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Multi-electron Polyanion Cathode, VOPO4, for High Energy Density Alkali-ion Batteries

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Multi-electron Polyanion Cathode, VOPO₄, for High Energy Density Alkali-ion Batteries

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Materials Science and Engineering

by

Yuh-Chieh Lin

Committee in charge

Professor Shyue Ping Ong, Chair
Professor Ping Liu
Professor Shirley Meng
Professor Yu Qiao
Professor Sheng Xu

2018
The Dissertation of Yuh-Chieh Lin is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California San Diego

2018
DEDICATION

To

my grandparents, parents and elder sister
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ABSTRACT OF THE DISSERTATION

Multi-electron Polyanion Cathode, VOPO$_4$, for High Energy Density Alkali-ion Batteries

by

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Doctor of Philosophy in Materials Science and Engineering

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Professor Shyue Ping Ong, Chair

Today’s commercial lithium-ion battery cathodes function on the basis of a single-electron transfer per transition metal. To attain significantly higher capacities, particularly in polyanionic compounds with higher voltages, achieving reversible multi-electron transfer per transition metal is necessary. In this thesis, we use first principles calculations to study the thermodynamics and kinetics of AVPO$_4$ (A = Li, Na), one of the most promising multi-electron cathodes for alkali-ion batteries, with the aim of providing crucial insights into its electrochemical performance and suggesting further optimizations. This thesis comprises three complementary projects.

In the first project, we demonstrated the stable cycling of more than one Li in solid-state-synthesized ε-LiVOPO$_4$ for the first time. Using joint first-principles calculations and experimental measurements, we presented a comprehensive analysis of the thermodynamics,
kinetics, and structural evolution of $\varepsilon$-Li$_x$VOPO$_4$ over the entire lithiation range ($x=0 \sim 2$). We unveiled two intermediate phases at $x = 1.5$ and 1.75 in the low-voltage regime ($x=1 \sim 2$) and showed that the capacity limitation in the high-voltage region is likely driven by Li mobility limitations whereas the increasing polarization in the low-voltage region is the result of structural changes. Finally, we predicted that $\varepsilon$-Li$_x$VOPO$_4$ is likely a pseudo-1D ionic diffuser with low electronic conductivity using DFT calculations, which suggests that nanosizing and carbon coating are crucial to achieve good electrochemical performance in this material.

In the second project, we conducted a combined first-principles and experimental study to evaluate the thermodynamic stability, voltage, band gap and diffusion kinetics for Li and Na intercalation in the $\beta$, $\varepsilon$ and $\alpha_I$ polymorphs of VOPO$_4$. We found that all VOPO$_4$ polymorphs remain reasonably stable with one alkali-ion insertion but are significantly destabilized with two alkali-ion insertion. We predicted that the $\alpha_I$ polymorph has higher Li$^+$ migration barriers and larger band gaps than the other polymorphs, which accounts for the relatively worse electrochemical cycling performance observed. On the other hand, only the layered $\alpha_I$ polymorph exhibits reasonably low barriers for Na$^+$ migration, which are consistent with observed electrochemical performances reported thus far in the literature. We also showed that differences in voltage, kinetics and rate capability of these different polymorphs for alkali-ion insertion can be ascribed to their fundamentally different VO$_6$/VO$_5$PO$_4$ frameworks.

In the final project, we synthesized all three major polymorphs of LiVOPO$_4$ ($\alpha_I$, $\beta$ and $\varepsilon$) using a single precursor, LiVOPO$_4\cdot$2H$_2$O, thereby minimizing effects of synthesis on the properties of the materials. We demonstrated that LiVOPO$_4$ undergoes the following phase transitions upon heating: LiVOPO$_4\cdot$2H$_2$O $\rightarrow$ $\alpha_I$-LiVOPO$_4$ $\rightarrow$ $\beta$-LiVOPO$_4$ $\rightarrow$ $\varepsilon$-LiVOPO$_4$. Metastable $\alpha_I$-LiVOPO$_4$ forms initially due to its structural similarity to the LiVOPO$_4\cdot$2H$_2$O precursor via H$_2$O removal.
Between the two almost energetically-degenerate \(\beta\) and \(\varepsilon\) polymorphs, formation of the \(\beta\) phase is favored in an oxidizing atmosphere, while \(\varepsilon\) is favored at high temperatures and an inert atmosphere. DFT defect calculations show that \(\beta\)-LiVOPO\(_4\) is more stable in the presence of O interstitials, while \(\varepsilon\)-LiVOPO\(_4\) is more stable in the presence of O vacancies. We also demonstrated that the calculated Wulff shape of \(\beta\)-LiVOPO\(_4\) shows an increased presence of facets with superior surface ion kinetics in an oxidizing atmosphere, which explains its improved rate performance relative to \(\varepsilon\)-LiVOPO\(_4\) in the high voltage regime.

In conclusion, the work completed in this thesis has provided critical new insights into the promising AVOPO\(_4\) family of multi-electron cathodes. A tightly integrated DFT and experimental effort has shed light on the phase stability and equilibria and kinetics of these cathodes across the entire lithiation range. Leveraging on these insights, we have optimized synthesis to achieve close to full two-electron cycling in the \(\beta\)-LiVOPO\(_4\) and \(\varepsilon\)-LiVOPO\(_4\).
Chapter 1. Introduction

1.1 Background

With growing concerns over the environmental, climate, and health impacts caused by using fossil fuels, various renewable energy sources, such as wind, solar and hydroelectric, are believed to be promising alternatives to support more sustainable economic growth. However, most renewable energy sources are intermittent in nature and hence must be complemented with an energy storage solution. Li-ion batteries (LIB) is regarded as one of the near-term solutions because of its combination of high energy and power density. Nowadays, LIB are widely used for the portable electronic devices such as cell phone, laptop, etc., and aggressively enter the large-scale high-power market, particularly the domain of sustainable hybrid/full electric vehicle.\(^1\)

In recent years, part of attention has been shifted to the Na-ion battery (NIB), due to the cost and abundance of Na.\(^2\)–\(^5\) Although the energy density of NIB may not reach that of LIB because Na is more than three times heavier than Li and the standard electrochemical potential of Na (2.71 V) is lower than Li (3.04 V) with respect to standard hydrogen electrode, NIB are competitive in the applications of a large grid support where the operation cost and longevity of the battery are more important aspects of a whole system.

Figure 1.1 shows the configuration of an alkali-ion battery (AIB), which is composed of cathode, anode and electronically insulating, ion-conducting electrolyte. Initially, all alkali ions are in the cathode sides and the battery system is assembled in “discharged” status. During charge, alkali ions are extracted from the cathode host, through the electrolyte, into the anode host. Meanwhile, electrons also move from cathode to anode through external electric circuit. The chemical potential of alkali ion is much higher in the anode than in the cathode and hence the electric energy is stored in the form of electrochemical energy. During discharge, the
Electrochemical energy is released in the form of electric energy. Typical cathodes are transition metal oxides, while the most common form of anode is graphitic carbon.

The energy density of a rechargeable AIB is governed primarily by the capacity and voltage of the active electrode materials, which have been the main focus in battery research. In most commercial cathodes, the maximum number of electrons transferred per cycle is in general less than one per transition metal, which ultimately limits achievable capacity. For example, the commercial LiCoO$_2$ can merely utilize ~0.5 Li or electron because full extraction of Li will lead to structure instability even though it has high theoretical capacity of 272 mAh/g. LiFePO$_4$ can achieve cycling of ~0.7 – 0.9 Li albeit with a lower voltage of ~3.45V. To further increase the energy density, a potential avenue is to develop multielectron alkali-ion cathodes, which can cycle more than one electron per transition metal.

### 1.2 Review of multi-electron AIB cathode

Metal fluorides as multielectron cathodes were first reported by Arai $et$ $al$; however, only one third of the theoretic capacity (236 mAh/g) of FeF$_3$ was demonstrated in a discharge voltage region from ~4.5 to 2 V, which was attributed to the poor electronic conductivity and questionable ionic conductivity. Later, FeF$_3$ : C-based carbon metal fluoride nanocomposites was shown with a reversible specific capacity of ~600 mAh/g but with large stepwise voltage gaps leading to large fluctuation in the power output. Almost at the same time, Li $et$ $al$. reported reversible lithium storage capacities of TiF$_3$ and VF$_3$ being realized as high as 500 – 600 mAh/g, due to a reversible formation and decomposition of LiF upon lithium insertion into the metal fluorides. Metal sulfides have also been investigated as potential positive-electrode materials. The advantage of metal sulfides is that the sulfur might participate in the multielectron redox reaction in addition to the transition metal leading to high energy density although their typical voltages are lower than those
of oxides. For example, crystalline TiS$_3$ was reported with reversible capacities greater than 300 mAh/g, involving more than two electrons during cycling process.$^8$–$^{11}$ However, the reversibility of TiS$_3$ was low, which might be attributed to the structural transformation from a trigonal prism to a more stable octahedron.$^9$–$^{11}$ Later, amorphous TiS$_3$ was reported with improved electrochemical performance due to the three-dimensional framework, which would be favorable for stabilizing its structure against the large volume changes in cycling process.$^{12,13}$ Recently, Li$_2$TiS$_3$ and Li$_3$NbS$_4$ were reported with high gravimetric energy densities of 850 and 780 Wh/kg corresponding to 2.5- and 3.5-electron processes, which are much higher than the 660 Wh/kg of LiCoO$_2$.$^{14}$ Although Li$_2$TiS$_3$ exhibited high capacity retention, the capacity faded quickly within 10 cycles probably due to the volume change. For oxides, $\omega$-Li$_x$V$_2$O$_5$, was reported enabling $\sim$1.5 Li$^+$ per transition metal ($\sim$300 mAh/g) leading to high energy density of 800 Wh/kg although the voltage range was large (1.9V–4V).$^{15}$ VOPO$_4$, with seven distinct polymorphs, was firstly systematically studied as Li$^+$ cathode by Azmi et al.$^{16}$ Although an approximately 4 V flat discharge potential were demonstrated in each phase, the cyclable capacities were far below its high theoretic capacity of $\sim$160 mAh/g for one Li$^+$ cycling. Recently, Chen et al. demonstrated a novel multielectron cathode, disordered Li$_2$VO$_2$F, which can deliver up to $\sim$1.8 Li$^+$ per transition metal ($\sim$420 mAh/g) at $\sim$2.5V corresponding to a high gravimetric energy density of $\sim$1000 Wh/kg.$^{17}$ Besides, it shows remarkable smooth voltage profile with no stepwise voltage gap and small increase in polarization. For multielectron NIB systems, Na$_3$(VO$_{1-x}$PO$_4$)$_2$F$_{1+2x}$ (0$\leq$$x$$\leq$ 1) was reported with high energy density ($\sim$520 Wh/kg) and good cycle life but with large voltage gap ($\sim$1.5V) due to V$^{3+}$ $\leftrightarrow$ V$^{5+}$ redox couples.$^{18}$ Na$_2$CoFe(CN)$_6$ was demonstrated with highly reversible two Na cycling ($\sim$150 mAh/g) and superior cyclability of 90 % over 200 cycles with reasonable voltage gap $< 1$V using both Co$^{2+}$ $\leftrightarrow$ Co$^{3+}$ and Fe$^{2+}$ $\leftrightarrow$ Fe$^{3+}$ redox couples.$^{19}$
Na$_{1.5}$VPO$_{4.8}$F$_{0.7}$ was achieved with the highest energy density ~600 Wh/kg in NIB.$^{20}$ Besides, it showed excellent rate capability due to open two-dimensional diffusional framework and small volume change ~2.9%. Recently α-VOPO$_4$ was demonstrated as one of the most promising Na$^+$ cathodes with a high reversible capacity of ~110 mAh/g.$^{21}$ After incorporation of conductive graphene oxide, an impressive capacity of ~150 mAh/g was achieved.

1.3 Motivation and overview

The typical cathode used in today’s rechargeable AIB operate on the transfer of a single-electron per transition metal, limiting achievable energy densities. Multi-electron polyanionic cathodes offer the potential to significantly increase energy densities by leveraging on the inductive effect of polyanion chemistries to increase voltage, and transfer of more than one electron per transition metal to increase capacity. In this thesis, we focus on the study of one of the most promising multi-electron cathode materials, AVOPPO$_4$, using first-principles calculations. We aim to predict the thermodynamic stability, kinetics and provide insights to improve the electrochemical performance of AVOPPO$_4$, as well as explain its experimental findings.

Project 1: Thermodynamics, Kinetics and Structural Evolution of ε-LiVOPO$_4$ over Multiple Lithium Intercalation. The majority of commercial cathodes today such as LiFePO$_4$ and LiCoO$_2$ operate on less than a single redox per transition metal, which limits capacities.$^6$ A potential path toward higher capacities is to develop multielectron cathodes that can reversibly cycle more than one electron per transition metal. Given ~4.5 V voltage limit of current commercial electrolytes stability, a previous high-throughput first-principles analysis has shown that only V and Mo have reasonable average voltages across multiple redox couples ($V^{3+} \rightarrow V^{5+}$ and $Mo^{3+} \rightarrow Mo^{6+}$) to be practical multielectron phosphate-based cathodes.$^{22}$ VOPO$_4$ is one of the promising multielectron cathode materials that can utilize $V^{3+} \rightarrow V^{5+}$ redox couples yielding a high
theoretical capacity of 305 mAh/g. However, the insertion/deinsertion behaviors of the first and second Li exhibit differently which limits the reversible capacity. In addition, there is disagreement over the number of intermediate phases in the low-voltage region. In this project, we conduct joint first-principles calculations and experimental measurements to study the thermodynamics, kinetics, and structural evolution of $\varepsilon$-Li$_x$VOPO$_4$ over the entire lithiation range ($x=0 \sim 2$).

**Project 2: Comparison of the polymorphs of VOPO$_4$ as multielectron cathodes for rechargeable alkali-ion batteries.** One of the key differences between NIBs and LIBs is the alkali radii, which could affect the properties of structure. The electrochemical performance can be very different even with the same crystal framework and the performance of NIB may not be poorer than its Li counterpart. For example, Ong et al. found surprising evidence that the barriers for Na-ion migration can potentially be lower than that for Li-ion migration in the layered structures. This is against the conventional belief that Na ion diffuses slower in the same host structures due to larger ionic size. Although the voltage of a sodium-ion cathode is generally ~0.5 V lower than that of its lithium counterpart, VOPO$_4$ remains a promising sodium-ion cathode with an expected high voltage of ~3.4 V yielding a high theoretical energy density of 258 mAh/g. Recently, one Na insertion into VOPO$_4$ phases are reported but there are still no studies for two Na insertions. In this thesis, we perform a combined first-principles and experimental study to evaluate the thermodynamic stability, voltage and diffusion kinetics for Li and Na intercalation in the $\beta$, $\varepsilon$ and $\alpha_I$ polymorphs of VOPO$_4$.

**Project 3: Rational Synthesis and Electrochemical Performance of LiVOPO$_4$ Polymorphs.** Among the seven polymorphs of VOPO$_4$, $\alpha_I$, $\beta$, and $\varepsilon$ phases are the most well-studied as multi-electron Li-ion cathodes due to the promising electrochemical performances
demonstrated.\textsuperscript{27,28} The $\alpha_I$ is the least reported among the various polymorphs due to difficulties in its synthesis. On the contrary, both the $\beta$ and $\varepsilon$ phases have been synthesized using a large plethora of methods, including hydrothermal,\textsuperscript{29–31} solid-state,\textsuperscript{31–33} and sol-gel.\textsuperscript{32,34} We previously reported that $\alpha_I$-LiVOPO$_4$ is metastable and $\beta$- and $\varepsilon$- LiVOPO$_4$ are stable with very similar thermodynamic stabilities. The close energies between $\beta$ and $\varepsilon$ phases might be one of the reasons for the observation of phase transformation between them in experiments.\textsuperscript{34,35} However, this energetic degeneracy makes the obtainment of each pure phase, and hence optimization of electrochemical performance as well as direct comparisons between experiments and theories challenging. In this thesis, we synthesize the three phases using the same precursor, LiVOPO$_4$·2H$_2$O, which is likely to minimize effects of synthesis on the properties such as stability and electrochemical performance. In addition, first-principles calculations are applied to study how O chemical potential affects LiVOPO$_4$ morphology and hence the electrochemical performance.

This thesis is divided into the following chapters:

- Chapter 2 presents a comprehensive analysis of the thermodynamics, kinetics, and structural evolution of $\varepsilon$-Li$_x$VOPO$_4$ over the entire lithiation range by combining first-principles prediction and experimental characterization.

- Chapter 3 presents a systematic first principles investigation, supported by careful electrochemical characterization and published experimental data, of the relative thermodynamic stability, voltage, band gap, and diffusion kinetics for alkali intercalation in $\beta$, $\varepsilon$ and $\alpha_I$ polymorphs of VOPO$_4$.

- Chapter 4 presents a thorough study on the effects of temperature and atmosphere on the stability and formation of $\alpha_I$-LiVOPO$_4$, $\beta$-LiVOPO$_4$ and $\varepsilon$-LiVOPO$_4$, using the same precursor, LiVOPO$_4$·2H$_2$O. In addition, DFT surface calculations are applied to study the
effect of O chemical potential on LiVOPO$_4$ morphology and hence the electrochemical performance.

• Chapter 5 summarizes the key findings in this thesis and presents suggestions for future research.
Figure 1.1 Schematic of the operation of alkali-ion battery.
Chapter 2. Thermodynamics, Kinetics and Structural Evolution of $\varepsilon$-LiVOPO$_4$ over Multiple Lithium Intercalation

2.1 Introduction

The rechargeable lithium-ion (Li-ion) battery$^{36-39}$ has become a dominant form of energy storage for the modern age. However, the energy densities, both gravimetric and volumetric, of today’s Li-ion batteries are still far below that necessary to displace gasoline combustion engines. For example, the capacities of the layered LiMO$_2$ cathodes$^{38}$ which have the highest theoretical energy density of current commercial cathodes, are capped at around 180 mAh g$^{-1}$, leading to corresponding calculated energy densities of around 1 kWh kg$^{-1}$ and 3 kWh L$^{-1}$. Other commercial cathodes have significantly lower energy densities, e.g., the high rate LiFePO$_4$$^{39}$ cathode has maximum theoretical energy densities of 587 Wh kg$^{-1}$ and 2 kWh L$^{-1}$. In commercial cells, the energy densities are even lower, the best not exceeding 250 Wh kg$^{-1}$ and 0.6 kWh L$^{-1}$.

