CATALYSIS OF OXYGEN REDUCTION REACTIONS
IN NON-AQUEOUS LITHIUM-AIR BATTERIES

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ABSTRACT OF DISSERTATION

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Abstract

As society continues to consume the world’s finite carbon fuel reservoir, the demand for high-performance energy storage devices that are capable of storing alternative forms of energy such as wind, solar and hydropower increases. Chapter one explains the implications of this matter and summarizes the current state-of-the-art lithium battery technologies. The chapter concludes with an introduction to the lithium oxygen battery couple and provides a review of more recent developments of this technology that have been reported.

Chapter 2 summarizes previously published studies of the effect of the electrolyte cation on the oxygen electrode behavior, explaining how these results are related to the hard-soft acid base concept. It then elaborates on these concepts by presenting a study of the superoxide redox couple in the presence of a hard acid cation lithium (Li$^+$), and a soft acid tetrabutyl ammonium cation (TBA$^+$), and finally the effect of adding water molecules to the soft acid electrochemical environment.

In the third chapter dimethyl sulfoxide (DMSO) is evaluated as a practical solvent for the rechargeable lithium air battery. Redox characteristics of the dissolved oxygen and its reduction products in the presence of lithium hexafluorophosphate (LiPF$_6$) supporting electrolyte were studied via cyclic, rotating disc (RDE) and ring-disc (RRDE) electrode voltammetry. The DMSO medium facilitates reversible reduction and oxidation processes in contrast to other solvent-based electrolytes studied. Galvanostatic discharge-charge cycling of the Li-O$_2$ cells has shown characteristics of rechargeability expected from voltammetric studies. Multiple high-efficiency discharge-charge cycles are possible if the depth of discharge of the carbon cathode is limited to avoid excessive passivation by the discharge products. The discharge voltage of this Li-O$_2$ cell is
higher than those of cells assembled with other non-aqueous organic electrolytes, an attribute ascribed to the stability of superoxide (O$_2^-$), the one-electron reduction product of oxygen.

Chapter 4 highlights the full reduction of O$_2$ to Li$_2$O, the ultimate chemistry desired for building a super-high-energy-density Li-air battery. Most investigations to date have identified Li$_2$O$_2$ as the discharge product which limits the specific energy of the Li-air battery to 3500 Wh kg$^{-1}$, about 67% of the theoretical value. Here, for the first time, we report the full reduction of O$_2$ to Li$_2$O in a Li-air cell using cobalt phthalocyanine-catalyzed carbon cathodes. Details of the oxygen reduction reaction mechanism have been discerned through cyclic voltammetry experiments in half cells as well as analysis of discharged Li-air cell cathodes by means of X-ray absorption spectroscopy and X-ray diffraction spectroscopic methods. The catalyst lowers the activation energy for O$_2$ reduction by forming a complex with superoxide, and enables the reduction of Li$_2$O$_2$ to Li$_2$O. In addition, the catalyst is effective in lowering the gap between the discharge and charge voltage plateaus, leading to an increase in the energy efficiency of the Li-air battery. The breakthrough in the discharge chemistry being reported could lead to the realization of the full potential of the Li-air battery.

Chapter 5 is a report on electrochemical data presented to show that catalysis of oxygen reduction reactions (ORR) in non-aqueous electrolytes are coupled to the donor number of the solvents through their ability to modulate the Lewis acidity of Li$^+$ with the formation of solvated Li$^+$. In high donor number solvents such as DMSO, the ORR proceeds via an outer Helmholtz sphere reaction pathway leading to a homogeneous catalysis of the reaction, irrespective of whether or not a catalyst is present in the carbon cathode. In low donor number solvents such as tetraethylene glycol dimethyl ether (TEGDME) and CH$_3$CN, catalyst such as CoPC, Pt and Au promote an inner Helholtz sphere reaction with the adsorption of O$_2$ and the ORR intermediates
on the catalyst surface. The catalysts in these electrolytes serve to increase the discharge voltage of Li-air cells compared to uncatalyzed ones as well as to promote the reduction of $O_2$ to $O_2^-$. The final chapter provides a conclusion and offers insight toward future directions in non-aqueous Li/O$_2$ battery research.
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List of Abbreviations and Symbols

