ADVANCED CATHODES AND ELECTROLYTES FOR LITHIUM-ION AND LITHIUM-AIR BATTERIES

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by

Christopher John Allen

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ABSTRACT OF DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of Northeastern University June, 2012
Abstract

Today we hold high expectations that supporting technologies will keep pace with the ever-changing lifestyles most of us lead. Batteries are perhaps the most important of these supporting technologies as they provide the energy to power the lifestyle devices. Various redox chemistries have been developed and engineered in the form of batteries over the past two centuries, paving the way for many such conveniences. Despite the success, they are still lacking the energy density required for future high energy demands such as hybrid, full electric vehicles and mobile devices with step changes in computing and transmission power. This is a critical limitation of intercalation based cathode chemistries for Li-ion batteries. Advancements in this arena as well as metal-O\textsubscript{2} batteries are welcome as portable power sources for the next line of energy hungry applications. The scope of chapter 1 is to provide a summary of current state-of-the-art lithium-ion and lithium-O\textsubscript{2} battery technologies.

In chapter 2, the synthesis and characterization of the Li-ion battery positive electrode materials $\alpha$-LiVOPO\textsubscript{4}, $\beta$-LiVOPO\textsubscript{4} and $\alpha$-Li\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} are discussed. They have been prepared as individual phases from a common precursor mixture by controlling the synthesis conditions. These phases result because of their distinct crystal symmetries and vanadium oxidation states. The synthesis involves the decomposition of a precursor mixture prepared from NH\textsubscript{4}VO\textsubscript{3}, NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, LiF and hexanoic acid, which when heat-treated under different conditions produced the three Li\textsubscript{w}V\textsubscript{x}O\textsubscript{y}(PO\textsubscript{4})\textsubscript{z} products. The materials were characterized by means of elemental analysis, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and Li cell data. The Li cycling performance and the accompanying structural effects on $\alpha$- and $\beta$-LiVOPO\textsubscript{4} were also studied under normal and deep discharge conditions using XAS to probe the local vanadium environment. XANES and EXAFS confirm reversible changes in the two structures when
intercalation does not exceed 1Li/VOPO$_4$. Deeper discharge revealed more disruption to both structures, including an additional 0.25 Å increase to the V=O bond length. A greater range in the VO$_6$ symmetry of α-LiVOPO$_4$ resulted in a more flexible accommodating host, in agreement with its improved low voltage performance compared to β-LiVOPO$_4$.

A new Fe-V mixed metal phosphate of the composition Li$_{1+x}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ has been synthesized and characterized as a single phase Li insertion/extraction cathode material for rechargeable lithium batteries and is the focus of chapter 3. Its tetragonal crystal structure revealed from X-ray diffraction and absorption spectral data exhibits little change with Li extraction and subsequent Li insertion. The charge/discharge cycling capacities obtained from Li cells is consistent with the structure. The presence of F in the material is essential to prepare a mixed metal phosphate with equal amounts of Fe and V in the crystal structure and is probably the key to our success in preparing one of the first single phase metal phosphate cathode materials.

Studies on ionic liquid electrolytes for Li-O$_2$ applications are the subject of chapters 4 and 5. Initial work discussed in chapter 4 covers oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) on glassy carbon (GC) and gold electrodes, investigated in a neat and a Li$^+$-containing room temperature ionic liquid (RTIL), 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide (EMITFSI). The presence of Li$^+$ significantly changes the ORR mechanism. While similar one-electron O$_2$/O$_2^-$ reversible couples result on both electrodes in neat EMITFSI, in the presence of added LiTFSI the initially formed LiO$_2$ decomposes to Li$_2$O$_2$. In addition, the ORR and OER in the Li$^+$ doped solution exhibits strong distinctions between the Au and GC electrodes. The voltammetric data on the Au electrode revealed a highly
rechargeable ORR yielding LiO\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2}, which undergoes multiple cycles without electrode passivation.

Oxygen reduction and evolution reactions (ORR and OER) were also studied in ionic liquids containing other singly charged cations having a wide range of ionic radii, or charge densities. Specifically, ORR and OER mechanisms were studied using cyclic and rotating disk electrode voltammetry in the neat ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR\textsubscript{14}TFSI) and in their solutions containing LiTFSI, NaPF\textsubscript{6}, KPF\textsubscript{6} and tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}). A strong correlation was found between the ORR products and the ionic charge density, including those of the ionic liquids. The observed trend is explained in terms of the Lewis acidity of the cation present in the electrolyte using an acidity scale created from \textsuperscript{13}C NMR chemical shifts and spin lattice relaxation (T\textsubscript{1}) times of \textsuperscript{13}C=O in solutions of these charged ions in propylene carbonate (PC). The ionic liquids lie in a continuum of a cascading Lewis acidity scale with respect to the charge density of alkali metal, IL and TBA cations with the result that the ORR products in ionic liquids and in organic electrolytes containing any conducting cations can be predicted on the basis of a general theory based on the Hard Soft Acid Base (HSAB) concept.

Conclusions and direction for future research are presented in Chapter 6.
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Scheme 2.3. Steps 1-2c represents possible phase formation mechanisms for the three compounds formed from one precursor mix. Table 1 provides tube furnace conditions given in parenthesis here.

Chapter 3

Scheme 3.1 Addition of two phases in forming the mixed metal phase

Scheme 3.2 Expected oxidation states for proposed phase before and after charge

Chapter 4

Scheme 4.1 Anion exchange reaction for the synthesis of EMITFSI

Scheme 4.2 ORR and OER in neat EMITFSI
Scheme 4.3 ORR and OER mechanism in 0.025 M Li⁺ in EMITFSI

Scheme 4.4 Li spiked or neat EMITFSI

Chapter 5

Scheme 5.1. Ionic liquid cations and anion studied in chapter 5

Scheme 5.2. Synthetic steps for production of PYRTFSI

Scheme 5.3. Neat EMITFSI and their TBA⁺ solutions

Scheme 5.4. 0.025M LiTFSI PYRTFSI

Scheme 5.5. 0.025M NaPF₆ EMITFSI

Scheme 5.6. 0.025M KPF₆ EMITFSI
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>δ</td>
<td>Resistivity</td>
</tr>
<tr>
<td>ε</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>ν</td>
<td>Scan rate</td>
</tr>
<tr>
<td>σ</td>
<td>Li⁺ conductivity, Warburg impedance factor</td>
</tr>
<tr>
<td>σ²</td>
<td>Debye-waller factor</td>
</tr>
<tr>
<td>ω</td>
<td>Frequency⁻¹ (impedance)</td>
</tr>
<tr>
<td>χ²</td>
<td>Statistical goodness of fit</td>
</tr>
<tr>
<td>A</td>
<td>Ampere, area</td>
</tr>
<tr>
<td>ac</td>
<td>Alternating current</td>
</tr>
<tr>
<td>Ah</td>
<td>Ampere hour</td>
</tr>
<tr>
<td>B.P.</td>
<td>Boiling point</td>
</tr>
<tr>
<td>C</td>
<td>Coloumb, concentration</td>
</tr>
<tr>
<td>CIF</td>
<td>Crystallographic information file</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase element</td>
</tr>
<tr>
<td>C rate</td>
<td>Rate of charge or charge</td>
</tr>
<tr>
<td>CTR</td>
<td>Carbothermal reduction</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>dc</td>
<td>Direct current</td>
</tr>
<tr>
<td>DN</td>
<td>Donor number</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>E</td>
<td>Electromotive force</td>
</tr>
<tr>
<td>E°⁺</td>
<td>Formal reduction potential</td>
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<tr>
<td>E₀</td>
<td>Absorption edge energy</td>
</tr>
<tr>
<td>Eₚa</td>
<td>Anodic peak potential</td>
</tr>
<tr>
<td>Eₚc</td>
<td>Cathodic peak potential</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended x-ray absorption fine structure</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>H</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>Iₚ</td>
<td>Peak current</td>
</tr>
<tr>
<td>iR</td>
<td>Ohmic voltage drop</td>
</tr>
<tr>
<td>HSAB</td>
<td>Hard soft acid base (theory)</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Center for Diffraction Data</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Stds</td>
</tr>
<tr>
<td>k</td>
<td>Photoelectron wavenumber</td>
</tr>
<tr>
<td>L</td>
<td>Liter, thickness</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>M⁺</td>
<td>Single charged cation</td>
</tr>
</tbody>
</table>
M.P.  Melting point
N  coordination number
n  Number of electrons transferred
n_c  Number of electrons transferred (faradaic)
O_eq  Equatorial oxygen
OER  Oxygen evolution reactions
OCPP  Open circuit potential
ORR  Oxygen reduction reactions
PDF  Powder diffraction file
q  Heat
R  Resistance, gas constant, interatomic distance
R_{ct}  Charge transfer resistance
RDE  Rotating disk electrode
RPM  Rotations per minute
R_s  Solution resistance
RTIL  Room temperature ionic liquid
S  Entropy, Siemen
s  Second
S_c  Schmidt number
SEI  Solid electrolyte interface
S_o^2  Amplitude reduction factor
SG  Space group
SOD  State of discharge
T  Temperature
T_1  Spin lattice relaxation time
TGA  Thermogravimetric analysis
V  Volt
\eta  Viscosity
W  Watt
Wh  Watt hour
W_{non-pV}  non-pressure-volume work
W_{pV}  pressure-volume work
X^-  Anion
XANES  X-ray near edge structure
XAS  X-ray absorption spectroscopy
XRD  X-ray diffraction
Z'  Real axis
Z''  Imaginary axis
Chapter 1. Introduction to Rechargeable Lithium Batteries

1.1 21st Century Portable Power Advancement

1.1.1 Motivation

Sustained energy sources necessary for personal transportation in the United States will inevitably be threatened with continued burning of fossil fuels at the current rate of consumption. According to the U.S. Department of Transportation, more than a quarter of the 800 million personal vehicles worldwide burn fossil fuels in the U.S.\textsuperscript{1} This contributes to the consumption of 0.5\% of proven oil reserves per year.\textsuperscript{2} The depleting resources and growing populations are projected to lead to an energy shortage in less than 50 years as seen in Figure 1.1. This foreseen crisis and geopolitical/environmental impact caused by fossil fuels, along with our increasing addiction to portable electronics, are two driving forces behind today’s energy research initiatives.

\textbf{Figure 1.1.} U.S. Energy Information Administration projected world oil production and demand.\textsuperscript{2}
Lithium-ion (Li-ion) batteries and advanced technology like Lithium-O$_2$ (also called Li-air) batteries offer present and future solutions to manage our dependence on these fossil fuels. Li-ion batteries already have an undeniable influence over our daily lives. Not only electric propulsion vehicles and mobile electronics, but also various energy dependent sectors such as load leveling infrastructure for intermittent power storage benefit utilize these batteries. In 2009, the Department of Energy under the Obama Administration granted $2.4 billion in funding to several Li-ion battery companies for the development of electric and electric-assist vehicle technologies in the U.S.\textsuperscript{3} Despite their ubiquity and invested interest, limits on energy density and high cost of commercialized Li-ion batteries have accelerated efforts to improve our understanding of battery chemistry on all fronts. In this thesis, select aspects of both Li-ion and the highly anticipated Li-O$_2$ chemistry are investigated.

\textbf{1.1.2 General Battery Electrochemistry}

In a closed system, harnessing electricity from charge transfer between redox reactions of two chemicals differing in their chemical potentials stored in the negative and positive electrodes is the basis for all battery chemistries. Electrochemical reactions at the respective positive and negative poles of the early dawned-Daniel cell can be visualized in Figure 1.2. Reduction of Cu$^{2+}$ occurs at the cathode and oxidation of Zn metal to Zn$^{2+}$ results at the anode yielding a 1.1 V reaction.
The voltage in the Daniel cell stems from the thermodynamics describing chemical spontaneity defined according to equation 1.1 (at standard state-o) as Gibbs free energy ($\Delta G^o$),

$$\Delta G^o = \Delta H^o - T \Delta S^o$$

(1.1)

Here, $H$ and $S$ are enthalpy and entropy, respectively. From the first law of thermodynamics as seen in equation 1.2,

$$\Delta U = q + w_{pV} + w_{non-pV}$$

(1.2)

the change in internal energy of the system ($\Delta U$) is equal to heat ($q$) plus total work ($w$). Under typical electrochemical conditions, (i.e. constant temperature and pressure) the limit for electrochemical work ($w_{non-pV}$) is equal to $\Delta G^o$, which translates into equation 1.3.

$$\Delta G^o = -nFE^o$$

(1.3)

The magnitude of $\Delta G^o$, proportional to the electromotive force ($E^o$), drives the reaction which determines the electrical energy produced, where $n$ is equal to the number of electrons
transferred and \( F \) is Faraday’s constant. There is always a decrease in \( \Delta G \) as the reaction proceeds. According to equation 1.3, spontaneous \( (\Delta G^o<0) \) changes correspond to positive \( \Delta E^o \) values. This lends predictable behavior to the charge transfer direction and magnitude between any two redox reactions from a Table of standard reduction potentials. An example is demonstrated in the redox reaction of Figure 1.2.

As current flows during cell operation, the voltage is drawn away from open circuit potential (OCP) at equilibrium to overcome kinetic limitations, principally from three sources. 1) charge transfer 2) mass transport and 3) iR loss, collectively known as polarization. Numerous “polarization” curves are displayed throughout this work as either current versus potential in linear voltage scan cyclic voltammetry (CV), or analogously as potential versus time in constant current cycling curves. All three polarization sources contribute to energy loss as either shifts in the CVs, or voltage drop during constant current cycling. The activation polarization (charge transfer) and concentration polarization (mass transport) will be discussed throughout the thesis. Ohmic polarization (iR loss) is removed prior to any analysis of the former two.

The theoretical capacity of an electrode reaction calculated in Ampere hour per gram (Ah/g) can be maximized with an increased e⁻ transfer/equivalent weight of active material ratio as seen in equation 1.4 to calculate capacity.

\[
\frac{\text{Number of } e^- \text{ transferred}}{\text{g/mole (active material)}} \times \left( \frac{96485 \text{ C}}{\text{mole}} \times \frac{1 \text{ A-s}}{1 \text{ C}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \right) = \frac{\text{Ah}}{g} \quad (1.4)
\]

The terms in brackets can be condensed to a constant of 26.8 Ah/mole. Charge and discharge capacity is also a measure of energy density in Watt hour per liter (Wh/L), also referred to as specific energy (Wh/kg), as seen below.
Energy density = \( V \times \frac{Ah}{L} = \frac{Wh}{L} \)  
Specific energy = \( V \times \frac{Ah}{kg} = \frac{Wh}{kg} \)

Consider a Li-F\(_2\) battery. A 6 volt reduction potential results from the reaction between electropositive Li and electronegative F\(_2\) as follows, \( \text{Li} + \frac{1}{2}\text{F}_2 \rightarrow \text{LiF} \). Together with a low formula weight, the cell yields the highest specific energy possible, > 6000 Wh/kg. The incompatible chemistry and handling concerns of the Li/F\(_2\) redox couple deems it impractical, but this example illustrates the desire to harness reactions of low molecular weight electrodes and products in order to maximize capacity. Rate capability of the charge/discharge cycling is expressed as power density in Watts per Liter (W/L).

1.1.3 Early Rechargeable Batteries

Starting in the late 18\(^{th}\) century, Italian scientists Alessandro Volta and Luigi Galvani competed for the rights to the first battery. Volta triumphed in that feud.\(^3\) The result was a primary (single discharge) battery with a Zn-Cu redox couple. A hundred years later came the birth of the secondary (rechargeable) Pb-acid battery, which paved the way for portable energy as we know it today. The full-cell discharge reaction is shown in Scheme 1.1 resulting in a nominal voltage of 2.0 V.

**Scheme 1.1.** Pb-acid battery reaction (discharge)

\[
Pb + PbO_2 + 2H_2SO_4 (aq) \rightarrow 2PbSO_4 + 2H_2O = 372 \text{ Wh/kg}
\]

Pb-acid chemistry, and later Thomas Edison’s Fe-Ni rechargeable battery, competed with steam- and gasoline-powered internal combustion engines (ICE) in the early automotive era of the late 19\(^{th}\) century.\(^3\) The Fe-Ni battery operates at 1.4V in alkaline electrolyte. Like Pb-acid, its chemistry employs a 2 e\(^-\)/equivalent active material discharge reaction, visible in Scheme 1.2.
Scheme 1.2 Fe-Ni battery reaction (discharge)

\[ 2 \text{NiOOH} + \text{Fe} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Ni(OH)}_2 + \text{Fe(OH)}_2 = 690 \text{Wh/kg} \]

Practically, these batteries achieve only a low percentage of their theoretical specific energies (in Wh/kg) listed in Schemes 1.1 and 1.2. Thus, a massive Pb-acid battery required for propulsion of automobiles in the early 20th century had limited driving range and did not fare well against the evolving ICE, eventually dominating the automotive industry. Overall, subtle inconveniences suffered by early battery technology such as frequent maintenance and long charging times also led to their downfall. But most central to their demise was the limited energy density and high cost, the same hurdles confronting the battery chemist a century later.

1.2 Li-ion batteries

1.2.1 Electrode Reaction Mechanisms

Commercial Li-ion batteries have been in use for more than two decades. These cells utilize intercalation compounds for both electrodes. They usually consist of a transition metal oxide, sulfide, or phosphate cathode active phase along with a graphite anode, activated with a Li\(^+\)-containing organic carbonate-based electrolyte. The cathode electrode is comprised of a blend of active material, conductive carbon, and binder. Li metal anodes offer excellent capacity at 3.86 Ah/g, but have been replaced by graphite because of safety concerns with the first commercialized cells introduced by Sony in 1991. Lithium is still used as an anode in primary batteries as well as in laboratory settings. Graphite’s high theoretical capacity (370 mAh/g), similar chemical potential to Li/Li\(^+\), and affordability made it a viable replacement for Li metal. Both cathode and anode can be visualized as a scaffolding host for Li\(^+\) as seen in Figure 1.3. In the discharge of a battery, chemical to electrical energy conversion occurs as Li\(^+\), extracted from
interstitial sites in the graphite crystal structure, pass through the ionically conducting electrolyte with electron charge compensation taking place on the metal center of the active cathode material. Electrons for work travel through the external circuit from the anode to the cathode to maintain electroneutrality. Upon charge the opposite reactions take place, resulting in rechargeability.

![Diagram of Li-ion battery de/insertion mechanism.](image)

**Figure 1.3.** Li-ion battery de/insertion mechanism.

The half and full-cell electrochemical reactions corresponding to the illustration in Figure 1.3 are shown in Scheme 1.3, where charging occurs from left to right as the cathode in this case, LiCoO$_2$, is oxidized. (This electrode maintains the title of cathode during charge and discharge.)
Scheme 1.3. Li-ion de/insertion chemical reaction with a LiCoO$_2$ cathode and graphite anode

$$Li_xCoO_2 = Li_{1-x}CoO_2 + xLi^+ + xe^- \quad \text{(cathode)}$$

$$C_6 + xLi^+ + xe^- = Li_xC_6 \quad \text{(anode)}$$

$$Li_xCoO_2 + C_6 = Li_{1-x}CoO_2 + Li_xC_6 \quad \text{(full-cell)}$$

Charge compensation occurs predominately on Co sites as Li$^+$ and electrons shuttle back and forth between anode and cathode. The cobalt oxidation state increases from Co$^{3+}$ towards Co$^{4+}$ during charge (Li$^+$ removal). The process is reversed during discharge.

1.2.2 Transition Metal Oxide and Phosphate Cathode Materials

LiCoO$_2$ and its derivatives represent one class of cathode materials for Li-ion batteries. A material of this crystal phase is incorporated into the majority of commercial Li-ion batteries manufactured today and has dominated the small scale (<1Ah) battery market for portable electronics. Patented by John Goodenough $^6$ in the early 1980’s, it has a layered rhombohedral structure. The two dimensional de/insertion of Li$^+$ reaction has proven extremely effective, while only reversibly cycling 0.5 Li/equivalent. Toxicity and high cost of Co oxide precursors ($25$/kg)$^5$ along with safety concerns have forced a shift towards metal substituted LiCo$_{1-x}$M$_x$O$_2$ (M =Ni,Al) phases with stoichiometries such as LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$ (NCA). NCA represents the most energy dense commercial Li-ion cathode with a capacity of 190 mAh/g, utilizing 0.7 Li/equivalent weight. At 3.6V, this phase yields a specific energy of 240 Wh/kg with a graphite anode in a commercial 18650 cell (a cylindrical cell with dimensions -18 mm diameter, 65.0mm long, see Figure 1.4 inset for image) The cycling profile of an 18650 cell seen in Figure 1.4 was
cycled at a C/20 rate. (i.e. 20 hour discharge) A C/n rate corresponds to a discharge of 1/n hours. The exact elemental composition of the active material is unknown, but a single-layered LiMO$_2$ phase was confirmed with x-ray diffraction.

More recently, a layered oxide consisting of a solid solution of Li$_2$MnO$_3$ and LiMO$_2$ (M=Co,Ni,Mn), namely the Li-rich Li[LiMnNiCo]O$_2$ (layered LMO), has received much attention. For example, Li[Li$_{0.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$]O$_2$ offers capacities of 250 mAh/g, translating into 280 Wh/kg in an 18650 cell. Currently, such chemistry suffers capacity fade and is limited

Figure 1.4. Typical cycling profile from an 18650 Li-ion cell featuring the LiCoO$_2$ active material. The cell was extracted from a laptop computer battery pack. C/20 cycling rate, Current= 200mA. The 18650 cell is visible in the inset.
to low current densities. But with improved performance and coupled with higher capacity anodes like Sn or Si, the battery could offer significant energy density improvements over the current state of the art.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Cell Voltage (V)</th>
<th>Capacity (mAh/g)</th>
<th>Specific Energy (mWh/g)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered LiCoO₂ cathode (2-d structure)</td>
<td>~4</td>
<td>140</td>
<td>560</td>
<td>High electronic and Li⁺ ion conductivity, revolutionized the portable electronics market</td>
<td>Expensive and toxic Co; safety concerns; only 50% of the theoretical capacity can be utilized</td>
</tr>
<tr>
<td>Spinel LiMn₂O₄ cathode (3-d structure)</td>
<td>~4</td>
<td>120</td>
<td>480</td>
<td>Inexpensive and environmentally benign Mn; high electronic and Li⁺ ion conductivity; excellent rate capability; good safety</td>
<td>Severe capacity fade at elevated temperatures (55 °C)</td>
</tr>
<tr>
<td>Olivine LiFePO₄ cathode (1-d structure)</td>
<td>~3.5</td>
<td>160</td>
<td>560</td>
<td>Inexpensive and environmentally benign Fe; covalently bonded PO₄ groups lead to excellent safety</td>
<td>Low electronic and Li⁺ ion conductivity; needs small particle size and carbon coating to realize high rate capability; high processing cost</td>
</tr>
<tr>
<td>Graphite anode</td>
<td>~0.1</td>
<td>370</td>
<td>—</td>
<td>Inexpensive and environmentally benign C; low operating potential maximizes cell voltage</td>
<td>SEI layer formation and lithium plating lead to safety concerns; high processing cost</td>
</tr>
</tbody>
</table>

Table 1.1. Pros and cons of major cathode and anode intercalation materials for commercial Li-ion cells. Note that practical specific energies of these cathodes can be as low as 25% of their theoretical values, even in the highly engineered 18650 cells. This is due to unused active materials, cell packaging, and polarization losses which occur during cycling.