The energy density of a cathode is given by the product of its voltage and its capacity. A push for high voltage reactions has motivated the strong interest in phosphate-based cathodes such as LiFePO$_4$ and LiMnPO$_4$ with increased voltage (relative to simple oxides) associated with the inductive effect of the PO$_4^{3-}$ polyanion.$^{39}$ The majority of commercial cathodes today operate on a single redox per transition metal on average, which ultimately limits capacities. A potential path toward higher capacities is to develop multielectron cathodes that reversibly cycle more than one electron per transition metal. Given the fact that current organic carbonate electrolytes can only support voltages up to around 4.5 V,$^{41}$ a previous high-throughput first-principles analysis$^{22}$ has shown that only V and Mo have reasonable average voltages across multiple redox couples ($V^{3+} \rightarrow V^{5+}$ and $Mo^{3+} \rightarrow Mo^{6+}$) to be practical multielectron phosphate-based cathodes.
The vanadyl phosphates with formula VOPO$_4$ are an interesting class of multielectron cathode materials that utilize the V$^{3+}$ ↔ V$^{4+}$ ↔ V$^{5+}$ couple. Indeed, insertion of two Li into the ε polymorph of VOPO$_4$ has been demonstrated.$^{23-25,42}$ However, there are distinct differences between the insertion/deinsertion behaviors of the first and second Li. The insertion of the first Li at $\sim$3--4.5 V$^4$ has been shown to be relatively facile and reversible with small overpotential. The insertion of the second Li, on the other hand, is associated with a much larger overpotential.$^{25}$ Although previous studies conclusively demonstrate that the first Li insertion takes place via a two-phase reaction, there is disagreement on the nature of the second Li insertion. Some works suggest the existence of several intermediate phases at $\sim$ Li$_{1.5}$VOPO$_4$ and Li$_{1.75}$VOPO$_4$, whereas Harrison et al.$^{24}$ suggest a single-phase region between Li$_{1.5}$VOPO$_4$ and Li$_2$VOPO$_4$.

In ε-Li$_x$VOPO$_4$, the VO$_6$ polyhedra share corners to form one-dimensional (1D) chains (see Figure 2.1). These chains are bridged by PO$_4$. All V ions are symmetrically equivalent in VOPO$_4$ (Cc spacegroup), whereas alternating V ions along the 1D chains are symmetrically inequivalent in LiVOPO$_4$ and Li$_2$VOPO$_4$ (P1 space group). It is only recently that a structure for the Li$_2$VOPO$_4$ end member has been proposed for a chemically lithated sample.$^{23,24}$ For historical reasons, the singly lithiated phase of ε-VOPO$_4$ is known as α-LiVOPO$_4$ based on the order of discovery. For the sake of clarity, we will adopt the convention proposed by Whittingham et al.$^{40}$ and refer to all lithiated members of ε-VOPO$_4$ with the ε prefix. Also, unless otherwise stated, formulas given without a prefix refer to the ε phase.

In this work, we demonstrate the stable cycling of more than one Li in solid-state-synthesized ε-LiVOPO$_4$ for more than 20 cycles for the first time. In contrast to previous work, we apply an integrated approach combining density functional theory (DFT) calculations, operando X-ray pair distribution function (PDF) and diffraction analysis, and extended X-ray
absorption fine structure (EXAFS) measurements to elucidate the thermodynamics, kinetics and structural evolution of $\varepsilon$-Li$_x$VOPO$_4$ over multiple Li intercalation. The main accomplishments include the identification of candidate stable structures for Li$_{1.5}$VOPO$_4$ and Li$_{1.75}$VOPO$_4$, the observation and explanation of a hysteretic V—O bond length evolution during low voltage cycling, and a discussion of the phase stability and ionic and electronic conductivity considerations in achieving good electrochemical performance in this material.

2.2 Experimental Methods

2.2.1 Synthesis

$\varepsilon$-LiVOPO$_4$ was prepared via solid state synthesis. Stoichiometric amounts of NH$_4$VO$_3$ (Aldrich, 99%), Li$_2$CO$_3$ (Fisher Scientific, $\geq$ 99%), and NH$_4$H$_2$PO$_4$ (Sigma-Aldrich, $\geq$ 99.99%) were mixed with acetone in a planetary ball mill for 4h. The isolated solid mixture was pressed into pellets and heated in argon atmosphere at 300 °C for 5h and then at 750 °C for 10h. The structure of the as-prepared material was verified using powder diffraction analysis and transmission electron microscopy (TEM). Nanocomposite $\varepsilon$-LiVOPO$_4$ was prepared by high energy ball-milling the as-synthesized material with Super P carbon black and PVDF (poly(vinylidene fluoride)) in a weight ratio of 75:15:10.

2.2.2 Electrochemistry

Electrodes were fabricated by casting the nanocomposite onto Al foil. Electrodes with 5–6 mg of active material of area 1.2 cm$^2$ were assembled into 2325-type coin cells with a Celgard 2400 separator (Hoechst Celanese), lithium metal foil (Aldrich) and liquid electrolyte (1 M LiPF$_6$ in 1:1 ethylene carbonate: dimethylcarbonate, EC:DMC). The thickness of the electrode was $\sim$40 μm. The electrochemical properties were investigated using VMP multichannel potentiostat (Bio-Logic). Cells were cycled galvanostatically at C/50 ($\sim$0.01 mA/cm$^2$) in the high voltage (3.0–4.5
V), low-voltage (1.5–3.5 V) and whole voltage (1.6–4.5 V) regimes. Cells were also cycled at C/20 (~0.02 mA/cm²) over the whole voltage range. The kinetics in the high- and low-voltage regimes were explored using GITT testing by applying C/50 current for 1.5 h followed by resting for 100 h at high voltage or 24 h at low voltage.

2.2.3 Operando Pair Distribution Function (PDF) and Diffraction Analysis

Operando X-ray scattering data were collected for ε-LiVOPO₄ based pellet electrodes within the AMPiX electrochemical cell.44 13 mm-diameter electrode pellets of 120–180 μm thick were prepared from the LiVOPO₄ nanocomposite as described previously. The electrode pellets were assembled into an electrochemical cell in an Ar-atmosphere glovebox with a glass fiber separator (Whatman GF/A), Li metal foil and liquid electrolyte (1 M LiPF₆ in 1:1 EC:DMC, from BASF). The cell was cycled galvanostatically at a constant current of 5 mA g⁻¹, in the voltage range of 3.5 V to 1.6 V to 3.5 V (LiVOPO₄ to Li₂VOPO₄ to LiVOPO₄).

X-ray scattering data were collected in 3 min exposures at beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory, using high energy X-rays (~58 keV, λ = 0.2114 Å) in combination with a large amorphous-silicon based area detector (PerkinElmer). Data were collected at 15 min intervals alternating between PDF and pXRD optimized configurations (equivalent to 0.015 Li intervals for each) during the first lithiation and delithiation cycle. Total scattering data suitable for PDF analysis were collected to high values of momentum transfer (Qmax ~ 22 Å).45,46 Diffraction data optimized for improved 2θ resolution were collected using a long sample-to-detector distance. The scattering images were reduced to one-dimensional data using fit2d.47

The large Q-range total scattering data were corrected for background scattering, Compton scattering and detector effects within pdfgetX2 and Fourier transformed to get G(r), the PDF.48
Structure models were refined against the PDF data and the corresponding partial pair contributions to the PDFs calculated within PDFgui.\textsuperscript{49} A spherical particle envelope parameter was used to model the particle size and/or length scale of ordering. The intensity and position of peaks corresponding to the V═O/P—O bond (ca. 2.0 Å) and the V—O bond (ca. 2.5 Å) were quantified by fitting Gaussian functions within fityk.\textsuperscript{50} The evolution of the crystallographic lattice dimensions and average structure was evaluated based on Rietveld refinement of the powder diffraction data within TOPAS.

\textbf{2.2.4 X-ray Absorption Spectroscopy}

X-ray absorption data were collected for Li$_3$VOPO$_4$ electrodes recovered at different states of charge at beamline 9-BM-B of the Advanced Photon Source, Argonne National Laboratory. The V k-edge ($E = 5.463$ keV) XANES and EXAFS spectra were acquired in transmission mode. A $k$-range of 1–7 Å$^{-1}$ was used in the Fourier transformed $R$-space functions. Data were processed in Athena and Artemis from the Demeter software package version 0.9.21.\textsuperscript{51}

\textbf{2.2.5 XRD and TEM}

High resolution X-ray synchrotron diffraction patterns were collected at beamlines X14A of National Synchrotron Light Source (NSLS) in Brookhaven National Laboratory (wavelengths 0.7801 Å) and 7B of APS (Advanced Photon Source) in Argon (wavelength 0.72775 Å). The Rietveld refinement of the X-ray diffraction patterns was done using the GSAS/EXPGUI package.

The morphology and particle sizes were first obtained by high resolution Scanning Electron Microscopy (SEM), ZeissSupra-55 field emission scanning electron microscope. Further transmission electron microscopy (TEM) characterization of the electrode particles was performed at Brookhaven National Laboratory. The powdered electrode sample was mixed in an alcohol solution in a small vial, and sonicated to ensure that the particles are well dispersed. The sample
was then drop-casted onto a lacey carbon TEM grid. The TEM images and selected area diffraction patterns (SAEDs) were obtained with a JEM-2100F (JEOL) operated at 200kV.

2.3 Computational Methods

All density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach. Appropriate functionals and parameters for each analysis were selected based on accuracy and computational cost considerations. Initial candidate structures for $\varepsilon$-VOPO$_4$, LiVOPO$_4$ and Li$_2$VOPO$_4$ were obtained from the experimental literature. Candidate intermediate structures Li$_x$VOPO$_4$ ($x = 0.25$, 0.5, 0.75, 1.25, 1.5 and 1.75) were derived by partially delithiating LiVOPO$_4$ or Li$_2$VOPO$_4$ and carrying out an enumeration of all symmetrically distinct orderings. All analyses were performed using the Python Materials Genomics (pymatgen) library.

2.3.1 Phase Equilibria and Voltage Profile

The energies of all Li$_x$VOPO$_4$ phases were calculated using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation functional with the application of an effective Hubbard $U$ of 3.25 eV for vanadium (GGA+$U$). The calculation parameters were based on the parameters used in the Materials Project. The key parameters are a plane wave energy cutoff of 520 eV and $k$-point density of at least 1000/(number of atoms in unit cell). All calculations were spin-polarized starting from a high-spin ferromagnetic configuration as a previous first-principles study has shown that the magnetic ordering has a small effect on the relative total energies in this system. We assessed the phase stability of Li$_x$VOPO$_4$ by constructing the pseudobinary VOPO$_4$–Li$_2$VOPO$_4$ phase diagram, as well as the full Li–V–P–O quarternary phase diagram with data from the Materials Project. The voltage profile was then constructed from the stable orderings.
also performed energy calculations using the screened hybrid Heyd–Scuseria–Ernzerhof (HSE) functional\textsuperscript{66} to obtain more accurate structural parameters, electronic structure, and voltages. Given the much greater computational expense of HSE calculations, these calculations were limited to only the lowest energy orderings at each composition obtained from the GGA+\(U\) calculations.

We assessed the phase stability of Li\(_{x}\)VOPO\(_{4}\) using two criteria.

- **Formation energies relative to end members.** We constructed the pseudo-binary VOPO\(_{4}\) – Li\(_2\)VOPO\(_{4}\) phase diagram by computing the formation energies \(\Delta E(x)\) of Li\(_{x}\)VOPO\(_{4}\) for \(x = 0 - 2\) relative to the end members. \(\Delta E(x)\) is given by the following equation:

\[
\Delta E(x) = E(Li_xVOPO_4) - \frac{2-x}{2} \times E(VOPO_4) - \frac{x}{2} \times E(Li_2VOPO_4)
\]

(1)

- **Comparison with all known phases in the Li-V-P-O system.** To determine how the thermodynamic stability of Li\(_{x}\)VOPO\(_{4}\) changes with lithiation, we constructed the Li-V-P-O quarternary phase diagram.\textsuperscript{64} The pre-computed energies of all Li-V-P-O phases were automatically queried using the Materials Project Application Programming Interface (API).\textsuperscript{63}

We then added the Li\(_{x}\)VOPO\(_{4}\) phases calculated in this study, and determined the energy above the convex hull, Ehull, of each phase of interest, which is a measure of the thermodynamic stability of a material at 0K. From the stable orderings along the lithiation path, we can calculate the average voltage for each adjacent pair of stable phases, Li\(_{x_1}\)VOPO\(_{4}\) and Li\(_{x_2}\)VOPO\(_{4}\) as follows:\textsuperscript{65}

\[
V = \frac{E(Li_{x_2}VOPO_4) - E(Li_{x_1}VOPO_4) - (x_2-x_1)E(Li)}{(x_2-x_1)e}
\]

(2)

Where E is the total energy as calculated using DFT, and e is the absolute value of the electron charge.
2.3.2 Vacancy Migration Barriers

Activation barriers for vacancy (\(v\text{Li}^+, v\) is used to denote a vacancy) migration in LiVOPO\(_4\) were calculated using the climbing image nudged elastic band method (CI-NEB).\(^{67,68}\) To avoid ambiguity regarding the localization of electrons, the standard PBE GGA functional (without application of the Hubbard \(U\)) was used, in line with the well-established practice in the literature.\(^{69}\) The CI-NEB calculations were carried out using a \(2 \times 2 \times 2\) supercell with formula \(\text{Li}_{31}\text{V}_{32}\text{O}_{32}\text{P}_{32}\text{O}_{128}\) (32 formula units with a Li vacancy) to minimize the interactions between periodic images. A \(\Gamma\) \(1 \times 1 \times 1\) \(k\)-point grid was used, and each image is relaxed until the forces on each atom are less than 0.02 eV/Å. Investigation of vacancy migration in Li\(_2\)VOPO\(_4\) was not carried out as the introduction of a vacancy leads to a substantial rearrangement of Li atoms in the crystal due to the large number of Li atoms in the unit cell.

2.3.3 Electronic Conductivity

The electronic conductivity of Li\(_x\)VOPO\(_4\) was assessed by calculating the band gaps and small polaron migration barriers using the HSE functional.\(^{70,71}\) A slow moving electron or hole in a dielectric crystal induces a local lattice distortion, which acts as a potential well that causes the charge carrier to become self-trapped. The quasiparticle formed by the charge carrier and its self-induced distortion is called a small polaron if the range of the lattice distortion is of the order of the lattice constant. In this work, we adopted the same methodology used previously by one of the coauthors to study of polarons in the LiMPO\(_4\) (\(M = \text{Fe, Mn}\)) olivines.\(^{72}\) In Li\(_x\)VOPO\(_4\), we can assume that electron transfer is confined within each 1D chain with no charge transfer through the PO\(_4\) polyanions. The maximum barrier calculated for the charge to move from one V atom to its nearest periodic image along the chain is an upper limit for the migration barrier. In VOPO\(_4\), polaronic charge carriers are electrons on V\(^{5+}\) sites. In LiVOPO\(_4\), polaron charge carriers can either
be holes or electrons on V\textsuperscript{4+}, forming a localized V\textsuperscript{5+} or V\textsuperscript{3+} state, respectively. In Li\textsubscript{2}VOPO\textsubscript{4}, it is assumed that polaronic charge carriers are holes on V\textsuperscript{3+} sites given the fact that further reduction of V beyond a two-electron process has thus far not been demonstrated. The polaron migration barriers were calculated using a ferromagnetic structure. Supercells containing 16 formula units (2 × 1 × 2 for VOPO\textsubscript{4} and 2 × 2 × 1 for LiVOPO\textsubscript{4} and Li\textsubscript{2}VOPO\textsubscript{4}) were used to minimize the interaction between periodic images while keeping computational costs at a reasonable level. The HSE functional was used for the polaron calculations. Similar to the LiMnPO\textsubscript{4} olivine studied previously,\textsuperscript{72} we found that a polaron cannot be localized in Li\textsubscript{x}VOPO\textsubscript{4} with the GGA+U functional, likely due to the strong hybridization between V and O. A fairly tight energy convergence criteria of 0.001 eV was used, with a minimal Γ 1 × 1 × 1 k-point grid.

2.3.4 Small polaron migration

In this work, we adopted the same methodology used previously by one of the co-authors to study of polarons in the LiMPO\textsubscript{4} (M = Fe, Mn) olivines.\textsuperscript{72} A hole (electron) polaron was formed on one of the transition metal ions by removing (adding) an electron to the fully relaxed Li\textsubscript{x}VOPO\textsubscript{4} supercell. Overall charge neutrality was preserved via a compensating background charge. If \{q\textsubscript{i}\} and \{q\textsubscript{f}\} denote the initial and final ion positions respectively, the migration of the polaron can then be described by the transfer of the lattice distortion over a one-dimensional Born-Oppenheimer surface, with a energy maximum at a configuration between \{q\textsubscript{i}\} and \{q\textsubscript{f}\}. To determine this maximum, we computed the energies for a set of cell configurations \{q\textsubscript{x}\} linearly interpolated between \{q\textsubscript{i}\} and \{q\textsubscript{f}\}, i.e.,

\[q\textsubscript{x} = (1-x)q\textsubscript{i} + xq\textsubscript{f}\] where 0 ≤ x ≤ 1.

The polaron migration barriers were calculated using a ferromagnetic structure. Supercells containing 16 formula units (2×1×2 for VOPO\textsubscript{4} and 2×2×1 for LiVOPO\textsubscript{4} and Li\textsubscript{2}VOPO\textsubscript{4}) were
used to minimize the interaction between periodic images, while keeping computational costs at a reasonable level. The HSE functional was used for the polaron calculations. Similar to the LiMnPO$_4$ olivine studied previously,$^{72}$ we found that a polaron cannot be localized in Li$_x$VOPO$_4$ with the GGA+U functional, likely due to the strong hybridization between V and O. A fairly tight energy convergence criteria of 0.001 eV was used, with a minimal $\Gamma$ $1\times1\times1$ k-point grid.

2.4 Results

2.4.1 Electrochemistry of $\varepsilon$-LiVOPO$_4$

The first effort of this work was to optimize the solid state synthesis of $\varepsilon$-LiVOPO$_4$ as the method originally proposed by Ateba Mba et al. was for LiVOPO$_4$F. $^{73}$ NH$_4$VO$_3$ was used as a V$^{5+}$ precursor, and pure $\varepsilon$-LiVOPO$_4$ was readily obtained at 750 °C. The high resolution X-ray diffraction pattern and TEM image of the as-synthesized and high energy ball-milled $\varepsilon$-LiVOPO$_4$ are given in Figure 2.2. After ball milling with super P carbon black, the micron-size as-synthesized LiVOPO$_4$ particles are fragmented, forming an agglomerate of smaller multigrained particles with a thin layer of carbon (thickness $\sim$2 nm) on the surface. The resulting clusters are less than 100 nm in size (see Figure 2.2e).

Figure 2.3a and b show the galvanostatic cycling of ball milled $\varepsilon$-LiVOPO$_4$ in the high-(3.0–4.5 V) and low-voltage (1.5–3.5 V) domains, respectively. The high-voltage V$^{4+/5+}$ plateau consistently delivers a reversible capacity of $\sim$105 mAh/g for up to 35 cycles, which corresponds to $\sim$0.65 Li. The charge–discharge profiles are similar after 25 cycles (insert of Figure 2.3a), but the initial charge curve is different. Electrolyte decomposition above 4.2 V leads to the initial capacity loss, as seen in Figure 2.3a These results are comparable with most previous reports on the cycling of VOPO$_4$ and LiVOPO$_4$. $^{24,53,74}$ In the low-voltage region, the capacity from the V$^{3+/4+}$ couple is close to 1 Li and stable for 25 cycles (see Figure 2.3b). The discharge–charge profiles
with steps are in agreement with many reports, suggesting the existence of intermediate phases at 1.5 and 1.75Li.\textsuperscript{23,24,74} The inset of Figure 2.3b compares the curves of the 1st, 10th, 20th, and 25th cycles.