\( \alpha \)  
Electron transfer coefficient

\( \varepsilon_r \)  
Dielectric constant

\( \Delta G \)  
Gibbs free energy

\( \Delta G_0 \)  
Standard Gibbs energy

\( \Delta-\mu \)  
XANES difference spectrum

\( \rho \)  
Density

\( \mu \)  
Absorption coefficient

\( \nu \)  
Kinematic viscosity or scan rate

\( \eta \)  
Overpotential; Dynamic viscosity / centipoise

\( \sigma^2 \)  
Debye -Waller factor

\( \theta \)  
Angle

\( \chi \)  
Mole fraction

\( \chi(k) \)  
EXAFS equation

\( \omega \)  
Rotation rate

\( \text{Å} \)  
1 \times 10^{-10} \text{ meters}

\( A \)  
Amperes

\( \text{BL} \)  
Butyrolactone

\( C_o^* \)  
Concentration of reactant in the bulk electrolyte

\( \text{CE} \)  
Counter electrode

\( \text{CMOS} \)  
Complementary metal oxide semiconductor

\( \text{CN} \)  
Coordination number

\( \text{CV} \)  
Cyclic voltammetry

\( \text{CoPC} \)  
cobalt phthalocyanine

\( \text{ct} \)  
Charge transfer

\( d \)  
Distance between crystal planes

\( D_0 \)  
Diffusion coefficient
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DEMS</td>
<td>Differential electrochemical mass spectrometry</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>DME</td>
<td>1,2 Dimethoxyethane</td>
</tr>
<tr>
<td>DN</td>
<td>Donor Number</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>EIA</td>
<td>Energy Information Administratio</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy Dispersive X-ray Analysis</td>
</tr>
<tr>
<td>EpC</td>
<td>Cathodic wave Peak potential</td>
</tr>
<tr>
<td>EpA</td>
<td>Anodic wave Peak potential</td>
</tr>
<tr>
<td>E&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Absorption edge energy</td>
</tr>
<tr>
<td>E&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Standard potential</td>
</tr>
<tr>
<td>ET</td>
<td>Electron transfer</td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volts</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended x-ray absorption fine structure</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>FSEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>HSAB</td>
<td>Hard Soft Acid Base</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>I</td>
<td>Electrical current / coulombs per second</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner Helmholtz plane</td>
</tr>
<tr>
<td>i</td>
<td>Current density,</td>
</tr>
<tr>
<td>i&lt;sub&gt;lim&lt;/sub&gt;</td>
<td>Diffusion limiting current</td>
</tr>
<tr>
<td>ip,a</td>
<td>Anodic peak current density</td>
</tr>
<tr>
<td>ip,c</td>
<td>Cathodic peak current density</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Standard rate constant</td>
</tr>
<tr>
<td>$k$</td>
<td>Photoelectron wavenumber</td>
</tr>
<tr>
<td>$L$</td>
<td>Ostwald coefficient / ml O$_2$ per ml liquid</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons transferred</td>
</tr>
<tr>
<td>$n^*$</td>
<td>Number of electrons transferred in rate limiting step</td>
</tr>
<tr>
<td>$[O]^a$</td>
<td>Activity of oxidized species</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz plane</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate; personal computers in Fig. 1.5</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant; photoelectron scattering path distance</td>
</tr>
<tr>
<td>$[R]^a$</td>
<td>Activity of reduced species</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>RIR</td>
<td>Reference Intensity Ratio</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring disk electrode</td>
</tr>
<tr>
<td>$S_0^2$</td>
<td>Many-body amplitude reduction term</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Small angle electron diffraction</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting Temperature</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>TBA</td>
<td>Tetrabutyl ammonium</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TEGDME</td>
<td>Tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>U.S.</td>
<td>United States of America</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
</tr>
<tr>
<td>W</td>
<td>Watt / Joule per second</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>wt.</td>
<td>Weight</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Chapter 1
Evolution of Lithium Battery Technologies

1.1 Battery Definition

A battery cell represents a union between two common forms of energy, electrical current and chemical bonds. The device has for over two centuries provided the world with a means to store energy in the form of chemical bonds which can later be released to liberate a flow of electrical charge, known as current, from the cell. This release of current from the cell is brought forth by the electrochemical charge transfer reactions occurring at the two separated electrodes in the cell container as shown in Figure 1.1 below for the Li/SO$_2$ battery.

During cell discharge, electrons liberated from the oxidation reaction occurring at the negative electrode (anode), in this case lithium, flow through an external load circuit to do work and then...
to the positive electrode (cathode) where a reduction reaction transfers the electrons back into the cathode active material SO$_2$. The balance of charge between the two electrodes is achieved by allowing Li$^+$ charge carriers in the form of ionic electrolytes to flow through an electrically insulating material, known as a separator, placed between the electrodes inside the cell. These charge transfer reactions occurring at each electrode, referred to as half-cell reactions, are specifically shown below in equations [1] and [2] for the Li/SO$_2$ cell.

Anode Reaction: \[ \text{Li} \rightarrow \text{Li}^+ + \text{e}^- \] [1]

Cathode Reaction: \[ \text{SO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{Li}_2\text{S}_2\text{O}_4 \] [2]

Cell Reaction: \[ \text{Li} + \text{SO}_2 \rightarrow \frac{1}{2} \text{Li}_2\text{S}_2\text{O}_4 \] [3]

For the Li/SO$_2$ cell the electrolyte is lithium bromide (LiBr) dissolved in acetonitrile (CH$_3$CN) solvent. As depicted in Figure 1.1, the carbon cathode is merely a substrate to carry out the reduction of the cathode active material SO$_2$ during discharge and to serve as a current collector. The flow of electrons from the anode to the cathode is induced by the existence of an electric field gradient between the two active electrode materials (Li and SO$_2$) which is analogous to the pressure in a tube of flowing liquid. In electrochemical terminology this force is referred to as the cell potential and is a thermodynamically derived parameter proportional to the change in free energy ($\Delta G^\circ_{\text{reaction}}$) of the electrochemical reaction in the cell as described in equation [4] below.

\[ \Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}} = -nFE^\circ_{\text{cell}} \] [4]
In this equation, \( F \) is Faraday’s constant, \( E_{\text{cell}}^o \) is the standard cell potential, and \( n \) is the number of electrons involved in the cell reaction. The relationship between the standard cell potential and the actual cell potential, \( E \), in a battery is related by the Nernst equation given in equation [5],

\[
E_{\text{cell}} = E_{\text{cell}}^o + \frac{RT}{nF} \ln \frac{[R]^a}{[O]^a} \tag{5}
\]

In equation [5], \( R \) is the gas constant and \([R]^a\) and \([O]^a\) are the activities of the reduced and oxidized reactants in the cell. For the Li/\( \text{SO}_2 \) cell, the value of \( E_{\text{cell}} \), known as the open-circuit voltage, is 3.1 \( \text{V} \). The practical operating voltage of a battery in fact deviates from this thermodynamic cell potential as shown in Figure 1.2.

**Figure 1.2.** Battery cell polarization curve

In this Figure, the thermodynamically derived voltage described by equation 1 is represented as the open-circuit voltage denoted by the dash-dot line at the highest potential. This value would correspond to the potential difference between the two electrodes in Figure 1.1a. Three experimental parameters are shown to lower the operating voltage from the thermodynamic voltage in this Figure, namely the IR loss, activation polarization, and concentration polarization.
The IR loss is produced by the electronic and ionic resistivities of the electrodes and of the electrolyte medium, respectively. It is referred to as “IR loss” because its behavior is analogous to the voltage drop induced by an electrical resistor which follows Ohm’s law shown as equation [5] below.

\[ V = I \times R \]  