Figure 1.5. Unit cells of the three major Li-ion cathode materials (metal-blue, Li-green O-red, P-yellow)
To put the specific energy values of NCA and layered LMO in context, recent calculations have determined that an electric vehicle with a single discharge 300 mile driving range will require a 580 Wh/kg or 1450 Wh/L battery. Certainly, the layered phases fall short of this value, but it is their cost which draws major attention toward more economical, albeit lower energy-dense alternatives for large scale batteries. The spinel LiMn$_2$O$_4$ and olivine LiFePO$_4$ phases represent the other two major classes of cathode active materials in commercial Li-ion cells. General properties of all three classes of materials are listed in Table 1.1 with crystal structures displayed in Figure 1.5.

LiMn$_2$O$_4$ is attractive because of its abundant and cheap metal oxide precursors among other attributes, but has historically suffered low discharge capacity and fast capacity fading. This is caused by dissolution of Mn$^{2+}$ as a result of the disproportionation of Mn$^{3+}$ to Mn$^{2+}$ and Mn$^{4+}$. Like LiCoO$_2$, LiMn$_2$O$_4$ has benefited from metal doping, which for LiMn$_2$O$_4$ reduces Mn dissolution. In fact, mixtures of both doped LiCo$_{1-x}$M$_x$O$_2$ and LiMn$_{2-x}$M$_x$O$_4$ (M=Ni,Al,Cu) are typically blended in commercial cell cathodes for enhanced performance.

The operating voltages at which Li$^+$ de-inserts are phase- and chemistry-specific. This voltage is due to both the electrostatic field (band structure) of the redox active metal, determined by the long range order of the structure, and also the ionic/covalent nature of the metal-anion bonding linkage. The energetics of the metal redox couple can therefore be tuned verses Li/Li$^+$ depending on the chemical composition of the crystal structure, a most significant ingenuity that led to the LiMPO$_4$ (M= Fe,Ni,Co) class of compounds.

Safety concerns regarding the use of metal oxide cathodes stems from the high valence redox couples found in chemistries such as LiCoO$_2$ (Co$^{3/4+}$) and LiNiO$_2$ (Ni$^{3/4+}$). Upon charge,
the oxidative nature of the metals is elevated, posing risk for release of oxygen from the electrolyte at high temperatures. This can lead to a dangerous condition called thermal runaway, where the electrode’s reaction at full charge is accelerated by flammable electrolyte. Lower redox couples such as Fe\(^{2/3+}\) in Fe\(_2\)O\(_3\) are less reactive, but their energy verses Li/Li\(^+\) is also lowered, yielding a lower operating voltage. Consider the atomic framework Fe-O-X-O (X=Fe,P). By increasing the covalency of the X-O bond with P in Fe-O-P-O via inductive electron withdrawal from the Fe, the Fe-O bond is weakened. This lowers the energy of the Fe\(^{2/3+}\) redox couple, therefore raising the energy difference between it and Li/Li\(^+\).\(^{12,13}\) The end result is a higher operating voltage, with inductive withdrawal from the Fe-O achieved from the PO\(_4\)\(^{3-}\) group in LiFePO\(_4\). Initially plagued by poor electronic conductivity and low rate cycling, it was realized that metal organic salts (M=Mg,Ti,Zr,Nb) incorporated into the synthesis, significantly enhance the conductivity (~10\(^8\) improvement).\(^{14}\) The exact source of the improved conductivity, either from metal doping of the phosphate (i.e. LiFe\(_{0.99}\)M\(_{0.01}\)PO\(_4\)), or carbon coating of LiFePO\(_4\), is still up for debate.\(^{15}\) Nano-sizing of the particles decreases Li\(^+\) diffusion path lengths, also contributing to enhanced kinetics and increasing power densities. Despite its low energy density, the low cost, high rate capable and safety features of this class of cathode materials currently makes it an attractive option for electric vehicle battery pack manufacturers.
<table>
<thead>
<tr>
<th>Phosphate stoichiometry</th>
<th>Cell Voltage (V)</th>
<th>Theoretical capacity (mAh/g)</th>
<th>Specific energy (mWh/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoPO₄</td>
<td>4.8</td>
<td>120</td>
<td>576</td>
<td>16</td>
</tr>
<tr>
<td>LiMnPO₄</td>
<td>3.9</td>
<td>140</td>
<td>546</td>
<td>17</td>
</tr>
<tr>
<td>*LiVOPO₄</td>
<td>3.9</td>
<td>166</td>
<td>647</td>
<td>18, 19</td>
</tr>
<tr>
<td>*Li₃V₂(PO₄)₃</td>
<td>3.8</td>
<td>(130/2Li;197/3Li)</td>
<td>494;750</td>
<td>20</td>
</tr>
<tr>
<td>LiVPO₄F</td>
<td>4.2</td>
<td>150</td>
<td>630</td>
<td>21</td>
</tr>
<tr>
<td>*Li₂FePO₄F</td>
<td>2.8</td>
<td>152</td>
<td>425</td>
<td>22, 23</td>
</tr>
<tr>
<td>Li₂(VO)₀.₅(Fe)₀.₅PO₄F₀.₅</td>
<td>3.0</td>
<td>225</td>
<td>675</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 1.2 Lithium metal phosphate phases and electrochemical properties. *-Exists in at least two distinct phases.

As seen in Table 1.2, other lithium metal phosphates with redox active chemistries more energy dense than LiFePO₄ have recently been developed. Unique properties of LiVPO₄F offer extended cycling, thermal stability, and an operating voltage greater than 500 mV relative to LiFePO₄. The Li₃V₂(PO₄)₃ is an attractive candidate for electric vehicle applications due to its high rate capability and energy density. In Chapters 3 and 4, several lithium vanadium (fluoro)phosphates explored for better understanding of their electrochemical and structural correlations during various cycling conditions are discussed.

1.2.3 Organic Carbonate-Based Electrolytes

Electrolytes for rechargeable Li batteries have several required properties in order to fulfill their principal role of an ion-transport medium between the two electrodes during charge
transfer. These properties are exemplified by the current state of the art organic carbonate-based electrolyte for Li-ion batteries, which meets the following set of conditions.26

The solvent must

1. be capable of dissolving high concentrations of Li\(^+\) salt (high dielectric constant (\(\varepsilon\)))
2. have low viscosity (\(\eta\)) to provide sufficient Li\(^+\) conductivity (\(\sigma\))
3. be stable in its liquid phase over a wide temperature range (high B.P., low M.P.), preferably -40\(^\circ\) to 70\(^\circ\) C
4. be environmentally stable

The Li\(^+\) salt must

1. be capable of dissolving in high concentrations in the organic solvent, dissociate to form electrolytes with conductivities of 10\(^{-3}\) to 10\(^{-2}\) S/cm, be thermally stable over the operating temperature of the battery, and exhibit non-toxicity

Both solvent and salt must remain un-reacted with the cathode, cell container, and reaction products within the battery. Properties of ethylene carbonate (EC) and di-methylcarbonate (DMC) solvents along with lithium hexafluorophosphate (LiPF\(_6\)), make up a typical electrolyte blend as 1:1 (by volume) EC:DMC:1M LiPF\(_6\). Structures of these solvents along with di-ethylcarbonate (DEC) are shown in Figure 1.6.
Similar qualities will be required of next-generation electrolytes with the added demand of improved stability at high voltages, up to 5V. Select Li-ion battery cathodes geared toward high energy applications cannot be utilized in carbonate electrolytes because of their high chemical potential versus Li/Li\(^+\). Materials like layered LMO, LiMn\(_{1.5}\)Ni\(_{0.5}\)O\(_4\), and olivine LiMPO\(_4\) (M=Co,Ni) with operating voltages > 4.7V offer improved energy density, but safety and performance considerations regarding electrolyte instability must also be considered.\(^8\)

1.3 Li-O\(_2\) batteries

1.3.1 Power of O\(_2\)

The lithium-oxygen (Li-O\(_2\)) couple is perhaps the most logical and economical candidate for the ultimate high energy battery. O\(_2\) is a good oxidizing agent and thus offers promise as a cathode in a variety of air battery (Li,Al,Si,Zn) and fuel-cell (H\(_2\),CH\(_3\)OH) chemistries. Together with the reducing power of Li as the anode, and an excellent equivalent weight/e\(^-\) transfer ratio of 15, the Li-O\(_2\) battery offers the highest theoretical energy density of any battery realized to date at 5220 Wh/kg as seen in Figure 1.7.
Efforts to develop the Li-O$_2$ battery into a sought-after commercially available technology have intensified in recent years. Such a breakthrough could alleviate concerns regarding cost and energy-deficient large scale Li-ion batteries, yet several hurdles need still be overcome.$^{27}$

The first non-aqueous Li-O$_2$ battery was developed by Abraham and co-workers$^{28}$ in 1996. Oxygen reduction on the O$_2$ electrode as seen in the schematic for Li-O$_2$ discharge in Figure 1.8, may result in several potential reaction products also listed in that Figure. In a Li-O$_2$ battery the O$_2$ cathode (carbon based) is exposed to gaseous O$_2$, which saturates the electrolyte. This initiates oxidation of the Li anode and formation of Li$_x$O$_y$ discharge products on the cathode. Li$_2$O$_2$, insoluble in non-aqueous solvent, is the primary discharge product.$^{28,29}$ The oxidation of insoluble Li$_2$O$_2$ results in large overpotentials and hence major energy inefficiency upon recharge due to polarization losses.
1.3.2 Elucidating ORR and OER in organic electrolyte

Work from our laboratory\textsuperscript{30,31} has advanced the understanding of non-aqueous electrolytes’ role in the product formation and how it influences the oxygen reduction reactions (ORR) during discharge, as well as oxygen evolution reactions (OER) during recharge. Elucidating ORR and OER pathways is crucial in tuning products for efficient rechargeability (i.e. reversibility), a major challenge facing this chemistry. Both the conducting salt and solvent influence the reaction pathway.

In studies of a series of non-aqueous electrolytes, prepared in dimethyl sulfoxide (DMSO), acetonitrile (MeCN), dimethoxyethane (DME), and tetraethylene glycol dimethyl ether (TEGDME), it has been determined that in the presence of a singly charged cation (M\textsuperscript{+}), the reduction of O\textsubscript{2} usually proceeds through an initial one-electron process as seen in reaction Scheme 1.4.

\textbf{Scheme 1.4.} One-electron reduction of dioxygen

\[ \text{M}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{M}^+ - \text{O}_2^- \]  \hspace{1cm} (1.4)
The resulting superoxide species ($O_2^-$) may be stabilized and cycled reversibly in the presence of large, soft acid cations like tetrabutyl ammonium (TBA$^+$), or take on more reduced states as peroxide ($O_2^{2-}$) or monoxide ($O_2^-$) in the presence of hard acid cations like Li$^+$, leading to irreversible electrochemistry. Thus hard-soft acid base chemistry based on Pearson’s work\textsuperscript{32} plays a key role in product stability. (This concept is discussed in more detail in Chapters 4 and 5.) Moreover, it was determined that these events can be controlled further by modulating the acidity of the Li$^+$, based on the Lewis basicity of the solvent. This solvent property is defined as Gutmann’s Donor Number (DN) in kcal/mole measured as the enthalpy ($-\Delta H$) of the 1:1 reaction between the solvent (the Lewis base) and SbCl$_5$ (the Lewis acid) in 1,2-dichlorethane.\textsuperscript{33} High donor numbers signify increased basicity. Li-O$_2$ cell cycling displayed reaction reversibility increasing as the solvent DN increased since a high DN solvent like DMSO “softens” the hard nature of Li$^+$. Based on the HSAB theory and ORR electrochemistry in the soft acid TBA$^+$, this is a favorable property of the cation to enhance reversibility. For this reason, recharging ORR products in Li$^+$ concentrated DMSO yields a separation between charge and discharge voltages as low as any reported O$_2$ electrode reactions (un-catalyzed or catalyzed) at 0.9V.\textsuperscript{34}

1.3.3 Ionic Liquids

It’s clear that the effect of the electrolyte in Li-O$_2$ electrochemistry differs compared to those requirements listed in section 1.2.3 for Li-ion batteries. Besides reaction product stability, the unique presence of a highly reactive reduced oxygen nucleophile, complications arising from proton based impurities entering the cell with the O$_2$ source, and electrolyte vapor pressures leading to solvent loss, are all additional factors that may affect cell performance based on the choice of electrolyte. Room temperature ionic liquids (RTIL) or (IL) as a class of solvents for Li-O$_2$ batteries offer potential benefits over molecular based electrolytes because they can be tuned
to have application specific physicochemical properties and functionality to counteract these factors. The electrochemical window, viscosity, hydrophobicity, and O$_2$ solubility are a few properties affecting cycling performance of a Li-O$_2$ battery that may be tailored based on the chosen cation and anion of the RTIL.

For example, both ions that make up the molten salt (or polyelectrolyte) contribute to the overall electrochemical window. In particular, anions which increase the electrolyte oxidation potential, important during OER, include triflates and fluoroborates. The 4-coordinated nitrogen based cations are more resistant to reduction, lowering their reduction potential. Cations in this class include ammonium, piperidinium, and morpholinium. These and other ions typical in RTILs are listed in Figure 1.9.

Electrochemical studies in RTILs were initiated in the 1980’s using N-butylpyridinium and 1-ethyl-3-methylimidazolium based ILs. To date, the few studies conducted on Li-O$_2$ cycling in ILs have also employed imidazolium along with pyrrolidinium based ILs, both of which displayed limited rechargeability.

![Figure 1.9. Cations (red) and anions (blue) typical in RTILs. Shaded ions represent those studied in this thesis.](image-url)
1.4 Scope of Thesis

This thesis involves select Li-ion (Ch. 2-3) and Li-O₂ (Ch. 4-5) battery contributions for the advancement of portable power applications. In Chapter 2, novel synthetic routes to distinguish closely related vanadium phosphate cathode materials are discussed. Namely, α-LiVOPO₄, β-LiVOPO₄, and α-Li₃V₂(PO₄)₃ have been synthesized as pure phases from the same precursor by controlling the synthesis conditions. We have gained an understanding of the relationship between atomic and electrochemical dynamics of the two-phase Li⁺ insertion vanadyl phosphates using X-ray absorption spectroscopy (XAS) coupled with electrochemistry. These studies led to the discovery of a new single phase Li⁺ insertion vanadyl fluoro-phosphate, Li₂Fe₀.₅(VO)₀.₅(PO₄)F₀.₅, the topic of Chapter 3. In-situ spectroelectrochemical studies using XAS have allowed us to pinpoint both V and Fe redox active sites during the single phase Li⁺ insertion process in this material.

Insight into ORR and OER mechanisms in RTILs for Li-O₂ batteries is the focus of the final two chapters. In Chapter 4, the electrochemical and chemical reversibility in an imidazolium based IL is investigated by monitoring the effect of both the O₂⁻ stabilized cation and the specific electrode surface in play (Au or glassy carbon). Finally in chapter 5, we expanded on those studies by including a pyrrolidinium IL along with the imidazolium IL concentrated with various single charged cation salts. The electrochemistry is complemented by ¹³C chemical shifts and T₁ NMR studies carried out by fellow graduate student Jaehee Hwang. From these studies a general mechanism for ORR in non-aqueous electrolytes has been formulated.
1.5 References


2.1 Introduction

Transition metal phosphate positive electrode materials now compete with layered and 3-D structured transition metal oxides and their derivatives for a share in the lithium-ion battery market. The phosphate group provides a thermally stable, high voltage electrode material attributed to the inductive effect of the PO$_4$ moiety, with these qualities exemplified by LiFePO$_4$. As described in Chapter 1, electrical transport limitations originating from low ionic and electronic conductivities have plagued such phosphate frameworks. Poor Li-ion cell charge/discharge performance ascribed to these problems, especially at high rates, have been alleviated with nanophase materials and metal ion doping with the result that high power LiFePO$_4$ cells are now a practical reality. However, certain metal phosphates such as $\alpha$-LiVOPO$_4$ and $\beta$-LiVOPO$_4$ have improved features such as a high theoretical specific capacity of 166 mAh/g at discharge voltages approximately 500 mV higher than that of LiFePO$_4$, which translates into a theoretical specific energy of 650 Wh/Kg in a Li cell. However, they yield only about 70% of their theoretical capacity at rates of C/50 to C/5. At a higher cycling rate (4.22C) $\alpha$-LiVOPO$_4$ has achieved 25% of its theoretical capacity. The reason for the poor practical performance of these materials is not fully understood. Interestingly, vanadium exists in a variety of stable valence states, useful in both increasing energy density via insertion of multiple Li/ equivalent and also for opening possibilities for new synthetic strategies.

Previously, LiVOPO$_4$ synthesis has been accomplished through multiple steps, combining one of seven open ($\varepsilon$+$\beta$) or layered ($\alpha_1, \alpha_2, \omega, \delta, \gamma$) VOPO$_4$ phases with a second lithiation step. Kerr et al and Gaubicher et al utilized the open VOPO$_4$ structures to synthesize $\alpha$-LiVOPO$_4$ from $\varepsilon$-VOPO$_4$ and $\beta$-LiVOPO$_4$ from $\beta$-VOPO$_4$, respectively. Both syntheses
utilized LiI in acetonitrile for the lithiation of VOPO$_4$. The resulting LiVOPO$_4$ shows discharge plateaus around 3.95 V vs Li/Li$^+$ with varying capacity as mentioned above. Comparing these two separate studies, $\alpha$-LiVOPO$_4$ yielded better cycling results than $\beta$-LiVOPO$_4$ (100 mAh/g at C/10 rate vs. 90 mAh/g at C/50 rate). In another study, $\delta$-VOPO$_4$ has been discharged and charged in a Li anode cell achieving 124 mAh/g at C/50 rates$^8$, although the capacity was cut nearly in half when the rate increased to C/10. Tetragonal $\alpha$-VOPO$_4$2H$_2$O was also electrochemically lithiated, yielding high initial capacity at 3.8 volts vs. Li (>100 mAh/g, C/5 rate) but with poor cycleability attributed to the water in the material.$^9$ Utilizing the same $\alpha$-VOPO$_4$ phase, superior long term cycling results were achieved by Barker et al$^{10}$ incorporating lithium into the $\alpha$-VOPO$_4$2H$_2$O structure via carbothermal reduction. The resulting $\beta$-LiVOPO$_4$ showed 120 mAh/g capacity at a C/20 rate.

The aforementioned syntheses require multiple phase formations in several steps as follows.

Various methods $\xrightarrow{\text{x-VOPO}_4}$ lithiation reactions $\xrightarrow{\text{Li-xVOPO}_4}$

In all of these, control of x-VOPO$_4$ (x =one of seven structures) is followed by a second lithiation step. Discharge voltage profiles and capacities of these VOPO$_4$ phases in Li cells have varied from 3.7 to 3.95 V and 25-125 mAh/g, respectively.$^8$

Here, we first look to capitalize on this range of vanadium oxidation states and distinct phases that provide a unique synthetic opportunity to determine structural connections that exist among $\alpha$-LiVOPO$_4$, $\beta$-LiVOPO$_4$, and $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$. This is done with an aqueous precursor-based synthesis yielding these three different active materials from the same starting material precursor mixture. This method is of interest for the following reasons; 1) it allows for product control from an in situ generated reducing agent, with the final structure dependent on sintering conditions (gas, flow rate, and temperature) used for the thermal decomposition of the precursor;
and 2) it yields several electrochemically active phases from one common precursor mix; and 3) it provides an explanation of how and why these different phases are formed.

Although a large oxidation state window is an important requisite for high energy cathodes, it also requires strain tolerance of the structure in order to avoid deterioration and/or phase transformation, as in the case of V$_2$O$_5$ cycled beyond 1 Li.$^{11}$ X-ray absorption spectroscopy (XAS) was utilized in order to understand electrochemical/structural correlations of α- and β-LiVOPO$_4$ during normal discharge to 3 volts and what is considered overdischarge to 2 volts. By correlating electrochemical properties with structural dynamics we have gained new insights into the structural differences between these close analogues. XAS is also used here to elucidate the cause of deep cycling capacity fade in these phases.

2.2 Experimental Methods

2.2.1 Synthesis

The three compounds, α-LiVOPO$_4$, β-LiVOPO$_4$, and α-Li$_3$V$_2$(PO$_4$)$_3$ were produced from a precursor mixture prepared in an aqueous process, followed by two sintering steps as seen in Scheme 2.1. Equivalent molar ratios of all starting materials, specifically, 0.8069 g NH$_4$VO$_3$ (Sigma Aldrich, 99.999%), 0.7934 g NH$_4$H$_2$PO$_4$ (Sigma Aldrich, 99.999%), 0.1789 g LiF (Sigma Aldrich, 99.99%), and 0.864 mL hexanoic acid (CH$_3$(CH$_2$)$_4$COOH) (Sigma Aldrich, 99.5%) were mixed in 300 ml H$_2$O for 24 hrs and then evaporated at 80° C. Low solubility of LiF required long mixing times; however, only this inorganic source of lithium gave the results presented here (see Results and Discussion). The resultant bright yellow cake was then dried, ground, pressed at 3000 psi, and sintered at 300° C for 3 hours under a constant argon flow. The final product depended on the subsequent four-hour sintering which varied in temperature, gas
flow rate in the tube furnace, and reducing atmosphere, consisting of either argon or 5% H₂/argon. These conditions are summarized in Table 2.1. Flow rates were determined using flow meter calibration data (Porter Instrument Co. Inc, Hatfield, PA). Heating rates were held constant for all samples at 4°C/minute. Thermal analysis including differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) on the precursor mixture after the 80°C evaporation step was performed in the range 25°-450°C and 25°-800°C, respectively, both at a heating rate of 4°/min under 45 mL/min N₂. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were contracted out to Geolabs Inc. (Braintree, MA) to determine elemental composition.

