Li_2VOPO_4	✔ α-$LiVOPO_4$/ε-$VOPO_4$
β-$LiVOPO_4$	orthorhombic	✔ β-Li_2VOPO_4	✔ β-$VOPO_4$
α_1-$LiVOPO_4$	tetragonal	✔ α_1-Li_2VOPO_4	✔ $VOPO_4$ (new phase)

- Chemical delithiation of the three forms of $LiVOPO_4$ suggests
  - α-$LiVOPO_4$ shows slower lithium mobility than the other two forms
  - a new layered $VOPO_4$ phase can be formed from α_1-$LiVOPO_4$

- Significant amount of aliovalent V^{3+} has been substituted for Co^{2+} in $LiCo_{1-3x/2}V_x\square_{x/2}PO_4$ ($0 \leq x \leq 0.07$) by a microwave-assisted synthesis process at < 260 °C. The samples disproportionate to $LiCoPO_4$ on heating to 600 °C, demonstrating the necessity of low-temperature methods.