The drop in voltage is directly proportional to the total electronic and ionic resistances of the cell. The second effect that lowers the operating voltage is activation polarization, named after the activation energy that defines the kinetic rates of reactions for the charge transfer (ct) processes. This effect includes contributions from both the anode and the cathode reactions. Finally, we have the concentration polarization which also lowers the operating voltage of a discharging battery. This effect is the result of the cell becoming depleted of the reactants which are necessary to feed the electrochemical charge transfer process. Figure 1.2 shows these effects as a function of increasing current, however the concentration term would also have the same effect as a function of time. As the cell continues discharging over time, the available concentration of the reactants continues to decrease. This depletion of reactants from the cell must necessarily correspond to a decrease in the discharge voltage (and in regards to a charging processes, an increase in charging voltage). As emphasized in Figure 1.2, all three of these parameters become increasingly influential on the operating voltage as the cell’s delivered current density increases. This is an important consideration as the power (P) delivered from the cell’s discharge current (I) is proportional to the voltage (V) at which it is delivered as described by equation [6].

\[ P = I \times V \]  

[6]
1.2 Battery Demand

Today, virtually all technologies are powered by an electrical current; even the modern internal combustion engine-powered automobile relies on an electrical current, provided by a battery, to start the engine initially. The consumption of electricity has indeed become of paramount importance to the existence of modern society and so humans have been relentlessly pursuing the development of battery technologies. The most attractive feature of a battery is that it provides mankind a means to carry the power of electricity wherever we go and release it in a controlled and useful manner when required. The demand for this portable capability continues to grow even more rapidly with the recent demand for portable hand-held electronic computers, telephones, cameras, and communication devices for both civilian and military uses. Additionally, modern advances in harvesting energy from the wind, sun, and tide will create a demand to store the energy when there is abundance so that it can be released during down times when the wind does not blow or the sun does not shine. Finally, it should be mentioned that an additional enormous demand for batteries will be realized if the vehicle transportation infrastructure transforms to an electrical propulsion fleet.

Although society has already begun to develop electric vehicles utilizing the battery technologies available, the full embracement of this transition will be dictated by two predominately financial issues. One is the supply and demand of fossil fuels superimposed by the environmental impact of fossil fuel consumption, and the other is the cost and performance associated with state-of-the-art battery technologies. As of now, the future state of these two matters can only be predicted. The U.S. Energy Information Administration’s historical track of global oil production over the last three decades plotted below in Figure 1.3 indicates that the world is still able to produce more and more oil every day.
It certainly will be necessary for the world to at least continue on this rate of increase as the population of consumers continues to grow alongside. Logically, if the global production begins to level off or even decrease substantially over short time periods, then a true economic pressure will exist for the price of oil products to inflate substantially. Currently, the price of gasoline is approaching 4 dollars per gallon in the United States, a mark that has already influenced the consumers’ demand for automobiles to be more fuel efficient. If the oil price were to inflate substantially, the popularity of the electric vehicle will certainly rise in conjunction.

The cost and performance of the available battery technologies is the other matter that will influence the popularity of the electric vehicle and is indeed the underlying thrust of this dissertation. The remaining introductory body will explain the importance of using lithium as a battery electrode and highlight the current state-of-the-art lithium battery technologies.

1.3 Lithium Battery Technologies
Naturally to improve this energy carrying technology we seek to increase the quantity of energy that can be packaged into a given battery container. The parameter that defines this quantity is referred to as specific energy and is telling how much electrical energy per mass of electroactive material is being liberated through the chemical to electrical energy conversion process. As shown in equation [7] below, this value is the product of the active electrode materials’ Coulombic capacity and the voltage at which this capacity is delivered.

\[
\frac{\text{mole active materials}}{\text{grams active materials}} \times \frac{\text{mole electrons}}{\text{mole active materials}} \times \frac{26.8 \text{Ah}}{\text{mole electrons}} \times V \times \frac{1000 \text{ grams}}{\text{Kilogram}} = \frac{\text{Wh}}{\text{kilogram}} \quad [7]
\]

In this equation, Faraday’s constant, which accounts for the magnitude of electrical charge corresponding to a mole of electrons, is conveniently expressed in terms of Ampere hours (Ah). As described in equation [4] above, the amount of energy available in the chemical bonds of the electroactive materials is dictated by their chemical identities, and so we refer back to the periodic table of elements as we consider possible ways to package batteries with the highest specific energy. Upon doing this we realize that the key to maximizing the specific energy in the battery container lies in the element lithium. Lithium is the third lightest element in the universe and is the lightest and most electropositive metal known, making it an optimal choice to serve as the negative electrode in a battery cell. This ultra-light anode element has already been coupled with many cathode active materials to produce numerous battery technologies summarized in Table 1 on the next page. Finally, the coupling of lithium with one of the lightest electronegative elements available, oxygen, would yield a battery with the second highest theoretical specific energy possible. The specific energy of the Li/O\textsubscript{2} cell is second only to that of the Li/F\textsubscript{2} couple,
but due to the abundance of oxygen in the earth’s atmosphere and the high toxicity of fluorine, the Li/O\textsubscript{2} couple is the best option for an ultra-high specific energy battery.

The initial development of lithium batteries was focused on primary battery technologies. Eventually, the reversible Li intercalation phenomenon was discovered and developed into the rechargeable lithium ion battery which has become an extremely successful secondary battery. Table 1 summarizes some of the most successful lithium battery advances available thus far. They are discussed in further detail below. Figure 1.4 compares the discharge profiles of some lithium battery cells with various aqueous based systems, highlighting the voltage advantage associated with the non-aqueous technologies.