Scheme 2.1. Overall synthetic Scheme

2.2.2 Electrochemical Measurements

The dc electronic conductivity measurements were done using pellets pressed at 5000 psi. The pellets, approximately 0.95 cm in diameter and 0.16 cm thick, were left unsintered in order to preserve labile phases with a consistent density around 1.85 g/cm³. They were then coated with conductive graphite and housed between copper current collectors in a delrin casing. The dc current-voltage data with the electrodes were obtained using an Autolab potentiostat. Impedance measurements were made on Li anode half cells, similar to those used in the
electrochemical cycling, in the range 100 kHz to 0.0008 Hz with a 5 mV potentiostatic sine-wave amplitude in order to determine chemical Li⁺ ion diffusion coefficients in the solid materials. All measurements were made at room temperature.

Galvanostatic charge/discharge cycling was performed on an Arbin Instruments cycler, which employed pressed electrodes comprised of 77% weight percent active material, 20% Super-P conductive carbon (TimCal Carbon and Graphite, Belgium), and 3% polyvinylidene fluoride (PVDF). Slurry made with N-methyl-2-pyrrolidone (NMP) was cast on aluminum foil and dried overnight at 100°C with typical active material loadings around 5 mg/cm². The active material and conductive carbon were mixed in either a Spex 8000 mill or Fritsch planetary mill for 3 hours. Swagelok Li half-cells (referred to as T-cells) were assembled in an argon environment and activated using a 1:1.2 by volume EC/DMC electrolyte consisting of 1 M LiPF₆. Whatman glass microfiber paper separated the active electrode and lithium foil counter electrode in the test cell.

2.2.3 X-ray Diffraction and Absorption

X-ray diffraction (XRD) measurements were performed using a Rigaku D-Max 2200 (Cu Kα₁,₂ radiation). Unit cell constants of powder patterns were refined with Expogui¹² and GSAS¹³ using Lebail pattern matching.

X-ray absorption measurements were collected in transmission mode at the V K-edge (5465 eV) at beam line X-18a of the National Synchrotron Light Source at Brookhaven National Laboratory, with a Si 111 crystal detuned 35% to reject higher harmonics. Scans were collected in four regions, -150 to -50 eV (5 eV steps), -50 to 200 eV (0.5 eV steps), 50 to 200 eV (1 eV steps), and out to 16k (0.05 k steps). Low cycling rates (C/75) were utilized and electrodes extracted from T-cells were packed under argon to avoid oxidation. The electrodes were
prepared as described above, however active material and conductive carbon were mixed using a zirconium mill to avoid metal contamination. Grafoil was used as the positive electrode substrate to ensure ample transmission at the V K-edge. A k range of 2-12.5Å⁻¹ and 2-11.5Å⁻¹ were used for α- and β-LiVOPO₄ in the Fourier transformed R space functions. Data processing was done in Athena, version 8.056, and Artemis, version 8.012 developed by Ravel and Newville.¹⁴

2.3 Results and Discussion

2.3.1 Synthesis of Electrode Materials in Controlled Atmosphere

NH₄VO₃ has been used as a source of V⁵⁺ in vanadyl phosphates prior to this report.¹⁵ Here, we capitalized on its decomposition products for use as part of an intercalation host, similar to that described previously¹⁶, seen in reaction Scheme 2.2.

\[
\begin{align*}
\text{NH}_4\text{VO}_3 & \xrightarrow{\Delta} \text{VO}_{2.5} + \text{NH}_3 + \frac{1}{2} \text{H}_2\text{O} \quad \text{V reduction} \quad \text{VO}_{2.5-x} + \text{NH}_3 \text{ oxidation products}
\end{align*}
\]

Scheme 2.2. Controlled formation of vanadium oxides with argon gas flow

In that study, it was found that the control of the generation of NH₃, a reducing agent, yielded various VO₂.₅₋ₓ stoichiometries by manipulating vanadium’s oxidation state. Although decomposition of NH₄VO₃ in air yields V₂O₅,¹⁷ under inert conditions the NH₃ residence times can be controlled via argon gas flow rates in the reaction tube. As a result, non-stoichiometric products with distinct electrochemistry formed,¹⁶ ranging from VO₁.₈₈ at the longest NH₃ residence time or slowest argon gas flow rate, to VO₂.₁₉ at the shortest residence time or fastest argon gas flow rate. Those VₓOᵧ non-stoichiometric compositions resulted because decomposed NH₄VO₃ allowed for varying levels of reaction between VO₂.₅ and NH₃, depending on the argon...
gas flow rate. We took a similar approach in forming the Li$_w$V$_x$O$_y$(PO$_4$)$_z$ framework in a one-pot reaction, revealing interesting relationships between these vanadium phosphates.

The overall procedure for the synthesis of Li$_w$V$_x$O$_y$(PO$_4$)$_z$ phases, depicted in Scheme 2.1, specifies two sintering steps. The TGA data in Figure 2.1 describes the weight losses accompanying the heating. Multiple grinding, pelleting, and sintering attempts allowed for maximum solid-state diffusion of starting materials as phase evolution occurs, while also increasing inter-particle contact in order to ensure reaction completion. The initial heating at 300°C is intended to remove excess water and allow for NH$_4$H$_2$PO$_4$ decomposition, in which the majority of its weight loss is known to occur between 150°C-210°C. These two contributions, along with the early decomposition of NH$_4$VO$_3$ are thought to make up the first half of the weight loss, evident in the TGA curve as it approaches 300°C seen in Figure 2.1. Corresponding DSC data (Figure 2.1 inset) also indicate large endothermic events in this temperature range. The first major peak at 160°C is in agreement with the dehydration of NH$_4$H$_2$PO$_4$(s) to NH$_4$H$_2$P$_2$O$_7$(s) + H$_2$O(g) confirmed by XRD in Reference 18. This NH$_4$H$_2$P$_2$O$_7$ solid phase deformation continues at 210°C as determined in that study. This most likely occurs here as well, alongside NH$_4$VO$_3$ decomposition, resulting in the large peak at 250°C due to endothermic V$_x$O$_y$ formation and consequent NH$_3$, H$_2$O, O$_2$, and N$_2$ gas production caused by that decomposition. Significant pellet enlargement was witnessed following the first sintering, which indicates substantial gas evolution.
Figure 2.1. TGA results of the precursor mixture (after the 80°C drying), heated at 4°/min under 45 cc/min N₂ flow from 25°-800°C. The phase formations, achieved with two heat applications are designated here revealing weight loss during each furnace treatment. Differential thermogram from 25°-450°C (inset), under identical heating ramp and N₂ flow as TGA.

The vanadyl phosphates form upon re-sintering the mixed phase intermediate to a minimum of 600°C. Temperatures below this, between 350°C and 390°C (Figure 2.1 inset) still in the range of thermal decomposition of NH₄VO₃, clearly shows two DSC endothermic peaks and TGA weight loss, believed to control phase evolution based on sintering conditions in this synthesis. In the first stage, VOPO₄ is thought to form from the reaction between NH₄VO₃ and NH₄H₂PO₄ as depicted in step 1 of Scheme 2.3. However, the NH₃ generated during the decomposition of NH₄VO₃ and NH₄H₂PO₄ would slightly reduce V⁵⁺ to form non-stoichiometric VO₁₋ₓPO₄ products with x depending on NH₃ residence times and/or additional reduction atmosphere provided by H₂/argon as seen in steps 2a-2b of Scheme 2.3. The end result is the formation of the two vanadyl phosphates. The numbers in parenthesis in Scheme 2.3 correspond
to tube furnace conditions as summarized in Table 2.1. (x is negative in certain cases for the two LiVOPO₄ phases due to V oxidation states greater than 4.) Only limited residence times of NH₃ can be expected as it evolves from the NH₄VO₃ + NH₄H₂PO₄ mixture in an open vessel, regardless of pellet pressure. Therefore H₂/argon provides continuous reducing power during the phase formations. At 600°C the low symmetry α-LiVOPO₄ triclinic phase formation occurs at relatively faster flow rates in both argon alone and 5% H₂/argon compared to the formation of β-LiVOPO₄. (This reaction was also favored at higher temperatures up to 750°C.) At slower flow rates the orthorhombic β-LiVOPO₄ is favored. The trend in flow rates seen here is consistent with the Li/V ratios in Table 2.1 determined using ICP-MS elemental analysis, XRD, and XAS results. The results suggest slightly higher oxidation states in the α phase due to shorter residence times of the reducing agent, whereas the β phase apparently requires longer reducing agent residence times, leading to lower oxidation states. Step 1 in Scheme 2.3 may occur prior to or concurrently with the final lithiation step, as hexanoic acid residues (e.g. RCOOLi) can quite
possibly act as a lithiating or chelating agent. Attempts without hexanoic acid during the synthesis led to various mixed phases, especially in the case of $\alpha$-LiVOPO$_4$, so its use may

Table 2.1 Reaction conditions resulting in the Li$_n$V$_4$O$_y$(PO$_4$)$_z$ products. Flow rates less than 45 cc/min argon or 10 cc/min H$_2$/argon were unknown due to limits of the calibration data.

<table>
<thead>
<tr>
<th>Argon</th>
<th>Flow Rate</th>
<th>Temperature ($^\circ$C)</th>
<th>ICP-MS</th>
<th>Li/V</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li/ V</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(g/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>45mL/min</td>
<td>$\geq$ 600</td>
<td>35.9</td>
<td>280</td>
<td>0.94</td>
</tr>
<tr>
<td>2.</td>
<td>&lt;45 mL/min</td>
<td>600</td>
<td>42.5</td>
<td>318</td>
<td>0.98</td>
</tr>
<tr>
<td>3.</td>
<td>150 mL/min</td>
<td>600</td>
<td>32.0</td>
<td>252</td>
<td>0.93</td>
</tr>
<tr>
<td>4.</td>
<td>&lt;10 mL/min</td>
<td>600</td>
<td>39.5</td>
<td>249</td>
<td>1.16</td>
</tr>
<tr>
<td>5.</td>
<td>10 mL/min</td>
<td>750</td>
<td>38.2</td>
<td>191</td>
<td>1.5</td>
</tr>
</tbody>
</table>

possibly impede further reduction to $\beta$-LiVOPO$_4$ if reducing conditions are mild enough. It should also be noted that alternative organic additions to this mix, such as citric acid in place of hexanoic acid, or Li acetate in place of LiF also led to increased impurities and lack of phase selectivity. The TGA plot in Figure 2.1 is consistent with our final product results, first by revealing a small plateau around 500°C consistent with poorly performing $\alpha$- and $\beta$-LiVOPO$_4$ phases that evolved in that temperature range. This plateau was followed by another 1% weight loss leading to the large TGA plateau at 600°C where better electrochemical performance was observed for both LiVOPO$_4$ phases.
By further altering the tube furnace environment, the formation of monoclinic $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ is also achieved from this precursor mixture. At 750°C under H$_2$/argon, $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ appears to form from full reduction of V$_2$O$_5$.P$_2$O$_5$ (from Scheme 2.3) leading to V$_2$O$_3$.P$_2$O$_5$ or VO$_{1-x}$PO$_4$ to VPO$_4$ ($x=1$). This is followed by lithiation as seen in 2c of Scheme 2.3. The formation of $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ is not evident in the TGA results of Figure 2.1 as no significant weight change is noticed at 750°C. The fluorophosphate, LiVPO$_4$F (V$^{3+}$) was the originally intended product under these conditions. However, it did not form. It appears that instead F was probably evolved as HF, which together with the NH$_3$ reacted with the quartz tube to form (NH$_4$)$_2$SiF$_6$. This phase solidified on the furnace walls and was identified from its XRD pattern as seen in Figure 2.2. Interestingly, the typical route to forming LiVPO$_4$F, using carbothermal reduction (CTR)$^{19}$ includes the same intermediate VPO$_4$ proposed here, yet its formation was not favorable under our conditions. This may be due to the one pot method we
have employed to prepare LiVPO₄F. This inevitably allows for NH₃ as a byproduct that in turn led to the products we found. The CTR method used previously to prepare LiVPO₄F involves a two-step reaction.

2.3.2 Phase Characterization and V Oxidation States

In Table 2.1, the α phase which formed according to condition 1 (at 750°C) and the β phase according to condition 4, yielded the best electrochemical performance and will be discussed in more detail. X-ray powder diffraction patterns of these two phases, along with α-Li₃V₂(PO₄)₃, are shown in Figure 2.3. Table 2.2 lists the refinement results along with space group (SG) and goodness of fit parameters ($\chi^2$). Unit cell parameters in Table 2.2 obtained from Lebail fits agree with the respective ICDD/JCPDS cards. Small impurity reflections are noted but were not identified due to lack of peaks. The lattice parameters of the β phase agree with a Li⁺ content > 1 when compared to literature cell volume constants that report a 1:1 Li:V ratio. Additional Li⁺ will expand the volume of the unit cell.

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDF #</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha,\beta,\gamma$</th>
<th>SG</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Li₀.₅V₀₁.₀PO₄</td>
<td>01-072-2253</td>
<td>6.7321(7)</td>
<td>7.1814(8)</td>
<td>7.8962(8)</td>
<td>89.833(2),91.277(2),117.032(2)</td>
<td>P₁</td>
<td>7.34</td>
</tr>
<tr>
<td>β-Li₁₁.₀VO₉.₅PO₄</td>
<td>01-085-2438</td>
<td>7.4478(6)</td>
<td>6.2917(5)</td>
<td>7.1798(6)</td>
<td>-</td>
<td>Pnma</td>
<td>8.52</td>
</tr>
<tr>
<td>α-Li₃V₂(PO₄)₃</td>
<td>01-072-7074</td>
<td>8.512(2)</td>
<td>8.593(2)</td>
<td>11.957(3)</td>
<td>90.443(6)</td>
<td>P₂₁/n</td>
<td>2.58</td>
</tr>
</tbody>
</table>
Vanadium K-edge x-ray absorption near edge structure (XANES) measurements of the two LiVOPO$_4$ phases and Li$_3$V$_2$(PO$_4$)$_3$ were made in order to determine any trends in oxidation state of these three compounds. The connection between oxidation state trend and absorption edge of the XANES is based on the increased energy needed to elevate a 1s electron as the metals valence electrons decrease due to a stronger nucleus/core electron attraction. In Figure

**Figure 2.3.** X-ray powder diffraction patterns of the three vanadium phosphate phases along with standard spectra. (*) represent un-indexed peaks.
2.4a, α-Li₃V₂(PO₄)₃ with a vanadium oxidation state near 3 shows a shift in its absorption edge to lower energies relative to the other two phases as seen in the rising portion of the spectra. The β- and α-LiVOPO₄ follow, with a slight shift in energy separating the two. This main absorption edge has been defined as the second peak in the derivative curve of vanadium oxides²⁰ (Figure 2.4b), which reveals the edge differences between the two LiVOPO₄ phases. Other factors affecting metal electron energy transitions and hence this edge position include interatomic distance and local vanadium coordination.²¹ However, the edge shift observed for the two LiVOPO₄ is consistent with the vanadium oxidation state in the α phase being slightly higher than that in the β phase. This is in agreement with the conclusion arrived at from elemental analysis and XRD.

**Figure 2.4.** Vanadium K-edge X-ray absorption near edge structure (XANES) spectra: (a) Normalized absorption and (b) derivative plots of α-Li₃V₂(PO₄)₃, β-LiVOPO₄, and α-LiVOPO₄.

### 2.3.3 Cycling Performance and Electrical Transport Properties

The first two charge/discharge profiles of the two vanadyl phosphates are shown in Figure 2.5. Galvanostatic cycling was conducted between 3.0–4.4 V at C/10 rates. Voltages
above 4.5 V led to active material or electrolyte degradation evidenced by irreversible capacity. The $\alpha$-LiVOPO$_4$, which undergoes phase transformation to monoclinic $\varepsilon$-VOPO$_4$ upon charge,$^4$ displays first cycle coulombic efficiency of only 79% as seen in Figure 2.5a, but the asymmetry of both charge/discharge capacities improve as quickly as the 2$^{nd}$ cycle. These features along with lowered voltage hysteresis seen in the 2nd cycle indicate improved reversibility of the system. The cycling capacity of this phase stabilizes at just over 100 mAh/g (Figure 2.5c). In Figure 2.5b the $\beta$ phase, which leads to orthorhombic $\beta$-VOPO$_4$ upon full charge,$^7$ also displays poor coulombic efficiency initially, but offers consistent discharge capacity over 80 mAh/g (Figure 2.5c). The slightly sloping cycling curves of the $\beta$ phase may be caused by a higher disorder of the vanadium sites. This trend was seen in the discharge of $\varepsilon$-VOPO$_4$ formed from tetragonal H$_2$VOPO$_4$.,$^{22}$ It should also be noted that high energy Spex milling was necessary to incorporate conductive carbon with the $\alpha$ phase. Planetary milling resulted in a 100 mAh/g lower first discharge capacity. This may explain the recent communications which reported poor capacities in the range of 10 to 12 mAh/g at rates no faster than C/50 for $\alpha$-LiVOPO$_4$.,$^{15,23}$ As synthesized, the $\alpha$-LiVOPO$_4$ particles were in the range of 2-5 microns determined using SEM as seen in Figure 2.6. Milling led to a uniform, 1 micron particle size for both Spex and planetary motion. Due to Spex ball milling’s inability to reduce particle size down substantially lower than the planetary mill, shorter diffusion paths are ruled out as the basis for increased capacity of the $\alpha$-LiVOPO$_4$ phase comparing the two milling techniques.
Figure 2.5. (a) $\alpha$-LiVOPO$_4$ and (b) $\beta$-LiVOPO$_4$ with first (solid) and second (dashed) cycle comparisons of Li cells at C/10 rates between 3.0 and 4.4 V (c) Discharge capacities verses cycle number of Li cells with $\alpha$- and $\beta$-LiVOPO$_4$ phases. All cycling was done at C/10 rates.
Electrical conductivity measurements also reveal consistencies that correspond to a higher vanadium oxidation in $\alpha$-LiVOPO$_4$ compared to $\beta$-LiVOPO$_4$. Two-point probe chronopotentiometric measurements were made using graphite painted pellets sandwiched between copper current collectors. The ionically blocking painted faces of the pellet allowed for
dc electronic conductivity calculations. Galvanostatic excitation of the cell was maintained for
100 seconds at room temperature, yielding a constant voltage response where resistance (R) was
extracted from the I-V curve based on Ohm’s law. Resistivity (δ) was determined using equation
2.1

\[ \delta = \frac{RA}{L} \]  

(2.1)

where A is the pellet area and L is the thickness. 1/δ yielded dc electronic conductivity, which
ranged from 5.5x10^{-11} to 1.8x10^{-10} S/cm for α-Li_{0.94}VO_{1.03}PO_4 and β-Li_{1.16}VO_{0.92}PO_4,
respectively. These values are very low, highlighting inherent limitations of ε and β-VOPO_4 as
high rate lithium transport media. They do correlate nicely with calculated V oxidation states of
the two respective compounds assuming they follow a semiconductor-like model. The electronic
configuration in α-Li_{0.94}VO_{1.03}PO_4 (V^{4.06}) is on the side of that of semiconducting V_2O_5, which
due to its empty conduction band has poor electronic conductivity compared to lower vanadium
oxides. Therefore, one might expect higher conductivity for the β-Li_{1.16}VO_{0.92}PO_4 (V^{3.68}) due to a
process similar to that of lithium intercalation into V_2O_5. Vanadium sites are reduced from V^{5+}
to V^{4+}, resulting in small polarons from the interaction of the V^{4+} unpaired electron and the polar
V_2O_5 leading to higher conductivity as intercalation proceeds via electron hopping between
mixed valence sites.\textsuperscript{24} Based on the oxidation states of α-Li_{0.94}VO_{1.03}PO_4 and β-Li_{1.16}VO_{0.92}PO_4,
the greater abundance of vanadium atoms with unpaired d electrons in the β form may increase
its conductivity through a similar semiconducting mechanism.

This conductivity trend between the two compounds is also supported by ac impedance
measurements. The same blocking electrode setup was used to analyze the ac impedance
spectrum of both α- and β-LiVOPO_4 at room temperature as seen in the Nyquist plot in Figure
2.7a.
Figure 2.7. (a) Impedance spectrum of pelletized $\alpha$-Li$_{0.94}$VO$_{1.03}$PO$_4$ (red) and $\beta$-Li$_{1.16}$VO$_{0.92}$PO$_4$ (black) along with simplified equivalent circuit. (b) In-cell impedance measurements of both materials along with $\text{Re } Z$ as a function $\omega^{-1/2}$ at low frequencies (inset).

Impedance spectroscopy along with dc conductivity measurements can be used to isolate ionic and electronic charge transfer contributions, consistent with similar strategies carried out earlier for LiFePO$_4$ and LiMnPO$_4$. Conductivity values were determined by fitting the impedance data based on the simplified equivalent circuit in Figure 2.7a with a constant phase element (CPE) representing double layer charging, in parallel with the charge transfer resistance ($R_{ct}$), representing bulk phase properties (ionic and electronic resistance). Figure 2.7a reveals one semicircle with high frequency extrapolation through the Real Z axis at zero ohm for both materials. The low frequency region of the spectrum corresponding to $R_{ct}$ yielded conductivities of $2.95 \times 10^{-10}$ and $4.4 \times 10^{-10}$ S/cm for $\alpha$-Li$_{0.94}$VO$_{1.03}$PO$_4$ and $\beta$-Li$_{1.16}$VO$_{0.92}$PO$_4$, respectively. The resistivity values ($\delta$) resulting in these conductivities were near to or lower than dc values, indicating these materials to be ionically insulating and their conduction to be primarily electronic. Like dc electronic conductivities, the ac calculations are consistently higher for $\beta$-
Li\textsubscript{1.16}VO\textsubscript{0.92}PO\textsubscript{4}, possibly due to its lower vanadium oxidation state. The results of both are listed in Table 2.3.

Also listed in Table 2.3 are the calculated chemical lithium diffusion coefficients for these two materials. Mass transport limitations are important considerations when determining the influence particle size may play in overall performance compared to conductivity contributions.