The cells were also cycled over the whole voltage range (1.6–4.5 V), as shown in Figure 2.3c and d. A high capacity of \(~\text{240 mAh/g}\) can be achieved for up to 20 cycles, corresponding to 1.65 Li with little dependence of capacity on the rate. Both plateaus deliver a similar capacity as when cycled separately. From Figure 2.3e, we see that the profiles of C/50 cycling evolve from step-like to more slope-like, especially at low-voltage, and the difference between voltage plateaus increases progressively, suggesting changes in the local structure. At C/20, this effect is more pronounced. These observations clearly suggest inherent kinetic limitations, particularly in the high-voltage regime. Indeed, sluggish kinetics in the high-voltage regime have been recently considered responsible for pronounced Li gradients and reduced capacity in hydrothermally synthesized $\varepsilon$-VOPO\textsubscript{4}.\textsuperscript{75} Overall, the electrochemical performance is consistent with previous reports, indicating that it is easier to intercalate Li into than to remove Li from $\varepsilon$-LiVOPO\textsubscript{4}. This is the first time cycling of multiple Li$^+$ in phosphates has been achieved for up to 20 cycles.

The kinetics in the high and low voltage regimes were explored using GITT testing. Figure 2.4a and b plot the capacity–voltage graph in the high- and low-voltage regions respectively, which is similar to the constant rate charge–discharge curves. The overpotentials and relaxation of the reactions in the high- and low-voltage plateaus in the green box are shown in Figure 2.4c. At low voltage, the discharge overpotential is \(~\text{32 mV}\), three times less than the high-voltage charge process (\(~\text{108 mV}\), and is comparable to the high-voltage discharge process (\(~\text{41 mV}\). This observation implies the intercalation process at high-voltage has to overcome a higher energy barrier than at low-voltage, which restricts the amount of lithium that can be reversibly extracted.
Electrolyte decomposition during high-voltage charging may further limit the amount of Li extracted. The transitions between $V^{3+}/V^{4+}$ and $V^{4+}/V^{5+}$, where more energy is needed for nucleation, always manifest the highest overpotentials. The voltage at low plateau region is stable in 24 h, and 100 h relaxation is insufficient for the high-voltage reaction to reach equilibrium. These observations conclusively demonstrate the faster kinetics reaction at the low-voltage region, indicating that it is easier to intercalate Li into than to remove Li from $\varepsilon$-LiVOPO$_4$.

Figure 2.5a shows the 0 K pseudobinary VOPO$_4$–Li$_2$VOPO$_4$ phase diagram calculated using the GGA+U and screened hybrid HSE functionals. For $0 \leq x \leq 1$, the phase diagram predicts that there are no stable intermediate phases, consistent with the two-phase behavior observed in our high-voltage cycling (see Figure 2.3a) and previous results.$^{23,24,62,75}$ Two stable intermediate phases are predicted at $x = 1.5$ and 1.75 for $1 \leq x \leq 2$, which is again consistent with the three plateaus observed during low voltage cycling (see Figure 2.3b). We find that the average voltages calculated using the HSE functional are in much better agreement with experiments compared to those calculated using GGA+U, possibly due to a better description of the strongly hybridized V–O bonds and the fact that the Hubbard $U$ value is a fitted average. Overall, we find that our computed HSE voltage profile is in fairly good agreement with the electrochemically measured profile (see Figure 2.3e) and values in the literature (see Table 2.1). This agreement gives us confidence that the intermediate structures obtained in our approach are reasonably close to the true ground state structures.

Figure 2.5b shows the calculated GGA+U $E_{\text{hull}}$ relative to all known Li–V–P–O phases for the stable orderings in the VOPO$_4$–Li$_2$VOPO$_4$ pseudobinary. The $E_{\text{hull}}$ is an estimate of the thermodynamic stability of a phase; stable phases have an $E_{\text{hull}}$ of 0, whereas increasing $E_{\text{hull}}$ indicates decreasing thermodynamic stability. We observe that although the $E_{\text{hull}}$ remains relatively
low up to \( \chi = 1 \), it rapidly increases upon further lithiation, which indicates that highly lithiated Li\(_x\)VOPO\(_4\) phases are thermodynamically unstable. All highly lithiated Li\(_x\)VOPO\(_4\) are predicted to be unstable with respect to a linear combination of Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), Li\(_3\)PO\(_4\), and vanadium oxides.

Figure 2.6 shows the symmetrically distinct VO\(_6\) environments extracted from the stable HSE-relaxed structures. In general, the HSE lattice parameters are in excellent agreement with the experimental lattice parameters\(^{23}\) (see Table 2.2) As the atomic positions of the intermediate Li\(_{1.5}\)VOPO\(_4\) and Li\(_{1.75}\)VOPO\(_4\) phases have not been reported previously, the DFT relaxed positions are given in Table 2.3 and Table 2.4. In agreement with previous findings,\(^{23,24}\) both the predicted Li\(_{1.5}\)VOPO\(_4\) and Li\(_{1.75}\)VOPO\(_4\) structures have \( P \overline{1} \) symmetry, though the lowest energy Li\(_{1.75}\)VOPO\(_4\) structure is a supercell that is twice the size of the primitive cell of Li\(_2\)VOPO\(_4\). It is, however, likely that Li disorder is present in Li\(_{1.75}\)VOPO\(_4\) given the presence of multiple orderings that are close in energy (and hence, potentially thermodynamically accessible at finite temperatures) to the ground-state ordering (see Figure 2.5a).

The calculated models of all intermediates were compared to the data collected for the ex-situ samples recovered from coin cells from electrochemical cycling and to the selected points of the operando data. Refinement of the lattice parameters (Figure 2.7) yielded a good fit for the long-range structure (beyond 15 Å), though significant deviations in the local structure remain. Further refinements of oxygen coordinates yielded excellent fits over all length scales (see Figure 2.8).

Partial pair contributions to the PDFs were calculated based on the refined model to identify the atom–atom pairs associated with different features in the experimental data (see Figure 2.9). The V has an asymmetric coordination environment, with one short V—O bond (1.62 Å) and five longer V—O bonds (\( \sim 1.99 \) Å). In the total PDF, the short V—O bond at \( \sim 1.6 \) Å overlaps with
the contribution from the P—O distance within the PO₄³⁻ anion. These bond lengths are in excellent agreement with the HSE-relaxed VO₆ environments for LiVOPO₄.

The operando PDF data, collected during lithiation and delithiation between \( x = 1 \) and \( x = 2 \), revealed marked changes in the local atomic structure and V coordination (Figure 2.10a). Continuous shifts in the 1.6 and 2.0 Å peak positions reflect changes in the average bond lengths, whereas the changes in peak areas correspond to changes in the average coordination number. Discontinuous changes were observed for the peak at \( \sim 3.3 \) Å, corresponding to the V(—O—)P distance. This likely reflects changes in the V—O—P angle associated with a relative rotations of the VO₆ and PO₄ polyhedra during the structural phase transitions. The changes in the local structure were quantified by fitting Gaussian functions to features in the PDFs up to 4 Å. Although the contributions from the P—O and short V—O bonds are not well resolved in the operando data, the PO₄ polyatomic anion geometry is not expected to change during cycling, so all changes in the feature at ca. 1.6 Å can be entirely attributed to changes in the V═O bond. The intensity and position of the feature associated with the P—O bond was fixed for the analysis.

More pronounced changes were observed for the V═O bond length compared to the V—O bond (Figure 2.10b). During the initial stage of reaction, corresponding to the transition between LiVOPO₄ and Li₁.₅VOPO₄, the short terminal V═O bonds elongate rapidly by 0.15 Å, whereas longer V—O interactions increase only by 0.008 Å. The elongation of the V═O bond is accompanied by a decrease in the relative intensity of this peak and a small, but not equivalent, increase in the intensity of the V—O feature at 2.0 Å. Once the V═O correlations are effectively eliminated, the longer V—O bond grows more rapidly. The average V—O bond lengthens most rapidly between Li₁.₅VOPO₄ and Li₁.₇₅VOPO₄ (2.014 Å to 2.026 Å), with slower changes again between Li₁.₇₅VOPO₄ and Li₂VOPO₄ (2.026 Å to 2.034 Å). The intensity weighted average of V—
O distance changes more continuously. The overall changes in V—O distance are reversed upon delithiation. These observations are consistent between the PDF measurements and the DFT computed structures (Figure 2.6).

Clear hysteresis is observed for the V—O features between lithiation and delithiation (Figure 2.11a). The V—O bond contracts more rapidly during delithiation compared to the elongation during lithiation. Correspondingly, stable intermediates appear to form ~0.1 Li earlier during delithiation than during lithiation (Li$_{1.6}$VOPO$_4$ vs Li$_{1.5}$VOPO$_4$) as is reflected by the relevant plateaus in the electrochemistry. The hysteresis within each V—O bond is noticeable throughout the entire composition range. The shorter V interactions exhibit large hysteresis associated with only the first Li$_{1.5-1.6}$VOPO$_4$ intermediate.

The V—O coordination number for V—O bonds of less than ~2.2 Å drops during the reaction (Figure 2.11b), which reflects either under-coordination of V or the formation of a long ~2.4 Å V—O bond. The initial V local environment has 1 short V═O and 5 longer V—O correlations on average. During the transformation from LiVOPO$_4$ to Li$_{1.5}$VOPO$_4$, the total intensity in the V—O features at 1.6 and 2.0 Å reduces from 6 to 5.5 O neighbors, suggesting that up to half of the V have an elongated V—O bond. This is supported by an increase in intensity for the features at 2.5 and 2.8 Å, which are primarily assigned to O—O distances. During charge, the V—O coordination drops to 5.5 beyond 1.75 Li, but this is not reversed by 1 Li.

The local V coordination environment for a set of ex-situ samples was determined via EXAFS. The Fourier transformed $k^2$ weighted data is plotted (offset for clarity) in Figure 2.12a. The peak around 1.5 Å is associated with the first coordination shell around the central absorbing atom. First coordination shell fits were performed using a model for the VO$_6$ octahedron, which included long and short apical bonds (created by displacing the central V along the z axis) as well
as four equivalent equatorial bonds. Bond lengths were determined by fitting unique ΔR values for all scattering paths and all samples. Coordination number (N) and amplitude reduction (S₀^2) were taken to be constant. A single Debye–Waller factor (σ²) and energy shift (E₀) were used for all scattering paths and samples. Consistent with the PDF analysis, we identify a short and equatorial V—O radial distance at ∼1.6 and 2.0 Å respectively. The presence of a long bond around 2.4–2.5 Å is also apparent from Figure 2.12c. The long bond length increases with increasing state of discharge and then recovers (with a clear overpotential) upon recharge. The observation of a long V—O bond length at ∼2.4 Å in our PDF and EXAFS measurements is consistent with previous EXAFS results by Allen et al.74

2.4.2 Ionic Conductivity

We investigated the migration barriers for vLi+ hopping in LiVOPO₄ using CI-NEB calculations. The unit cell of LiVOPO₄ contains two crystallographically distinct Li sites (labeled Li1 and Li2) that form percolating 1D chains, as shown in Figure 2.13. We investigated all hops between nearest neighbor Li sites (A → B, B → C, D → E, E → F, A → G and A → H, see Figure 2.13a for labeling scheme). The results are shown in Figure 2.14.

For the 1D path A → B → C, both hops A → B and B → C involve the migration through the space between two VO₆ octahedra, resulting in fairly similar activation barriers of 244 and 214 meV respectively. For the 1D path D → E → F on the other hand, the migration local environments are extremely different for hops D → E and E → F. The D → E hop takes place through two VO₆ octahedra (similar to hops A → B and B → C), but the much smaller channel size results in a significantly higher migration barrier of 600 meV. Unlike the previous hops, the E → F hop passes through two PO₄ tetrahedra instead of VO₆ octahedra. In fact, the midpoint of E → F hop is found to be lower in energy than the end points, which we attribute to a reduction in the electrostatic
repulsion between nearest neighbor Li$^+$ with the introduction of a vacancy. Overall, we find that the effective migration barriers (across the entirety of each path) for the Li1 (A → B → C) and Li2 (D → E → F) paths are 244 and 703 meV respectively. This suggests that vLi$^+$ migration is likely to be relatively facile at least along the Li1 1D chains. Interchain vacancy migration barriers (A → G and A → H) are found to be significantly higher at 815 and 1199 meV.

We may estimate the diffusion coefficient $D$ of LiVOPO$_4$ using transition-state theory as follows: $D = a^2 \times \nu \times \exp(-E_a/k_B T)$ (1) where $a$ is the length of a diffusion jump, $\nu$ is the attempt frequency, $E_a$ is the activation energy, and $k_B T$ is Boltzmann’s constant times the temperature. Using a typical phonon frequency of $10^{12}$ Hz, the diffusion coefficient at 300 K for LiVOPO$_4$ in the dilute limit is estimated to be $6.73 \times 10^{-8}$ cm$^2$ s$^{-1}$ (based on the lowest activation energy 1D channel), which is in relatively good agreement with the lithium chemical coefficient obtained from GITT or electrochemical impedance spectroscopy measurements ($10^{-10}$ to $10^{-9}$ cm$^2$ s$^{-1}$).$^{42}$

2.4.3 Electronic Conductivity

The calculated densities of states (DOSs) of Li$_x$VOPO$_4$ are shown in Figure 2.15. We find that all Li$_x$VOPO$_4$ phases have a fairly large band gap (2.25–2.99 eV), though the band gap decreases with increasing lithiation. The calculated band gap of LiVOPO$_4$ (2.63 eV) is comparable with previous experimental measurements and theoretical calculations (2.13 and 2.78 eV respectively).$^{77}$

Figure 2.16 summarizes the calculated migration barriers for the various polaron in Li$_x$VOPO$_4$ and provides a comparison to polaron migration barriers previously calculated for the olivine LiFePO$_4$ and LiMnPO$_4$ cathode materials$^{72}$ using the same computational methodology. In
general, we find that the polaron migration barriers in the Li$_x$VOPO$_4$ to be higher than those in LiFePO$_4$ and comparable to those in LiMnPO$_4$.

2.5 Discussion

$\varepsilon$-VOPO$_4$ is a highly promising cathode material due to its potential ability to intercalate two Li per vanadium to achieve a very high theoretical capacity of 318 mAh g$^{-1}$.\textsuperscript{23-25,42} In contrast to previous efforts, we have demonstrated in this work the stable cycling of solid-state synthesized $\varepsilon$-LiVOPO$_4$ over more than one Li for more than 20 cycles. Furthermore, our combined DFT, operando PDF, and EXAFS analysis have yielded new insights into the thermodynamic and kinetic factors influencing the electrochemical performance in this material.

In general, the electrochemical performance obtained in this work is consistent with the earlier reports.\textsuperscript{23,24,42,78} The discharge–charge profiles, with steps at $\sim$3.9, 2.5, 2.2, and 2.0 V, suggest the existence of intermediate phases at $x = 1.5$ and 1.75. It should be noted that there is some minor disagreement on the low voltage regime in the experimental literature. Although previous works\textsuperscript{23,24,78} agree on the existence of an intermediate phase at $x = 1.5$, these works disagree on whether there is a second intermediate phase at $x = 1.75$,\textsuperscript{23,78} or a solid solution regime for $1.5 \leq x \leq 2$.\textsuperscript{24} Our results support the former findings, though the $x = 1.75$ phase is only slightly below the tie-line formed by the Li$_{1.5}$VOPO$_4$ and Li$_2$VOPO$_4$ phases.

From our electrochemical cycling data in Figure 2.3, we may make the observation that it is somewhat easier to intercalate Li into LiVOPO$_4$ than to remove Li from LiVOPO$_4$. However, intercalation of Li into LiVOPO$_4$ is associated with increasing polarization with cycling. Our results suggest that the limitation in extracting Li from LiVOPO$_4$ at high voltage is kinetic in nature, whereas the increasing polarization during intercalation at low voltage is probably due to thermodynamically driven structural changes.
From NEB calculations, we find that LiVOPO$_4$ is a pseudo-1D vacancy diffuser, with much lower effective migration barriers for the Li1 path (244 meV) than for the Li2 path (703 meV). The barriers for the Li1 path are also significantly lower than the Li migration barriers in the charged VOPO$_4$ material (463 meV) calculated by Mueller et al.$^{69}$ This suggests that (a) initial extraction of Li is likely to take place from the Li1 channel, and (b) there may be asymmetry in the kinetics between charge and discharge for $0 \leq x \leq 1$. This observation is consistent with the results of our GITT measurements, which find much lower overpotentials for high-voltage discharge compared to high-voltage charging. It could account for why full extraction of Li from LiVOPO$_4$ is difficult, as well as the larger polarization observed at the end of charge in most experiments.$^{23,25,42}$ It should be noted that the computed vacancy migration barriers in this work are different from those recently calculated by Ling et al.,$^{62}$ who concluded that vacancy migration in LiVOPO$_4$ follows a 2D network. However, as noted by the authors themselves, the relaxed LiVOPO$_4$ structure in Ling et al.$^{62}$'s work shows significant deviation from the experimental structure, and their GGA+$U$ NEB migration barriers are for a combination of ionic and electron migration.

The DFT calculations, PDF and EXAFS analysis provide strong evidence of thermodynamically driven structural changes during Li insertion into LiVOPO$_4$. First, the DFT calculated phase diagram show that the Li$_x$VOPO$_4$ phases are highly unstable for $x > 1$, with $E_{\text{hull}}$ as high as 81 meV per atom for the Li$_2$VOPO$_4$ end member. Second, operando PDF and EXAFS data show evidence of a clear hysteresis in VO$_6$ local environments during low-voltage cycling. In particular, an irreversible increase in a V—O long bond at $>2.4$ Å is observed. The long V—O bond at $>2.4$ Å found in both PDF and EXAFS local structure analysis of the cycled samples, as well as in a previous EXAFS study by Allen et al.,$^{74}$ but it is not reflected in the VO$_6$ environments.
of the DFT-relaxed or experimentally derived Li$_x$VOPO$_4$ structures. VO$_6$ environments with a long V—O bond close to that observed (>2.3 Å) are known for HVOPO$_4$, which shares the same VO$_6$—PO$_4$ connectivity as ε-Li$_x$VOPO$_4$. DFT relaxations of both HVOPO$_4$ and H$_2$VOPO$_4$ derived by substituting H for Li in LiVOPO$_4$ and Li$_2$VOPO$_4$, respectively, also show a significant extension in certain V—O bond lengths. Accordingly, we speculate that the observed >2.4 Å V—O bond is associated with H incorporation into the Li$_x$VOPO$_4$ structure, perhaps as a H/Li solid solution. Hydride formation is known to occur for V-based catalysts in organic solution. Here, we believe the H likely results from electrolyte decomposition. A recent detailed study of the thermal stability of cathodes by some of the authors provides strong evidence that the charged VOPO$_4$ tends to oxidize the electrolyte to form H$_x$VOPO$_4$. The structural distortions resulting from this H incorporation may provide an explanation for the increasing polarization during cycling. The investigation of this hypothesis will be the subject of future work.

The DFT results on the ionic and electronic conductivity in Li$_x$VOPO$_4$ emphasize the importance of nanosizing and carbon coating in achieving good electrochemical performance. The pseudo-1D nature of the diffusion pathways in Li$_x$VOPO$_4$ (this work and the work of Mueller et al.), similar to the olivine Li$_x$MPO$_4$ cathodes, makes nanosizing crucial for maintaining facile Li conduction, given the fact that inevitable channel blocking defects at the macroscopic limit would limit the conductivity in 1D diffusers. We also find Li$_x$VOPO$_4$ to be a large band gap insulator throughout the entire lithiation range, and calculated polaron migration barriers are similar to those in the olivine LiMPO$_4$ systems. Therefore, carbon-coating and nanosizing are essential for electronic conductivity as well. It should be noted that this result is contrary to the previous measurements of Song et al., who found VOPO$_4$ (10$^{-6}$ S cm$^{-1}$) to have a much higher electronic conductivity compared to LiFePO$_4$ (10$^{-8}$–10$^{-10}$ S cm$^{-1}$). It is our wish that future
experiments into the electronic conductivity across different states of charge, especially for the $x = 1$ and $x = 2$ end members, would be carried out to more conclusively verify the first-principles predictions and previous experimental results.