Figure 1.4. Discharge profiles of various aqueous and non-aqueous battery cells overlaid from Linden’s Handbook of Batteries.
<table>
<thead>
<tr>
<th>Cathode Active Material</th>
<th>Cell Reaction</th>
<th>Open Circuit Voltage</th>
<th>Specific Energy Wh Kg$^{-1}$</th>
<th>Operational Characteristics</th>
<th>Battery Type</th>
<th>Year of Invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>Li + SO$_2$ → $\frac{1}{2}$ Li$_2$S$_2$O$_4$</td>
<td>3.1</td>
<td>1170 270</td>
<td>Low temperatures; High currents</td>
<td>Primary</td>
<td>1972$^4$</td>
</tr>
<tr>
<td>SOCl$_2$</td>
<td>4 Li + 2 SOCl$_2$ → 4 LiCl + S + SO$_2$</td>
<td>3.65</td>
<td>1470 500</td>
<td>High operating voltage</td>
<td>Primary</td>
<td>1973$^4$</td>
</tr>
<tr>
<td>CF$_3$</td>
<td>xLi + (CF)$_x$ → xLiF + xC</td>
<td>3.1</td>
<td>2260 250</td>
<td>Autoclavable high power pace maker</td>
<td>Primary</td>
<td>1969$^5$</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>Li + Mn$^{(IV)}$O$_2$ → Mn$^{(III)}$O$_2$(Li$^+$)</td>
<td>3.5</td>
<td>1005 230</td>
<td>Long Shelf Life</td>
<td>Primary</td>
<td>1975</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>LiC$<em>6$+ Li$</em>{1-x}$CoO$<em>2$↔ Li$</em>{1-x}$C$_6$ + LiCoO$_2$</td>
<td>3.95</td>
<td>560 110</td>
<td>1000s of cycles</td>
<td>Secondary</td>
<td>1980$^6$</td>
</tr>
<tr>
<td>S</td>
<td>2 Li + S ↔ Li$_2$S</td>
<td>2.2</td>
<td>2566 500</td>
<td>High Specific energy</td>
<td>Secondary</td>
<td>1962$^7$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2 Li + O$_2$ → Li$_2$O$_2$</td>
<td>3.10</td>
<td>3620 —</td>
<td>Highest Specific Energy (Developmental stage)</td>
<td>Secondary</td>
<td>1996$^8$</td>
</tr>
<tr>
<td></td>
<td>4 Li + O$_2$ → 2 Li$_2$O</td>
<td>2.91</td>
<td>5220 —</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1. Popular lithium batteries and their corresponding performance characteristics.
1.3.1 Primary Lithium Batteries

Li/SO₂

This cell technology, as described in equations [1-3], functions by the electrochemical reduction of SO₂ which is dissolved into the electrolyte solvent during cell construction. The electrolyte utilized in this cell is lithium bromide (~1.8 M) dissolved in acetonitrile (CH₃CN). Lithium metal is not stable in acetonitrile and will undergo chemical reaction to form 3,5-diamino-2,4-hexenenitrile, methane, and lithium cyanide. However, Li metal is extremely stable in acetonitrile-containing SO₂ due to the in-situ formation of a lithium dithionite (Li₂S₂O₄) film on the Li metal surface as depicted Figure 1.1. This Li stabilizing film, generally known as the solid electrolyte interphase (SEI), is capable of conducting lithium ions and serves as a protective barrier preventing the lithium foil from reacting with the solvent. Cells are packaged with an excess of SO₂ (typically up to 70 wt. % of the electrolyte) to minimize the possibility of an accidental reaction between the lithium foil and CH₃CN in the event that the SO₂ is depleted first. The great chemical stability of this SEI is responsible for the exceptional shelf life of these cells. Furthermore, the acetonitrile-based electrolyte has high ionic conductivity even at low temperatures. As a result, the cell has a reputation for yielding good discharge performance even at temperatures as low as -40°C. Typically, a high surface carbon is used as a substrate to support the cathode reaction. Due to the need for the cell to be pressurized with highly flammable and toxic electrolyte, the battery is not sold to the general public but remains an important technology for various applications in the military.
Li/SOCl₂

In this cell SOCl₂ (boiling point, 75.8 °C and melting point -104.5 °C) serves both as the active cathode material and the solvent for the electrolyte salt LiAlCl₄. Usually, a 1.5-1.8 M solution of LiAlCl₄ in SOCl₂ is used. As in the case of the Li/SO₂ battery, the SOCl₂ is reduced on a high surface area carbon electrode current collector during cell discharge. The discharge products are LiCl, S and SO₂ as shown in Table 1. The LiAlCl₄ is effective in complexing with the SO₂ produced in the discharge to keep it in solution, thereby preventing excessive buildup of gas pressure in the cell. The complex formed between SO₂ and LiAlCl₄ with a composition of LiAl(SO₂)₃Cl₄ has high ionic conductivity, which serves to maintain low internal resistance and the high discharge rate capability of the cell even as SOCl₂ is consumed during discharge. The Li anode forms a LiCl protective surface film that contributes to its long shelf-life. One of the strongest attributes of this cell is this long shelf-life, making it an attractive option as a backup power supply for many applications. The Li/SOCl₂ cell has a high operating voltage of about 3.5 V and an outstanding ability to operate at both extremely low and high temperatures. The discharge profile is characterized by a very steady voltage plateau and at low current densities the cells can provide constant voltage for years of operation, making them suitable to power CMOS memory and remote instrumentations.¹ It is fully capable of operating up to 140°C and as a result has found use in down-hole applications in petroleum drilling. Due to the high energy density, the cell has shown a propensity for safety hazards, which has limited its widespread consumer use. A low rate version of this battery is used in metering applications.
Li/(CF)_x

The lithium carbon monofluoride ((CF)_x) cell is perhaps the highest theoretical specific energy primary battery with 2260 Wh/Kg. This battery technology has proven performance for low power demands and excellent shelf life. Additionally, the cell can withstand the temperatures of autoclaving processes without major detrimental effect on performance, making it a good choice for use as power source for implantable medical devices like pacemakers.\textsuperscript{11} The cell is constructed usually with a lithium tetrafluoroborate (LiBF4) electrolyte dissolved in butyrolactone (BL) or propylene carbonate (PC). As the cell undergoes discharge, LiF and carbon are formed as discharge products (Table 1). The carbon thus produced causes an increase in the conductivity of the cathode matrix and lowers the internal cell resistance, thereby minimizing the cell voltage drop commonly found during the discharge of many Li cells. These performance characteristics have secured its utility for many consumer applications.\textsuperscript{1}

Li/MnO\textsubscript{2}

This cell is one of the earliest intercalation-based lithium batteries and has become the most popular primary cell available on the commercial market. Electrolytic MnO\textsubscript{2} is used as the cathode material. The electrolyte comprises a solution of lithium perchlorate electrolyte (LiClO\textsubscript{4}) dissolved in a solvent mixture of propylene carbonate and 1,2 dimethoxyethane (DME). The discharge reaction, as shown in Table 1, proceeds via the electrochemical intercalation of Li\textsuperscript{+} into the interstitial sites of the MnO\textsubscript{2} crystal with simultaneous injection of electrons into the conduction bands of MnO\textsubscript{2}. This cell uses the same type of MnO\textsubscript{2} used in the alkaline batteries but has been shown to tolerate higher discharge rates. The Li/MnO\textsubscript{2} cell also has an advantage over the aqueous alkaline cells in its operating temperature range with performance from -20 to 55 °C. The cell has an outstanding safety reputation and is available in a 9V battery size.
comprising three cells in series. Such design includes a pressure vent and a positive temperature coefficient element as a safety feature for protection in the event of thermal runaway at high power output.\footnote{1} These batteries are used in many household and industrial applications.