### Table 2.3. Summary of charge transfer properties for LiVOPO\textsubscript{4} phases.

<table>
<thead>
<tr>
<th></th>
<th>Electronic conductivities (S/cm)</th>
<th>Li\textsuperscript{+} diffusion coefficient (cm\textsuperscript{2}/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dc</td>
<td>ac</td>
</tr>
<tr>
<td>α-Li\textsubscript{0.94}VO\textsubscript{1.03}PO\textsubscript{4}</td>
<td>5.5x10\textsuperscript{-11}</td>
<td>2.9x10\textsuperscript{-10}</td>
</tr>
<tr>
<td>β-Li\textsubscript{1.16}VO\textsubscript{0.92}PO\textsubscript{4}</td>
<td>1.8x10\textsuperscript{-10}</td>
<td>4.4x10\textsuperscript{-10}</td>
</tr>
</tbody>
</table>

Impedance spectroscopy was again utilized for these measurements\textsuperscript{26} and Li cells in the lithiated (discharged) state prior to charging were tested as seen in Figure 2.7b. Depressed semicircles are again evident for both α-Li\textsubscript{0.94}VO\textsubscript{1.03}PO\textsubscript{4} and β-Li\textsubscript{1.16}VO\textsubscript{0.92}PO\textsubscript{4} followed by steeply sloped inclines in the low frequency region of the spectrum, known as the Warburg impedance region, which is related to mass transfer resistance. Both kinetic and mass transfer controlled regions are defined within the frequency range 100 kHz to 0.0008 Hz. The chemical diffusion coefficient (D) values were extracted according to equation 2.2, where R is the gas constant, T is temperature, A the electrode surface area, n is electron transfer per molecule of LiVOPO\textsubscript{4},

\[
D = \frac{R^2r^2}{2A^2n^4F^4c^2\sigma^2}
\]  

(2.2)

F is Faraday’s constant, c is concentration of lithium ions, and σ, known as the Warburg factor, can be extracted from the slope of the plot, \( Z' \) versus the reciprocal square root of frequency (\( \omega^{-1/2} \)) at low frequencies as seen in the inset of Figure 2.7b from equation 2.3,
\[ Z' = R_s + R_{ct} + \sigma \omega^{-1/2} \]  

where \( R_s \) is the solution resistance. Values of \( 3.0 \times 10^{-15} \) and \( 2.4 \times 10^{-15} \) cm\(^2\)/s for \( \alpha \)- and \( \beta \)-LiVOPO\(_4\), were obtained. These values are very low, highlighting inherent limitations of \( \varepsilon \) and \( \beta \)-VOPO\(_4\) as high rate lithium transport media.

In Figure 2.8, the first two constant current cycles of a Li/\( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) cell are presented along with extended cycling data (inset). The capacity corresponds to 1.6 Li per mole of the phosphate, or 106 mAh/gram. During charge, the first two plateaus correspond to removal of 0.5 Li each, followed by extraction of a second Li starting at 4 V. Two-phase behavior is maintained throughout charge and discharge in this voltage range.\(^{27}\) These data confirm its formation under the more intense reducing conditions as described in Table 2.1. Compared to the two LiVOPO\(_4\) phases, transport properties of \( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) are apparently less troublesome with a reported lithium diffusion coefficient of \( 10^{-9} \) cm\(^2\)/s.\(^{28}\)

![Figure 2.8](image-url)  

**Figure 2.8.** A Li/\( \alpha \)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) cell cycled between 3.0-4.3 volts at C/20 along with extended cycling (inset). The first cycle capacity corresponds to the de-insertion of 1.6 Li per Li\(_3\)V\(_2\)(PO\(_4\))\(_3\) or 106 mAh/gram.
2.3.4 Structural Effects Accompanying Li Insertion and Extraction in $\alpha$- and $\beta$-LiVOPO$_4$ using XAS

The effects of Li de/insertion on the structures of $\alpha$- and $\beta$-LiVOPO$_4$ were studied using x-ray absorption spectroscopy (XAS). These phosphate electrodes are normally cycled between 3 and 4.4 V but in our structural studies the electrodes were discharged down to 2 V in order to determine their reversible capacities under such deep discharges and the consequences of overlithiation on the crystal structures of the materials. It is of interest that overlithiated active materials provide not only increased energy density, but the higher capacity can also be used for compensating the irreversible capacity in the first charge due to electrolyte reduction and solid electrolyte interface (SEI) formation on graphite anodes. Reversible cathode capacity at low voltages can also afford protection from over-discharge of the cell. Probing the VO$_6$ octahedral environment, which is conducive to XAS studies, allowed us to determine changes in short range atomic order in $\alpha$- and $\beta$-LiVOPO$_4$ which was monitored throughout the first cycle.

Figure 2.9. V K-edge XANES spectra of $\alpha$-LiVOPO$_4$ and $\beta$-LiVOPO$_4$ before and after the 1$^{\text{st}}$ charge cycled at a C/75 rate. The labeled features include the pre-edge (1), main edge (2), and 1s-4p electronic transition (3)
The $\alpha$- and $\beta$-LiVOPO$_4$ achieved first cycle charge capacities of 140 and 130 mAh/g respectively at 0.01 mA/cm$^2$ (C/75) cycling rate. This corresponds to the removal of 0.84 Li in the $\alpha$ and 0.78 Li in the $\beta$. (These charging profiles can be seen in the insets of Figure 2.17a and 2.17b.) V K-edge XANES spectra in Figure 2.9 compare uncycled $\alpha$- and $\beta$-LiVOPO$_4$ with spectra of their fully charged states. Substantial changes in the spectral profile occur following delithiation. The first feature in the XANES spectra is the pre-edge peak labeled 1 in Figure 2.9, which is typical in vanadium oxides. X-ray absorption spectroscopy follows dipole selection rules and this dipole forbidden $s\rightarrow d$ electronic transition is allowed due to $p$ orbital character in the final unoccupied d states as a result of $V_{3d}/V_{4p}$ and $O_{2p}$ mixing. Increased intensity in this feature is observed at full charge due to decreased V-O bond lengths and lower VO$_6$ symmetry resulting in further VO$_6$ distortion as a result of Li removal. The phase change of $\alpha$-LiVOPO$_4 \rightarrow \epsilon$-VOPO$_4$ provokes a greater response in the VO$_6$ environment compared to $\beta$-LiVOPO$_4 \rightarrow \beta$-VOPO$_4$ with a pre-edge intensity change of 0.19 in the former, nearly double that of the latter (0.1). The main edge step in the spectra (labeled 2) associated with the steep increase in absorption, reveals a rigid shift to higher energy following lithium extraction due to charge compensation on the V sites. Evidence of this V oxidation during Li removal is also visible in the
positive shift of the pre-edge feature as well as the shifted white line feature labeled 3 in Figure 2.9. This third feature, affected by the coordinating atoms surrounding the photoabsorber, is due to V 1s electronic transitions to non-binding V 4p states, (referred to as a 1s→4p feature) and is discussed further below.

1\textsuperscript{st} cycle discharge curves of both phases in Figure 2.10 show the various points of XAS measurements labeled as states of discharge (SOD) a-f. Nearly 2 Li insert into these structures in the high and low voltage regions. Corresponding XANES spectra at the six states of discharge are shown in Figure 2.11a and 2.11b for both phases. The trends in spectral features described above during charge are reversed following Li intercalation in the high voltage region (SOD a-d). Figure 2.11c compares the uncycled phases with SOD d. Good agreement of these spectra is qualitative proof that both VO$_6$ symmetry and V electronics are reversible if cycling is limited to
≤ 1 Li/VOPO₄. This is consistent with cycling data in Figure 2.5c. The EXAFS results in Table 2.4 comparing VO₆ bond lengths of the uncycled materials with SOD d also support these XANES results.

**Figure 2.11.** V K-edge XANES spectra of (a) α-LiₓVOPO₄ and (b) β-LiₓVOPO₄ at various states of Li insertion during the first discharge. (c) XANES comparison of the uncycled materials to their electrodes following SOD d. (d) XANES spectra of both phases compared at the two discharge extremes.

During the low voltage discharge, increased VO₆ symmetry and charge compensation on the V sites continues as seen in the reduced pre-edge intensity and main edge shift of corresponding XANES spectra in Figures 2.11a and b. The 1s→4p feature, which shows
increased intensity during the first Li insertion, is followed by peak broadening and loss of intensity during the low voltage region despite moving towards more negative energies. This may be due to changes in the symmetry of the four equatorial oxygens ($O_{eq}$) alluded to in the case of $V_2O_5$ during deep discharge. These LiVOPO$_4$ phases, which can be viewed with VO$_5$ pyramidal geometry like $V_2O_5$, exhibit trends suggesting decreasing symmetry of these equatorial oxygens as a result of low voltage Li insertion. This conclusion is also based on trends in the EXAFS discussed below.

**Table 2.4.** First shell VO$_6$ fits$^\dagger$ for $\alpha$- and $\beta$-LiVOPO$_4$ and Li$_x$VOPO$_4$ at various SOD.

<table>
<thead>
<tr>
<th></th>
<th>$V=O$ (Å)*</th>
<th>$V-O$ (Å)* (equat.)</th>
<th>$V-O$ (Å)* (trans)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Uncycled</td>
<td>1.63</td>
<td>1.64</td>
<td>1.94</td>
</tr>
<tr>
<td>Li$_x$VOPO$_4$ SOD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. $x=0$</td>
<td>1.57</td>
<td>1.58</td>
<td>1.91</td>
</tr>
<tr>
<td>b. $x=0.24$</td>
<td>1.60</td>
<td>1.60</td>
<td>1.93</td>
</tr>
<tr>
<td>c. $x=0.48$</td>
<td>1.61</td>
<td>1.62</td>
<td>1.94</td>
</tr>
<tr>
<td>d. $x=0.73$</td>
<td>1.61</td>
<td>1.63</td>
<td>1.95</td>
</tr>
<tr>
<td>e. $x=1.2$</td>
<td>1.71</td>
<td>1.74</td>
<td>1.94</td>
</tr>
<tr>
<td>f. $x=1.47, 1.76$</td>
<td>1.90</td>
<td>1.87</td>
<td>2.02</td>
</tr>
<tr>
<td>2$^{nd}$ discharge</td>
<td>1.91</td>
<td>1.89</td>
<td>2.00</td>
</tr>
</tbody>
</table>

$^\dagger$See text for fitting procedure and omitted parameters.

The XANES spectra of $\alpha$- and $\beta$-LiVOPO$_4$ at the two extremes of the 1$^{st}$ discharge cycle are compared in Figure 2.11d. The fully charged (SOD a) $\alpha$ phase exhibits a slightly higher pre-edge peak than the $\beta$, indicative of a more distorted VO$_6$ at 4.4 volts (intensity of 0.54 vs 0.49). A higher V oxidation state in the $\alpha$ phase is also apparent based on its relative edge shift to
higher energies at full charge. This edge shift is in agreement with the higher charge capacity achieved in the α phase compared to the β. Similarly, the full discharge XANES region is compared in Figure 2.11d. The main edge feature of both phases is in agreement, evidence of the close nature of their V oxidation states at full discharge, and thus similar Li content at SOD f. The difference in full discharge capacities of 50 mAh/g is consistent with a higher Li content in the β phase upon full charge, resulting in a lower discharge capacity. The α phase VO₆ at this point is almost fully symmetric as seen in its reduced pre-edge intensity at 0.078 compared to the β-phase at 0.19. Comparing these XANES spectra suggests a more accommodating Li pathway during the insertion of 1.76 Li into ε-VOPO₄ visible in the greater pre-edge intensity range here. With similar Li content of both phases at SOD f, the nearly fully restored inversion symmetry of the α phase indicates added mobility of the V atom through the VO₆ during discharge to 2 volts. This is opposed to the β phase which maintains significant pre-edge intensity, thus a more rigid structure following deep discharge.

The atomic displacement during the first cycle was also monitored in the EXAFS region of the spectra in order to compare quantitatively the local changes surrounding the V absorbing atom. Magnitudes of the Fourier transformed k³ weighted data offset on the y-axis in Figure 2.12a and 2.13b reveal several peaks corresponding to the coordination shells surrounding the V center in both phases. Peaks below 1 Å have no structural significance. The first prominent peak at 1.5 Å can be assigned to the first V-O coordination shell. This is followed by an additional 3-4 peaks extending to 3.5 Å which include V-P and V-O single scattering paths along with various multiple scattering paths contributing significant amplitude to these outer shell peaks in both phases. Note that phase shift corrections have not been made so peaks are at lower than expected values. The fits, made in R space, were restricted to the
Figure 2.12. Fourier transformed $k^3$ weighted EXAFS offset on the y-axis. (a) $\alpha$-Li$_x$VOPO$_4$ and (b) $\beta$-Li$_x$VOPO$_4$ at the six states of discharge in the first cycle. The insets display overlaid spectra.
Figure 2.13. Local environment of a V absorbing atom in α-LiVOPO₄. The VO₆ 1+4+1 (Vanadyl)+(Oeq)+(Trans) EXAFS fitting model along with the outer P (orange), V (grey), O (red), and Li (purple) framework are highlighted.

Figure 2.14 Typical fit in both (a) R and (b) k⁳ space for the VO₆ first shell of the vanadyl phosphates.
first shell with the following constraints. The first shell VO$_6$ wide distribution of bond lengths (1.65-2.25 Å) were incorporated using a 1+4+1 model, illustrated in Figure 2.13. Only the α phase local environment is shown due to close similarities between both vanadyl phosphates at this range. Bond lengths (R) were determined by fitting ΔR values for the short vanadyl, long trans, and 4 equatorial bonds (O$_{eq}$). Coordination numbers (N) were held constant and one Debye-Waller factor ($\sigma^2$) along with one photoelectron energy shift (E$_0$) were fit for the three paths. The fit values for $\sigma^2$ ranged from 0.0007-0.0043 Å$^2$ and E$_0$ remained within +/- 10 eV. An amplitude reduction ($S_0^2$) value of 0.69 was determined by fitting vanadium foil. Fractional atomic coordinates from α$^{\text{ref.31}}$-and β$^{\text{ref.32}}$-LiVOPO$_4$ were used for theoretical EXAFS calculations. A representative fit in both R and k space is provided in Figure 2.14.

The first shell VO$_6$ peak amplitudes of both phases in Figure 2.12 vary only slightly during the upper voltage discharge plateau, until the 3 volt region at SOD d where the intensity rises. This trend, more apparent in the insets of Figure 2.12a and 2.12b, indicates increased symmetry surrounding the V absorber following the insertion of the first Li.$^{33}$ This peak then declines during SOD e and f in both phases. As mentioned above, the 1s→4p region in Figures 2.11a and 2.11b also shows declining intensity in this voltage region, attributed to asymmetry in the first shell equatorial oxygens. In agreement, the majority of the EXAFS first shell peak amplitude in Figure 2.13 originates from the 4 equatorial V-O single scattering paths as determined by Feff, the software used to generate the theoretical EXAFS. This O$_{eq}$ asymmetry appears to also affect the longer range order seen in the EXAFS outer shells between 2-3.5 Å visible in the SOD f, namely irregular behavior compared to the lower Li levels. This can be ascribed to the V-O$_{eq}$-P connection in these phases (see Figure 2.13) since single and multiple scattering paths including the O$_{eq}$ and P scattering atoms contribute significantly to these outer
peaks. Thus XANES and EXAFS suggest a lower degree of symmetry within the $O_{eq}$ coordination as a result of overlithiation in these structures.

As mentioned above, the XANES pre-edge feature signifies a possible 1s-3d transition. This comes as a result of mixing of $V_{3d}+V_{4p}$ and $V_{3d}+O_{2p}$ orbitals, which is due to the lack of an inversion center in the VO$_6$ or short V-O bond lengths. The results from first shell fits of the EXAFS in Table 2.4 reveal interesting correlations regarding these pre-edge peak trends. Throughout the normal discharge range between 4.4-3 V (SOD a-d), all three sets of bond lengths in the 1-4-1 configuration display isotropic change along with relatively small loss in

![Figure 2.15. Pre-edge intensity (green) and V=O bond length (red) as a function of Li content for six states of discharge. Arrows indicate the trends during discharge.](image-url)
pre-edge intensity. In Figure 2.15, the pre-edge intensity and V=O bond length during the 1\textsuperscript{st} discharge are plotted vs Li\textsubscript{x} for both phases. The V=O bond length increases approximately 0.05 Å during the normal discharge range in both phases. However, the V=O bond increases an additional 0.25 Å between SOD d and f in both phases, 3 times that of the O\textsubscript{eq} or long V-O trans bonds. The pre-edge intensity decreases at similar rates. Note that the α phase pre-edge intensity extends to greater extremes due to a more dynamic VO\textsubscript{6} as mentioned above. The results are consistent with the work of Wong et al.\textsuperscript{20} who correlated the intensity of the pre-edge peak to the size of the VO\textsubscript{x} “molecular cage” using several vanadium oxides with different polyhedral distortion. The molecular cage is defined as the average bond distance of the nearest neighbors surrounding the V atoms. In that study the V=O bond length alone was determined to contribute 55% of the total intensity to the pre-edge feature. Figure 2.15 confirms this trend during Li insertion into vanadyl phosphates as well, since the changes in this bond distance vary at similar rates to the pre-edge intensity during discharge. The exception is the β phase at SOD f. Although the V=O bond increases nearly as much as α phase at full discharge, the β phase still maintains significant pre-edge intensity. This could be attributed to the unchanged V-O trans bond at full discharge, resulting in a smaller molecular cage. But assuming the trans bond alone has a minor influence in determining the VO\textsubscript{6} cage size, a more plausible cause for the larger β pre-edge is sustained distortion in the VO\textsubscript{6} geometry. In other words, both phases have larger VO\textsubscript{6} octahedrons as a result of overlithiation, but the VO\textsubscript{6} geometry of the β phase retains its distortion, even after the insertion of nearly 2 Li.

Slight differences between α and β-LiVOPO\textsubscript{4} seen here in the XAS were also noticeable in their respective synthetic conditions. These differences reflect the subtleties between both structures. The major difference between the two phases is the orientation of VO\textsubscript{6} as seen in
Figure 2.16. The polyhedra lie in stacks along the b-axis. The VO$_6$ severe distortion leads to apical connections along this axis with alternating short and long V-O bonds. In the $\alpha$ phase, they are staggered due to alternating orientations of the PO$_4$ along the a-axis, but in the $\beta$ phase they lie eclipsed. As suggested in Reference 32, $\beta$-LiVOPO$_4$ also has smaller lithium sites compared to $\alpha$-LiVOPO$_4$ which may not be conducive to full VO$_6$ inversion symmetry.

Figure 2.16. Crystal structures of $\alpha$-LiVOPO$_4$ (top) and $\beta$-LiVOPO$_4$ (bottom). Lithium (green), and oxygen (red) are configured with distorted octahedral VO$_6$ (gray) and PO$_4$ (orange).
Visible differences in the slopes comparing the 1st and 2nd Li insertion in Figure 2.15 also relate directly to the reversibility of these phases. The shallow slope in the upper voltage plateau (b,c,d), shows little change in distortion or size of the VO$_6$. This is followed by increased rates of change during deeper discharge at SOD e and f. As seen in this report as well as others,$^{4,7}$ both
phases have proven to cycle reversibly between LiVOPO$_4$-VOPO$_4$. But as a result of low voltage discharge, hysteresis pursues during the 2$^{\text{nd}}$ cycle charge as seen in Figure 2.17a and 2.17b. The majority of Li removal in the second charge occurs in the high voltage region and approximately 70% less charge capacity is achieved in the 2$^{\text{nd}}$ cycle below 2.5 volts compared to the first discharge. The insets of Figure 2.17a and 2.17b compare the asymmetry between the first and second charge at high voltages revealing the increased capacity above the plateau at 4.1 volts. Despite the hysteresis, the 1$^{\text{st}}$ and 2$^{\text{nd}}$ cycle discharge curves are in agreement, confirming the

![Figure 2.18](image_url)

*Figure 2.18. (a-b) XANES spectra of $\alpha$–Li$_3$V$_2$(PO$_4$)$_3$ along with various states of discharge during the first two cycles of both vanadyl phosphates. The insets magnify the main edge region. (c-d) EXAFS $k^3$ weighted spectra of select states of discharge from the first and second cycle.*
reformation of $\varepsilon$-VOPO$_4$ and $\beta$-VOPO$_4$ at 4.4 V. Only 70% coloumbic efficiency in the second cycle results with visible capacity loss comparing the first two discharges.

In Figure 2.18a and 2.18b, select XANES spectra from the first two discharge curves are compared to $\alpha$–Li$_3$V$_2$(PO$_4$)$_3$ to better understand the behavior of the VO$_6$ environment of the vanadyl phosphates in the low voltage region. In Figure 2.18a, the pre-edge intensity of the $\alpha$ phase at SOD f and $\alpha$–Li$_3$V$_2$(PO$_4$)$_3$ are in good agreement. This is evidence of the extreme reduction in the $\alpha$ phase VO$_6$ distortion since $\alpha$–Li$_3$V$_2$(PO$_4$)$_3$ has a near symmetric VO$_6$. The main edge of both phases at SOD f is shifted slightly positive of $\alpha$–Li$_3$V$_2$(PO$_4$)$_3$, indicating a vanadium oxidation state close to three. (This main edge is magnified in the inset of Figure 2.18a and 2.18b.) It appears however that the $\alpha$ phase is maintained even at this high Li content, verified by XRD. The same is true for the $\beta$ phase as confirmed with in-house XRD measurements of an extracted electrode.

Also in Figure 2.18a and 2.18b, slight shifts occur in the XANES edge following the second cycle discharge relative to SOD f. This is due to a higher vanadium oxidation state after the 2$^{nd}$ discharge. Both $\alpha$ and $\beta$ 2$^{nd}$ discharge edge positions fall in between their respective SOD e and f, consistent with the capacity loss after the second cycle. VO$_6$ bond lengths however are very similar to the 1$^{st}$ cycle full discharge as seen in Table 2.4. It appears that the irreversible capacity corresponding to Li$_{0.3}$ lost in the 2$^{nd}$ discharge in both phases leads to restored order in these structures visible in the increased intensity of the 1$s$$\rightarrow$4$p$ region in the XANES spectra. Also, in Figure 2.18c and 2.18d the EXAFS first shell amplitude increases after the 2$^{nd}$ discharge and the outer shell peaks return to order resembling sod e from the first discharge. These features may give insight into the Li “tolerance limit” during deep discharge in these vanadyl phosphates.
2.4 Conclusions

$\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ and $\alpha$- and $\beta$-LiVOPO$_4$ have been synthesized from one precursor mixture under sintering tube furnace atmosphere control. A plausible mechanism for the various phase formations is provided with analytical results by means of TGA and DSC. Small differences in gas flow results in $\alpha$- and $\beta$-LiVOPO$_4$, with $\alpha$-Li$_3$V$_2$(PO$_4$)$_3$ forming under more intensive reducing conditions. Elemental analysis and XANES spectra support slightly higher oxidation states in the $\alpha$ phase relative to the $\beta$, the result of varying the residence times of the reducing agent. Monitoring structural changes of these vanadyl phosphates using XAS reveals that XANES features including the pre-edge and 1s$\rightarrow$4p transition can predict Li reversibility as gleaned from comparing different states of discharge in the normal and low voltage region. Although extreme changes to the VO$_6$ symmetry do not favor long term reversibility in these vanadyl phosphates during deep discharge, such observations may be useful in testing/designing new high density vanadium phosphates spanning wide oxidation state ranges.