### 2.6 Conclusion

To conclude, we have demonstrated that solid-state synthesized LiVOPO$_4$ can be stably cycled over 1.65 Li for more than 20 cycles. About 65% of the theoretical capacity was achieved during delithiation from LiVOPO$_4$ to VOPO$_4$ in the high-voltage regime, whereas almost 100% of theoretical capacity was obtained during lithiation of LiVOPO$_4$ to Li$_2$VOPO$_4$ in the low-voltage regime, albeit with increasing polarization. Using a combination of DFT calculations, GITT measurements, operando PDF analysis and EXAFS spectra, we show that the capacity limitations during delithiation is likely to be driven by Li mobility limitations, whereas the increasing polarization during lithiation is the result of structural changes. We also show that Li$_x$VOPO$_4$ is likely to be a pseudo-1D ionic conductor with low electronic conductivity, for which nanosizing and carbon coating is essential to achieve good electrochemical performance.

Figure 2.1 Crystal structure of VOPO₄, showing polaron migration along 1D VO₆ chains.
Figure 2.2 (a) High-resolution X-ray diffraction pattern of ε-LiVOPO₄ (wavelength \( \lambda = 0.72775 \) Å); (b) High resolution X-ray diffraction patterns of as-synthesized and high energy ball milled ε-LiVOPO₄ (wavelength \( \lambda = 0.78013 \) Å); (c) TEM image of ε-LiVOPO₄ Particles.
Figure 2.3 Galvanostatic charge–discharge cycling of ε-LiVOPO₄: (a) high voltage cycling within 3–4.5 V (C/50) and (b) low voltage cycling in the range of 1.5–3.5 V (C/50). Two lithium cycling from 1.6 to 4.5 V (c) at C/50 and (d) C/20 (1C = 159 mA/g); (e) Comparison between experimental voltage curve at 50C and HSE calculated voltage profile.
Figure 2.4 GITT capacity-voltage profiles of $\varepsilon$-LiVOPO$_4$ in the (a) high voltage and (b) low-voltage domains. (c) Voltage vs time graph of the magnified marked region. C/50 current was applied for 1.5 h before rest; 24 h relaxing for low voltage and 100 h for high voltage.

Figure 2.5 (a) Calculated pseudobinary VOPO$_4$–Li$_x$VOPO$_4$ phase diagram using the HSE (blue) and GGA+U (green) functionals. Squares, unstable structures; circles, stable structures; lines, convex hull. (b) Calculated energies above the convex hull for stable orderings in the pseudobinary VOPO$_4$–Li$_x$VOPO$_4$ system in GGA+U. The convex hull is calculated with respect to all phases in the full Li–V–P–O calculated phase diagram.

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<th>Voltage step $\left(x_1 - x_2\right)$</th>
<th>GGA+U</th>
<th>HSE</th>
<th>Expt.</th>
<th>Literature</th>
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<td>1.63</td>
<td>1.72</td>
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<td>7 – 9</td>
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Figure 2.6 Symmetrically distinct VO₆ local environments in LiₓVOPO₄ from structures relaxed using HSE calculations. Large sphere: vanadium ion. Small sphere: oxygen ion.
Table 2.2 Comparison of calculated lattice parameters of stable Li$_x$VOPO$_4$ structures with the experimental lattice parameters.

<table>
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<th>$x$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\alpha$ (°)</th>
<th>$\beta$ (°)</th>
<th>$\gamma$ (°)</th>
<th>Volume (Å$^3$)</th>
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Figure 2.7 Refinements of all Li$_x$VOPO$_4$ based on the calculated structures, lattice parameters refined, atomic positions fixed.

Figure 2.8 Refinements of all intermediates based on the HSE-relaxed structures, lattice parameters, and oxygen atomic positions.
Figure 2.9 Structural model of LiVOPO$_4$.

Figure 2.10 (a) Operando PDF data obtained during cycling of LiVOPO$_4$ in the range 3.5–1.6–3.5 V. (b) Peak positions corresponding to the V—O and V═O bonds, and the intensity-weighted average value. Experimental data, open markers; HSE calculated distances, red closed markers.
Figure 2.11 Changes in V—O bond lengths and coordination showing hysteresis during lithiation and delithiation.

Figure 2.12 EXAFS analysis of ex-situ LiVOPO₄ cathodes at various states of charge. (a) First shell fits using an asymmetric model for the VO₆ octahedron including long and short apical bonds, and four equivalent equatorial bonds. (b) V—O bond lengths at different states of charge. (c) Normalized XANES spectra used for the fitting.
Figure 2.13 Crystallographically distinct Li in LiVOPO$_4$ and investigated diffusion paths in LiVOPO$_4$ viewed along (a) [100] and (b) [110] directions. A total of six different vacancy hops were investigated. Using the labeling scheme in (a), hops A → B and B → C form a 1D channel comprising only Li1 sites, whereas hops D → E and E → F form a similar 1D channel comprising only Li2 sites. In addition, hops from one 1D channel to another (hops A → G and A → H) were also investigated.
Figure 2.14 Calculated GGA CI-NEB migration barriers for various vacancy hops in LiVOPO$_4$. 
Figure 2.15 Orbital projected densities of states of Li$_x$VOPO$_4$ from HSE calculations.
Figure 2.16 Comparison of calculated HSE polaron migration barriers for Li$_x$VOPO$_4$ with olivine LiFePO$_4$ and LiMnPO$_4$ from ref $^{72}$. 
Chapter 3. Comparison of the polymorphs of VOPO$_4$ as multi-electron cathodes for rechargeable alkali-ion batteries

3.1 Introduction

The typical cathode used in today’s rechargeable alkali-ion batteries are layered oxides with formula A$_x$MO$_2$, where A is an alkali-ion (Li/Na) and M is a transition metal or mixture of transition metals.$^{92,93}$ These cathodes, as well as other common cathodes such as LiFePO$_4$, operate on the transfer of a single-electron per transition metal, limiting achievable energy densities. Multi-electron polyanionic cathodes offer the potential to significantly increase energy densities by leveraging on the inductive effect of polyanion chemistries to increase voltage, and the transfer of more than one electron per transition metal to increase capacity.

Several families of materials have been investigated as potential multi-electron polyanionic cathodes for rechargeable alkali-ion batteries. For example, the Li$_2$MSiO$_4$ (M = Fe, Co, Mn) silicates have theoretic capacities > 333 mAh/g,$^{95}$ but exhibit poor rate capability due to poor intrinsic ionic conductivity.$^{96-99}$ In phosphates, a previous high-throughput first-principles study has shown that only V and Mo can attain reasonable average voltages across multiple redox couples ($V^{3+} \rightarrow V^{5+}$ and $Mo^{3+} \rightarrow Mo^{6+}$) as practical multi-electron cathodes.$^{100}$ Extensive studies have been carried out on Li$_3$V$_2$(PO$_4$)$_3$, Li$_5$V(PO$_4$)$_2$F, Li$_9$V$_3$(P$_2$O$_7$)$_3$(PO$_4$)$_2$,$^{101-105}$ but achieving reversible cycling remains a challenge, especially for with the high $V^{4+}$/V$^{5+}$ redox couple. Na$_3$V$_2$(PO$_4$)$_3$ has been reported with excellent rate capability and good cycling performance up to ~1.4 Na due to open NASICON structure, but with low theoretical capacity of ~120 mAh/g.$^{106}$ Na$_3$V$_2$(PO$_4$)$_2$F$_3$ has been demonstrated promising with reversible capacity ~128 mAh/g at ~3.75V using $V^{3+}$/V$^{4+}$ along with good rate capability and capacity retention.$^{107,108}$

Among the candidate multi-electron polyanionic chemistries, the A$_x$VOPO$_4$ (A = Li, Na)
vanadyl phosphates are among the most promising, with good electrochemical performance having been achieved for both lithium and sodium-ion insertion. By utilizing both the \( V^{3+/4+} \) and \( V^{4+/5+} \) redox couples, VOPO\(_4\) has a high theoretical capacity of 305 mAh / g Li\(_2\)VOPO\(_4\) or 258 mAh / g Na\(_2\)VOPO\(_4\). Depending on synthesis conditions, VOPO\(_4\) can crystallize in one of seven polymorphs, namely, \( \alpha_1 \) (P4/n), \( \alpha_0 \) (P4/n), \( \beta \) (Pnma), \( \delta \) (P4\(_2\)/mbc), \( \varepsilon \) (Cc), \( \omega \) (P4\(_2\)/mmc) and \( \gamma \) (Pbam). We will henceforth refer to all lithiated/sodiated phases of VOPO\(_4\) polymorphs using the prefix associated with the VOPO\(_4\) phase, as proposed by Whittingham et al. For example, even though the singly lithiated phase of \( \varepsilon \)-VOPO\(_4\) is designated as \( \alpha \)-LiVOPO\(_4\) in the literature based on the order of discovery, we will instead refer to this phase as \( \varepsilon \)-LiVOPO\(_4\) to establish a clear correspondence between the phases at different levels of intercalation. Among the seven polymorphs, the \( \beta \), \( \varepsilon \) and \( \alpha_1 \) forms are arguably the most well-studied as multi-electron cathodes for both Li-ion and Na-ion chemistry. For Li-ion chemistry, reasonable multi-electron cycling has been achieved in all three phases, with reversible capacities of up to \(~80\), \(~225\) and \(~240\) mAh/g having been achieved for \( \beta \), \( \varepsilon \) and \( \alpha_1 \) respectively. For Na-ion chemistry, on the other hand, electrochemical cycling performance has been mixed. Monoclinic NaVOPO\(_4\), which is structurally similar to \( \varepsilon \)-LiVOPO\(_4\), was first reported by Song et al. with a reversible capacity of \(~90\) mAh/g. More recently, He et al. investigated \( \alpha_1 \)-NaVOPO\(_4\) and \( \beta \)-NaVOPO\(_4\) obtained from corresponding Li phases and showed that while a relatively high capacity of \(~150\) mAh/g can be achieved in \( \alpha_1 \)-NaVOPO\(_4\) with the incorporation of reduced graphene oxide, a large irreversible capacity loss is observed during the cycling of \( \beta \)-NaVOPO\(_4\).

It is evident from these previous studies that different polymorphs with the same chemistry
(VOPO$_4$) can exhibit radically different electrochemical performances for Li-ion and Na-ion chemistry. The VOPO$_4$ polymorphs therefore present a unique opportunity for us to probe the interplay between host structure and alkali-ion chemistry, and its corresponding effect on thermodynamic stability, voltage and diffusion kinetics. To our knowledge, no other cathode chemistry present a similarly diverse polymorphism.$^{93}$

In this work, we performed a systematic first principles investigation, supported by careful electrochemical characterization and published experimental data, of the relative thermodynamic stability, voltage, band gap, and diffusion kinetics for alkali intercalation in $\beta$, $\varepsilon$ and $\alpha$ polymorphs of VOPO$_4$. The primary effort is focused on the relative electrochemical performance of Li$^+$ insertion in the different polymorphs of VOPO$_4$, for which both density functional theory (DFT) data and experimental results are presented. To further probe the relationship between structure and electrochemical properties, we have also investigated the insertion of the larger Na$^+$ ion into the same hosts using DFT calculations only. We find that all three VOPO$_4$ polymorphs remain reasonably stable with one alkali-ion insertion, but become significantly less stable with two alkali-ion insertion. We will show that the significantly different cycling performances for Li$^+$ insertion in the different VOPO$_4$ polymorphs can be linked to the differences in Li$^+$ migration barriers, which in turn can be correlated to topological descriptors such as bottleneck size. Finally, we will demonstrate that the migration of the larger Na$^+$ ion is much more sensitive to bottleneck size compared to Li$^+$, and discuss this effect in the context of electrochemical performances already reported in the literature. These results provide crucial insights, such as the importance of structural selection, into the design of new multi-electron cathodes for Li-ion and Na-ion batteries.

3.2 Computational methods

All density functional theory (DFT) calculations were performed using the Vienna Ab
initio Simulation Package (VASP)\textsuperscript{126} within the projector augmented-wave approach,\textsuperscript{127} and all analyses were performed using the Python Materials Genomics (pymatgen) library\textsuperscript{128} and the pymatgen-diffusion add-on.\textsuperscript{129}

### 3.2.1 Generating initial structures

Initial structures of $\varepsilon$-VOPO$_4$ (ICSD # : 415924), $\varepsilon$-LiVOPO$_4$ (ICSD # : 184602), monoclinic NaVOPO$_4$, (ICSD # : 188088), $\beta$-VOPO$_4$ (ICSD # : 9413), $\beta$-LiVOPO$_4$ (ICSD # : 80613), and $\alpha$-VOPO$_4$ (ICSD # : 108983) were obtained from Inorganic Crystal Structure Database (ICSD).\textsuperscript{119} The initial structure for $\varepsilon$-Li$_2$VOPO$_4$ is based on that reported by Bianchini \textit{et al.}\textsuperscript{116} It should be noted that the monoclinic form of NaVOPO$_4$ is structurally similar to $\varepsilon$-LiVOPO$_4$, albeit with a different space group and only one symmetrically distinct Na site (instead of two symmetrically distinct Li sites in $\varepsilon$-LiVOPO$_4$). Henceforth, we will refer to this monoclinic form as $\varepsilon$-NaVOPO$_4$. As the structures of $\beta$-Li$_2$VOPO$_4$, $\beta$-Na$_2$VOPO$_4$, $\varepsilon$-Na$_2$VOPO$_4$, $\alpha$-NaVOPO$_4$, $\alpha$-Li$_2$VOPO$_4$ and $\alpha$-Na$_2$VOPO$_4$, have not yet been reported, we obtained candidate structures by identifying potential alkali intercalation sites using a Voronoi tessellation-based algorithm, followed by an enumeration of all symmetrically distinct alkali orderings. It should be noted that it is known that the $\alpha$$_1$ polymorph exhibits alkali-ion site disorder,\textsuperscript{111,114,130} and all sites with non-zero occupancies reported in experiments were considered in the structural enumeration. The structure with the lowest energy computed via DFT was then used as the representative structure for subsequent studies of voltage and migration barriers.

### 3.2.2 Total energy calculations

The total energies of all $A_x$VOPO$_4$ ($x = 0, 1, 2$) polymorphs were calculated using the Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA)\textsuperscript{131} functional with
the application of an effective Hubbard $U$ of 3.25 eV for vanadium (GGA+$U$), similar to that used in the Materials Project. All calculations were spin-polarized starting from a high-spin ferromagnetic configuration given that previous works have found magnetic effects to have a minimal impact on relative energies. Similar to parameters used in the Materials Project, a plane wave energy cutoff of 520 eV and $k$-point density of at least 1000/(number of atoms in unit cell) was used for all calculations. To estimate the thermodynamic stability of $A_xVOPO_4$ polymorphs, we evaluated their energy above the hull ($E_{\text{hull}}$) by constructing the corresponding $A$-V-P-O quaternary phase diagrams, wherein the energies of compounds other than those of primary interest in this work were extracted from Materials Project using the Materials Application Programming Interface. Stable phases have an $E_{\text{hull}}$ of 0, whereas increasing $E_{\text{hull}}$ indicates decreasing thermodynamic stability.

3.2.3 Electronic structure calculation

The electronic band gap of all $A_xVOPO_4$ polymorphs ($x = 0, 1$ and 2) were calculated using the screened hybrid Heyd-Scuseria-Ernzerhof functional (HSE06) with a $k$-point density of 500 per atoms in the unit cell.

3.2.4 Climbing-image nudged elastic band calculations

The barriers for $A^+$ ion and alkali vacancy $v_A^-$ (lower case $v$ is used to denote an alkali vacancy to distinguish it from upper case V for vanadium) migration in VOPO$_4$ and $A$VOPO$_4$ polymorphs, respectively, were calculated using the climbing image nudged elastic band (CI-NEB) method. To avoid ambiguity regarding the localization of electrons, the PBE functional without Hubbard $U$ was used, in line with the well-established practice in the literature. For $v_A^-$ migration calculations, the CI-NEB calculations were carried out using $2 \times 2 \times 2$ supercells with
formula $A_{31}V_{32}O_{32}P_{32}O_{128}$ (32 formula units) for the $\beta$ and $\varepsilon$ polymorphs, and $A_{15}V_{16}O_{32}P_{16}O_{80}$ (16 formula units) for $\alpha$ polymorph to minimize the interactions between periodic images. Likewise, $2 \times 2 \times 2$ supercells with formula of $A_{1}V_{32}O_{32}P_{32}O_{128}$ for $\varepsilon$ and $\beta$ polymorphs, and $A_{1}V_{16}O_{32}P_{16}O_{80}$ for $\alpha$ polymorph were used to calculate single A$^+$ ion migration barriers. A $\Gamma$-centered $1 \times 1 \times 1$ $k$-point grid was used for $\varepsilon$ and $\beta$ polymorphs, while a $2 \times 2 \times 2$ $k$-point grid was used for the $\alpha$ polymorph. The image-dependent pair potential approach was used to obtain better initial guesses of the NEB paths.$^{129,142}$ The atomic coordinates in each image were relaxed until the force components on each atom were less than 0.03 eV/Å. No compensating background charge was applied.

It should be noted that we did not attempt to study $v_A^-$ migration in $A_2VOPO_4$. We find that the creation of a vacancy results in significant rearrangement of the alkali ions in $A_2VOPO_4$ due to the large number of the alkali ions in proximity with one another.

### 3.3 Experimental methods

$\beta$-, $\varepsilon$- and $\alpha$-LiVOPO$_4$ were synthesized from LiVOPO$_4$·2H$_2$O precursor obtained by a hydrothermal method modified from previous reports.$^{7,18}$ V$_2$O$_5$ (Aldrich, $\geq 99.6\%$), oxalic acid (Sigma-Aldrich, $\geq 99.0\%$), and phosphoric acid (Fisher Scientific, 85%) were stirred in ethanol and water for 18 hours. LiOH·H$_2$O (Sigma, $\geq 99.0\%$) was then added, and the mixture was stirred for another 4 hours. The mixture was then placed in a 4748 Type 125 mL PTFE-lined reactor (Parr Instrument Co.) and heated to 160 °C for 48 hours. The hydrothermally synthesized LiVOPO$_4$·2H$_2$O was filtered and washed with water, ethanol, and acetone, then dried at 80 °C. The different LiVOPO$_4$ phases were then synthesized by annealing the hydrated precursor in different environments for 3 hours:
• \( \beta \)-LiVOPO\(_4\): At 600 °C in O\(_2\)
• \( \varepsilon \)-LiVOPO\(_4\): At 750 °C in Ar
• \( \alpha_1 \)-LiVOPO\(_4\): At 300 °C in Ar

Powder X-ray diffraction (XRD) data were collected at room temperature with a Bruker D8 Advance diffractometer with Bragg-Brentano geometry using a Cu Ka source (\( Ka1 = 1.54053 \) Å, \( Ka2 = 1.54431 \) Å). This instrument utilizes a Lynx-Eye 1D position sensitive detector (192 channel Si strip detector) with a primary and secondary radius of 280 mm. Routine pattern indexing and phase identification was done using the PDF-2015 software package, while the TOPAS software package (Bruker AXS, version 5.0) was used for Rietveld refinement.