1.3.2 Secondary Lithium Batteries

Early efforts to develop secondary Li batteries involved the use of Li metal anodes and Li intercalation cathodes such as TiS$_2$ and V$_6$O$_{13}$\cite{12,13}. Although rechargeable Li cells exhibiting 100-200 charge/discharge cycles have been developed, they did not experience commercial success due to safety hazards associated with the reactivity of the high surface area Li metal which accumulates in the cell during cycling. The search for an alternative anode for secondary lithium batteries led to the discovery of graphite as a reversible Li intercalation electrode and coupling this anode with the already existing LiCoO$_2$ cathode began the era of Li-ion batteries.

C/LiCoO$_2$

Perhaps one of the most commercially successful examples of lithium batteries is the rechargeable “rocking chair” lithium-ion (Li-ion) intercalation cell. These cells function via the reversible shuttling of Li$^+$ charge carriers into and out of electrode materials referred to as “hosts” with the simultaneous injection or extraction of charge compensating electrons. With the recent surge in demand for portable electronic devices like laptop computers and cell phones, the Li-ion batteries have become a technology that virtually everyone carries in their pockets. Figure 1.5 below shows a summary of the recent growth in world-wide market sales for this battery
The standard Li-ion cell is composed of two Li intercalation electrodes, a graphite anode and a lithiated transition metal oxide cathode such as lithium cobalt oxide (LiCoO$_2$). The discharging and charging of this battery is achieved through the simultaneous Li$^+$ intercalation and extraction into and out of the host cathode and anode materials with charge compensation achieved via electrons flowing over the external load circuit as depicted in Figure 1.6. The cell is constructed in the discharged state with the Li residing in the cathode. The cell is activated by charging it first. The reversible cell reaction is depicted in equation [8].
Recent research efforts have been involved in the production of variations of LiCoO$_2$ cathode material to fine tune the performance of the Li-ion cell and cost of the battery. Additionally, a wide variety of cathode host materials have been found to be successful toward accommodating Li$^+$ intercalation reversibly and a worldwide research effort is currently in progress to find alternate materials with significantly higher capacity than that of LiCoO$_2$. Efforts are also underway to develop anodes alternative to graphite with much attention paid to Li alloying
materials such as silicon and tin. Depending on the application, cell design can be adjusted to accommodate many different shapes and sizes using both liquid organic electrolytes and solid state polymer electrolytes and compatible packaging technologies. Thus far, the major share of the Li-ion battery market has been as power sources for consumer electronics. However, there is a large push to expand the market into larger scale applications like electric vehicles, aircrafts, robotics and utility energy storage.

At the end of the 2010 calendar year the world was introduced to what would become the best-selling all-electric vehicle available to date, the Nissan Leaf, reaching a total of 50,000 units sold as of February 2013. Consumers in both The United States and Japan have purchased nearly equivalent amounts while those in Europe, especially Norway, have also purchased a significant fraction of the total sales. The vehicle is equipped with an $18,000 lithium ion battery characteristic of a 24 kWh capacity. The 300 kg battery pack has a specific energy of 140 Wh kg\(^{-1}\) and can deliver up to 90 kW of power with a top speed over 90 mph. The battery has the capacity to drive the vehicle between 47 and 138 miles per charge, depending on the driving conditions, and after 10 years is expected to retain between 70% and 80% of its initial capacity.\(^{16}\)

While the range of this vehicle is great enough to carry most individuals through their daily commute to and from work, it certainly is not adequate for longer driving trips. In order to make the electric vehicle an attractive option for more consumers, the range of the vehicle will need to be increased as much as possible to make it competitive with the internal combustion engine-driven automobiles. It has been established that in order to achieve this level of competitiveness, the EV range will have to be increased to 300 miles per charge, which roughly corresponds to a battery with a specific energy of 500 Wh Kg\(^{-1}\).\(^{17}\) Two battery technologies currently in developmental stage show promise to meet this demand. The lithium/sulfur battery is one such
technology and its progress will be discussed below. The other technology is the lithium/oxygen battery, which has an order of magnitude higher specific energy than the lithium ion battery and is the main subject of this dissertation.

**Li/S**

The lithium/sulfur couple has an attractive theoretical specific energy 5-fold greater than the state-of-the-art lithium ion intercalation battery. This battery was initially investigated in the 1960s by incorporating a solid phase $S_8$ cathode into the conductive carbon support. This design failed to display substantial cycleability and was plagued by large polarization losses at high current densities, likely due to the poor conductivity of the $S_8$ material. Soon after these initial attempts, it was discovered by Brummer et al\textsuperscript{18} that the sulfur compound could be solubilized as lithium polysulfides, $\text{Li}_2\text{S}_n$, where $n$ is between 5 and 8. In fact the partially reduced sulfur compounds are highly soluble in many organic solvents such as DMSO and THF with the latter dissolving greater than 10 molar sulfur as $\text{Li}_2\text{S}_n$. This finding was incorporated into the invention of a new type of Li/S battery where the sulfur cathode was introduced into the cell as a dissolved partially reduced species.\textsuperscript{19} While utilizing a partially reduced sulfur cathode sacrifices a fraction of the specific energy, the overall change is beneficial as the feasible current densities are much higher for the soluble cathode system and the cycleability is also improved as compared to the solid phase $S_8$ cathode. Additional developments in this battery technology were achieved by revisiting the design of a completely solid state sulfur cathode.\textsuperscript{20} In this development a nano-architected cathode was prepared, which infused a carbon nanotube array with the solid phase sulfur material. This design proved to enhance the performance in two ways. First, the electrical contact between the cathode active material and the conductive carbon support was much more intimate, negating much of polarization losses typically experienced with a solid state sulfur
cathode. Second, the discharge products are inherently trapped in the carbon matrix and therefore much less susceptible to migrate to the anode and undergo parasitic side reactions which are believed to limit the cycleability of the sulfur cathode.