2.5 Acknowledgements

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2.6 References


Chapter 3. Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$, a New Mixed Metal Phosphate Cathode Material

3.1 Introduction

The olivine LiFePO$_4$, developed into a power-dense Li insertion cathode for Li-ion batteries, has found commercial success over the last decade. Several features inherent in the material are responsible for this, including low cost, non-toxicity, and an iron redox center. From an energy density perspective, LiVOPO$_4$, which exists in various crystallographic phases as described in Chapter 2, is also an attractive polyanionic material offering a two-phase discharge plateau several hundred millivolts higher than LiFePO$_4$. But unlike LiFePO$_4$, the vanadyl phosphates have not yet overcome rate limiting processes related to poor electronic conductivities and/or low Li$^+$ diffusion which confine them to low rate charge/discharge cycling.

Even more recently, fluorinated derivatives of Fe and V phosphates have also received attention. For example, the LiMPO$_4$F (M=Fe,V) phases crystallize in a triclinic P-1 space group, isostructural to tavorite and amblygonite.$^{1,2}$ These phases exhibit Li extraction voltages of 2.8V for (Fe$^{2+}$/3$^+$) and 4.1V (V$^{3+}$/4$^+$) as well as large three dimensional Li pathways for good ionic conductivity. An orthorhombic Li$_2$FePO$_4$F phase also forms via ion exchange with its sodium analogue, and results in a solid solution single phase cycling profile, unique to metal phosphate materials.$^3$ It is this electrochemical feature which brought to our attention the mixed metal (fluorophosphate) presented here.

Combining features of the three phosphate moieties, V=O, FeO$_x$, and Fe-F$_y$ into a single phase material, Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$, was the focus of this work. Synthetic attempts involved typical solid state techniques. The Fe-V mixed metal fluorophosphate synthesized here responds
electrochemically as having a single phase material with Li extraction/insertion processes at V and Fe redox active sites.

3.2 Experimental methods

3.2.1 Synthesis

Synthesis of the Fe/V compound was carried out using a two-step heat treatment preceded by intimate mixing of the precursors. In an acetone slurry, appropriate amounts of iron(II) oxalate (Alfa Aesar, 99.999%), ammonium metavanadate (Aldrich, 99.999%), lithium fluoride (Aldrich, 99.98%), and ammonium dihydrogenphosphate (Aldrich, 99.999%) were mixed in a zirconium vial for five hours with a Spex ball mill. The resultant mixture was dried, pressed at 3000 psi, and heated for 350°C for 3 hours under argon. The Fe/V phase formed following the second 4 hour heat treatment at 600 °C under a 5%H₂/Argon blend of purge gas.

3.2.2 Phase Determination

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV diffractometer (Cu Kα₁,₂ radiation). Unit cell constants of the powder pattern were refined with Expgui⁴ and GSAS⁵ using Lebail pattern matching. Prior to XRD measurements, extracted T-cell electrodes were disassembled in a glove box and washed with ethylmethyl carbonate (EMC) to remove excess salts. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were contracted out to Galbraith Laboratories, Inc. (Knoxville, TN) to determine elemental composition.
3.2.3 T-cell and In Situ Cell Electrochemical Measurements

Compression fitted Li half-cells (T-cells) with 1 M LiPF$_6$ 1:1.2 EC/DMC electrolyte were utilized to collect galvanostatic cycling data on an Arbin Instruments battery cycler. Pressed cathodes consisted of 77% active material, 20% carbon black, and 3% PVDF binder resulting in active material loadings of approximately 5mg/cm$^2$. Active material and carbon black were mixed in a Spex stainless steel vial for 3 hours. The in-situ spectroelectrochemical half-cell which was used for the x-ray absorption near edge structure (XANES) measurements consisted of a Li anode, Whatman glass microfiber separator and the cathode mix painted onto a substrate (Al or grafoil). The cell was housed between two steel plates with polyester-protected windows to allow for x-ray transmission along with a silicon gasket to provide a hermetic seal. The cell is shown in action at the beamline in Figure 3.1.

3.2.3 X-Ray Absorption

X-ray absorption measurements were collected in transmission mode at the V K-edge (5465 eV) and Fe k edge (7112 eV) at beam line X-18a of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, with a Si 111 crystal detuned 35% to reject higher harmonics. Grafoil was used as the positive electrode substrate to increase transmission signal at the V edge and Al was utilized at the Fe edge to avoid Fe contamination originating from grafoil. Preparation of triclinic $\alpha$-Li$_x$VOPO$_4$ and collection of XAS data for this phase is described in Chapter 2. Data processing was done in Athena, version 8.056 developed by Ravel and Newville.$^6$
3.3 Results and Discussion

3.3.1 Mixed Metal Phase Synthesis Strategy

Initial efforts at synthesizing lithiated Fe-V mixed metal phosphates without F led to mixtures of LiFePO$_4$, Li$_3$Fe$_2$(PO$_4$)$_3$, Li$_3$PO$_4$ and V$_2$O$_3$ when Li acetate or Li$_2$CO$_3$ were used as Li sources. The synthesis conditions were not favorable, possibly due to structural differences between the LiFePO$_4$ and LiVOPO$_4$ frameworks. Olivine LiFePO$_4$, which does share the same space group as orthorhombic $\beta$-LiVOPO$_4$ (Pnma) has recently been shown to substitute up to 0.25 moles of Fe with V using a low temperature microwave synthetic route.$^7$

We succeeded in synthesizing the Fe-V mixed metal compound, Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$, by incorporating fluorine into its crystal structure. We can see that by including LiF along with the V, Fe and P starting materials in atomic ratios proportional to the two lithiated metal phosphates,
Li$_2$FePO$_4$F (Fe$^{2+}$) and Li$_2$VOPO$_4$ (V$^{3+}$), the mixed metal phase is formed as represented in Scheme 3.1.

\[
\text{Li}_2\text{FePO}_4\text{F} \cdot \text{Li}_2\text{VOPO}_4 \rightarrow \text{Li}_4\text{Fe(VO)(PO}_4)_2\text{F} \quad \text{(i.e. Li}_{2}\text{Fe}_{0.5}\text{(VO)}_{0.5}\text{(PO}_4)_0.5\text{F}_{0.5})
\]

**Scheme 3.1** Addition of two phases in forming the mixed metal phase

This material represents a discharged metal phosphate with Fe and V in Fe$^{2+}$ and V$^{3+}$ oxidation states, respectively. Oxidation of V and Fe sites, and hence removal of 1.5 Li, would result in Li$_{0.5}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$ as depicted in Scheme 3.2.

\[
\text{Li}_2\text{Fe}_{0.5}\text{(VO)}_{0.5}\text{(PO}_4)_0.5\text{F}_{0.5} \rightarrow -1.5\text{Li} \rightarrow \text{Li}_{0.5}\text{Fe}_{0.5}\text{(VO)}_{0.5}\text{(PO}_4)_0.5\text{ (Fe}^{2+},\text{V}^{3+})
\]

**Scheme 3.2** Expected oxidation states for proposed phase before and after charge

The theoretical capacity of 1 Li into Li$_{0.5}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ (Fe$^{2+},$V$^{4+}$) is 150 mAh/g. For further insertion of Li with reduction of V to V$^{3+}$ is 225 mAh/g for 1.5 Li/Li$_{0.5}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$ (Fe$^{2+},$V$^{3+}$).

### 3.3.2 X-Ray Diffraction and Phase Determination

The X-ray powder pattern of Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ presented in Figure 3.2 can be indexed to a tetragonal phase isostructural with Li$_{1+x}$MOSiO$_4$ (M=V,Ti), ICDD # 01-089-5553. The tetragonal phase is designated here with the $\alpha_1$- prefix due to its close relation to the tetragonal $\alpha_1$-VOPO$_4$, not to be confused with triclinic $\alpha$-LiVOPO$_4$. Lebail pattern matching (red circles) was utilized to fit the pattern and resulted in a $\chi^2$ of 11.1. Trigonal $\alpha$-Fe$_2$O$_3$ (01-071-
Figure 3.2. X-ray powder diffraction pattern and unit cell Le Bail refinement of tetragonal $\alpha_1$-Li$_{1+x}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ (see Table 1) along with triclinic $\alpha$-LiVOPO$_4$ (P-1, $a=6.584(9)$ $b=7.00(1)$ $c=7.925(9)$ $\alpha=91.4(1)$ $\beta=90.4(1)$ $\gamma=116.4(1)$) and $\alpha$-Fe$_2$O$_3$ (R-3C, $a=5.030(7)$ $b=5.030(3)$ $c=13.74(1)$ $\alpha=90$ $\beta=90$ $\gamma=120$) impurity phases. The observed (blue), calculated (red circle) and difference spectrum are displayed. $\chi^2 = 11.1$.

5088) and triclinic $\alpha$-LiVOPO$_4$, (01-072-2253) phases present as small impurities were also included in the fit. Electrochemistry and X-ray data presented below show that these phases are present in very small amounts and they, particularly the low voltage Li inserting Fe$_2$O$_3$, contribute little capacity. The unit cell dimensions of the tetragonal phase in Table 3.1 agree well with a $\alpha_1$-Li$_{1+x}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$ framework described above and are the focus of this work.
Table 3.1 Unit cell values for the $\text{Li}_{1+x}\text{Fe}_{0.5}\text{(VO)}_{0.5}\text{(PO}_4\text{)}_{0.5}$ calculated from the Lebail fit

<table>
<thead>
<tr>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha,\beta,\gamma$</th>
<th>SG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$-$\text{Li}<em>{1+x}\text{Fe}</em>{0.5}(\text{VO})_{0.5}(\text{PO}<em>4)</em>{0.5}$</td>
<td>6.395 (4)</td>
<td>6.395(4)</td>
<td>4.381(2)</td>
<td>90</td>
<td>P4/nmm</td>
</tr>
</tbody>
</table>

Based on atomic ratios before and after heat treatment as listed in Table 3.2, fluorine’s presence within the structure appears to be dependent on the Fe content. It’s only when the F and Fe sources are used that this phosphate phase formed. This is consistent with direct interaction between the Fe and F ions, possibly in the form of $\text{FO}_4\text{F}_2$ chains as in the triclinic phase.

Table 3.2. Precursor and post-synthesis atomic ratios as determined by ICP-MS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Pre-synthesis</th>
<th>ICP-MS (wt %)</th>
<th>Post-synthesis</th>
<th>Intended phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4</td>
<td>6.76</td>
<td>3.7</td>
<td>4</td>
</tr>
<tr>
<td>V</td>
<td>1</td>
<td>13.3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>15.8</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>5.85</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>17.7</td>
<td>2.1</td>
<td>2</td>
</tr>
</tbody>
</table>

$\text{Li}_2\text{FePO}_4\text{F}$ fluorinated phosphate. The $\text{Li}_2\text{FePO}_4\text{F}$ phase however is not believed to constitute the triclinic phase in Figure 3.2, as unit cell constants of triclinic $\text{Li}_2\text{FePO}_4\text{F}$ are not consistent with the triclinic phase in this work. A previous attempt to synthesize fluorophosphate compounds in a one pot reaction without Fe resulted in the total loss of F yielding $(\text{NH}_4)_2\text{SiF}_6$. Therefore, interdependence between Fe and F plays a key role in this synthesis and the resulting electrochemically active product. The tetragonal phase of the mixed metal fluorophosphate tetragonal phase can be visualized in Figure 3.3 with alternating VO$_5$ and FeO$_4$F chains in the c
direction interconnected by PO₄ groups. Referring to the CIF file of ICDD # 01-089-5553 mentioned above, 0.5 fluorine atoms are proposed to substitute at the O₁ position. This oxygen is axial to FeO₄.

![Crystallographic view of tetragonal α₁-LiFe₀.₅(VO)₀.₅(PO₄)ₐ₀.₅(PO₄)F₀.₅ with alternating VO₅ (grey) and FeO₄F (purple) chains. Li-green, F-blue, O-red, P-orange.](image)

**Figure 3.3.** Crystallographic view of tetragonal α₁-LiFe₀.₅(VO)₀.₅(PO₄)ₐ₀.₅(PO₄)F₀.₅ with alternating VO₅ (grey) and FeO₄F (purple) chains. Li-green, F-blue, O-red, P-orange.

### 3.3.3 Charge/Discharge Cycling Performance

Galvanostatic cycling in Figure 3.4 shows typical single phase Li de/insertion behavior visible in the sloping charge and discharge profile. Note that characteristic two-phase voltage plateaus during Li insertion in either triclinic/tetragonal⁹ LiₓVOPO₄ at 3.9V and/or 2.4-2.0V are not present. In order to observe a near equilibrium voltage curve and maximize Li removal/insertion, cycling was done at a C/55 rate. The first charge (3.3-4.4V) results in a capacity of 106 mAh/g. Following a first cycle discharge capacity of around 185 mAh/g (4.4-
2.0V), capacities of approximately 160 mAh/g are achieved over the next several cycles as seen in Figure 3.3b. During continued cycling, capacity loss occurs below 2.5V. Extended cycling is shown in Figure 3.5 with some capacity loss over 15 cycles at a C/40 rate.

In Table 3.3, the atomic ratios of all elements relative to Li indicate ratios close to the intended final phase following heat treatment. Considering the first cycle charge capacity, it is more likely that Li-deficient Li\(_{1+x}\)Fe\(_{0.5}\)(VO)\(_{0.5}\)(PO\(_4\))\(_{0.5}\)(Fe\(^{2+}\),V\(^{4+}\)) is the major phase, with excess elemental mass contributing to the impurities. The first cycle discharge capacity of 185 mAh/g at 2 V is also consistent with that same impurity weight percent considering further lithiation to form Li\(_2\)Fe\(_{0.5}\)(VO)\(_{0.5}\)(PO\(_4\))\(_{0.5}\). (i.e. about 20% Fe\(_2\)O\(_3\) and α-LiVOPO\(_4\) combined.) Li insertion into α-Fe\(_2\)O\(_3\) occurs between 2.5-1.5V with x in Li\(_x\)Fe\(_2\)O\(_3\) dependent on Fe\(_2\)O\(_3\) particle size\(^{10}\). XANES data presented below reveals little to no Fe charge compensation in this region.

---

**Figure 3.4.** a) Initial charge/discharge curve of the Li\(_{1+x}\)Fe\(_{0.5}\)(VO)\(_{0.5}\)(PO\(_4\))\(_{0.5}\) phase and b) first five cycles at 1x10\(^{-2}\) mA/cm\(^2\) cycled between 2.0-4.4V.
3.3.4 X-Ray Measurements: In Situ XANES and XRD of Extracted Electrodes

In order to understand charge compensation on the two metal centers during cycling for the proposed phase, in-situ XANES measurements were made at various points along the first galvanostatic discharge at both the V and Fe K-edge. Those measurements are highlighted by hash marks in Figure 3.6. The V edge XANES spectra during discharge are presented in Figure 3.7a. The pre-edge peak located around 5471 eV represents dipole forbidden 1s-3d final state transitions. This transition is allowed due to vanadium 3d and 4p hybridized orbitals, which are

![Figure 3.5](image.png)

**Figure 3.5.** Capacity as a function of cycles in the voltage range of 2.0-4.4V. Charge/discharge current =1.3x10^{-2} mA/cm^2
Figure 3.6. First cycle discharge profile from 4.4-2.0V at 1x10^{-2} mA/cm^2. Hash marks indicate points of XANES measurements. Shaded regions highlight the two V/Fe transition voltage ranges.

Figure 3.7. V k-edge in-situ XANES spectrum. a) the first discharge (4.4V-2.0V) after the initial charge to 4.4V  b) XANES of select voltages compared to the triclinic \( \alpha \)-LiVOPO_4 at various states of discharge.
overlapped with oxygen 2p orbitals. The peak initially shifts 1.4 eV from 5471.4 eV to 5470 eV in the upper voltage region of the discharge. This shift is consistent with a transition from $V^{5+}$ to $V^{4+}$ based on work by Wong et. al.,$^{11}$ who measured a 1.1 eV pre-edge shift difference between $V_2O_5 (V^{5+})$ and $V_2O_4 (V^{4+})$. Little change occurs in this peak thereafter until below 2.8V, where it loses intensity continuously until 2.0V. Intensity changes in this peak reflect changes in the VO$_6$ distortion as a result of Li intercalation. This intensity loss can serve as a qualitative tool to monitor the degree of VO$_6$ distortion in vanadium phosphates, which appears to be much less than in other Li$_x$VOPO$_4$ phases. Comparison of this phase to $\alpha$-Li$_x$VOPO$_4$ is discussed further below.

The main V absorption edge, which is expected to shift to lower energies as the V oxidation state decreases during Li intercalation, has been defined as the second peak in the first derivative curve for vanadium oxides.$^{11}$ Alternatively, the midpoint in the edge step has also been used to compare metal phosphate oxidation states during cycling.$^{12}$ Taking this latter approach, (at 0.6 absorption units) shifts in the edge occur in the upper voltage range until 3.1 V, consistent with the pre-edge shifts. The lack of edge movement from 3.1V to 2.6V represents an inactive voltage range for the V sites. This is followed by another visible shift in the main edge region from 2.6V-2.0V. About half of the total pre-edge intensity loss occurs between 2.8V and 2.6V, before V charge compensation restarts at 2.6V. This may imply that Li intercalation at the Fe sites in the mid voltage range has an indirect effect on the V environment, increasing its VO$_6$ symmetry without any effect on the V oxidation state.
To estimate the V oxidation state range during discharge, Figure 3.7b compares the XANES spectrum at the two charge extremes against the triclinic $\alpha$-Li$_x$VOPO$_4$ at various states of discharge. The edge positions at the midpoint of the XANES spectra of both fully charged species are in close agreement, suggesting a V oxidation state close to five at 4.4 V for the $\alpha_1$-Li$_{1.5}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ phase. The edge position at 2.6V as V reduction restarts is consistent with a V$^{4+}$ state comparing it to triclinic $\alpha$-Li$_{0.75}$VOPO$_4$. At full discharge (2.0V), the edge position shifts further in the direction of $\alpha$-Li$_{1.75}$VOPO$_4$ ($V^{\text{+3.25}}$) and so it appears the formal V oxidation state is close to 3 at 2.0V. Comparing the pre-edge region of these two phosphate

Figure 3.8. a) X-ray diffraction patterns of electrodes with Al substrates extracted from T-cells at the two charge extremes. (black)-4.4V and (red)-2.0V  b) Expanded view of select 2-theta range. + denotes $\alpha$-Fe$_2$O$_3$ impurity.
phases during discharge, both the magnitude and variation in intensity is more extreme for the triclinic Li$_x$VOPO$_4$ phase. This feature reflects key differences in the VO$_6$ environment of this new phosphate phase. Two-phase behavior is essentially prevented by restricting crystal structure relaxation during Li removal as a result of an extended network of FeO$_4$F$_2$ interconnecting the VO$_6$ polyhedra. Moreover, previous accounts of F doping into metal oxides such as spinel (i.e. LiMn$_{2-y-z}$Li$_y$M$_z$O$_{4-n}$F$_n$ (M = Ti, Ni, and Cu) have resulted in better capacity retention, attributed to less lattice strain during cycling. XRD patterns of extracted α$_1$-Li$_x$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)$_{0.5}$F$_{0.5}$ electrodes at the two charge extremes in Figure 3.8a also appear to exhibit very little lattice strain. Comparing the two end members of this phase, only slight 2-theta shifts to select peaks of the tetragonal phase are visible. Most notable are the shifts of the 200 and 201 peaks in Figure 3.8b with tick marks clarifying the shift. There also appears to be no evolution of any new peaks at these voltages during cycling, which is further evidence of a single phase Li insertion mechanism.

In situ Fe K-edge XANES data are presented in Figure 3.9. The shifts in the main edge during discharge between 3.6-2.5V indicating Fe reduction are reflected in the mid cycling profile of Figure 3.6. The range of edge shifts in Figure 3.9, midway up the absorption edge between 4.4 and 2.0 V, spans approximately 4.5 eV. Deb et. al. shows a similar range of shifts in the XANES spectra between LiFePO$_4$ and the fully charged FePO$_4$ state, an indication that Fe$^{3+}$ to Fe$^{2+}$ state is achieved here. Also in agreement with that work is the behavior of the small pre-edge peaks during discharge. These peaks are expanded in the inset of Figure 3.9 and can be assigned to t$_2$ and e$_g$ electronic transitions at 7112 eV and 7114 eV, respectively. The strong presence of an e$_g$ transition at full charge is consistent with increased distortion of an octahedrally coordinated Fe$^{3+}$ complex.
Comparing both V and Fe edge shifts during discharge, regions of Fe inactivity in the upper (>3.6V) and lower (<2.6V) voltage region reflect voltage range charge compensation in the V environment. This is illustrated in Figure 3.6 with the highlighted regions representing switching potential ranges. In the upper voltage region, V reduction is responsible for the first 30-60 mAh/g. According to XANES spectra in Figure 3.9 below 3.6V, charge compensation is initiated on the Fe sites resulting in approximately 60-100 mAh/g. The ranges in capacity come as a result of uncertainties in switching potentials due to voltage-capacity profile gaps between measurements. In the region around 2.6V following Fe reduction, an Fe$^{2+}$ and V$^{4+}$ state is

![Figure 3.9](image-url)  

**Figure 3.9.** Fe k-edge in-situ XANES spectra during the first discharge (4.4V-2.0V) after the initial charge to 4.4V.
achieved. The proposed structure of $\alpha_1$-$\text{Li}_{1.5}\text{Fe}_{0.5}(\text{VO})_{0.5}(\text{PO}_4)\text{F}_{0.5}$, which satisfies the oxidation states (Fe$^{2+}$, V$^{4+}$) has a 150 mAh/g theoretical capacity. The 120 mAh/g capacity achieved at 2.6V represents 80% of its theoretical capacity. The lower voltage region below 2.6V is a result of V$^{4+}$ to V$^{3+}$ reduction according to XANES data. At full discharge, the 180 mAh/g is also consistent with an 80% yield of the 225 mAh/g theoretical capacity considering the Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)F$_{0.5}$ phase following reduction of V$^{4+}$ to V$^{3+}$. Removing impurity phases $\alpha$-LiVOPO$_4$ and $\alpha$-Fe$_2$O$_3$, the likely cause of this lower than calculated capacity loss will be the next step in further developing this new Fe-V mixed phase cathode material.

### 3.4 Conclusions

A new cathode material exhibiting single phase Li extraction-insertion processes in Li cells has been identified. Based on x-ray powder diffraction, x-ray absorption and Li cell capacity data, the material has a tetragonal crystal structure with the stoichiometry Li$_{1+x}$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)F$_{0.5}$. It shows a unique single phase behavior for a metal phosphate positive electrode material during Li extraction and subsequent insertion in Li cells. The presence of F in the structure is the key to the formation of the mixed metal cathode material. During discharge, the single phase Li insertion manifests itself in the limited variation of the VO$_6$ environment (as revealed by the XANES pre-edge spectra) along with low crystal strain as identified from XRD data.