Electrodes were prepared by high-energy ball-milling LiVOPO\(_4\) with graphene for 30 minutes. Polyvinylidene fluoride (PVDF) was then added to the mixture, resulting in a LiVOPO\(_4\):graphene:PVDF ratio of 75:15:10. A slurry was formed by dissolving the mixture in n-methyl-2-pyrrolidinone (NMP), which was then cast onto a carbon-coated Al foil and dried at 60 °C. Electrodes with areas of 1.2 cm\(^2\) and active mass loadings of 2-3 mg were punched and assembled into 2325-type coin cells with pure lithium chip (MTI) as the counter and reference electrodes, a Celgard 2400 separator (Hoechst Celanese) as the separator, and 1 M LiPF\(_6\) in 1:1 v/v ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. Electrochemical tests were conducted using a VMP multichannel potentiostat (Bio-Logic). Capacities were measured through galvanostatic charge-discharge tests from 3 to 4.5 V at current densities from 5 \( \mu \)A/cm\(^2\) (C/50) to 250 \( \mu \)A/cm\(^2\) (C/1, where C is defined as 158.57 mAh/g). Diffusion coefficients were estimated from cyclic voltammetry (CV) data using the Randles–Sevcik equation.\(^{143}\) Cells were run through CV at 0.05, 0.1, 0.2, and 0.5 mV/s, between 1.5 and 4.5 V.
3.4 Results

3.4.1 Crystal structures of $A_xVOPO_4$ polymorphs

Figure 3.1 shows the fully-relaxed, lowest-energy structures of $A_xVOPO_4$ polymorphs ($x = 0, 1$) from GGA+$U$ calculations. The alkali orderings for the lowest energy structures are similar for the Li and Na forms of the $\varepsilon$ and $\beta$ polymorphs. For $\alpha$, the lowest energy orderings are different for Li and Na, though we have found that the energy is not especially sensitive to the alkali ordering; there are > 10 structures with energies within 10 meV of the ground state. It is well-established in the literature that $\alpha$-LiVOPO$_4$ and $\alpha$-NaVOPO$_4$ are disordered at room temperature,$^{111,114}$ and our calculations support these observations.

We have synthesized $\beta$-, $\varepsilon$- and $\alpha$-LiVOPO$_4$ polymorphs, and the X-ray diffraction patterns (see Figure 3.2) confirm the formation of pure $\beta$-, $\varepsilon$- and $\alpha$-LiVOPO$_4$ phases. Overall, the measured cell parameters of the as-synthesized LiVOPO$_4$ polymorphs (see Table 3.1) are in good agreement with the DFT counterparts, with the largest volume difference being ~5.6% in the case of $\alpha$-LiVOPO$_4$. Our calculated cell parameters for the Na$_x$VOPO$_4$ polymorphs are also in good agreement with those reported in literature.$^{110-112}$

3.4.2 Thermodynamic stability and intercalation voltage

We evaluated the thermodynamic stability of $A_xVOPO_4$ polymorphs ($x = 0, 1, and 2$) by computing their energy above convex hull ($E_{\text{hull}}$).$^{135}$ The results are shown in Figure 3.3a. For VOPO$_4$, we find that the most stable polymorph is $\beta$, whereas the most stable polymorphs of AVPO$_4$ for Li and Na versions are $\beta$ and $\varepsilon$, respectively. For LiVOPO$_4$, Ling et al.$^{62}$ previously found that $\varepsilon$-LiVOPO$_4$ is ~10 meV/atom lower in energy than $\beta$-LiVOPO$_4$, whereas our calculations find that $\beta$-LiVOPO$_4$ is ~5 meV/atom lower in energy than $\varepsilon$-LiVOPO$_4$. This is likely
due to different parameters, e.g. $U$ value utilized in the calculations. Nevertheless, such small energy differences indicate that both $\varepsilon$- and $\beta$- have similar thermodynamic stability. All $A_2VOPO_4$ ($x = 0$ and $1$) polymorphs have an $E_{\text{hull}}$ of $\sim 30$ meV/atom or less up to one alkali insertion, indicating that they are likely metastable and can be stabilized at finite temperatures. This is consistent with their synthesizability in experiments.$^{122,123,125,144,145}$ $\beta$-VOPO$_4$ forms upon heating of $\varepsilon$-VOPO$_4$, indicating that $\beta$-VOPO$_4$ is more stable, while the opposite is true for LiVOPO$_4$ polymorphs. In our experiments, $\beta$-LiVOPO$_4$ forms at 600 °C in O$_2$, while further heating to 700 °C leads to the formation of $\varepsilon$-LiVOPO$_4$. The reports on direct synthesis methods of $\alpha$-VOPO$_4$ are scarce and variable, which makes it difficult to evaluate its stability.$^{146-148}$ $\alpha$-LiVOPO$_4$ can be formed at lower temperatures either from structurally related precursor LiVOPO$_4$·2H$_2$O$^{121}$ or in microwave-assisted hydrothermal synthesis$^{118}$, indicating that it is the least stable among the three considered LiVOPO$_4$ phases. This is consistent with the higher calculated $E_{\text{hull}}$ of $\alpha$ compared with the $\beta$ and $\varepsilon$ phases, and we speculate that the known alkali-ion disorder in $\alpha$ may play a role in entropically stabilizing this polymorph.

Of the three NaVOPO$_4$ polymorphs, direct high-temperature synthesis has only been reported for $\varepsilon$-NaVOPO$_4$ as of now$^{125}$; the $\beta$- and $\alpha$- polymorphs are formed by ion exchange from the Li counterparts,$^{111,112}$ which is consistent with our DFT calculations showing that $\varepsilon$-NaVOPO$_4$ is significantly more stable than the $\beta$ and $\alpha$ equivalents. For A$_2$VOPO$_4$ polymorphs, our calculations clearly show that they have much higher $E_{\text{hull}}$, suggesting that they are thermodynamically more unstable compared to their AVOPO$_4$ counterparts. In particular, we note that the different polymorphs of Na$_2$VOPO$_4$ have extremely different $E_{\text{hull}}$, with the $\beta$ form being the least stable and the $\varepsilon$ form being the most stable. None of A$_2$VOPO$_4$ polymorphs have been synthesized directly so far; instead, they have been obtained by chemical and electrochemical
lithiation of corresponding LiVOPO$_4$ polymorphs. This is consistent with the calculated reduced stability of $x = 2$ phases.

We have also constructed the 0K phase diagrams of AVOPO$_4$ polymorphs for Li and Na (see Figure 3.4). Our results show that there are no intermediate phases in the high voltage regime VOPO$_4$-AVOPO$_4$, which agree with experimental findings in literature. In the low voltage region AVOPO$_4$-A$_2$VOPO$_4$, there are two intermediate phases at 1.5 and 1.75 for the $\varepsilon$ polymorph intercalated with Li, which is in good agreement with previous experimental findings. Although our calculations indicate that there is an intermediate phase for the $\beta$ polymorph at $x = 1.5$ for both Li and Na, there is no clear experimental evidence so far. This might be due to the relatively poor crystallinity of the samples by either low-temperature synthesis method proposed by He et al. or ball-milling.

Figure 3.3b shows the calculated voltage profiles of the different polymorphs for Li and Na insertions, respectively. We find that the average voltage for Li insertion is about 0.33-0.69 V higher than for Na insertion, in line with the observed voltage differences in other host structures.

Figure 3.5 shows the cyclic voltammetry (CV) curves measured at several sweep rates over the 1.5 V to 4.5 V voltage range. Each peak at a specific voltage corresponds to an electrochemical reaction. In the high-voltage regime, all three polymorphs show a single peak for the LiVOPO$_4$ to VOPO$_4$ transformation at 4.2, 4.1, and 4.0 V for $\beta$, $\varepsilon$, and $\alpha$-LiVOPO$_4$, respectively. The observed voltage trend of $\beta > \varepsilon > \alpha$ agrees with the trend from first principles calculations (see Figure 3.3b). The computed and measured average voltages for the first redox process ($V^{4+/5+}$) are also in excellent agreement with reported experimental voltages in the literature ($\beta$-LiVOPO$_4 \approx 3.9$ V, $\beta$-NaVOPO$_4 \approx 3.3$ V, $\varepsilon$-LiVOPO$_4 \approx 3.95$ V, $\varepsilon$-NaVOPO$_4 \approx 3.6$ V, $\alpha$-LiVOPO$_4 \approx 3.7$ V, $\alpha$-NaVOPO$_4 \approx 3.4$ V).
In the low-voltage region ~2V, only one peak is observed for $\beta$ and $\alpha$-LiVOPO$_4$, while three distinct peaks are observed for $\varepsilon$-LiVOPO$_4$ during charging/discharging. These findings suggest that there are no intermediate phases for insertion of Li in $\alpha$- and $\beta$-LiVOPO$_4$, but there are two intermediate phases at $\sim x = 1.5$ and $x = 1.75$ for insertion of Li into $\varepsilon$-LiVOPO$_4$, which are in agreement with the calculated $\alpha$-Li$_x$VOPO$_4$ phase diagram and our recent studies of $\varepsilon$-LiVOPO$_4$.\cite{109,113,151} The voltages measured from the experimental CV data follows the trend $\alpha > \varepsilon > \beta$, which is again in agreement with the first principles calculations.

### 3.4.3 Alkali ion migration barriers

**$\beta$-A$_x$VOPO$_4$.** There is only one symmetrically distinct $v_{A^+}$ diffusion path in $\beta$-AVOPO$_4$, which is denoted as path A-B along [010] direction (see Figure 3.6a). We find the barriers of $v_{Li^+}$ and $v_{Na^+}$ migrations in $\beta$-LiVOPO$_4$ and $\beta$-NaVOPO$_4$ are 239 and 255 meV, respectively, and the barriers of Li$^+$ and Na$^+$ migration in $\beta$-VOPO$_4$ are 346 and 541 meV, respectively.

For $\beta$-A$_x$VOPO$_4$ ($x = 0, 1$), both Li$^+$ and Na$^+$ exhibit 1D diffusion along the [010] direction, in line with the previous simulation and experimental results.\cite{62,112} We notice that our computed $v_{Li^+}$ diffusion barrier in $\beta$-LiVOPO$_4$ (239 meV) differs substantially from a previous study by Ling et al. (150 meV).\cite{62} This may be due to the fact that the GGA+$U$ functional was employed in that study, whereas we used GGA functional in the current study to avoid any mixing of the diffusion barrier with a charge transfer.

**$\varepsilon$-A$_x$VOPO$_4$.** The barriers for $v_{Li^+}$ migration in $\varepsilon$-LiVOPO$_4$ have already been reported in our recent work,\cite{109} and we will briefly summarize the key results here. The two 1D paths, path A$\rightarrow$B$\rightarrow$C (formed by Li1 sites) and path D$\rightarrow$E$\rightarrow$F (formed by Li2 sites) in Figure 3.7a, have
barriers of 244 and 703 meV, respectively. Significantly higher barriers of > 800 meV are found for inter-chain migration (paths A→G and A→H). In comparison, the migration barriers for $v_{Na^+}$ in ε-NaVOPO$_4$ are much higher, with barriers exceeding 1eV for all paths (Figure 3.7b). We have tested the sensitivity of this result to the functional used; similar results are obtained with the PBEsol functional$^{152}$, even though the lattice parameters are much closer to that of the experimental values.

At the beginning of discharge, there are three distinct paths for A$^+$ diffusion in ε-VOPO$_4$. For paths A→B, A→C and A→D, the barriers for Li$^+$ migrations are 271, 629 and 637 meV, respectively, and those for Na$^+$ migrations are 516, 674, and 694 meV, respectively (see Figure 3.8a). We note that our calculated Li$^+$ migration barriers are somewhat lower than the values of 463 (1D), 738 (2D), 1215 (3D) meV previously reported by Mueller et al.$^{141}$ We believe that the difference is due to the fact that a delithiated ε-LiVOPO$_4$ framework with triclinic symmetry was used in Mueller et al.’s work, whereas the experimentally observed ε-VOPO$_4$ with monoclinic symmetry is used in this work.

$\alpha$-A$_x$VOPO$_4$. For $\alpha$-LiVOPO$_4$, there are four distinct $v_{Li^+}$ diffusion paths, denoted as paths A→B, A→C, A→D and A→E in Figure 3.9a, with calculated barriers of 728, 762, 449, and 328 meV, respectively. In $\alpha$-NaVOPO$_4$, there are three distinct $v_{Na^+}$ diffusion paths, denoted as paths A→B, A→C and A→D in Figure 3.9b, with calculated barriers of 263, 1409 and 565 meV, respectively. The much higher barrier of 1409 meV in path A→C is likely due to the much shorter distance of the two VO$_6$ octahedra to the path (see Table S1 in SI). As it is well-established that alkali ions in $\alpha$-AVOPO$_4$ are disordered, we also evaluated the $v_{Na^+}$ migration barriers for the $v_{Li^+}$ paths shown in Figure 3.9a. We find that the $v_{Na^+}$ migration barriers for A→B, A→C, A→D
and $A \rightarrow E$ are 651, 548, 261 and 123 meV, respectively, which in all instances are lower than the corresponding $v_{Li^+}$ migration barriers.

For $\alpha$-VOPO$_4$, three distinct diffusion paths for Li$^+$ are identified, denoted as paths $A \rightarrow B$, $A \rightarrow C$ and $A \rightarrow D$ in Figure 3.10a with calculated barriers of 276, 282 and 284 meV, respectively. Such similar barriers are likely due to the similar local environments of barrier bottlenecks of these three paths (see Table 3.2). In the case of single Na$^+$ migration, the barriers of $A \rightarrow B$, $A \rightarrow C$ and $A \rightarrow D$ are 438, 2308 and 427 meV, respectively. The much higher barrier of the $A \rightarrow C$ path is likely due to the much shorter Na-O and Na-V distances than those in the $A \rightarrow B$ and $A \rightarrow D$ paths (see Table 3.2).

3.4.4 Electronic band gap

Figure 3.13 shows the calculated electronic band gaps of $A_x$VOPO$_4$ ($x = 0, 1$ and 2) polymorphs. All polymorphs are found to have band gaps $> 2.1$ eV, indicating that they are insulators. The electronic band gaps of the $\beta$ and $\epsilon$ polymorphs decrease with alkalination, but the electronic band gap of $\alpha$ polymorph increases by $> 0.6$ eV upon the insertion of first alkali ion and then decreases by $\sim 1$ eV when the second alkali ion is inserted. We will discuss the reasons for this different behavior in the Discussion section. Overall, our electronic band gap calculations suggest that carbon coating is critical for improving the electron conduction in these polymorphs.

3.4.5 Electrochemical performance

We have performed a rate test for all the three LiVOPO$_4$ polymorphs and calculated Li diffusion coefficients from the cyclic voltammetry data. Figure 3.14 shows the electrochemical performance for one-Li cycling between LiVOPO$_4$ and VOPO$_4$ (3 to 4.5 V) at various current densities. Though the high-voltage capacities for all polymorphs fall short of the theoretical 159 mAh/g, $\beta$-LiVOPO$_4$ exhibits the highest capacity of all the three phases ($\sim 90$ mAh/g) at C/20,
followed by $\varepsilon$-LiVOPO$_4$ and $\alpha$-LiVOPO$_4$, both exhibiting capacities of $\sim$80 mAh/g. At a higher rate of C/10, the $\beta$ polymorph does not experience significant capacity loss, while the capacities of $\varepsilon$ and $\alpha$ polymorphs drop to below 70 mAh/g. With further current increase to 1C, the $\beta$ and $\varepsilon$ polymorphs show similar capacity retention of about 50%, while the $\alpha$ polymorph retains only 40% of its capacity. When the current rate is decreased to C/50, all the polymorphs show similar capacities, around 90 mAh/g. These observations indicate that the $\varepsilon$ and $\alpha$ polymorphs clearly suffer more capacity loss at high rates, which are indicative of poorer Li diffusion kinetics in these polymorphs relative to the $\beta$ polymorph.

The high-voltage cycling of $\beta$- and $\varepsilon$-LiVOPO$_4$ at C/10 have previously been reported by Allen et al.$^{124}$ The capacities for $\beta$-LiVOPO$_4$ reported in that work are similar to our measurement. The $\varepsilon$-phase shows higher capacity of about 120 mAh/g, but it should be noted that a significant part of this capacity comes from the sloping part of the electrochemical curve, which is absent in our sample (see Figure 3.15). The true high-voltage plateau at about 3.86 V is the same in both works. The electrochemistry of $\alpha$-LiVOPO$_4$ at C/10 was also reported previously,$^{113,121}$ but in a larger voltage range between 2.5 V and 4.4 V, resulting in capacities of 100 to 120 mAh/g. Such differences in the electrochemical performances may be attributed to differences in morphology (see Figure 3.16) caused by different synthesis and ball-milling methods, and by the electrode preparation technique, in particular the amount and kind of carbon used. Our data obtained for three different polymorphs synthesized from the same precursor and employing the same electrode preparation indicates that $\beta$-LiVOPO$_4$ exhibits the highest capacity, followed by $\varepsilon$-LiVOPO$_4$ then $\alpha$-LiVOPO$_4$. We will discuss the observed electrochemical performance in the context of the calculated alkali migration barriers and band gaps.
From the CV, we estimated the apparent diffusion coefficient from the plot of the current versus the square root of the scan rate \((\nu^{1/2})\) (see Figure 3.17) via the Randles–Sevcik equation:

\[
i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}C\nu^{1/2}
\]

where \(i_p\) is the current at an electrochemical reaction, \(n\) is the number of electrons participating in one mole of the reaction, which is one in this case. \(A\) is the electrode-electrolyte interface area, \(D\) is the apparent diffusion coefficient, \(C\) is the mole concentration of Li-ions in the electrode, and \(\nu\) is the scan rate. In our calculations, the electrode-electrolyte interface is approximated to be the electrode area. Special care was also taken so that cells would have similar mass loadings to avoid introducing variations in the current experienced by the materials due to differences in mass loading.

Table 3.3 shows the estimated apparent diffusion coefficients for the insertion of Li to VOPO\(_4\) and the removal of Li from LiVOPO\(_4\). These values are calculated from the peaks in the CV curves above 3V. Specifically, the insertion of Li to VOPO\(_4\) is observed as a peak with a negative current while the removal of Li from LiVOPO\(_4\) is observed as a peak with a positive current. We find that the \(\beta\) polymorph has the highest diffusion coefficient at the start of both charge and discharge in the high voltage regime, followed by \(\alpha\) and then \(\varepsilon\). Quantitative comparison of these results with the CI-NEB migration barriers summarized in Figure 3.12 is difficult, given that the diffusion coefficients estimated from the CV are total diffusivities for the polycrystalline electrode, while the calculations are based on perfect crystals. Nevertheless, we may make several useful qualitative observations. In general, the CI-NEB calculations predict the \(\beta\) polymorph has the lowest migration barriers for Li\(^+\), albeit only in 1D. This agrees with the experimentally observed diffusion coefficients in Table 3.3. Between the \(\varepsilon\) and \(\alpha\) polymorphs, the effective barriers for 1D Li\(^+\) diffusion are very similar in these two phases, while the effective
barriers for >1D Li$^+$ diffusion are significantly lower in the $\alpha$ phase. Therefore, we speculate that >1D diffusion may account for the higher diffusivity observed in the $\alpha$ phase in experiments. Nevertheless, we observe that all three polymorphs have reasonably low diffusion barriers for Li$^+$.  