Despite the ongoing research to improve the lithium sulfur battery performance, already there exists a successful implementation of the existing soluble sulfur technology. The Sion Power company, which holds over 100 patents for the development of their technologies, already has proven a practical secondary battery characteristic of 350 Wh Kg\(^{-1}\). In a laboratory setting their cells achieve 500 Wh Kg\(^{-1}\) and the company aspires to optimize this performance further to 600 Wh Kg\(^{-1}\); however, additional engineering is required to bring the laboratory performance into a practical cell. Although this achievement is only a fraction of the theoretical energy available, it is already twice the value of state-of-the-art lithium ion batteries. The company showcased its achievements by powering the world’s longest flight duration of an unmanned aircraft in 2010, which was powered at night by the company’s lithium sulfur battery and by photovoltaics and sunlight during the day. The flight lasted 14 consecutive days at times reaching altitudes of 70,000 feet and was exposed to external temperatures of -75°C. The Li/S battery is currently utilized by the military to power unmanned aerial vehicles.

\[\text{Li/O}_2\]

The invention of the non-aqueous lithium oxygen battery occurred during the study of the stability of a lithium ion polymer battery electrolyte. These findings were first published in 1996. Researchers at EIC Laboratories in Norwood, Massachusetts were collecting the gas phase headspace from partially discharged Li/graphite intercalation cells for mass spectral analysis in order to understand the electrolyte degradation mechanism. After pausing the discharge and extracting the gas sample from the cell, the researchers would restart the discharge
and noticed that the cell voltage would spike up to approximately 3 volts and show a small amount of capacity before dropping back to the initial discharge voltage as shown below in Figure 1.7.

![Figure 1.7. Discharge profile of the Li/C pouch cell used in the gas extraction experiment](image)

They hypothesized that this spike was caused by an incidental addition of atmospheric oxygen into the cell via the syringe extraction procedure and later proved the cause of the voltage increase by modifying the cell container to include a gas permeable window at the cathode as shown below in Figure 1.8.
Figure 1.8. Photograph of the Li/C pouch cell modified by the addition of a gas permeable window at the cathode.\textsuperscript{21}

The research team used this cell design to conduct the initial characterizations of the discharge performance of a Li/O\textsubscript{2} cell (Figure 1.9) and reported their discovery as a potentially revolutionary high energy density battery in the Journal of the Electrochemical Society.\textsuperscript{8}

Figure 1.9. The discharge curve for the first Li/O\textsubscript{2} cell\textsuperscript{8}
The discharge of the cell proceeds via the electrochemical reduction of oxygen gas which is dissolved in the electrolyte. The oxygen gas could be either carried in the cell container or possibly acquired from the ambient atmosphere as in a “lithium-air” battery. The theoretical specific energy calculations shown in Table 1 above include the mass of the oxygen and still show an order of magnitude increase in specific energy as compared to a traditional lithium ion cell. The initial discovery of the system proved the existence of lithium peroxide as the discharge product which could be electrochemically recharged from the cathode. However, it is noteworthy to mention that the full reduction of oxygen to the monoxide product corresponds to an even greater specific energy (as shown in Table 1) than the reaction pathway that leads to peroxide.

1.3.3. Development of Li⁺-conducting electrolytes for Li/O₂ cells

Approximately five years after the initial discovery by Abraham and Jiang,⁸ a renewed interest in further development of the Li/O₂ battery occurred. This second wave of research described further below was conducted utilizing already established non-aqueous lithium ion conducting electrolytes similar to those utilized in intercalation-based lithium ion batteries.²²⁻²⁴ Generally, lithium hexafluorophosphate (LiPF₆) salt was dissolved in an organic solvent or a solvent mixture including various blends of the organic carbonate solvents, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), ethylene carbonate (EC), and propylene carbonate (PC), dimethyl sulfoxide (DMSO), gamma-butyrolactone (g-BL), and ethers like 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), 2-methyltetrahydrofuran (2Me-THF) and dioxolane (DOL). Some properties of these solvents are tabulated in Table 1.2 below. Figure 1.10 shows the molecular structures of the solvents of interest in this thesis.
Table 1.2. Properties of various solvents relevant to the development of the Li/O$_2$ battery. Ostwald coefficient in cm$^3$ O$_2$/cm$^3$ liquid ($L$), density in g/cm$^3$ ($\rho$), viscosity in centipoise ($\eta$), and relative dielectric constant ($\varepsilon_r$). Superscript $^{24}$ Solvent Donor numbers (DN) $^{25}$ and melting temperatures ($T_m$)$^{15}$ have also been included.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$L$</th>
<th>$\rho$</th>
<th>$\eta$</th>
<th>$\varepsilon_r$</th>
<th>DN</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.0330</td>
<td>0.998</td>
<td>1.00</td>
<td>78.54</td>
<td>33.0</td>
<td>0</td>
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<tr>
<td>EC$^{2,b}$</td>
<td>0.0425</td>
<td>1.338</td>
<td>1.85$^b$</td>
<td>89.60</td>
<td>16.4</td>
<td>36.4</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.0620</td>
<td>1.096</td>
<td>1.99</td>
<td>46.45</td>
<td>29.8</td>
<td>19</td>
</tr>
<tr>
<td>$g$-BL</td>
<td>0.0918</td>
<td>1.125</td>
<td>1.75</td>
<td>41.77</td>
<td>18.0</td>
<td>-43.5</td>
</tr>
<tr>
<td>PC</td>
<td>0.0940</td>
<td>1.198</td>
<td>2.53</td>
<td>64.40</td>
<td>15.1</td>
<td>-48.8</td>
</tr>
<tr>
<td>DOL</td>
<td>0.1632</td>
<td>1.060</td>
<td>0.58</td>
<td>7.10</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>DMC</td>
<td>0.2107</td>
<td>1.070</td>
<td>0.59</td>
<td>3.12</td>
<td>-</td>
<td>4.6</td>
</tr>
<tr>
<td>DME</td>
<td>0.2122</td>
<td>0.860</td>
<td>0.46</td>
<td>7.20</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>EMC</td>
<td>0.2280</td>
<td>1.007</td>
<td>0.65</td>
<td>2.96</td>
<td>-</td>
<td>-53</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.2354</td>
<td>1.006</td>
<td>0.65</td>
<td>2.28</td>
<td>0.1</td>
<td>10</td>
</tr>
<tr>
<td>DFC</td>
<td>0.2409</td>
<td>0.960</td>
<td>0.75</td>
<td>2.82</td>
<td>16.0</td>
<td>-74.3</td>
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<tr>
<td>THF</td>
<td>0.2467</td>
<td>0.889</td>
<td>0.46</td>
<td>7.40</td>
<td>20.0</td>
<td>-108</td>
</tr>
<tr>
<td>2-MeTHF</td>
<td>0.2677</td>
<td>0.848</td>
<td>0.47</td>
<td>6.24</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>DOL:DME</td>
<td>0.1840</td>
<td>0.952</td>
<td>0.51</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Ostwald coefficient calculated from PC:EC 50:50 w/w mix.
$^b$ Viscosity at 40°C.