### 3.5 Acknowledgments

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National Laboratory, was provided by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

3.6 References


Chapter 4. The oxygen electrode rechargeability in an ionic liquid for the Li air battery

4.1 Introduction

In our continuing efforts to develop practical electrolytes for the non-aqueous Li air battery,\textsuperscript{1-4} we have studied O\textsubscript{2} electrode processes in the ionic liquid 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide, (EMITFSI). The use of room temperature ionic liquids (RTILs) in Li air batteries is attractive due to their low-flammability, hydrophobic nature, low vapor pressure, wide potential window and high thermal stability. In particular, the extended anodic voltage window in RTILs is of interest as the presence of cathode catalysts, frequently employed in the Li air system, can shorten the potential window of many organic electrolytes (e.g; carbonate solvents) and affect cell performance. The influence of solvents on the kinetics of the ORR products and/or the nature of the oxidation reactions in the Li-air cell is now recognized.\textsuperscript{3-8} Previous studies have reported on the O\textsubscript{2} one-electron reduction product superoxide, O\textsubscript{2}\textsuperscript{-}, and its electrochemistry in different RTILs\textsuperscript{9-12}, yet a good understanding of the influence of Li\textsuperscript{+} on the oxygen electrode in these media has not yet been obtained. In this chapter, we have investigated in detail ORR and OER in a RTIL doped with Li salt on both GC and Au electrodes to establish the reaction mechanism and products and their rechargeability. Surprisingly, we have found a strong influence of the nature of the electrode material and the charging potential on the rechargeability of the O\textsubscript{2} electrode, along with changes in ORR and OER when a Li salt is present. These results are reported.
4.2 Experimental Methods

4.2.1 Synthesis of EMITFSI

The 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide was synthesized via anion exchange as shown in reaction Scheme 4.1.

\[
\text{EMITFSI} = \text{EMIBr} + \text{LiTFSI} \rightarrow \text{EMITFSI} + \text{LiBr}
\]

An aqueous solution containing 1-ethyl-3-methylimidazolium bromide (EMIBr)-98\(^+\%\) (Alpha Aesar) and lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI)-98\(^+\%\) (Alpha Aesar) was stirred at 80\(^\circ\) C for 3 hours until the materials reacted completely. The solution was then diluted in dichloromethane to reduce the products viscosity and washed several times with water. Further purification was carried out with decolorizing carbon using a carbon mass equal to 20\% of the product in a 1:1 volumetric ratio of product to ethyl acetate, mixed overnight at 70\(^\circ\)C. The liquid phase was isolated by vacuum filtration and purified again with neutral alumina using an alumina mass equal to 50\% of the product, mixed overnight at room temperature. Following vacuum filtration, the product was finally isolated and dried under vacuum for 24 hours at 130\(^\circ\) C to remove residual water and solvent. Typical batch sizes yielded approximately 100 grams with 80-85\% yields. \(^1\)H NMR, 10mM in CO(CD\(_3\))\(_2\) δ/ppm relative to TMS (s, 9.08, 1H), (t, 7.81, 1H), (t, 7.74, 1H), (q, 4.43, 2H), (s, 4.09, 3H), (t, 1.58, 3H). A moisture content less than 25 ppm was confirmed with Karl Fisher coulometry.
### 4.2.2 Electrochemical methods

Cyclic voltammetry (CV) measurements were performed on an Autolab potentiostat (Eco Chemie B.V.) equipped with a frequency response analyzer for iR correction. A conventional three electrode setup was used which included a planar glassy carbon (diameter = 6mm) or Au (diameter = 5mm) disk working electrode along with a platinum counter electrode. The reference electrode consisted of a silver wire immersed in a 0.1 M AgCF$_3$SO$_3$ solution contained in a glass tube placed close to the working electrode, separated with a Vycor frit. Potentials were converted to the Li/Li$^+$ reference electrode by measuring the potential of the Ag/Ag$^+$ electrode against a Li foil and are used throughout this Chapter. Gas purging of the IL solutions (1 hour of argon followed by 1 hour of oxygen) and the electrochemistry were carried out in a controlled atmosphere glove box.

Full Li-O$_2$ cells were tested using Li foil on Cu substrate and O$_2$ electrodes made with Vulcan XC72R or Ketjan 600 carbon on Panex cloth with a nickel substrate (typical loadings around 3-4 mg/cm$^2$). At high potentials, aluminum, typically used as the O$_2$ electrode substrate, is corroded in the presence of TFSI.$^{13}$ In order to activate the O$_2$ electrodes they required soaking in O$_2$ bubbled EMITFSI prior to cell assembly. This is likely due to the electrolyte’s high viscosity (30-60 mPa), which may inhibit atmospheric O$_2$ saturation in this class of electrolyte. O$_2$ purge of the cell and cell cycling are also carried out in the controlled atmosphere glove box interfaced to an Arbin battery cycler.

### 4.3 Results and Discussion

#### 4.3.1 Oxygen electrochemistry in neat EMITFSI
The oxygen reduction (ORR) and evolution (OER) reactions on glassy carbon (GC) and gold (Au) electrodes were studied in neat and Li$^+$-containing room temperature ionic liquid, EMITFSI. Cyclic voltammetry (CV) data in neat EMITFSI at various scan rates on Au and GC electrodes are shown in Figure 4.1. Anodic to cathodic peak area ratios are approximately 1 at all scan rates and cathodic and anodic peak currents ($I_p$) are proportional to the square root of the scan rate (see Figure 4.1 right side). On the GC electrode, oxidation of the reduction product(s) extends several hundred mV more positive of that on Au. Interestingly, Au seems to enhance oxidation reactions in this electrolyte, in line with observations involving Li$^+$-stabilized O$_2^-$ on this surface discussed below.

![Figure 4.1. Cyclic Voltammograms of O$_2$ saturated EMITFSI at Au and GC electrodes (left). Randles-Sevcik plots (right) for the cathodic and anodic peak currents which includes experimental data along with one and two electron theoretical fits (see equation 4.1). Scan rates, I=25 mV/s, II=45 mV/s, III=65 mV/s, IV=85 mV/s, V=100 mV/s, VI=200 mV/s, VII=300 mV/s, VIII=500 mV/s. (Au electrode) Argon saturated solution scanned at 100 mV/s.](image-url)
A linear response between the magnitudes of the peak currents ($I_p$) vs scan rate ($v^{1/2}$) in the Randles-Sevcik plots (Figure 4.1 right side) is evidence of a diffusion-limited process on both electrodes. According to equation 4.1 for a reversible system,

$$I_p = 2.69 \times 10^5 n^{3/2} A \ D^{1/2} \ C \ v^{1/2}$$

(4.1)

$n$ is number of electrons, $A$ is electrode area ($cm^2$), $D$ is the $O_2$ diffusion coefficient (7.3x$10^{-6}$ cm$^2$/s) or $O_2^-$ diffusion coefficient (2.7x$10^{-6}$ cm$^2$/s), $C$ is concentration of electroactive species (3.9 x$10^{-6}$ moles/cm$^3$), and $v$ is scan rate (V/s). $D$ and $C$ were taken from ORR studies in EMITFSI at a Au microelectrode.\textsuperscript{14} Scan rates up to 500 mV/s on Au show linearity of the plot presented in Figure 4.1. Comparing experimental values to theoretical plots of $n$=1,2, the ORR reaction in EMITFSI unequivocally consists of a one electron $O_2/O_2^-$ redox couple, in agreement with previous reports.\textsuperscript{14,15} The reversibility of the couple is similar to ORR in tetrabutylammonium (TBA$^+$) doped non-aqueous solvents.\textsuperscript{2,3} There it was concluded that the soft acid, TBA$^+$, stabilizes the soft base $O_2^-$, in agreement with Pearson’s hard soft acid base (HSAB) theory, thus limiting the reduction of the complex to one electron. The EMI$^+$ resembles TBA$^+$ in soft acidity and its ability to stabilize $O_2^-$ seen here. The noticeable asymmetry between the cathodic and anodic peak shapes is attributed to different diffusion rates between $O_2$ and $O_2^-$ in this media,\textsuperscript{14} likely due to the strong ion-pairing between $O_2^-$ and EMI$^+$.\textsuperscript{16} This is consistent with the notion of the EMI$^+$ soft acid strongly stabilizing the superoxide soft base. The predominant $O_2$ electrochemistry in EMITFSI can be summarized according to the reactions depicted in Scheme 4.2.

\textbf{Scheme 4.2} ORR and OER in neat EMITFSI

\textbf{Cathodic}

$$EMI^++O_2+e^- \rightarrow EMI^+--O_2^-$$
Anodic

\[
\text{EMI}^+ + \text{O}_2^- \rightarrow \text{EMI}^+ + \text{O}_2 + e^-
\]

As seen in Figure 4.2, lowering the cathodic switching potential to 1.4 V leads to a second reduction peak. The two cathodic peaks are referred to as C1 and C2. Since no reduction of the EMI\(^+\) occurs in this voltage region, visible from the background scan of the argon purged electrolyte, this current is probably due to the reduction of EMI\(^+\)--O\(_2^-\) to form peroxide, stabilized by EMI\(^+\) (i.e. EMI\(^+\)--O’--O’--EMI\(^+\)). Comparing this reaction on the two electrode surfaces, the C1:C2 current ratio is 20% higher on Au. This was determined from integrated peak areas and signifies less reduction of the EMI\(^+\)--O\(_2^-\) on the Au surface at lower voltages. Also, the anodic peak at 2.2 V corresponding to the oxidation of the superoxide complex (EMI\(^+\)--O\(_2^-\)) is decreased to a shoulder on GC. A second anodic peak at >2.5 V is seen in the scans following the cathodic sweep to 1.4 V which we ascribe to the oxidation of the peroxide. The oxidation peak potentials of the superoxide and peroxide products are slightly lower on GC compared to those on the Au electrode. These observations suggest that Au may stabilize the superoxide and peroxide as Au--O\(_2^-\) and Au--O\(_2^{2-}\) more effectively than GC, providing them longer lifetimes, while also requiring higher oxidation overpotentials. In fact, the oxidation potentials of the superoxide and peroxide appear sensitive to not only the electrode surface but also, as seen below, to the counter-ion as well. We will see later that Li\(^+\)- and H\(^+\)- stabilized superoxides and peroxides have higher overpotentials than the EMI\(^+\) stabilized products in this ionic liquid, which is consistent with their relative acidities. Also, unlike Li\(^+\) (see reference 3), the EMI\(^+\) stabilized superoxide ion does not disproportionate to peroxide, although it can be electrochemically reduced to it, providing further support to the soft Lewis acidity of EMI\(^+\).


Figure 4.2. Cyclic Voltammograms comparing low (red dash) and high (green solid) cathodic voltage limits at Au and GC in O$_2$ saturated and Argon saturated EMITFSI. Scan rate is 100 mV/s.

4.3.2 Influence of Li salt on ORR and OER

The O$_2$ reduction mechanism in EMITFSI is strongly influenced by the presence of Li$^+$. In Figure 4.3a, the ORR in 0.025 M LiTFSI-doped EMITFSI is compared on both GC and Au electrodes. The irreversible electrochemical peak profile is substantially similar to that found in
Li$^+$-conducting organic electrolytes. The ORR onset potentials are similar on both electrodes; however, cathodic peak shape differences (i.e. usually indicative of different transfer coefficients, $\alpha$) signify perhaps a buildup of adsorbants (for example from the chemical decomposition of the ORR product) on the surface of GC. $E_{pc}$ and $E_{pa}$ peak separation are also similar on both electrodes, as is the anodic to cathodic charge ratio. (~0.96 for both electrodes). Apart from the anodic peak A1 (which is very minor here) seen on Au due to the oxidation of superoxide ion-paired with EMI$^+$, oxidation peaks at A2 and A3 in Figure 4.3a are at the same
positions on both GC and Au during the first cycle. The appearance of two oxidation processes following what appears to be a single reduction reaction suggests that the ORR is accompanied by chemical reactions. A most significant observation is that the ORR performance on these surfaces deviates during subsequent scans. The first five repetitive cycles on GC in Figure 4.3b show diminishing peak currents indicative of electrode surface passivation, as well as loss of the shoulder on the anodic profile at 3.7 V. On Au in Figure 4.3c on the other hand, little loss in current occurs during subsequent cycles revealing a chemically reversible (but electrochemically irreversible) reaction.

The scan rate dependence of the ORR on Au as seen in Figure 4.4 was investigated in an attempt to quantify electron transfer of the irreversible reaction occurring at Cl in the presence of Li salt. The $I_{pc}$ (cathodic peak current) versus the square root of the scan rate plot (Figure 4.4 inset) is linear, indicating a diffusion-controlled reaction. The buildup of Li$_x$O$_y$ products on the Au electrode surface does not appear to be a limiting factor in this solution, as revealed by the linearity of the plot. According to equation 4.2 for irreversible diffusion controlled reactions,$^{17}$ $I_{pc}$ is proportional to the square root of $\alpha n_c$. The value of this product, along with passivation may contribute to the loss in cathodic peak current following the addition of Li$^+$, but diffusion control appears to dominate at these relatively fast scan rates.

$$I_{pc} = 2.99 \times 10^5 n (\alpha n_c)^{1/2} A D^{1/2} C v^{1/2}$$ (4.2)

Here, $n_c$ is the number of electrons in the charge transfer step and $\alpha$ is the transfer coefficient. Assuming $n = n_c$ at $I_{pc}$ and using D and C values from Randles-Sevcik plots above, a one-electron transfer is likely as seen in the inset of Figure 4.4. The theoretical $n = 1$ plot can be fitted to the
Figure 4.4. Cyclic Voltammograms and cathodic peak currents (Ipc) as a function of scan rate ($\nu^{1/2}$) (inset) for 0.025 M LiTFSI doped O$_2$ saturated EMITFSI on a Au electrode. Theoretical plots for one and two electron transfers are calculated from equation 2 for irreversible charge transfer. Scan rates, I=25 mV/s, II=45 mV/s, III=65 mV/s, IV=85 mV/s, V=100 mV/s, VI=200 mV/s.

The experimental data when $\alpha$ equals 0.27. This value for $\alpha$ is not unreasonable given the electrochemical irreversibility of the one electron reaction.

To elucidate the origins of the ORR resulting in the multiple anodic peaks, their amplitudes following incremental cathodic limits are compared in Figure 4.5a. The major reactions between 1.9 and 4.6 V deduced from these studies are proposed in Scheme 4.3, and further explained below.

Scheme 4.3 ORR and OER mechanism in 0.025 M Li$^+$ in EMITFSI
Cathodic

\[ \text{EMI}^+ + \text{O}_2 + e^- \rightarrow \text{EMI}^+ - \text{O}_2^- \]  
\[ \text{Li}^+ + \text{O}_2 + e^- \rightarrow \text{LiO}_2 \]  
\[ 2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \] (chemical)

Anodic

\[ \text{EMI}^{\text{H}2} - \text{O}_2^- \rightarrow \text{EMI}^+ + \text{O}_2 + e^- \]  
\[ \text{LiO}_2 \rightarrow \text{Li}^+ + \text{O}_2 + e^- \]  
\[ \text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + \text{O}_2 + 2e^- \]

Peak A2 evolves first after the cathodic switching voltages starting at 2.19 V. From Figure 4.4, a one-electron transfer can be inferred at C1. Due to the different Lewis acidity of competing cations, (EMI$^+$ vs. Li$^+$), LiO$_2$ is likely the predominant product from that reaction as it will attract the superoxide because of its significantly stronger acidity due to the very high charge density. However, the stability of the resulting LiO$_2$ is poor as expected from the HSAB theory. This is indeed what is observed here as some of the LiO$_2$ decomposes to Li$_2$O$_2$ as shown in Scheme 4.3. The reactions in Scheme 4.3 are similar to what we previously observed in organic electrolytes,$^{3,4}$ and later confirmed by Peng et al.$^{18}$ The sustained LiO$_2$ is believed to oxidize at A2. The peak at A3 is assigned to the oxidation of Li$_2$O$_2$. Both A2 and A3, although different in amplitude, share nearly the same cathodic potential dependence until a cathodic switching potential of 1.91 V on C1. Thus some LiO$_2$ appears to disproportionate to Li$_2$O$_2$, resulting in subsequent two-electron oxidation at A3. At 1.91 V on C1, A2 is maximized and A3 continues to increase following cathodic switching potentials reaching the end of C1. This behavior strongly supports disproportionation of LiO$_2$ to Li$_2$O$_2$. The development of A1 on Au,
beginning after the potential is switched at 1.91 V on C1 is likely due to oxidation of some stabilized EMI$^+$--O$_2^-$ ion-pair.

**Figure 4.5.** (a) Cyclic Voltammograms of O$_2$ saturated EMITFSI/0.025 M LiTFSI swept to various cathodic limits. (b) CVs of O$_2$ saturated EMITFSI with and without 0.025 M LiTFSI. Scan rate is 100 mV/s. Labeled peaks correspond to reactions described in Schemes 1-3.
We observed a Li concentration dependence on the anodic peaks intensities, which supports these peak assignments. In a separate experiment we increased the LiTFSI concentration five times (0.125 M), which led to the loss of peak A1 as seen in Figure 4.3d. Also in this solution, a higher amount of A3 is found relative to A2. These findings suggest an overall increase in the amount of Li-oxides formed, leading to disproportionation of LiO₂ to form higher amounts of Li₂O₂. Our results are consistent with the recent work in reference 18 utilizing in-situ Raman spectroscopy to analyze LiₓOᵧ products in acetonitrile and their assignment of the oxidation peak potentials.

As seen in Figure 4.5b, there is a 10 fold decrease of A1 in 0.025 M LiTFSI EMITFSI compared to the neat solution, consistent with the argument regarding relative acidities of the two cations. The lack of A1 current on GC (Figure 4.3b) is presumably due to an inability of the electrode to stabilize EMİ⁺--O₂⁻ in the presence of Li salt. This is in agreement with the conclusion presented above regarding the decreased stability of O₂⁻ on GC when the potential is swept cathodically to 1.4 V. Furthermore, the loss of the shoulder (A3) and subsequent passivation during cycling on GC in Figure 4.3b appears to be caused by Li₂O₂ build up on the electrode. Au displayed similar electrode passivation if the anodic switching potential remained below A3, resulting in only trace current for the reactions at C1, A1, and A2.

\[
\text{Figure 4.6. EMİ}^+ \text{ highlighting the proton at the C2 position}
\]
4.3.3 Proton Contribution to the ORR

Interestingly, when the anodic limit is extended beyond 4 V in O₂ saturated neat EMITFSI (Figure 4.5b), a very small peak in the vicinity of A3 also exists. A proton source in the neat solution, likely from the carbon at the 2-position of EMI⁺ (shown in Figure 4.6) may result in H₂O₂ as seen in Scheme 4.4. Given the overall increase in the A3 peak area in the Li spied EMITFSI compared to the neat solution, concurrent H₂O₂ (albeit at very low levels) and Li₂O₂ oxidation is likely here.

Scheme 4.4 Li spiked or neat EMITFSI

Cathodic

\[ \text{EMI-H}^+ + \text{O}_2 + e^- \rightarrow \text{HO}_2^- \quad \text{(C1)} \]
\[ 2\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(chemical)} \]

Anodic

\[ \text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + \text{O}_2 + 2e^- \quad \text{(A3)} \]

4.3.4 Preliminary Li-O₂ Cell Performance in EMITFSI

Full cell Li-O₂ air testing has been initiated using 0.5 M LiTFSI EMITFSI to accompany voltammetric data. The first charge-discharge cycle at 0.1 mA/cm² using the Vulcan O₂ electrode in Figure 4.7 reveal two plateaus during first discharge at 2.45 V and 2.05 V. Based on the low discharge capacity following the first plateau (250 mAh/g) it’s plausible that Li₂O₂ formation at 2.45 V is followed by further reduction (Li₂O₂ + 2(Li⁺ + e⁻)\rightarrow 2Li₂O at 2.05 V. Thus the electrode is essentially choking out at 250 mAh/g due to the relatively low surface area Vulcan carbon, leading to the second reduction step. Modest rechargeability is seen during the following charge.
Turning to higher surface area carbon, improved discharge performance was apparent using Ketjan 600 compared to the Vulcan (solid lines) as seen in Figure 4.8. Discharge capacity doubled and the lower plateau at 2.05 V is not present, consistent with the argument above. Despite increased polarization, similar performance is seen on the O₂ electrode in neat EMITFSI in Figure 4.8. Further cycling with Au catalyst, along with X-ray diffraction and spectroscopic analysis of the cycling products will be part of the future work. It is relevant here to recall a previous study that demonstrated promising Li air cell cycling performance using carbon-supported Au and Pt cathodes in an organic electrolyte.²⁰ The carbon-supported Au electrode catalyzed the reduction reaction in that study.

Figure 4.7. Galvanostatic cycling 0.5M LiTFSI EMITFSI at 0.1mA/cm² on Vulcan XC72 carbon
Figure 4.8. Galvanostatic cycling at 0.1mA/cm$^2$ on two distinct carbon O$_2$ electrodes. Electrolyte- 0.5M Li LiTFSI EMITFSI (solid line) and neat EMITFSI (dashed line)

4.4 Conclusions

A most unexpected and practically useful observation is the ability to repeatedly cycle the O$_2$ electrode on Au in the presence of Li salts and other ionic influences between 1.5 and 4.6 V with little loss in capacity utilization. A cartoon summarizing the competing ions at the O$_2$ electrode is illustrated in Figure 4.9. In this ionic liquid, the gold surface is particularly beneficial for the oxidation reactions, with much improved cycling compared to the GC.
The O$_2$ reduction and evolution reactions in the room temperature ionic liquid EMITFSI show strong influence of the presence of Li salt leading to markedly different reaction mechanisms. The nature of electrode affects the reaction mechanism with gold showing the ability for high efficiency recharging of the oxygen electrode as evidenced by multiple cycles without passivation. Our data suggest that ionic liquids are promising electrolytes for rechargeable Li-air batteries and the selection of an electrolyte that is stable to both the Li and oxygen electrode is indicated as a major future direction of research.

4.5 Acknowledgment

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4.6 References


Chapter 5. Oxygen Reduction Reactions in Ionic Liquids and the Formulation of a General ORR Mechanism

5.1 Introduction

As previously discussed in Chapter 1, limits on energy density and the high cost of commercialized Li-ion batteries have accelerated efforts for alternative rechargeable battery systems such as the non-aqueous Li-O\(_2\) battery, first realized 15 years ago.\(^1\) The 5220 Wh/kg theoretical energy density of Li-O\(_2\) is 7-8 times that of today’s best Li-ion battery and it offers a long term solution to energy independence.