3.5 Discussion

The lithium vanadium phosphate Li$_x$VOPO$_4$ polymorphs have been studied as potential multi-electron cathodes that can enable high energy-density lithium-ion batteries.$^{109,114-117}$ Their Na analogs, on the other hand, have been explored only fairly recently as potential cathode materials for Na-ion batteries.$^{110-112}$ In this work, we have attempted to provide a systematic assessment of the three most common VOPO$_4$ polymorphs – $\beta$, $\varepsilon$ and $\alpha$ – in terms of key properties such as stability, voltage and alkali migration barriers using first principles calculations supported by experimental characterization in this work as well as those in literature.

We find that all three VOPO$_4$ polymorphs show reasonable stability for one Li insertion, though the insertion of a second Li is accompanied by a significant decrease in stability with relatively high $E_{\text{hull}}$ of ~80 meV/atom. All polymorphs are predicted to show two-phase behavior in the high voltage regime. In the low-voltage regime, $\beta$ phases are predicted to have intermediate phases of $\beta$-A$_{1.5}$VOPO$_4$ while there are $\varepsilon$-Li$_{1.5}$VOPO$_4$ and $\varepsilon$-Li$_{1.75}$VOPO$_4$ for $\varepsilon$ phases. For $\alpha$ phases, they are predicted to still exhibit two-phase behavior. We suspect that the absence of $\beta$-Li$_{1.5}$VOPO$_4$ in our experiment might be due to the poorer crystallinity from ball-milling. Another reason may be that we used relatively fast charge rate.

We may interpret the measured electrochemistry for Li intercalation in the context of the calculated Li$^+$ migration barriers and the electronic band gap. The calculated $v_{Li^+}$ and Li$^+$ migration barriers for minimally 1D diffusion are relatively similar between the $\beta$ (239 meV and 255 meV, respectively, see Figure 3.12) and $\varepsilon$ (244 meV and 271 meV, respectively) polymorphs. The $\alpha$
(328 meV and 276 meV, respectively) polymorph has somewhat higher barriers, especially at the beginning of charge. The calculated band gap for $\alpha$ LiVOPO$_4$ is also significantly higher than that of $\beta$ and $\epsilon$. We would speculate that the better performances of the $\beta$ and $\epsilon$ over $\alpha$ for Li$^+$ intercalation can be attributed to their lower barriers for Li$^+$ and smaller band gap (higher electronic conductivity).

In contrast, the three polymorphs are predicted to have very different performances as Na-ion multi-electron cathodes. Of the three polymorphs, $\beta$ polymorph becomes extremely unstable with two Na insertion ($E_{\text{hull}} = 126$ meV), and it also exhibits high barriers at the beginning of discharge. Though the $\epsilon$ polymorph remains the most stable for up to two Na$^+$ insertion, the barriers for Na$^+$ migration are extremely high, especially at the beginning of charge from $\epsilon$-NaVOPO$_4$ (> 1.5 eV). On the contrary, $\alpha$ polymorph is predicted to show a combination of reasonable stability and sufficiently low barriers for 2D Na$^+$ migration. These findings are in general agreement with the observed electrochemical performance reported in the literature which shows that $\beta$-NaVOPO$_4$ and $\epsilon$-NaVOPO$_4$ have comparatively worse reversibility and lower cycling capacity.$^{112,125}$ In contrast, cycling of $\alpha$-Na$_x$VOPO$_4$ has been demonstrated with relatively high capacity of $\sim$150 mAh/g.$^{111}$

We may attribute the differences in the electrochemical performance for Li and Na of the VOPO$_4$ polymorphs to their fundamentally different arrangements of VO$_6$/VO$_5$-PO$_4$ frameworks. $\beta$ and $\epsilon$ polymorphs have rigid 3D VO$_6$-PO$_4$ frameworks where the barriers of alkali migration are determined to a large degree by void space between the structural framework. The significantly higher density of $\epsilon$-VOPO$_4$ and $\epsilon$-NaVOPO$_4$ compared to $\beta$-VOPO$_4$ and $\beta$-NaVOPO$_4$ (see Table 3.1) leads to much higher barriers for Na$^+$ migration. On the contrary, the $\alpha$ polymorph has a layered structure, with 2D layers of alkali ions sandwiched between layers of VO$_5$-PO$_4$ stacked in
the $a$ lattice direction. Such a structure, which bears significant similarity to the layered AMO$_2$ structures, can expand to accommodate the larger Na$^+$ ion, leading to low migration barriers and reasonable electrochemical performance. Indeed, we find that $\alpha$-NaVOPO$_4$ has a much larger inter-layer spacing of $\sim$3.70 Å compared to $\alpha$-LiVOPO$_4$ ($\sim$3.02 Å), which has been shown to strongly affect the alkali migration barrier in the O3 and P2 layered AMO$_2$ materials.$^{93,153}$

We should also point out that the inter-layer spacing of the $\alpha$ polymorph is substantially reduced by $\sim$0.7 Å upon full de-alkalination. This implies that the alkali ion migration at fully de-alkaliated $\alpha$-VOPO$_4$ may be less facile, especially for Na$^+$ due to its larger ionic radius as compared to Li$^+$. Indeed, this is in line with our migration barrier calculations for $\alpha$-NaVOPO$_4$.

To further elaborate the correlation between the framework topology and alkali ion migration, we have estimated the bottleneck size ($r_c$), which is defined as the radius of the largest free sphere that can pass through the diffusion network formed by the structural framework, of all the AVOP$O_4$ polymorphs using the open source Zeo++ software$^{154,155}$ (see Figure 3.12). In general, we find that the computed bottleneck size is approximately inversely correlated to the lowest percolating migration barrier when comparing between close-packed $\beta$ and $\epsilon$ polymorphs. We also note that while the vacancy migration barrier in NaVOPO$_4$ is lower than that for Na$^+$ migration in VOPO$_4$ for the $\beta$ and $\alpha$ polymorphs due to a significant increase in channel size with one Na insertion, the vacancy migration barriers in $\epsilon$-NaVOPO$_4$ are much higher than that for Na$^+$ migration in $\epsilon$-VOPO$_4$ as there is negligible change in bottleneck size with on Na insertion. However, although the layered $\alpha$ always has the largest bottleneck size among the alkaliated and fully dealkaliated AVOP$O_4$ polymorphs (e.g 1.57 Å and 1.61 Å for $\alpha$-LiVOPO$_4$ and $\alpha$-NaVOPO$_4$, respectively), the associated lowest percolating migration barrier can be higher than that in the other two polymorphs, as shown in the case of LiVOPO$_4$. This suggests that the migration barrier
does not barely depend on $r_c$, but also the local VO$_6$/VO$_5$-PO$_4$ arrangement.

The VO$_6$/VO$_5$-PO$_4$ arrangement may also account for the electronic structure changes with alkali insertion. As can be seen from Figure 3.13, the band gap of $\alpha$ sharply increases with the insertion of the first Li/Na ($x = 1$), followed by a sharp decrease with the insertion of the second Li/Na ($x = 2$). In contrast, the band gaps of $\beta$ and $\varepsilon$ follow a monotonic decreasing trend upon alkali insertion. We speculate that there are two possible reasons for the observed trends. First, V is in a square pyramidal VO$_5$ environment in $\alpha$, and in octahedral VO$_6$ environment in $\beta$ and $\varepsilon$. From the DOS of the different A$_x$VOPO$_4$ polymorphs (see Figure 3.18), we may observe that the vbm and cbm of the AVOPO$_4$ ($x = 1$) are dominated by V $d$ orbitals. The $d_{xz}$ and $d_{yz}$ orbitals in a square pyramidal environment lie below the $t_{2g}$ orbitals of the octahedral environment due to the breaking of the degeneracy of the $t_{2g}$ orbitals from the distortion. This may have resulted in additional stabilization for the first electron added to $\alpha$, resulting in an increase in the band gap. Second, as highlighted earlier, $\alpha$ comprises layers of VO$_5$-PO$_4$ stacked in the $a$ crystallographic direction, while $\beta$ and $\varepsilon$ comprises 3D networks of interconnected VO$_6$-PO$_4$. $\alpha$ undergoes an expansion in the $a$ crystallographic direction upon the insertion of the first Li/Na (see Table 3.1), which may have contributed to the increase in band gap.

Finally, the DFT and experimental insights suggest several avenues for improving the performance of VOPO$_4$ polymorphs for alkali intercalation. We note that the $\beta$ and $\varepsilon$ exhibit low alkali diffusion barriers only in 1D, and only the $\alpha$ has low alkali barriers in 2D. All three polymorphs are predicted to be large band gap insulators, with $\alpha$ exhibiting a particular large increase in band gap for the single alkali insertion. These features – fast 1D conduction and electronic insulator – are similar to the well-known LiFePO$_4$ cathode. Similar to LiFePO$_4$, we
expect that nanosizing is critical in the VOPO$_4$ polymorphs to minimize the occurrence of blocking defects that causes capacity loss$^{85}$, as well as to shorten conduction length scales in view of their insulating nature. However, these requirements need to be balanced against the higher reactivity of VOPO$_4$ compared to FePO$_4$, which we expect to be exacerbated with nanosizing. Enhancing the electronic conductivity of VOPO$_4$ through coating with conductive materials (e.g., various forms of carbon)$^{156,157}$ would also be critical, and some coating materials may have the additional benefit of serving as a protective layer to mitigate reactions with the electrolyte.

### 3.6 Conclusion

In summary, we have conducted a combined first-principles and experimental study to evaluate the thermodynamic stability, voltage, band gap and diffusion kinetics for Li and Na intercalation in the $\beta$, $\varepsilon$ and $\alpha$ polymorphs of VOPO$_4$. We find that the three VOPO$_4$ polymorphs remain reasonably stable with one alkali insertion, but become significantly less stable with two alkali insertion. For Li$^+$ insertion, either ionic or electronic conduction can be the limiting factor in performance. For Na$^+$ insertion, performance is likely to be diffusion-limited, with only the $\alpha_1$ polymorph exhibiting reasonable migration barriers for Na$^+$ migration. The main reason is that larger size of the Na$^+$ makes it particularly sensitive to changes in bottleneck size as a result of the fundamentally different VO$_6$/VO$_5$-PO$_4$ frameworks of the different polymorphs. These results provide crucial insights, such as the importance of structural selection, into the design of new multi-electron cathodes for Li-ion and Na-ion batteries.

Chapter 3 is, in full, a reprint of the material “Comparison of the polymorphs of VOPO$_4$ as multi-electron cathodes for rechargeable alkali-ion batteries” as it appears in Journal of Materials Chemistry A, Y. C. Lin, M. F. V. Hidalgo, I. H. Chu, N. A. Chernova, M. Stanley Whittingham and S. P. Ong, 2017, 5, 17421–17431. The dissertation author was the primary investigator and
author of this paper. All calculations and corresponding data analysis were done by the author. The experimental portion of the work – synthesis, characterization and data analysis were done by collaborator, M. F. V. Hidalgo.
Figure 3.1 Lowest-energy structures of AVOPO\textsubscript{4} polymorphs (A=Li, Na). Yellow and green spheres denote Na\textsuperscript{+}, and Li\textsuperscript{+} respectively. The red octahedrons refer to VO\textsubscript{6} unit and the purple tetrahedrons refer to PO\textsubscript{4} units.

Figure 3.2 XRD patterns for all LiVOPO\textsubscript{4} polymorphs synthesized in this work.
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<th>β (°)</th>
<th>γ (°)</th>
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Figure 3.3 (a) Calculated $E_{\text{hull}}$ for $A_x\text{VOPO}_4$ polymorphs ($A=\text{Na and Li}; x=0, 1$ and $2$). (b) GGA+$U$ average voltages of $A_0\text{VOPO}_4$-$A_1\text{VOPO}_4$ and $A_1\text{VOPO}_4$-$A_2\text{VOPO}_4$ polymorphs.
Figure 3.4 Pseudo-binary phase diagram for A$_x$VOPO$_4$ (A=Li and Na) polymorphs. The red squares and blue circles denote unstable and stable structures, respectively. The black line is the convex hull.

Figure 3.5 Cycling voltammetry for (a) $\beta$, (b) $\epsilon$, and (c) $\alpha_I$ polymorphs of Li$_x$VOPO$_4$. 
Figure 3.6 Migration paths and barriers for (a) $\nu_{A^+}$ and (b) $A^+$ migration in $\beta$-AVOPO$_4$ and $\beta$-VOPO$_4$, respectively. The labeled values in (a) and (b) are the corresponding barriers for Li$^+$ (Na$^+$) and $\nu_{Li^+}$ ($\nu_{Na^+}$) migrations in meV. Purple spheres denote $A^+$.

Figure 3.7 Migration paths and barriers for (a) $\nu_{Li^+}$ in $\varepsilon$-LiVOPO$_4$ and (b) $\nu_{Na^+}$ in $\varepsilon$-NaVOPO$_4$. The labeled values are the corresponding CI-NEB migration barriers in meV. Green and yellow spheres denote Li$^+$, and Na$^+$, respectively.

Figure 3.8 Migration paths and barriers for $A^+$ in $\varepsilon$-VOPO$_4$. The labeled values are the corresponding CI-NEB barriers for Li$^+$ (Na$^+$) migration in meV. Purple spheres denote $A^+$. 
Figure 3.9 (a) Migration paths and barriers for $v_{A^+}$ in the lowest energy alkali ordering for (a) $\alpha_I$-LiVOPO$_4$ and (b) $\alpha_I$-NaVOPO$_4$. Purple and yellow spheres denote alkali ions. The labeled values in (a) are barriers of $v_{Li^+}$ ($v_{Na^+}$) migration and those in (b) are barriers of $v_{Na^+}$ migration in meV.

Figure 3.10 Migration paths and barriers for $A^+$ in $\alpha_I$-VOPO$_4$. The labeled values are the corresponding barriers of Li$^+$ (Na$^+$) migration in meV. Purple spheres denote $A^+$. 


Table 3.2 The CI-NEB migration barriers and the associated local environment information in A<sub>x</sub>VOPO<sub>4</sub>. A* stands for the alkali-ion in the transition state of a migration path. The minimum distances from A* to oxygen, vanadium and phosphorus are abbreviated as Min A*-O, Min A*-V and Min A*-P, respectively.

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<td>α-NaVOPO&lt;sub&gt;4&lt;/sub&gt; + v&lt;sub&gt;Na&lt;/sub&gt;+</td>
<td>A→B</td>
<td>263</td>
<td>2.166</td>
<td>3.523</td>
<td>2.988</td>
</tr>
<tr>
<td></td>
<td>A→C</td>
<td>1409</td>
<td>2.045</td>
<td>2.560</td>
<td>4.023</td>
</tr>
<tr>
<td></td>
<td>A→D</td>
<td>565</td>
<td>2.152</td>
<td>3.217</td>
<td>2.865</td>
</tr>
<tr>
<td>α-NaVOPO&lt;sub&gt;4&lt;/sub&gt;* + v&lt;sub&gt;Na&lt;/sub&gt;+</td>
<td>A→B</td>
<td>651</td>
<td>2.198</td>
<td>3.030</td>
<td>2.818</td>
</tr>
<tr>
<td></td>
<td>A→C</td>
<td>548</td>
<td>2.195</td>
<td>3.004</td>
<td>2.762</td>
</tr>
<tr>
<td></td>
<td>A→D</td>
<td>261</td>
<td>2.163</td>
<td>3.312</td>
<td>2.819</td>
</tr>
<tr>
<td></td>
<td>A→E</td>
<td>123</td>
<td>3.637</td>
<td>2.176</td>
<td>2.940</td>
</tr>
<tr>
<td>α-VOPO&lt;sub&gt;4&lt;/sub&gt; + Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>A→B</td>
<td>438</td>
<td>2.176</td>
<td>3.754</td>
<td>2.744</td>
</tr>
<tr>
<td></td>
<td>A→C</td>
<td>2308</td>
<td>1.889</td>
<td>2.257</td>
<td>3.886</td>
</tr>
<tr>
<td></td>
<td>A→D</td>
<td>427</td>
<td>2.112</td>
<td>3.430</td>
<td>2.743</td>
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Figure 3.11 Calculated CI-NEB migration barriers in AₓVOPO₄ polymorphs (A=Li and Na; x=0 and 1). The labels are associated with those in Table 3.2.
Figure 3.11 Calculated CI-NEB migration barriers in $A_x$VOPO$_4$ polymorphs ($A=$Li and Na; $x=0$ and 1). The labels are associated with those in Table 3.2. (Continued)
Figure 3.11 Calculated CI-NEB migration barriers in $A_x$VOPO$_4$ polymorphs ($A=$Li and Na; $x=0$ and 1). The labels are associated with those in Table 3.2. (Continued)
Figure 3.12 Calculated bottleneck size (top) and migration barriers (bottom) of (a) $v_{A^+}$ in AVOPO$_4$, and (b) $\Lambda^+$ in VOPO$_4$ in which bottleneck size and migration barrier are denoted as $r_c$ and $E_a$, respectively. $\alpha_{I}$-NaVOPO$_4$ with the same alkali ordering as the $\alpha_{I}$-LiVOPO$_4$ is denoted as $\alpha_{I}$-NaVOPO$_4$*. The dashed lines in the bottleneck size plot are drawn only to guide the eyes.

Figure 3.13 Calculated band gaps from the HSE density of states of $A_x$VOPO$_4$ polymorphs ($x = 0, 1, 2$).
Figure 3.14 Electrochemical performance of LiVOPO$_4$ polymorphs at different current densities.

Figure 3.15 Galvanostatic charge-discharge curves for different LiVOPO$_4$ polymorphs at a charge-discharge rate of C/10.

Figure 3.16 SEM images of (left to right) $\beta$-, $\varepsilon$-, and $\alpha_I$- LiVOPO$_4$ after ball-milling. Scale bars are 200 nm.
Figure 3.17 Current vs $\nu^{1/2}$ plots for the high-voltage transformation in (a) $\alpha_I$, (b) $\beta^-$, and (c) $\epsilon$-LiVOPO$_4$.