Figure 1.10. Molecular structure of (a) TEGDME (b) DME (c) EC (d) DMSO (e) CH$_3$CN. Hydrogen atoms are white, Carbon atoms are gray, nitrogen atoms are blue, oxygen atoms are red, sulfur atoms are yellow.
The donor number of the solvents, which is a measure of their Lewis basicity, has been included in this table for the purpose of gauging the strength of the lithium cation’s Lewis acidity, which is also expectedly present in the electrolyte solution of a Li/O₂ cell. This is an important electrolyte property that will influence the stability of the soft base reduction products formed from O₂ during discharge. As has been shown,²⁶-²⁹ the reactivity of the superoxide intermediate formed from the reduction of O₂ is strongly correlated to the Lewis acidity of the cation in solution, a topic which will be presented in greater detail in Chapter 2. Thus, considering the review of findings presented below regarding the electrolyte’s stability, attention needs to be focused on preventing the superoxide and peroxide intermediate reduction products of O₂ from undergoing side reactions with the solvent medium in order to successfully develop a secondary Li/O₂ technology. As we have seen thus far and will continue to realize throughout this dissertation, the electrolyte selection is an imperative choice that brings forth the success of lithium anode based batteries, and usually functions as more than just an ionic charge carrier.

The aforementioned second wave of research appeared to be making progress toward establishing a cycleable Li/O₂ cell until it was hypothesized in early 2010 that the stability of the electrolyte solvent was inhibiting the reversibility of the redox couple.³⁰ This notion was further substantiated by applying more sophisticated analytical techniques involving mass spectral analysis of the gaseous products contacting the cathode in-situ, which showed that the galvanostatic charging cycle in organic carbonate electrolytes does not produce oxygen gas but instead produces carbon dioxide.³¹ The release of carbon dioxide from the cathode is presumably a consequence of the electrochemical decomposition of the electrolyte and not the reversible cycling of the oxygen electrode. Initially, galvanostatic cycling of the Li/O₂ cell in carbonate-based electrodes was perceived to be evident of a reversible oxygen electrode.³² As of now, it
seems to be universally accepted that the carbonate-based electrolytes alone (without additives) are not chemically stable for prolonged cycling of the Li/O₂ cell. As a consequence of this finding, researchers began examining the stability of other electrolytes in-situ during cycling. Afterwards it was reported that both the linear and cyclic glymes (specifically tetraethylene-glycoldimethylether, 2-methyltetrahydrofuran, and 1,3 dioxolane) also might not support extensive cycling of the oxygen electrode as evident by the lack of Li₂O₂ signal in the diffraction analysis of the cathode after five galvanostatic charge/discharge cycles. Although the peroxide reduction product was detectable after the first discharge, its absence after subsequent discharges, in conjunction with the detection of a mixture of side reaction products in the cathode, led the authors to conclude that the ether-based electrolytes are unsuitable for extensive Li/O₂ cycling. It is important to mention, however, that these reports regarding the tetraglyme-based electrolyte are not consistent with other published findings which show the Li/O₂ cell can be cycled up to 100 times with excellent coulombic efficiency. The tetraglyme-based electrolyte was further investigated utilizing the DEMS analysis of the gas phase headspace in-situ and it was reported that the electrolyte solvent decomposes during both discharge and charge of the cell (evident by the detection of CO₂ in the cathode headspace) during the first cycle and more so in subsequent cycles (this same finding was reported for the DMSO solvent as well). Again, in regards to the DMSO stability, it is noteworthy to mention that this finding is not entirely congruent with other published works. Additionally, special attention has been devoted toward studying the stability of the 1,2 dimethoxyethane (DME) based electrolyte and based on the DEMS analysis in addition to the study of the XANES, SAED, and TEM results it has been concluded that this ether is also not suitable for prolonged cycling of the oxygen electrode at least in the presence of a high surface carbon cathode substrate. These recent
developments suggest careful analysis of the discharge products utilizing multiple analytical techniques should be employed in order to investigate the stability of the electrolyte materials and confirm the presence of a truly cycleable oxygen electrode. In summary, most of the electrolytes studied thus far have been shown, at least in some studies, to undergo parasitic side reactions with O\textsubscript{2} reduction products which lead to the electrochemical decomposition of the electrolyte. Research investigations must continue to bring further understanding of the cell reactions.

Lastly the acetonitrile-based electrolytes have been shown to be the most stable solvent based electrolyte (showing 90% coulombic efficiency) in the same DEMS experiments discussed above.\textsuperscript{40} Coincidently, we have been using this electrolyte for some time in our laboratory for O\textsubscript{2} electrochemistry investigations.\textsuperscript{28,29,42} This is one of the electrolyte solvents selected to conduct our catalyst characterizations included in Chapters 4 and 5. As mentioned above in the Li/SO\textsubscript{2} cell description, the lithium anode itself is not chemically stable in the acetonitrile solvent and so establishing a long cycle life secondary Li/O\textsubscript{2} cell with this solvent will require further developments including the identification of a suitable SEI forming additive. In the meantime, the Li/O\textsubscript{2} cell is still advantageous as a primary or low cycle life secondary battery due to its super-high specific energy.