A primary concern facing this power source is the inefficient rechargeability of insoluble \(\text{Li}_x\text{O}_y\) discharge products which accumulate on the \(\text{O}_2\) electrode.\(^2\) This issue was addressed in chapter 4 since it leads to poor cell performance, stemming from large cathode impedances and the associated voltage gaps between oxygen reduction reactions (ORR) and oxygen evolution reactions (OER).\(^3\),\(^4\) Our recent work on the mechanism of ORR in non-aqueous electrolytes has revealed that the properties of the organic solvent play a significant role in the nature of the final reduction product formed, and the stability of the intermediates through which the conversion of \(\text{O}_2\) to \(\text{Li}_2\text{O}\) occurs in the discharge of a Li-O\(_2\) cell. We have gained this insight from a detailed study of the ORR intermediates and products in a series of organic electrolytes \(^5\),\(^6\) judicially selected on the basis of their Lewis acid-base properties as defined by Guttmann donor and accepter numbers. The Guttmann donor number (DN) measures the electron donating capacity of the solvent to form complexes with Lewis acids such as \(\text{Li}^+\).
Ionic liquids as a class of electrolytes for Li batteries offer several potential advantages over traditional non-aqueous organic solvents. Besides negligible vapor pressure, high ionic conductivity and non-flammability, they can be designed to offer enhanced hydrophobicity and large electrochemical stability windows which are highly desirable for their use in the Li-air battery. In chapter 5, we have continued the study of oxygen reduction and evolution reactions (ORR and OER, respectively) in two ionic liquids (IL), namely, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (EMITFSI), and 1-methyl-1-butyl-pyrrolidinium bis-(trifluoromethanesulfonyl)imide (PYR\textsubscript{14}TFSI). The PYR\textsubscript{14} cation is abbreviated as PYR throughout chapter 5. The cations and common anion of these ionic liquids are shown in Scheme 5.1.

The ORR and OER mechanisms were studied using cyclic and rotating disk electrode voltammetry (CV and RDE, respectively) in the neat ionic liquids and in their solutions containing singly charged cation salts which included LiTFSI, NaPF\textsubscript{6}, KPF\textsubscript{6}, and
tetrabutylammonium hexafluorophosphate (TBAPF$_6$). A correlation between the ORR products and the Lewis acidity of the cation present in the electrolyte was developed with the help of an acidity scale of the various cations, including those of the ionic liquids. The acidity scale was created from $^{13}$C NMR chemical shifts and spin lattice relaxation ($T_1$) times, specifically of the $^{13}$C=O moiety, of the solutions of these salts in propylene carbonate (PC). Remarkably, we have found that the ionic liquids lie in a continuum of falling Lewis acidity scale with respect to the charge density of alkali metal, ILs, and TBA cations with the result that the ORR products in ionic liquids and in organic electrolytes containing any conducting cations can be predicted on the basis of a general theory based on the Hard Soft Acid Base (HSAB) concept. These results are presented in detail in this chapter. The present results complement our recent work which provided initial evidence for the correlation between the charge density of ions and the ORR products.$^{5,6}$ This work provides experimental evidence for the ability of the HSAB theory to explain ORR mechanism and reaction products in any non-aqueous electrolytes, and, perhaps, even in aqueous electrolytes.

5.2 Experimental

5.2.1 Synthesis and Characterization of PYRTFSI

The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PYRTFSI), were synthesized through an aqueous ion exchange reaction. The details of the synthesis and purification of EMITFSI are described in chapter 4. The 1-methyl-1-butyl-pyrrolidinium triflourosulfonylamide (PYRTFSI) ionic liquid two-step synthesis is summarized in Scheme 5.2. As seen in step 1 of Scheme 5.2, an addition reaction between N-methylpyrrolidine and 1-iodobutane yielded 1-methyl-1-butyl-pyrrolidinium iodide (PYR$_{14}$I). The reaction was carried
out at room temperature in ethyl acetate for 24 hours, vacuum filtered, and further dried under vacuum at 100°C overnight. Lithium trifluorosulfonylamide (LiTFSI) diluted in water, was then mixed with PYR₁₄I for several hours to yield the product shown in step 2 of Scheme 5.2. The PYR₁₄TFSI was washed several times with water and further purified with decolorizing carbon and activated neutral alumina as described in section 4.2 of chapter 4. Finally, it was heated at 130°C under vacuum and stored in a controlled atmosphere glove box. All handling of the iodide containing compounds was done in the absence of light to avoid oxidation of I⁻ to I₂. Currently, the product yield is on the 100 gram scale.

Scheme 5.2. Synthetic steps for production of PYR₁₄TFSI

Structures were confirmed with ¹H NMR in CO(CD₃)₂: δ/ppm relative to TMS (m, 3.71, 4H), (m, 3.52, 2H), (s, 3.24, 3H), (s, 2.32, 4H), (m, 1.90, 2H), (m, 1.45, 2H), (t, 0.98, 3H). A H₂O content below 25 ppm was verified with Karl Fisher coulometry.
5.2.2 Electrochemical methods

Cyclic voltammetry (CV) measurements were performed on an Autolab potentiostat (Eco Chemie B.V.) equipped with a frequency response analyzer for iR correction. Electrochemical O₂ half-cell studies were carried out in a controlled atmosphere argon glove box outfitted with a high purity O₂ gas source (99.995%). The O₂ half-cell consisted of a planar glassy carbon (diameter = 6mm) or Au (diameter = 5mm) disk working electrode, Ag/Ag+ reference electrode, and Pt mesh counter electrode. The reference electrode, comprised of 0.1M silver trifluoromethanesulfonate (AgCF₃SO₃) (99%, Sigma Aldrich) EMITFSI housed with a vycor frit, was measured vs. Li/Li⁺, the voltage scale reported throughout this chapter.

5.2.3 ¹³C NMR measurements

Propylene carbonate (PC) (anhydrous, 99.7%, Sigma-Aldrich) was used as the solvent for all NMR measurements along with various salts, including lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Purolyte), lithium hexafluorophosphate (LiPF₆) (Purolyte) sodium hexafluorophosphate (NaPF₆) (98%, Sigma-Aldrich), potassium hexafluorophosphate (KPF₆) (98%, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆) (Fluka), and the two ionic liquids, EMITFSI and PYRTFSI.

¹³C NMR samples run on a Varian 400MHz NMR utilized external referencing to preserve salt-solvent interactions. The tube configuration consisted of three components: 1) Wilmad NMR tube (100mHz, Economy) with 1M salt solutions in propylene carbonate. 2) inner PYREX® capillary melting point reference tube with acetone d-6, Tetramethyldisilane (TMS) (1% v/v). 3) Masterflex® peroxide-cured silicone to hold the capillary melting point tube in place. Electrolyte preparation and tube assembly was done in a controlled atmosphere argon glove box. Before all NMR experiments, the instrument was locked on acetone d-6 placed in the capillary
tube. The $^{13}$C chemical shifts of PC and its solutions were referenced to the $^{13}$C peaks of TMS. Inversion-recovery $^{13}$C $T_1$ measurements utilized the same tube configuration and were made on a Varian 500 MHZ instrument. The $90^\circ$ pulse-width was calibrated on each sample before measuring $T_1$, and eight acquisition arrays were used. Two scans were taken for each sample.

5.3 Results and Discussion

5.3.1 Effect of Soft Cations on Neat IL Electrochemistry

An initial look at the role cations play on ORR can be gleaned from the cyclic voltammograms (CVs) obtained with and without 25 mM TBA$^+$ in O$_2$ saturated EMITFSI and PYRTFSI. These CVs measured on Au and glassy carbon (GC) working electrodes are presented in Figure 5.1. There is no significant change in ORR following addition of TBA$^+$. Increasing the TBA$^+$ concentration 20X to 0.5M made no change to the peak positions. An estimate of formal potentials (E$^{\text{f}}$) in both neat ILs can be calculated based on peak potentials (E$_{pa}$+E$_{pc}$/2). The 120 mV lower reduction potential of PYR$^+$ relative to EMI$^+$ on both surfaces may be explained by the slightly higher solvating ability of EMI$^+$ cation with O$_2^-$, in agreement with the observations of Sawyer $^7$ who correlated a higher O$_2$ formal reduction potential with improved electrolyte solvating ability of O$_2^-$. It can be seen from the data in Table 5.1 that EMI$^+$, with a smaller ionic radius or charge density (hence stronger Lewis acidity as explained below) appears to exhibit improved solvation of the O$_2$ reduction product compared to PYR$^+$ which has a larger ionic radius.

The reversible processes exhibited in the CVs in Figure 5.2 have been established to be the one electron reduction of O$_2$ to O$_2^-$ from the linear response between the magnitudes of
cathodic peak currents \((I_p)\) vs scan rate \((\nu^{1/2})\) in the Randles-Sevcik plots as shown in Figure 5.2 inset for \(O_2\) in PYRTFSI (negative currents). The oxidation of \(O_2^-\) to \(O_2\) is also shown (positive currents). In all solutions of Figure 5.1 the ORR involve diffusion limited processes on both electrodes. According to equation 1 for a reversible system,

\[
I_p = 2.69 \times 10^5 n^{3/2} A D_{O_2}^{1/2} C_{O_2} \nu^{1/2}
\]

\(n\) is number of electrons, \(A\) is electrode area \((\text{cm}^2)\), \(D_{O_2}/O_2^-\) is the \(O_2/O_2^-\) diffusion coefficient \((1.8 \times 10^{-6} \text{cm}^2/\text{s} \text{ and } 0.86 \times 10^{-6} \text{cm}^2/\text{s} \text{ respectively})\), \(C_{O_2}\) is concentration of electroactive species \((13.6 \times 10^{-6} \text{ moles/cm}^3)\), and \(\nu\) is scan rate \((\text{V/s})\). Comparing experimental values to theoretical plots of \(n = 1, 2\) (Figure 2 inset), the ORR reaction in PYRTFSI unequivocally consists of a one electron \(O_2/O_2^-\) redox couple, in agreement with initial IL ORR reports \(^9,10\) including our results presented in chapter 4.

**Figure 5.1.** Cyclic Voltammograms on a Au and GC electrode in \(O_2\) saturated EMITFSI and PYRTFSI both with (red) and without (black) 0.025M TBAPF\(_6\). Scan rate= 100 mV/s
<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic radius (pm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>60</td>
<td>11</td>
</tr>
<tr>
<td>Na⁺</td>
<td>96</td>
<td>11</td>
</tr>
<tr>
<td>K⁺</td>
<td>133</td>
<td>11</td>
</tr>
<tr>
<td>EMI⁺</td>
<td>239</td>
<td>12</td>
</tr>
<tr>
<td>PYR⁺</td>
<td>330</td>
<td>13</td>
</tr>
<tr>
<td>TBA⁺</td>
<td>494</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 5.1: Crystallographic ionic radii of cations used in both ORR and NMR studies.

Figure 5.2. Cyclic voltammetry of PYRTFSI on a Au electrode at various scan rates (25-500 mV/s) indicated with arrows. Inset- Randles-Sevcik analysis for n = 1 (red circle), n = 2 (blue square), and experimental (triangle).
The ORR reactions in ILs are those in equations of Scheme 5.3, which are changed little with the addition of TBA$^+$ cations and the anodic and cathodic reactions can be represented as depicted in equations C1 and A1, respectively.

**Scheme 5.3.** Neat EMITFSI and their TBA$^+$ solutions

Cathodic

\[ \text{EMI}^+ + O_2 + e^- \rightarrow \text{EMI}^{+ -} \quad \text{C1} \]

Anodic

\[ \text{EMI}^{+ -} \rightarrow O_2 \rightarrow \text{EMI}^+ + O_2 + e^- \quad \text{A1} \]

**5.3.2 Rotating Disk Electrode Voltammetry**

Rotating disk electrode (RDE) polarization curves were generated in both ILs to gain further support for the above ORR reactions formulated from the CV, and to see if there are differences in the kinetics of the ORR in the two IL electrolytes, which differ in their viscosities and hence mass transport properties. RDE polarization curves in Figure 5.3a reveal some differences between these two ILs during ORR under forced convective conditions. The ORR onset potential is approximately 200 mV higher in EMITFSI, in agreement with quiescent electrochemistry in Figure 5.1. The mass transport limiting current region below 1.8V reveals noticeable differences in ORR transport properties between the two IL cations. EMITFSI is unable to reach a convection controlled steady-state current at either 400 or 2500 RPM at 10mV/s. The criteria needed to achieve steady-state RDE current following a potential step is dependent on scan rate and rotation speed along with properties intrinsic to the electroactive
species and solvent. For example, the Schmidt number (Sc), a ratio of solvent kinematic viscosity to O\textsubscript{2} diffusion coefficient as seen in Table 5.2, favors improved mass transport at low

**Figure 5.3.** RDE polarization curves on a Au electrode. a) O\textsubscript{2} saturated neat PYRTFSI (green) and EMITFSI (black) at 400 (solid) and 2500 (dashed) RPM at 10 mV/s. (b) EMITFSI with 0, 10, and 15mM LiTFSI at 400 RPM and 10mV/s. Inset- Expanded view of ORR onset region. (c) ORR in neat EMITFSI at 5 mV/s, 400-1000 RPM and corresponding Koutecky- Levich plot at 1.82 V (inset).
values. (kinematic viscosity is calculated from the solvent’s dynamic viscosity divided by density). Yet the Sc of PYRTFSI is an order of magnitude higher than EMITFSI, which conflicts with limiting current behavior in Figure 5.3a. An explanation for this may be found from the higher charge density of EMI$^+$. 

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Density (g/cm$^3$)</th>
<th>Dynamic viscosity (mPa s)</th>
<th>O$_2$ diffusion coefficient (cm$^2$/s)</th>
<th>Schmidt number (S$_c$)</th>
<th>ORR Tafel slope (mV/dec)</th>
<th>Transfer Coefficient ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMITFSI</td>
<td>1.518 (15)</td>
<td>0.33 (16)</td>
<td>7.3x10$^{-6}$ (17)</td>
<td>2.9x10$^5$</td>
<td>120</td>
<td>0.49</td>
</tr>
<tr>
<td>PYRTFSI</td>
<td>1.39 (13)</td>
<td>0.640 (8)</td>
<td>1.8x10$^{-6}$ (8)</td>
<td>3.6x10$^5$</td>
<td>101</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Table 5.2.** Ionic Liquid properties. References to select values are indicated in parenthesis.

Mass transport limiting currents in the neat EMITFSI were achieved at lower scan rates and rotation speeds (i.e. 5mV/s, 400-1000 RPM) seen in Figure 5.3c. This was determined by extrapolating to the origin of the Koutechy-Levich plot (inset), which relates current as a function of electrode rotation speed. In doing so we found no contribution of kinetically limiting current at 1.82V and lower, indicative of a mass transport controlled region.$^{18}$ The ORR Tafel slopes extracted from RDE data and listed in Table 5.2 reveal slightly enhanced kinetics in neat EMITFSI relative to PYRTFSI. Using these slopes, transfer coefficients of 0.49 and 0.59 were calculated for the one-electron ORR, as shown in equation C1 of Scheme 5.3 in EMITFSI and PYRTFSI, respectively.

**5.3.3 Effect of Alkali Metal Cations on ORR in Ionic Liquids**

Figure 5.4a illustrates the influence of Li$^+$ on the ORR electrochemistry in PYRTFSI. At a 25 mM LiTFSI concentration, the final ratio of products differed slightly from that found in
EMITFSI, recently presented in a preliminary communication. Those data are presented here for clarity in Figure 5.4b. The PYRTFSI cathodic peak current and potential at C1 in Figure 5.4a and potential at C1 in Figure 5.4a are in agreement with a one-electron reduction to form LiO$_2$. Non-aqueous Li-O$_2$ cell electrochemistry also supports an initial one electron product. A second reduction peak (C2) follows at 1.8V, a consequence of further reduction of O$_2$ to form O$_2^-$ and PYR--O$_2^-$ ion pairing. The negative shift in reduction potential for the PYR--O$_2^-$ relative to EMI--O$_2^-$ along with mass transport differences described in Figure 5.3 may account for the different behaviors in these Li$^+$ spiked ILs. Following ORR, oxidation of multiple reduction

![Figure 5.4. Cyclic Voltammograms (CVs) at 100 mV/s on a Au electrode. (a) 0.025MLiTFSI in PYRTFSI. Inset-CVs at various cathodic limits of 1.95V and higher. (b) 0.025 LiTFSI in EMITFSI](image-url)
products is evident in the anodic sweep of Figure 5.4a. Peak A1 results from ORR products at C2, since a cathodic voltage limit of 1.95V eliminates peak A1. (see Figure 5.4a inset) In that illustration, the decrease in cathodic limit from 2.23 to 1.95V results in formation of peak A2 followed by peak A3. Hence these peaks are assigned to the oxidation of LiO2 and Li2O2, respectively, with the reactions summarized in Scheme 5.4. These assignments are consistent with our previous results and those of others.5,6,21 Consistency between reaction time scales (at different cathodic limits) and respective A2:A3 peak area ratios are in agreement with the reaction sequence in Scheme 5.4. At cathodic limits >1.95V (Figure 5.4a inset), the extent of LiO2 disproportionation is limited due to reaction time constraints. Its abundance and hence oxidation exceeds that of Li2O2. Increasing the reaction time for LiO2 decomposition leads to more Li2O2, as seen in the decreased A2:A3 ratio in Figure 5.4a following a cathodic limit of 1.5V. The fact that PYR\(^+\)--O\(^2^-\) ion pair can be seen at potentials below where LiO2 is formed suggests that the Li2O2, whose oxidation is seen at A3 is formed from the chemical decomposition reaction shown in Scheme 5.4, and not from the electrochemical reduction of LiO2.

**Scheme 5.4.** 0.025M LiTFSI PYRTFSI

**ORR**

1. Li\(^+\) + O\(_2\) + e\(^-\) → LiO\(_2\) \(\text{C1}\)

2. 2LiO\(_2\) → Li\(_2\)O\(_2\) + O\(_2\) \(\text{chemical}\)

3. PYR\(^+\) + O\(_2\) + e\(^-\) → PYR\(^+\)--O\(^2^-\) \(\text{C2}\)

**OER**

4. PYR\(^+\)--O\(^2^-\) → PYR\(^+\) + O\(_2\) + e\(^-\) \(\text{A1}\)
5. \( \text{Li}_2\text{O}_2 \rightarrow \text{Li}^+ + \text{O}_2 + e^- \quad \text{A2} \)

6. \( \text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + \text{O}_2 + 2e^- \quad \text{A3} \)

Relative to \( \text{Li}^+/\text{EMITFSI} \), cyclic voltammograms of \( \text{O}_2 \) in the 25 mM \( \text{Na}^+/\text{EMITFSI} \) presented in Figure 5.5 reveal only subtle changes. The single ORR peak followed by multiple OER peaks witnessed here is signature of an electron transfer followed by a chemical decomposition reaction like that seen in \( \text{Li}^+ \) solution. Consequently, both \( \text{Li}^+ \) and \( \text{Na}^+ \) ORR likely share a similar reaction sequence in this IL. The probable ORR and OER products are given in Scheme 5.5.

\textbf{Scheme 5.5. 0.025M NaPF}_6\text{ EMITFSI}

**ORR**

1. \( \text{Na}^+ + \text{O}_2 + e^- \rightarrow \text{NaO}_2 \quad \text{C1} \)

2. \( 2\text{NaO}_2 \rightarrow \text{Na}_2\text{O}_2 + \text{O}_2 \quad \text{(chemical)} \)

**OER**

3. \( \text{NaO}_2 \rightarrow \text{Na}^+ + \text{O}_2 + e^- \quad \text{A2} \)

4. \( \text{Na}_2\text{O}_2 \rightarrow 2\text{Na}^+ + \text{O}_2 + 2e^- \quad \text{A3} \)

Initially, no EMI--\text{O}_2^- products form on the GC electrode in the presence of either 25mM \( \text{Li}^{+\text{iv}} \) or in \( \text{Na}^+ \), as seen in Figure 5.5a. Insulation of the GC electrode after several cycles, likely due to insoluble \( \text{Na}_2\text{O}_2 \) coverage, does initiate EMI--\text{O}_2^- oxidation as seen in the 20\textsuperscript{th} cycle. Like \( \text{Li}^+ \) containing IL, the \( \text{NaO}_2 \) ORR product with oxidation at A2 evolves first following low voltage cathodic limits in Figure 5.5b. Peak A3 intensity grows as the cathodic limit is expanded.
Figure 5.5. Cyclic Voltammograms of 0.025M NaPF₆ in EMITFSI on a GC electrode at 100 mV/s (a) Select cycles: 1ˢᵗ (black), 2ⁿᵈ (blue), and 20ᵗʰ (red) scan. (b) Scans extending to various cathodic limits as listed in the inset.

and reaction time scales increase, a result of NaO₂ chemical decomposition to Na₂O₂. The high voltage peaks in Figure 5.5 may come as a result of oxidation of proton-stabilized oxide formation (e.g. H₂O₂) from EMI⁺ or residual H₂O in solution as was discussed in Chapter 4.

In a 25 mM K⁺/EMITFSI solution, one ORR peak at C1 is followed by unique anodic features between 2.1 and 2.8V in Figure 5.6a. Despite the 500 mV peak separation between the major cathodic and anodic processes, consistent rechargeability of ORR and OER products is
Figure 5.6. (a) Cyclic Voltammograms of O\textsubscript{2} saturated 0.025M KPF\textsubscript{6} in EMITFSI at 100 mV/s on a GC electrode. cycle 1 (black), cycle 20 (red) (b) Incremental cathodic limits ranging from 2.38V to 1.19V (c) Various scan rates (10-300 mV/s). Inset shows expansion on anodic peaks.
observed after 20 cycles. The ORR reaction sequence presented in Scheme 5.6 accounts for the anodic features in Figure 5.6 and is described further below. The [EMI$^+\cdot$O$_2^-\cdot$K$^+$] represents a transition state for the conversion of EMI$^+$--O$_2$ to O$_2$--K$^+$. However, direct ion pairing of O$_2^-$ with K$^+$ cannot be ruled out.