Table 3.3 Apparent diffusion coefficients from CV data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$x = 1$ (Li vacancy diffusion)</th>
<th>$x = 0$ (Li ion diffusion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Li$_3$VOPO$_4$</td>
<td>$11 \pm 3$</td>
<td>$7 \pm 3$</td>
</tr>
<tr>
<td>$\epsilon$-Li$_3$VOPO$_4$</td>
<td>$3 \pm 1$</td>
<td>$4 \pm 2$</td>
</tr>
<tr>
<td>$\alpha$-Li$_3$VOPO$_4$</td>
<td>$6 \pm 1$</td>
<td>$6 \pm 1$</td>
</tr>
</tbody>
</table>
Figure 3.18 Calculated hybrid HSE density of states of A\textsubscript{x}VOPO\textsubscript{4} polymorphs (A=Li and Na; x=0, 1, 2). The computed band gaps are also labeled in each of the sub-figures.
Chapter 4. Rational Synthesis and Electrochemical Performance of LiVOPO$_4$

Polymorphs

4.1 Introduction

Li-ion batteries utilizing intercalation chemistry are currently the most prominent form of energy storage for portable electronic devices and electric vehicles due to their high energy density.$^{162-167}$ Unfortunately, the capacity of most commercially available cathode materials is limited by the fact that the cathode material can only store up to one Li$^+$ ion per redox center. Thus, there is a large interest in materials which can intercalate multiple electrons per redox center.$^{168-175}$ One such material is lithium vanadyl phosphate, or LiVOPO$_4$.$^{29,176,177}$ The V$^{5+}$/V$^{4+}$ and V$^{4+}$/V$^{3+}$ redox couples at 4.0 V and 2.5 V, respectively, allow for the intercalation of up to two Li$^+$ ions per vanadium through the formation of VOPO$_4$ ↔ LiVOPO$_4$ ↔ Li$_2$VOPO$_4$ during the operation of the battery. This results in a high theoretical capacity of 305 mAh/g and a specific energy of over 900 Wh/g.$^{30,178,179}$

Three major polymorphs of LiVOPO$_4$, $\alpha$-, $\beta$-, and $\varepsilon$-LiVOPO$_4$, have been previously reported and synthesized through different methods. The $\alpha$ phase (tetragonal, P4/nmm)$^{27,180-182}$ has a layered structure exhibiting 2D Li diffusion, and is the least reported among the different polymorphs due to difficulties in its synthesis. On the other hand, the $\beta$ phase (orthorhombic, Pnma)$^{183-185}$ has 1D diffusion channels while the $\varepsilon$ phase (triclinic, P-1)$^{29,33,184,186,187}$ has pseudo-1D diffusion channels. Unlike $\alpha$, both the $\beta$ and $\varepsilon$ phases have been synthesized using a large plethora of methods, including hydrothermal,$^{29-31}$ solid-state,$^{31-33}$ and sol-gel.$^{32,34}$

A complete understanding of the differences between these phases is essential to identifying which polymorph is best suited as a cathode material in a Li-ion battery. Thermodynamic calculations have reported previously that $\alpha$ is metastable relative to both $\beta$ and
which have very similar stabilities.\textsuperscript{176,187} Additionally, the different phases have been observed and reported either transforming between one another or appearing as impurities.\textsuperscript{34,35,184,188} However, since the difference in stability of these phases is small, minute differences in synthesis would greatly influence the individual properties of the polymorphs. This makes it difficult to conduct a thorough comparison of different properties of the polymorphs.

To address this challenge, we show in this study that all three polymorphs can be synthesized from a single precursor, LiVOPO\textsubscript{4}·2H\textsubscript{2}O, through careful control of synthesis conditions. By utilizing a single precursor, it is possible to minimize effects of synthesis on the properties such as stability and electrochemical performance, allowing for more direct and accurate experimental and theoretical comparisons. In addition, we demonstrated that the limitations to the electrochemical performance of LiVOPO\textsubscript{4} due to electronic and ionic conductions can be remedied with carbon coating, nano-sizing and morphology control.\textsuperscript{29,176} Guided by DFT surface calculations, we demonstrate how control of the O chemical potential may be used to control morphology to promote the formation of facets with facile Li intercalation\textsuperscript{189–191} for high rate performance.

4.2 Experimental methods

4.2.1 Synthesis of LiVOPO\textsubscript{4}·2H\textsubscript{2}O and different LiVOPO\textsubscript{4} polymorphs

The LiVOPO\textsubscript{4}·2H\textsubscript{2}O precursor was synthesized using a hydrothermal method modified from previous reports.\textsuperscript{42} V\textsubscript{2}O\textsubscript{5} (Aldrich, >99.6%), oxalic acid (Sigma-Aldrich, >99.0%), and phosphoric acid (Fisher Scientific, 85%) were dissolved in ethanol and water, and stirred for 18 hours. LiOH·H\textsubscript{2}O (Sigma, >99.0%) was then added, and stirred for another 4 hours. The solution was hydrothermally synthesized in a 4748 Type 125 mL PTFE-lined reactor (Parr Instrument Co.) and heated to 160 °C for 48 hours. The product was filtered and washed with water, ethanol, and
acetone, then dried overnight at 60 °C. The precursor was heated to different temperatures and environments for 3 hours in order to form the different LiVOPO₄ polymorphs. Specifically, α-LiVOPO₄ forms at 300 °C in Ar, β-LiVOPO₄ forms at 600 °C in O₂, and ε-LiVOPO₄ forms at 750 °C in Ar. Amorphized LiVOPO₄·2H₂O was prepared by subjecting the precursor to high-energy ball-milling for 30 minutes.

4.2.2 Materials characterization

Powder X-ray diffraction (XRD) data was collected using a Bruker D8 Advance diffractometer utilizing a Cu Ka source (Ka1 = 1.54053 Å, Ka2 = 1.54431 Å) over the 2θ range of 10 ° – 80 ° and a step size of 0.02 °. Indexing, phase identification, and Rietveld refinement were conducted using the TOPAS software package (Bruker AXS, version 5.0) and the PDF-2015 software package. Thermogravimetric analysis coupled with mass spectrometry (TG-MS) was performed using a TG 209 F1 Iris coupled to a QMS 403 Aeolos Mass Spectrometer (260-TG/MS Netzsch). In-situ diffraction data were collected using high-energy X-rays (λ = 0.2113 Å) provided by beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory. Diffraction images were recorded in transmission geometry using an amorphous Si detector, and integrated with GSAS-II using a CeO₂ standard (SRM674b) as calibrant. Powder samples were loaded in quartz capillaries and slightly compressed between two plugs of quartz wool. Capillaries were placed in the flow-cell/furnace and O₂ or He was flown (4 cc/min) through the capillary during the heating. When He was flown through the cell, a residual gas analyzer (Pfeiffer PrismaPlus QMG 220 M2 mass spectrometer) was attached to the outlet to monitor released gases. Transmission electron microscopy was conducted by dispersing the as-synthesized β- or ε-LiVOPO₄ particles in ethanol, sonicating thoroughly, and then dropping the solution onto the carbon film coated copper grid. Microstructure characterization was performed on a Talos F200X
S/TEM (Thermo fisher Scientific, USA) equipped with a field emission gun (FEG) operated at accelerating voltage of 200 kV.

4.2.3 Electrochemical Performance Testing

Electrochemical performance was evaluated by using the LiVOPO₄ as a cathode material in 2325-type coin cells. The cathodes were prepared by first subjecting the LiVOPO₄ with graphene to high-energy ball-milling for 30 minutes. Polyvinylidene fluoride (PVDF) was then added to the mixture, resulting in an LiVOPO₄:graphene:PVDF ratio of 75:15:10, and formed into a slurry using n-methyl-2-pyrrolidinone (NMP) as the solvent. The slurry was cast onto a carbon-coated Al foil and dried at 60 °C. Electrodes with areas of 1.2 cm² and active mass loadings of ~2.5 – 4.5 mg were punched and served as the cathodes. The cell was assembled with a pure lithium chip (MTI) as the counter and reference electrodes, a Celgard 2400 separator (Hoechst Celanese) as the separator, and 1 M LiPF₆ in 1:1 v/v ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. The cells were cycled at a rate of C/40 (C defined as 317 mAh/g) using a VMP multichannel potentiostat (Bio-Logic) from 1.5 V to 4.5 V at current densities from 16 – 28 μA/cm². Rate tests were conducted from C/100 up to C/2, then back to C/100, at 5 cycles each. Galvanostatic Intermittent Titration Technique (GITT) runs were conducted by discharging the cells at C/100 for 1.5 hours and letting them rest for 100 hours (high-voltage region) or 50 hours (low-voltage region).

4.3 Computational methods

All first-principles calculations in this work were performed using the Vienna ab initio simulation package (VASP) with the projected augmented wave (PAW) method. The Hubbard U extension to the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional with a U value of 3.25 V for vanadium was adopted, and all calculations were
initialized in a ferromagnetic high spin configuration given that previous studies have shown that magnetic effects to have a minimal impact on relative energies.\textsuperscript{62} A plane wave energy cutoff of 520 eV and k-point density of at least 1000/(number of atoms in the unit cell) were used for bulk relaxations of α\textsubscript{I}-, β\textsubscript{-}, and ε-Li\textsubscript{x}VOPO\textsubscript{4} (x = 0, 1). All other parameters are consistent with those used by the Materials Project for all calculations unless stated otherwise.\textsuperscript{61} All data analysis was performed using the Python Materials Genomics (pymatgen) library.\textsuperscript{56}

4.3.1 Gibbs free energy

Phonon calculations using density functional perturbation theory as implemented in the Phonopy code were carried out for β\textsubscript{-}, ε\textsubscript{-} and α\textsubscript{I}-Li\textsubscript{x}VOPO\textsubscript{4} (x = 0, 1).\textsuperscript{192} The Gibbs free energy of each phase was then obtained based on the quasi-harmonic approximation. More stringent energy and force convergence criteria of 10\textsuperscript{-8} eV and 10\textsuperscript{-4} eV/Å, respectively, were used for these calculations.

4.3.2 Defect formation energy

The defect formation energies (E\textsubscript{d}) of O-vacancy and O-interstitial defects were calculated using the following equations:

\[
\text{O-vacancy: } E_d = E_{Li_3V_3P_3O_{159}} - E_{Li_3V_3P_3O_{160}} + \Delta \mu_O \\
\text{O-interstitial: } E_d = E_{Li_3V_3P_3O_{161}} - E_{Li_3V_3P_3O_{160}} - \Delta \mu_O
\]

where \(\Delta \mu_O = \mu_O - \frac{1}{2} \mu_{O_2}^0\) being the oxygen chemical potential relative to \(\mu_{O_2}^0\) (the reference chemical potential of O\textsubscript{2} gas at standard temperatures and pressure). The defect concentration of 3.125\% was simulated by creating (vacancy or interstitial) defects in a 2 \times 2 \times 2 supercell for β\textsubscript{-} and ε-Li\textsubscript{x}VOPO\textsubscript{4} and 4 \times 2 \times 2 supercell for α\textsubscript{I}-Li\textsubscript{x}VOPO\textsubscript{4} (x = 0, 1). The structure was relaxed until the energy and forces are converged to 10\textsuperscript{-4} eV and 0.05 eV/Å, respectively.
4.3.3 Surface

Surface energies were calculated using the slab method, with the specific implementation and parameters as described in Tran et al.\textsuperscript{193} Similar to previous work on the LiFePO\textsubscript{4} cathode, only non-polar terminations that do no break P-O bonds were investigated.\textsuperscript{190,194} Only surfaces up to a max Miller index of 2 were considered, resulting in 29, 18, 19 and 19 facets for \textepsilon-LiVOPO\textsubscript{4}, \textepsilon-VOPO\textsubscript{4}, \beta-LiVOPO\textsubscript{4}, and \beta-VOPO\textsubscript{4}, respectively. We investigated non-polar, symmetric O adsorption on both surfaces of the slab using the algorithm implemented in pymatgen.\textsuperscript{195} Only slabs corresponding to the facets appearing on the clean Wulff shapes of \beta- and \textepsilon-LiVOPO\textsubscript{4} were investigated. To calculate the surface energy, we used the surface grand potential:

\[ \gamma = \frac{1}{2A} [E^{slab} - \sum N_i \mu_i] \]

where \( E^{slab} \) is the total energy of the slab with \( i \) unique species, \( \mu_i \) is the chemical potential of a specie \( i \) and \( N_i \) is the total number of \( i \) atoms in the slab. Further details are given in the SI for interested readers.

4.4 Results

4.4.1 Phase transformation upon heating LiVOPO\textsubscript{4}

Pure-phase LiVOPO\textsubscript{4}·2H\textsubscript{2}O (Figure 4.1) is used as a precursor to form the different polymorphs of LiVOPO\textsubscript{4}. From thermogravimetric analysis (TGA), we observe that both temperature and atmosphere are key factors which cause different changes within the precursor (Figure 4.2). We can directly identify these specific changes using in-situ XRD while heating LiVOPO\textsubscript{4}·2H\textsubscript{2}O (Figure 4.3) and use Rietveld refinement to quantify the relative amounts of each LiVOPO\textsubscript{4} polymorph at each specific temperature (Figure 4.4). Two major observations can be made. Firstly, we observe that heating LiVOPO\textsubscript{4}·2H\textsubscript{2}O results in the formation of \alpha-LiVOPO\textsubscript{4},
followed by β-LiVOPO$_4$, then ε-LiVOPO$_4$. This trend is seen in both Ar and O$_2$. Secondly, we observe that a large amount of β-LiVOPO$_4$ can only form in an oxidizing atmosphere.

Ex-situ XRD of heated LiVOPO$_4$$\cdot$2H$_2$O (Figure 4.5) and Rietveld refinement of these spectra (Figure 4.6) also show similar trends, where LiVOPO$_4$$\cdot$2H$_2$O → α$_I$-LiVOPO$_4$ → β-LiVOPO$_4$ → ε-LiVOPO$_4$, and higher amounts of β-LiVOPO$_4$ only form when the samples are heated in an oxidizing atmosphere. In fact, heating LiVOPO$_4$$\cdot$2H$_2$O at 600 °C in Ar, air, and O$_2$ results in 48%, 93%, and 97% β-LiVOPO$_4$, respectively, with the remainder being ε-LiVOPO$_4$. The ex-situ runs also show that these phases are stable upon cooling, with the final phases with highest purity (Figure 4.7) taken for further testing.

The LiVOPO$_4$$\cdot$2H$_2$O to α$_I$-LiVOPO$_4$ transformation can be attributed to fact that the α$_I$-LiVOPO$_4$ structure is analogous to the LiVOPO$_4$$\cdot$2H$_2$O structure (Figure S6), but without the water and with a slight shift in the Li position. At higher temperatures, the lack of α$_I$-LiVOPO$_4$ and the presence of β- and ε-LiVOPO$_4$ are in agreement with ex-situ heating of α$_I$-LiVOPO$_4$. This shows that α$_I$-LiVOPO$_4$ transforms into both β- and ε-LiVOPO$_4$ (Figure 4.9 & Figure 4.10) at these higher temperatures. Additionally, it is observed that the reverse reaction, that is, the transformation of β- and ε-LiVOPO$_4$ into α$_I$-LiVOPO$_4$, is not possible (Figure 4.11) In fact, when α$_I$-LiVOPO$_4$ is kept at 300 °C in Ar (the conditions for the LiVOPO$_4$$\cdot$2H$_2$O → α$_I$-LiVOPO$_4$ transformation) for extended periods, it slowly transforms into a mixture of β- and ε-LiVOPO$_4$. All these observations suggest that α$_I$-LiVOPO$_4$ is metastable relative to β- and ε-LiVOPO$_4$.

Figure 4.12 presents the calculated Gibbs free energies of α$_I$, β-, and ε-LiVOPO$_4$ within the temperature range of 0 – 1000 K. We observe that the Gibbs free energies of ε-LiVOPO$_4$ and β-LiVOPO$_4$ are almost degenerate (within 3 meV/atom of each other) and much lower than that of α$_I$-LiVOPO$_4$ at all temperatures of interest. This clearly indicates that the α$_I$ phase is the most
unstable phase, which is consistent with our experimental observations and previously reported calculations.\textsuperscript{16,29}

The phase distribution when heated for extended periods in Figure 4.13 shows that \(\beta\)-LiVOPO\(_4\) readily transforms into \(\varepsilon\)-LiVOPO\(_4\) when heated at 750 °C in Ar. Similarly, \(\varepsilon\)-LiVOPO\(_4\) also transforms into \(\beta\)-LiVOPO\(_4\) when heated at 600 °C in O\(_2\), albeit at a slower rate.

4.4.2 Role of Oxygen in the Phase Stability of the LiVOPO\(_4\) Polymorphs

It is observed in both in-situ and ex-situ heating of LiVOPO\(_4\)-2H\(_2\)O that the presence of O\(_2\) in the atmosphere during heating has a drastic effect on the relative ratios of \(\beta\)- and \(\varepsilon\)-LiVOPO\(_4\). This effect of O\(_2\) on stability can be more clearly demonstrated when heating amorphized LiVOPO\(_4\)-2H\(_2\)O. Figure 4.14 shows that, when heated to 600 °C, amorphized LiVOPO\(_4\)-2H\(_2\)O forms \(\beta\)-LiVOPO\(_4\) in O\(_2\) or \(\varepsilon\)-LiVOPO\(_4\) in Ar. This result shows that, independent of temperature, the preferential formation of \(\beta\)- or \(\varepsilon\)-LiVOPO\(_4\) is largely dictated by the presence of O\(_2\) in the atmosphere.

In order to further understand the effect of O\(_2\) on the stability of these phases, we monitored the changes in the XRD patterns (Figure 4.15), weight (Figure 4.17), and release of gasses (Figure 4.16 & Figure 4.17) as \(\beta\)-LiVOPO\(_4\) transforms into \(\varepsilon\)-LiVOPO\(_4\). We observe from our in-situ XRD data that the onset of the \(\beta\)-to-\(\varepsilon\) transformation at around 630 °C matches well with the onset of O\(_2\) release, as detected by the RGA (Figure 4.16). Additionally, the O\(_2\) signal diminishes once the maximum amount of \(\varepsilon\)-LiVOPO\(_4\) is formed. This alignment of the XRD and RGA data show that the formation of \(\varepsilon\)-LiVOPO\(_4\) and the release of O\(_2\) are related. Similarly, the loss of O\(_2\) can be detected and quantified using a TG-MS. The maximum weight loss coincides with the maximum amount of detected O\(_2\) loss, both at around 650 °C. This fits with the observations made from the \(\beta\)-to-\(\varepsilon\) in-situ XRD. Additionally, the thermogram shows that the amount of O\(_2\) lost during heating
is ~0.078% of the total weight, which is ~0.0065 moles of O per mole of LiVOPO$_4$. These suggest that ε-LiVOPO$_4$ has more O-vacancies than β-LiVOPO$_4$, and that these vacancies affect the stability of both phases.

Figure 4.18 presents the calculated defect formation energies of O vacancies and interstitials in β- and ε-LiVOPO$_4$ relative to Δµ$_O$. We find that at low oxygen chemical potentials (higher temperatures, reducing atmosphere), the most stable defect structure is that of ε-LiVOPO$_4$ with oxygen vacancies. Conversely, at high oxygen chemical potentials (lower temperatures, O$_2$ atmosphere), the most stable defect structure is that of β-LiVOPO$_4$ with oxygen interstitials.

The calculated dopant formation energies of O-vacancies in β-LiVOPO$_4$ are larger than that of ε-LiVOPO$_4$, while the energies of the O-interstitials of β-LiVOPO$_4$ are lower than that of ε-LiVOPO$_4$. These findings suggest that β-LiVOPO$_4$ is more likely to form in the presence of O-interstitials, and ε-LiVOPO$_4$ is preferred in the presence of O-vacancies. These calculation results are consistent with the experimental observations above.

4.4.3 Surface stability of LiVOPO$_4$ polymorphs

For β- and ε-LiVOPO$_4$, all facets remain non-polar after structural relaxations. It is shown that LiO$_6$ and VO$_6$ octahedral are cut through, leading to undercoordinated Li and V atoms on the surface in each orientation. The lowest-energy structures of each facet are provided in CIF format in Table 4.1.

Figure 4.19 plots the fractional areas of the different facets on the Wulff shape against Δµ$_O$ for β- and ε-LiVOPO$_4$ along with insets of the Wulff shapes constructed based on surface energies in Figure 4.20. For a max Miller index of 2, there are 19 and 29 symmetrically distinct facets for the clean β- and ε-LiVOPO$_4$, respectively. However, only 11 and 12 of these facets are thermodynamically stable on the Wulff shapes of clean β- and ε-LiVOPO$_4$, respectively. The
calculated surface energies for most facets of $\beta$-LiVOPO$_4$ are on somewhat higher than those reported in a recent work by Li et al.$^{191}$, and we attribute these differences to slightly different parameter settings. One exception is the (101) facet of $\beta$-LiVOPO$_4$, which we calculate to be 0.98 J/m$^2$, (0.42 J/m$^2$ lower than the value reported by Li et al.). We also find that the (121), (102), (212), (211), (221), and (112) facets, which were not considered by Li et al., to contribute to the Wulff shape of clean $\beta$-LiVOPO$_4$ as well.