**Scheme 5.6.** 0.025M KPF$_6$ EMITFSI

**ORR**

1. EMI$^+$ + O$_2$ + e$^-$ $\rightarrow$ EMI$^+$-- O$_2^-$  
2. EMI$^+$-- O$_2$ + K$^+$ $\rightarrow$ [EMI$^+$-- O$_2$--K$^+$]  
3. [EMI+--O$_2$ --K$^+$] $\rightarrow$ O$_2^-$ --K$^+$ (chemical)

**OER**

4. EMI$^+$--O$_2$ $\rightarrow$ EMI$^+$ + O$_2$ + e$^-$  
5. [EMI$^+$-- O$_2$--K$^+$] $\rightarrow$ EMI$^+$ + O$_2$ + K$^+$  
6. O$_2$--K$^+$ $\rightarrow$ O$_2$ + K$^+$ + e

**5.3.4 Correlation of Cation Radius with its Lewis Acidity**

The ORR and OER results presented above show a correlation between the nature of the conducting cation present in the IL electrolytes and the nature of ORR products formed and their oxidation potentials. An obvious difference among the various cations studied is the relative ionic radii (Table 5.1). Since ORR products, whether it is O$_2^-$ or O$_2$$^{2-}$, do not differ substantially in their ionic size but only in their relative Lewis basicity, a most probable property of the cation that influences the stability of the ORR products is the Lewis acidity. In order to shed light on this view, we devised an experiment to measure the relative Lewis acidity of the various cations including those of the ionic liquids examined. It is based on the fact that salt cations (M$^+$) in non-
aqueous electrolytes are generally solvated by the solvent by forming acid-base complexes $M^+ (\text{solvates})_n (X^-)$ where $X$ is the anion of the conducting salt. The value of $n$ in Li salt solutions is believed to be four. We hypothesized that the $^{13}$C NMR chemical shift and spin lattice relaxation times ($T_1$) of the C=O functional group in propylene carbonate (PC) due to interaction (or formation of acid-base complex) with each of the cations studied would provide information of the relative acidity of the cations. Although the Li$^+$ to solvent molar ratio in a 1M Li salt solution is much less than four, only one $^{13}$C signal will be seen because of the rapid exchange of the solvated and unsolvated solvent molecules with Li$^+$ in the NMR time scale.$^{22}$ A cation with stronger Lewis acidity would form a stronger complex with C=O, and hence would exhibit a larger $^{13}$C=O chemical shift relative to PC. The very large IL and TBA cations with their low charge densities would exhibit the least Lewis acidity and therefore probably the least chemical shift change. The chemical shift data would be complemented by the $^{13}$C=O spin relaxation times with the shortest $T_1$ in solutions of the salt having the strongest Lewis acid cations.

5.3.4.1 $^{13}$C NMR

The $^{13}$C NMR spectra highlighting the $^{13}$C=O chemical shifts of PC with and without the various salts including the ionic liquids are presented in Figure 5.7a. This plot shows that in LiTFSI and NaPF$_6$ salt solutions, Li$^+$ and Na$^+$ ions are strongly solvated to the carbonyl oxygen atoms of PC since they have the largest negative chemical shifts (less $^{13}$C shielding) relative to PC while K$^+$ and the three large cations, TBA$^+$, EMI$^+$, and PYR$^+$ are weakly coordinated. Comparing LiPF$_6$ and LiTFSI, the counter anion is shown here to have little effect on the $^{13}$C shift. Since all of the ions studied have the same single positive charge, the radius (and, hence, ionic volume) is roughly inversely proportional to the charge density, which is a measure of the Lewis acidity. Therefore, $^{13}$C NMR chemical shifts of the C=O provide a measure of the
Figure 5.7. (a) $^{13}$C NMR chemical shifts of the propylene carbonate (PC) carbonyl carbon, concentrated with various 1M salt solutions, 1M LiPF$_6$ (Li$^+$), 1M LiTFSI (Li$^+$), NaPF$_6$ (Na$^+$), KPF$_6$ (K$^+$), EMITFSI (EMI$^+$), PYRTFSI (PYR$^+$), and TBAPF$_6$ (TBA$^+$). The structure of PC is shown in the inset. (b) C(=O) $^{13}$C chemical shifts relative to neat PC as a function cation ionic radius.
complexing ability of the Lewis base C=O (by donating the electron pair on O) with the Lewis acid cations, and hence the relative acidity of the cations. This effect is illustrated in Figure 5.7b with a cascading chemical shift as a function of ionic radius for these cations. The cations of the ionic liquids are shown to have similar weak acidity as TBA+ with similar $^{13}$C chemical shifts closer to neat PC, while the $^{13}$C peaks are farther downfield for Li+ and Na+ solutions indicating their strong Lewis acidity. K+ has an intermediate Lewis acidity among the cations studied and its electrochemistry clearly supports it.

5.3.4.2 $^{13}$C NMR spin-lattice relaxation

To gain additional information on the relative acidity of the various cations from solvent-salt interactions with PC as a reference, the $^{13}$C longitudinal relaxation times ($T_1$), also called spin-lattice relaxation times, were measured using $^{13}$C NMR. The $T_1$ measurements were conducted on all carbon atoms of propylene carbonate in the presence of the various salts. A typical compilation of inversion recovery spectra for 1M LiPF$_6$ in PC obtained with various delay times is shown in Figure 5.8.

The $T_1$ of the four PC carbons atoms are plotted as a function of cation radius (Lewis acidity) in Figure 5.9. Comparing trends of all four carbon environments, overall relaxation efficiency increases (i.e shorter $T_1$) as the number of protons attached to carbon increases (C=O>C-H>CH$_2$). The effect of different cations on $T_1$ times is most pronounced on the carbonyl carbon. Random and rapid motion of neat PC molecules yield the longest relaxation time for the given carbon transition frequency. The Li+, which deshields the carbonyl carbon most effectively as seen in Figure 5.7, produces the most efficient relaxation and shortest $^{13}$C=O $T_1$ time. The strong Lewis acidity of the solvate which forms, Li$^+$--(C=O)$_n$--TFSI$^-$
Figure 5.8. $^{13}$C NMR inversion recovery spectra to calculate $T_1$ for 1M LiPF$_6$ EMITFSI with partially relaxed spectra.

Figure 5.9. Calculated $^{13}$C NMR $T_1$ values of propylene carbonate with various 1M salt solutions, propylene carbonate (neat PC), LiPF$_6$ (Li$^+$), LiTFSI (Li$^+$), NaPF$_6$ (Na$^+$), KPF$_6$ (K$^+$), EMITFSI (EMI$^+$), PYRTFSI (PYR$^+$), and TBAPF$_6$ (TBA$^+$).
may inhibit internal motion within PC to shorten the $T_1$. An increase in radius of the coordinating cation yields longer $T_1$ times up until the EMI$^+$ coordination, where relaxation times decrease again. Molecular motion, diffusion, and rotation are all modes which contribute to the relaxation process. Lack of charge density and the soft acid nature of the largest cations PYR$^+$ and TBA$^+$ appear to enhance relaxation, perhaps through a different means related to the way they interact with the solvents than the smaller cations. $^{13}$C NMR in Figure 5.7 revealed only slight chemical shifts in the C=O environment for either PYR$^+$ or TBA$^+$ medium. A decrease of $n$ in the cation$^+-(\text{C}=\text{O})_n-\text{TFSI}^-$ complex with these larger cations may enhance molecular tumbling during relaxation and improve their $T_1$ relaxation. Nevertheless, the $T_1$ data support the view based on $^{13}$C=O chemical shifts that Li$^+$ is the strongest Lewis acid in these electrolyte solutions while TBA$^+$ and IL$^+$ behave as very weak acids with little point charge interactions with PC as pictured in Figure 5.10.

![Figure 5.10. Propylene carbonate (in brackets) complexed with Li$^+$. C-grey, O-red, and Li-purple. The hydrogen’s are omitted.](image)
5.3.5 The Correlation Between ORR and OER Processes and Relative Acidity of the Cation in the Electrolyte

As we have seen earlier, there is no significant change in ORR following addition of TBA\(^+\). We can estimate relative Lewis acidities according to the inverse of their atomic radii. The large single charged cations with more shielded, polarizable valence electrons makes the three cations TBA\(^+\), EMI\(^+\), and PYR\(^+\) soft acids. They confer exceptional stability to the one-electron ORR product O\(_2^-\), which is a soft base, as M\(^+\)--O\(_2^-\), (M= PYR, EMI). This affords one-electron reversibility, consistent with our previous observations in organic electrolytes.\(^{5,6,23}\)

The effect of hard acids on the ORR products is evident in solutions containing Li and Na salts. Both Li\(^+\) and Na\(^+\) are hard acids in the ionic liquids, in agreement with their behavior previously observed in organic electrolytes. In O\(_2\) solutions containing LiTFSI in Figure 5.4, for example, the cathodic peak current versus scan rate and potential are in agreement with a one-electron reduction of O\(_2\) to form LiO\(_2\), which then may disproportionate to Li\(_2\)O\(_2\). An initial one electron product was confirmed in chapter 4 with scan rate dependent studies in Li concentrated EMITFSI resembling closely the voltammetry behavior observed here. Furthermore, the presence of both LiO\(_2\) and/or Li\(_2\)O\(_2\) as ORR products have been identified from in situ Raman spectro-electrochemistry in organic electrolyte and X-ray diffraction patterns of Li-air cell discharge product.\(^{21,23}\) The softness of O\(_2^-\) relative to O\(_2\)\(^2^-\) favors chemical decomposition of an unstable LiO\(_2\) to form the hard(Li\(^+\))-hard(O\(_2\)\(^2^-\)) product in Li\(_2\)O\(_2\). These data confirm the general trend in the nature of the ORR products vested in the Hard Soft Acid Base (HSAB) theory of Pearson\(^{24}\) that hard acids want to be associated with hard bases while soft acids associate with soft bases. Although hard acids such as Li\(^+\) and Na\(^+\) have a strong electrostatic attraction toward soft bases such as O\(_2^-\), they cannot remain as stable LiO\(_2\) or NaO\(_2\) because of the stability
founded in the HSAB theory. The cations investigated in this work listed in Table 1 rank in terms of Lewis acid hardness in the manner, TBA+<PYR+<EMI+<K+<Na+<Li+.

In the NaPF$_6$ solution, the oxidation of the NaO$_2$ at A2 evolves first following low voltage cathodic limits in Figure 5.5b. The intensity of peak A3 assigned to the oxidation of Na$_2$O$_2$ grows as the cathodic limit is expanded and reaction time scales increase, a result of the chemical decomposition of NaO$_2$ to Na$_2$O$_2$ caused by the hard acid Na$^+$ to hard base O$_2^{2-}$ stabilization interaction.

Lewis acidity differences between EMI$^+$ and K$^+$ are apparently not substantial enough for ORR products to be ion paired with either EMI$^+$ or K$^+$ to dominate the reaction. As seen in Figure 5.6b, increments in the cathodic voltage limit results in an initial broad anodic feature following a cathodic limit of 2.0V (highlighted in red) in the vicinity of peak A1. The broadness may come as a result of the intermediate (EMI$^+$--O$_2^{2-}$--K$^+$), which is oxidized at A2. Peak A2 achieves improved resolution as the cathodic limit is decreased towards the 1.2V limit (blue curve). At these lower voltages, this transitioning species probably transforms to O$_2^{2-}$--K$^+$ and is oxidized at A3. Cycling over a range of scan rates illustrated in Figure 5.6c further clarifies the time dependence of this reaction. Peak A3 intensity dominates at slower scan rates (10-65mV/s) on the right side of the hash mark (expanded in Figure 5.6c inset). This is followed by a gradual intensity change in favor of peak A2 at faster scan rates. The degree of softness from the cations in steps 1-3 of Scheme 5.6 stabilizing the superoxide, directly determines shifts in oxidation potentials and hence affects the degree of reversibility.

The trend of shifting oxidation potentials extends to the OER peak positions of all four cations in EMITFSI as summarized in Figure 5.11. The OER overpotentials of cation-- O$_2^{2-}$ ion
pairs increases as a function of cation hardness. According to HSAB theory, stronger, covalent bond character is more favorable for soft/soft interactions resulting in improved equilibrium of the redox species at the electrode surface and better reversibility. As the cation hardness increases, it imparts instability in the cation--O$_2^{2-}$ ion pair which coupled to chemical decomposition to form the peroxide, forces redox concentrations farther from Nernstian-like conditions. The strongly ion-paired O$_2^{2-}$--M$^+$ (where M = Li and Na) ORR products are oxidized at the highest anodic potentials. Some uncompensated resistance on the electrode surface from insoluble product accumulation may in part also contribute to this occurrence.
5.3.6 ORR Mechanism in Non-Aqueous Electrolytes

The results presented here provide strong evidence for the role cations play in controlling the reaction mechanism and products of $\text{O}_2$ reduction reactions in ionic liquids with strong correlations between the Lewis acidity of the cations and basicity of the ORR products. For conducting cations, the Lewis acidity is inversely proportional to the ionic charge density as confirmed by the NMR data. For oxygen reduction products, basicity decreases in the order $\text{O}_2^2->\text{O}_2->\text{O}_2^-$. With this concept it is now possible to predict the mechanism and stability of ORR products in ionic liquids. The findings in this work unify our previous observations in organic electrolytes$^5$ and lead to the formulation of a general theory for predicting ORR mechanism and products in non-aqueous electrolytes based on the HSAB concept. The results in the ionic liquid media with a mixture of cations, specifically $\text{IL}^+$ and $\text{Li}^+$ or $\text{Na}^+$, provides unambiguous evidence for the Lewis acidity of the cation to stabilize the reaction products. All soft acid cation-containing electrolytes such as $\text{IL}^+$ and/or $\text{TBA}^+$ provides a happy medium for the highly reversible one electron $\text{O}_2/\text{O}_2^-$ process. When a strong Lewis acid such as $\text{Li}^+$ or $\text{Na}^+$ is present, even at low concentrations, it dominates the reaction mechanism ultimately leading to the formation of the stable hard base products $\text{O}_2^{2-}$ or $\text{O}^2$. The CV results in ionic liquids that contained $\text{Li}^+$ show clear evidence for the chemical disproportionation of $\text{LiO}_2$ to $\text{Li}_2\text{O}_2$ in order to satisfy the stability requirements underlying the HSAB concept.

The $^{13}\text{C}$ NMR chemical shift and $T_1$ data also provide further support to the view of solvation of strong acid cations such as $\text{Li}^+$ and $\text{Na}^+$ in organic electrolytes for these ions to exist as solvated ions $\text{M}^+$(solvent)$_n$. Interestingly, the NMR data show that the large, soft acid cations $\text{IL}^+$ and $\text{TBA}^+$ are little solvated through point charge $(\text{C}=\text{O} \rightarrow \text{M}^+)$ complexation between the solvents and the cations. The interactions between the soft acid cations $\text{TBA}^+$ or $\text{IL}^+$ and organic
solvents such as PC, acetonitrile, dimethyl sulfoxide or dimethoxyethane leading to the formation of their respective electrolyte solutions probably involve dipole-dipole or dipole-induced dipole involving dispersion energy. The solvation of Li\(^+\) in organic solvents evidenced by the NMR data also provides support to our earlier proposal\(^6\) for the modulation of the Lewis acidity of the hard acid Li\(^+\) by the basicity of the organic solvents in Li\(^+\)-conducting non-aqueous electrolytes. As mentioned earlier, in a non-aqueous electrolyte composed of a solution of a Li salt in an organic solvent, the solvent complexes with the Li\(^+\) through the donor electrons on its oxygen, nitrogen or other heteroatom to form solvent-separated ion pairs. Typically, the Li\(^+\) is solvated by four solvent molecules to form ion pairs of the general formula, Li\(^+\)(solvent)\(_4\) --X\(^-\), where X is the anion of the Li salt.\(^{25}\) Li\(^+\), because of its small ionic radius and the resulting high positive charge density, is a hard Lewis acid. However, the formation of the solvates, Li\(^+\)(solvent)\(_4\) --X\(^-\), modulates (lowers) the acidity of Li\(^+\) in organic electrolytes. The extent to which Li\(^+\) acidity is lowered by solvation depends on the Gutmann Donor (DN) number, which is measure of the basicity or electron donating property of the solvent. A higher donor number solvent lowers the acidity of Li\(^+\) to a greater extent to make it a softer Lewis acid than by a solvent possessing a lower donor number. We have found a strong correlation between the modulated Lewis acidity of the Li\(^+\)-solvates formed, judiciously chosen for their DN differences, and the ORR mechanism as well as the ultimate products of ORR.\(^6\) Dimethyl sulfoxide\(^{26}\) with a donor number of 29.8 lowers the Lewis acidity of Li\(^+\) to the extent that it provides a longer lifetime for O\(_2\)^-- as Li\(^+\)(DMSO)\(_n\)-- O\(_2\)^--.

The ORR and OER results in ionic liquids presented here together with our earlier observations in organic electrolytes\(^6\) leads to an all-encompassing theory based on the HSAB concept to predict the ORR mechanism and products in non-aqueous electrolytes, summarized in
Figure 5.12. HSAB concepts also provide an explanation for the very transient or lack of existence of $O_2^-$ in aqueous electrolytes where the strong acid $H^+$ wants to stabilize the strong base $O_2^{2-}$ or $O^2-$ with the result that the observed ORR products in aqueous acid electrolytes are $H_2O_2$ and $H_2O$. Indeed the one-electron reduction of $O_2$ may be first ORR step in the aqueous electrolytes as in the non-aqueous electrolytes.

Figure 5.12. Illustration describing the general mechanism for ORR product formation based on HSAB theory. $M^+$ is a singly charged cation.

5.4 Conclusions

A strong correlation was found between the ORR products and the ionic charge density of the conducting cations in non-aqueous electrolytes. The observed trend is explained in terms of the Lewis acidity of the cation present in the electrolyte using an acidity scale created from $^{13}$C NMR chemical shifts and spin lattice relaxation ($T_1$) times of $^{13}$C=O in solutions of the salts of these charged ions in propylene carbonate. The ionic liquids lie in a continuum of cascading
Lewis acidity scale with respect to the charge density of alkali metal, IL and TBA cations with the result that the ORR products in ionic liquids and in organic electrolytes containing any conducting cations can be predicted using a general theory based on the Hard Soft Acid Base (HSAB) concept.

5.5 Acknowledgement

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5.6 References


Chapter 6. Conclusions and Future Direction

6.1 Lithium-ion batteries

Capitalizing on the proven advantages of Li-ion batteries involves further discovery and understanding of unknown high energy density chemistries like the recently revealed layered LMO material discussed in chapter 1. Vanadium phosphates investigated in chapters 2 and 3 also offer great potential for energy dense cathodes because of their large span in oxidation states \((V^{2-}\text{ to } V^{5+})\) in which V is stable. Based on equation 1.4, this relatively high electron transfer number is indication of potentially high theoretical capacities for corresponding vanadium oxides, silicates, and phosphates. Notably, the large V oxidation range capable in reduction of both VOPO\(_4\) and \(V_2(PO_4)_3\) \((V^{3-5+})\) investigated in chapter 2, yields capacities \(\geq 200 \text{ mAh/g}\) for such stoichiometries. Different reduction environments under controlled temperatures revealed that phase formation conditions could be specifically tuned to form \(\alpha\)-Li\(_3\)V\(_2\)(PO\(_4\))\(_3\), \(\alpha\)- and \(\beta\)-LiVOPO\(_4\), all from the same precursor mixture. Despite stoichiometric similarities, excellent phase selectivity of \(\alpha\)- and \(\beta\)-LiVOPO\(_4\) was achieved through this synthesis route. These vanadyl phosphates exhibited conductivities and diffusion coefficients typical of other metal phosphates \((\sim 10^{-11} \text{ S/cm} \text{ and } 10^{-15} \text{ cm}^2/\text{s}, \text{ respectively})\), which was reflected in a poor two-phase cycling performance of \(\text{Li}_{1-x}\)VOPO\(_4\) at all but very slow rates \((\leq C/10)\). The cycling of this first Li could however be de/inserted repeatedly, in agreement with XAS observations showing only slight structural deviations compared to the parent structure. The 1 volt step drop during insertion of the 2\(^{\text{nd}}\) Li in LiVOPO\(_4\) led to significant cycle fade. This is consistent with increased structural disruption witnessed in the XAS measurements, especially in the displacement of the V=O bond. In order to circumvent the disadvantages associated with this voltage drop in Li\(_{1+x}\)VOPO\(_4\) and
still benefit from the wide V redox range, both Fe and F introduced into the tetragonal LiVOPO$_4$
structure in equal molar ratios with V resulted in the new single phase material, Li$_2$Fe$_{0.5}$(VO)$_{0.5}$(PO$_4$)F$_{0.5}$. In situ XANES revealed both $V^{3.5+}$ and $Fe^{2.3+}$ redox active sites between a 4.5V and 2.0V cycling window encompassing a single crystallographic phase. XANES and XRD observations displayed minimal changes to short and long range order during discharge as a result of the fluorinated mixed metal Li$^+$ insertion environment. More detailed crystallographic refinements of this tetragonal structure will bring better understanding to the chemical environment which results in the single phase electrochemistry and improved Li insertion and extraction behavior in high capacity electrodes for Li-ion batteries.

6.2 Lithium-O$_2$ batteries

Advancing the electrochemical performance of the Li-O$_2$ battery will entail research and development related to several aspects of its operation. Discussion in chapter 1 made reference to non-aqueous Li-O$_2$ challenges which are most critical; some are listed here.

1. Knowledge of ORR and OER reaction mechanisms for custom design of electrolyte, O$_2$
electrode, catalysis, etc. to maximize energy and coloumbic cycling efficiencies

2. Formulation of oxidation and reduction resistant Li$^+$ electrolyte stable in the presence of a catalytic O$_2$ electrode, to identify decomposing electrolyte products resulting in coloumbic contribution to the ORR

3. O$_2$ electrode with engineered porous structure optimized to house reaction products, maximize capacity, and current densities
4. Specific practical considerations include; realization of a high capacity Li composite (e.g. Si-carbon) anode or safe alternative for Li metal, implement O$_2$-permeable electrode membrane to exclude parasitic reactants from the cell.

Several of these issues are not relevant to the work presented in the chapters 4 and 5 due to the lack of any extensive Li-O$_2$ cell cycling. Rather, an understanding of ORR and OER product formation in ionic liquid electrolytes through half-cell electrochemistry has allowed us to confront directly the challenges related to problem No.1 in the list above. The O$_2$ reduction chemistry in ionic liquid can now be explained from the perspective of HSAB theory, with the resulting products being influenced greatly by the acidic nature of the conducting cation. Moreover, oxidation of the products in IL is indeed electrode dependent as determined by the unique behavior of the Au verses the GC electrode. ORR trends, solidified with $^{13}$C NMR, and previous observations in non-aqueous solvents in our laboratory, will be complemented greatly from further studies to promote the formation of reversible (i.e. soluble) discharge products for better cycling efficiency based on this established theory. This may include systematic design of a Li$^+$ conducting ionic liquid electrolyte blended with organic solvent (e.g. dipolar high DN solvents) in hopes of bringing this battery steps closer to a mobile application near you.