The Wulff shape of $\beta$-LiVOPO$_4$ becomes more anisotropic as $\Delta \mu_O$ increases, finally forming a rectangular rod under extreme oxidizing conditions enclosed by the (001), (100), and (010) planes. A similar behavior in the evolution of the Wulff shape for $\varepsilon$-LiVOPO$_4$ is observed as the fractional area of the (100) facet sharply increases as $\Delta \mu_O$ increases beyond -3 eV.

In Figure 4.21, TEM images of the particles of $\beta$- and $\varepsilon$-LiVOPO$_4$ show that the $\beta$-LiVOPO$_4$ is enclosed at the top by the (001) plane and to the sides with the (010) and (100) planes while $\varepsilon$-LiVOPO$_4$ is enclosed at the top by the (100) plane, both of which are in excellent agreement with the dominant facets on calculated Wulff shapes. However, the (210) facet which is present in the experimental particle morphology is not present in the Wulff shape evolution of $\beta$-LiVOPO$_4$ (Figure 4.19(a)).

4.4.4 Surface redox potentials

Table 4.2 shows the calculated redox potentials to extract Li from different facets on the Wulff shape of LiVOPO$_4$. The surface potentials vary from 4.51 to 3.03 V and 4.63 to 3.12 V for $\beta$-LiVOPO$_4$ and $\varepsilon$-LiVOPO$_4$, respectively. The calculated bulk redox potentials for $\beta$-LiVOPO$_4$ and $\varepsilon$-LiVOPO$_4$ are 3.83 and 3.80 V, respectively, which are in good agreement with the experimental voltage of ~4.0 V.$^{21,31,51}$

4.4.5 Comparison of electrochemical performance of LiVOPO$_4$ polymorphs
Figure 4.22a shows the charge-discharge curve of the first cycle of each of the LiVOPO$_4$ polymorphs. We can observe that β-LiVOPO$_4$ has the highest capacity among the different phases, which may be attributed to its better kinetics, and the higher rate capability on the surfaces of β-LiVOPO$_4$ as seen in the longer high-voltage plateau. This larger capacity is maintained over several cycles, as seen in Figure 4.22b. Figure 4.23 also shows that the experimental voltage of each plateau for both the high- and low-voltage regions also fits well with theoretical voltage calculations which we reported previously.

The high-voltage rate capability test in Figure 4.24a shows that all three phases experience the expected capacity loss as they are cycled at higher rates, and regain this lost capacity when cycled at lower rates. This is in agreement with the GITT data in Figure 4.24b, which shows that each phase experiences comparable voltage changes when reaching equilibrium upon rest. A similar analysis can be conducted in the low-voltage region, shown in Figure 4.25a. First, we observe that α$_I$-LiVOPO$_4$ experiences a similar loss in capacity when cycled at higher rates. Interestingly, β- and ε-LiVOPO$_4$ show barely any loss of capacity when cycled at higher rates in the low-voltage region. This is also observed in the GITT in Figure 4.25b, where both β- and ε-LiVOPO$_4$ only experience a small overpotential, while α$_I$-LiVOPO$_4$ experiences a large change in voltage. This indicates that both β- and ε-LiVOPO$_4$ have better kinetics in this low-voltage regime. We also observe for all polymorphs that the low-voltage region nearly reaches the full theoretical capacity, while the high-voltage region is still lacking in capacity.

4.5 Discussion

In summary In our previous study, we showed that, in regard to thermodynamic stability, α$_I$-LiVOPO$_4$ <<< ε-LiVOPO$_4$ ≤ β-LiVOPO$_4$ at 0 K. In this study, we found the phase stability
from 0 – 1000 K exhibits the same trend for the three phases via calculating Gibbs free energies. In particular, β- and ε-LiVOPO₄ show little difference in Gibbs free energy, which explains why there is a small amount of ε-LiVOPO₄ always involved when synthesizing β-LiVOPO₄ at low temperatures in either O₂ or Ar atmospheres. Additionally, the energetics suggests that it might be possible to reversibly transform between these two phases. We can observe this transformation by taking ex-situ XRD of β-LiVOPO₄ heated in the conditions used to synthesize ε-LiVOPO₄ and vice versa.

We have also clearly shown that O₂ plays an important role in the formation of β-LiVOPO₄ over ε-LiVOPO₄. The lower O-interstitial formation energy in β-LiVOPO₄ indicates that it forms more favorably in O-rich environments. In contrast, ε-LiVOPO₄ is the preferred phase in O-deficient environments due to its lower O-vacancy formation energy. Consequently, at high temperatures above 750 °C in Ar atmosphere, we can achieve pure ε-LiVOPO₄. In addition, we found that the rate of transformation from β-LiVOPO₄ into ε-LiVOPO₄ at 750 °C is much faster than that of the reverse process at 600 °C. This is likely because the transformation from β-LiVOPO₄ into ε-LiVOPO₄ via O₂ release at high temperatures is kinetically more favorable than the reverse reaction via O₂ incorporation at low temperatures. Furthermore, the rate of atom rearrangement for transformation is faster at higher temperature.

For β-LiVOPO₄, we found that (001), (100), and (010) are the dominant facets on the Wulff shape under extreme oxidizing conditions, which are confirmed via TEM. In addition, we found that the (100) and (010) facets have redox potentials of 3.18 V and 3.71 V, respectively, lower than the 3.83 V of the bulk, in agreement with the results reported by Li et al.¹⁹¹ The lower surface redox potentials can lead to easier Li-ion extraction and hence increasing the surface area of these two facets in oxidizing environments would facilitate the rate capability of β-LiVOPO₄ on the
surface. In contrast, the dominant facet of $\varepsilon$-LiVOPO$_4$ is (100) under the extreme oxidizing condition, which has a redox potential of 3.82 V, higher than 3.80 V of bulk. This indicates oxidizing atmosphere is likely with little effect on improving the performance of $\varepsilon$-LiVOPO$_4$. The improved rate capability of $\beta$-LiVOPO$_4$ on the surface along with its better ionic kinetics$^{176}$ may explain why it achieves the best electrochemical performance among the three phases studied.

4.6 Conclusion

In summary, we conducted a thorough study on the effects of temperature and environment on the stability and formation of the different polymorphs of LiVOPO$_4$ using a single precursor, LiVOPO$_4$·2H$_2$O (Figure 4.26). Heating the precursor resulted in the following transformation: $\alpha$-LiVOPO$_4$ $\rightarrow$ $\beta$-LiVOPO$_4$ $\leftrightarrow$ $\varepsilon$-LiVOPO$_4$. The phase stability from 0 – 1000 K via Gibbs free energy calculations for the three phases is: $\alpha$-LiVOPO$_4$ $\ll$ $\varepsilon$-LiVOPO$_4$ $\leq$ $\beta$-LiVOPO$_4$, which is consistent with the experimental phase transformation process. The higher O-interstitial and lower O-vacancy defect formation energies of $\beta$-LiVOPO$_4$ and $\varepsilon$-LiVOPO$_4$, respectively, indicate that $\beta$-LiVOPO$_4$ and $\varepsilon$-LiVOPO$_4$ preferentially form in O-rich and O-deficient environments, respectively. Consequently, we can achieve the largest amount of $\beta$-LiVOPO$_4$ phase in oxidizing atmospheres and pure $\varepsilon$-LiVOPO$_4$ phase in Ar atmospheres at high temperatures (> 750 °C). The evolution of Wulff shapes with O chemical potentials indicates that only the surface rate performance of $\beta$-LiVOPO$_4$ can be improved by synthesis under O-rich environments. The calculated dominant facets of $\beta$-, and $\varepsilon$-LiVOPO$_4$ are further verified on the experimental particle morphologies by TEM. Finally, extensive electrochemical testing shows that of the three LiVOPO$_4$ phases, the $\beta$ phase is the most promising cathode material with the highest capacity and best rate capability. This may be attributed to its superior ionic kinetics and rate performances on the surfaces as the particle size approaches the nanoscale.
Chapter 4 is, in full, a preprint currently being prepared for submission for publication of the material “Rational Synthesis and Electrochemical Performance of LiVOPO$_4$ Polymorphs”, Marc F. V. Hidalgo, Yuh-Chieh Lin, Antonin Grenier, Dongdong Xiao, Richard Tran, Huolin Xin, Jennifer Donohue, Fredrick O. Omenya, Iek-Heng Chu, Zhenbin Wang, Xiangguo Li, Natasha A. Chernova, Karena W. Chapman, Guangwen Zhou, Shyue Ping Ong, and M. Stanley Whittingham. The dissertation author was a co-primary investigator and author of this paper. All calculations and corresponding data analysis were done by the author. The experimental portion of the work – synthesis, characterization and data analysis were done by collaborator, M. F. V. Hidalgo.
Figure 4.1 Rietveld refinement of as-synthesized LiVOPO$_4$·2H$_2$O.

Figure 4.2 Thermal studies of LiVOPO$_4$·2H$_2$O via (a) TG-MS in Ar, showing loss of water, and (b) TGA in different atmospheres.
Figure 4.3 In-situ XRD of heated LiVOPO$_4$·2H$_2$O in (a) He and (b) O$_2$, with arrows showing characteristic peaks for each polymorph.

Figure 4.4 Phase quantification of in-situ XRD of LiVOPO$_4$·2H$_2$O heated in (a) He and (b) O$_2$. 
Figure 4.5 Ex-situ XRD of heated LiVOPO$_4$$\cdot$2H$_2$O in (a) Ar and (b) air.

Figure 4.6 Phase quantification of ex-situ XRD of LiVOPO$_4$$\cdot$2H$_2$O heated in (a) Ar and (b) air.
Figure 4.7 Rietveld refinement of purest phase (a) $\alpha_\text{I}$, (b) $\beta_\text{I}$, and (c) $\varepsilon$-LiVOPO$_4$. 

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Figure 4.8 Crystal structure of (a) $\alpha_I$-LiVOPO$_4$ and (b) LiVOPO$_4$·2H$_2$O, showing the orientation of the PO tetrahedral (magenta), VO$_6$ octahedra (blue), Li (aqua) and water (red and yellow).

Figure 4.9 XRD patterns of $\alpha_I$-LiVOPO$_4$ heated in conditions to form $\beta$- and $\varepsilon$-LiVOPO$_4$.

Figure 4.10 Phase quantification showing $\alpha_I$-LiVOPO$_4$ heated in conditions for the formation of (a) $\beta$- (600 °C in O$_2$) and (b) $\varepsilon$-LiVOPO$_4$ (750 °C in Ar).
Figure 4.11 XRD of $\alpha_r$, $\beta_r$, and $\varepsilon$-LiVOPO$_4$ heated at conditions for the formation of $\alpha_r$-LiVOPO$_4$ (300 °C in Ar) for 50 hours.

Figure 4.12 Calculated Gibbs free energies ($G$) of $\alpha_r$, $\beta_r$, and $\varepsilon$-LiVOPO$_4$ as a function of temperature.
Figure 4.13 Phase quantification of (a) β-LiVOPO$_4$ transformation to ε-LiVOPO$_4$ (750 °C, Ar) and (b) ε-LiVOPO$_4$ transformation to β-LiVOPO$_4$ (600 °C, O$_2$).

Figure 4.14 XRD of amorphized LiVOPO$_4$·2H$_2$O before and after heating at 600 °C in different atmospheres.
Figure 4.15 In-situ XRD of a mostly $\beta$-LiVOPO$_4$ sample heated in He.

Figure 4.16 Phase quantification of in-situ XRD heating of a majorly $\beta$-LiVOPO$_4$ sample in He and RGA signal of O$_2$. 

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Figure 4.17 TG of β-LiVOPO$_4$ in Ar and coupled MS signal of O$_2$.

Figure 4.18 Calculated defect formation energies of (a) O-vacancy and (b) O-interstitial for β- and ε-LiVOPO$_4$ with respect to Δμ$_O$. To avoid decomposition of LiVOPO$_4$, -2.08 < Δμ$_O$ < -0.74 eV, as indicated by the dash lines.
### Table 4.1 Surface energies of symmetrically distinct facets of β- and ε-LiVOPO$_4$ with miller-index < 3.

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**β-LiVOPO$_4$**

**ε-LiVOPO$_4$**
Figure 4.19 The fractional area of different facets and the Wulff shape as a function of $\Delta \mu_O$ for (a) $\beta$- and (b) $\varepsilon$-LiVOPO$_4$. 
Figure 4.20 The evolution of surface energy of different facets with $\Delta \mu_O$ for (a) $\beta$- and (b) $\varepsilon$-LiVOPO$_4$.

Figure 4.21 TEM image of (a) $\beta$- and (b) $\varepsilon$-LiVOPO$_4$ showing the major facets.
Table 4.2 Calculated redox potentials for the extraction of Li from different surfaces on the Wulff shape of LiVOPO$_4$, with the bulk potential provided for comparison.

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Figure 4.22 Comparison of the (a) first charge-discharge curves and (b) cycling performance, all at C/40, of the different LiVOPO$_4$ polymorphs.
Figure 4.23 Experimental vs theoretical voltage plateaus in the (a) high- and (b) low-voltage regions of the different LiVOPO$_4$ polymorphs, cycled at C/40.

Figure 4.24 Comparison of the (a) rate capability and (b) GITT in the high-voltage region of the different LiVOPO$_4$ polymorphs.

Figure 4.25 Comparison of the (a) rate capability and (b) GITT in the low-voltage region of the different LiVOPO$_4$ polymorphs.
Figure 4.26 Summary of experimental phase transformations between the different polymorphs of LiVOPO$_4$. 
Chapter 5. Summary and outlook

Multi-electron polyanion cathodes offer the potential for achieving both high voltage and high capacity in rechargeable AIB. In this thesis, we focused on the study of one of the promising multielectron cathodes, AVOPO$_4$. (A = Li, Na). Using first-principle calculations, we predicted the thermodynamic stabilities, kinetics and surface properties of AVOPO$_4$, which elucidate the experimental findings and serve to guide experiments in improving the electrochemical performance of AVOPO$_4$.

Firstly, we conducted a joint experimental and first-principles computational analysis of the thermodynamics, kinetics structural evolution of the highly promising ε-Li$_x$VOPO$_4$ cathode over its entire lithiation range (0 ≤ x ≤ 2). Using both GGA+U and HSE calculations, we find that consistent with previous experimental data, there are no intermediate phases predicted to be stable in the region of 0 ≤ x ≤ 1, and two stable intermediate phases are identified at x = 1.5 and 1.75. We also find that the thermodynamic stability decreases with the incorporation of the second lithium into ε-VOPO$_4$, suggesting that there are inherent challenges to achieving stable two-electron cycling. Using a combination of DFT calculations, GITT measurements, operando PDF analysis and EXAFS spectra, we show that the capacity limitations during delithiation is likely to be driven by Li mobility limitations, whereas the increasing polarization during lithiation is the result of structural changes. In terms of electronic conductivity, we find ε-Li$_x$VOPO$_4$ to be a large band gap insulator across the entire lithiation range, and calculated small polaron migration barriers are similar to those of the olivine LiMPO$_4$ cathodes. Finally, we demonstrate that LiVOPO$_4$ is likely to be a one-dimensional diffuser using climbing-image nudged elastic band calculations. These results highlight the importance of nano-sizing and carbon coating in achieving good electrochemical performance in this material.
In the second project, we performed a combined first-principles and experimental study to evaluate the thermodynamic stability, voltage and diffusion kinetics for Li and Na intercalation in the \( \beta, \varepsilon \) and \( \alpha \) polymorphs of VOPO\(_4\). We find that all A\(_x\)VOPO\(_4\) polymorphs remain reasonably stable with one alkali intercalation, but significantly destabilizes with two alkali ion intercalation. The electronic band gap calculations suggest that carbon coating is critical for improving the electron conduction in A\(_x\)VOPO\(_4\) (A=Li, Na; \( x=0, 1, 2 \)). The computed alkali diffusion barriers indicate that the alkali diffusion of A\(_x\)VOPO\(_4\) (A=Li, Na; \( x=0, 1 \)) are more facile in \( \alpha \) polymorph compared to \( \beta \) and \( \varepsilon \) polymorphs, especially for the larger Na\(^+\) ion. The primary reason is that larger size of the Na\(^+\) makes it particularly sensitive to changes in bottleneck size as a result of the fundamentally different VO\(_6\)/VO\(_5\)-PO\(_4\) frameworks of the different polymorphs. These results provide crucial insights, such as the importance of structural selection, into the design of new multi-electron cathodes for Li-ion and Na-ion batteries.

In the third project, we conducted a thorough study on the effects of temperature and environment on the stability and formation of the different polymorphs of LiVOPO\(_4\) using the identical precursor, LiVOPO\(_4\)•2H\(_2\)O. The phase stability from 0 – 1000 K via Gibbs free energy calculations for the three phases is: \( \alpha \)-LiVOPO\(_4\) \(<\ll \varepsilon \)-LiVOPO\(_4\) \( \leq \beta \)-LiVOPO\(_4\), which is consistent with the experimental phase transformation process: \( \alpha \)-LiVOPO\(_4\) \( \rightarrow \beta \)-LiVOPO\(_4\) \( \leftrightarrow \varepsilon \)-LiVOPO\(_4\). By O-defect calculations, we showed that \( \beta \)-LiVOPO\(_4\) and \( \varepsilon \)-LiVOPO\(_4\) preferentially form in O-rich and O-deficient environments, respectively. Indeed, we achieved the largest amount of \( \beta \)-LiVOPO\(_4\) phase in oxidizing atmospheres and pure \( \varepsilon \)-LiVOPO\(_4\) phase in Ar atmospheres at high temperatures (> 750 °C). The study of effect of O chemical potential on particle morphology indicates that only the surface rate performance of \( \beta \)-LiVOPO\(_4\) can be improved by synthesis under O-rich environments. The calculated dominant facets of \( \beta \)-, and \( \varepsilon \)-LiVOPO\(_4\) are further verified on
the experimental particle morphologies by TEM. Finally, we performed extensive electrochemical testing demonstrating that β phase is the most promising cathode material with the highest capacity and best rate capability among the three phases. This may be ascribed to its superior ionic kinetics and rate performances on the surfaces as the particle size approaches the nanoscale.

To date, there are much fewer works on multielectron than single-electron systems in LIB and NIB, which might be attributed to (1) the instability of the active material in both charged and discharged states, (2) the large volume change making reversibility difficult and (3) the large gap of stepwise voltages due to phase transformations leading to fluctuated power output. The large voltage gap can be ascribed to the large difference of voltage contribution from the multiple redox couple of transition metal. Hautier et al. proposed a mixing-transition-metal strategy to design multielectron phosphate-based cathodes active in the voltage stability window. This also potentially minimized the voltage gaps by the effective redox couples of both transition metals. Besides V, Mo, Cr, Ni, Bi, Sb are shown potentially with small voltage difference across multiple redox reactions in phosphates, which can be guidance to look for novel small-voltage-gap cathodes. We believe in the near future, computational tools will be critically important to facilitate new electrode materials discovery, development and optimization, at the same time minimizing the traditional experimental trials.
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