1.4 Scope of the Dissertation

The organization of the electrochemical studies herein is divided into two centralized themes, both pertinent to the development of the lithium/O\textsubscript{2} battery chemistry. The first is an investigation of the electrolyte medium and its influence on the reaction pathways. In this regard, Chapter 2 will compare the oxygen electrode reactivity separately in supporting electrolytes of both hard and soft acid cations and explain the effect of adding protons to the soft acid
electrolyte environment. Chapter 3 will focus on the development of high donor number DMSO-based electrolytes and explain how this electrolyte has the capacity to function as a homogeneous catalyst by stabilizing the superoxide reduction intermediate, which was detected as a soluble intermediate for the first time in a Li$^+$-based electrolyte.\(^{27}\)

The second theme of the investigation is on the effects of incorporating a catalytic material into the high surface area conductive carbon support utilized to collect the current from the cathodic reduction of oxygen. Focusing on this theme, Chapter 4 will highlight the structural identity of a cobalt phthalocyanine derived catalyst material and discuss its effect on the ORR process. Both \(O_2/O_2^{-n}\) half-cell voltammetric results as well as \(Li/O_2\) full cell performance and product characterization will be shown. Also included will be the insitu XAS studies with the \(\Delta\mu\) analysis to elucidate the role of the CoPC on the ORR process as well as the use of XAS to detect the effect of galvanostatic cycling on the stability of the macrocyle molecule. The results of ORR product analysis conducted both by XRD and SEM with EDAX mapping will be presented.

Chapter 5 will tie the two centralized themes together through a study of precious metal disc electrodes as catalyst surfaces for the oxygen electrode in both low and high donor number based electrolyte solvents. A discussion of the catalysts’ influence will be offered from the perspective of inner sphere vs. outer sphere electron transfer processes and explain how the electrode material can influence these events.

Chapter 6 will end with a final conclusion and provide direction for future research investigations.
1.5 References


14. A. E. data courtesy of Christophe Pillot, France.


Chapter 2

Stability of the Oxygen Reduction Product Superoxide and its Dependence on the Cation Species in Solution

2.1 Introduction

The influence of the electrolyte cation on the oxygen reduction pathway in non-aqueous solvent-based electrolytes relevant to the Li/O\textsubscript{2} battery was first reported by Ó’Laoire et al\textsuperscript{1} and is summarized below. It was shown that alkali metal cation-based electrolytes caused major changes in the voltammetric response of the oxygen electrode in comparison to the larger quaternary ammonium cation- (tetrabutyl ammonium ion, TBA\textsuperscript{+})-based electrolytes. Specifically, the reversible one electron O\textsubscript{2}/O\textsubscript{2}\textsuperscript{-} couple observed in the TBA\textsuperscript{+}-based electrolytes, as shown in equation [1],

\[
O_2 + e^- \rightarrow O_2^- \quad \text{[1]}
\]

is completely transformed in the presence of the alkali metal cations to a multistep irreversible reduction which initiates via [1] and is then followed by chemical disproportionation or electrochemical reduction to peroxide depending on the voltammetric sweep rate and the radius of the alkali metal cation as shown in equation [2] and [3] respectively.

\[
2O_2^- \rightarrow O_2^{2-} + O_2 \quad \text{[2]}
\]
\[
O_2^- + e^- \rightarrow O_2^{2-} \quad \text{[3]}
\]

It was explained that the presence of the second oxygen reduction step (whether electrochemical or chemical) in the alkali metal-based electrolytes was a result of the Lewis acidity of the alkali cation being much greater than that of the TBA\textsuperscript{+}. These concepts have become widely adopted in the development of the Li/O\textsubscript{2} battery with currently 135 citations in peer-reviewed publications.\textsuperscript{2} A means to quantify the difference in Lewis acidity of various cations in solution was provided by \textsuperscript{13}C NMR chemical shifts of the carbonyl carbon in propylene carbonate (PC) solvent.\textsuperscript{3} The
cation of the conducting salt in solution complexes with the carbonyl oxygen (\( \text{C}=\text{O} \)) of propylene carbonate which in turn causes a chemical shift in the \( ^{13}\text{C} \) NMR spectrum of the carbonyl carbon in proportion to the electron acceptor strength (Lewis acidity) of the cation.

**Figure 2.1.** (a) \( ^{13}\text{C} \) NMR chemical shifts of the propylene carbonate (PC) carbonyl carbon, in its various 1 M salt solutions. 1 M LiPF\(_6\) (Li\(^+\)), 1 M 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) \( ^{13}\text{C} \) chemical shifts relative to neat PC as a function cation ionic radius.\(^4\)

The NMR data in Figure 2.1 show a greater than 1 ppm difference in the chemical shift relative to neat PC when comparing the Li\(^+\) cation solution to the one containing TBA\(^+\) cation and it was
shown that the extent of the chemical shift was a function of the cations’ radii, which are correlated to their Lewis acidities.\(^3\)

It is understood that the oxygen reduction product, superoxide, \(O_2^-\), is a relatively soft Lewis base due to its larger dinuclear radius and singular negative charge. Therefore, this reduction product forms stable complexes in the electrolyte environment which contains soft Lewis acids like the TBA\(^+\) in accordance with Pearson’s Hard Soft Acid Base (HSAB) theory.\(^5\) This stabilization prevents the oxygen from reducing further and allows for a completely reversible one electron couple in the soft acid cation electrolyte. In contrast, the superoxide decomposes further in the presence of the alkali metal cation resulting in the formation of an insoluble film of Li\(_2\)O\(_2\) at the electrode interface.\(^1\)

2.2 Experimental Methods

2.2.1 Half-cell voltammetry measurements

Anhydrous grade \(\geq 99.8\%\) acetonitrile (CH\(_3\)CN), and electrochemical grade tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) were purchased from SigmaAldrich and used as received. Purolyte\textregistered lithium hexafluorophosphate (LiPF\(_6\)) certified to contain less than 20.0 ppm water was purchased from Novolyte Technologies and used as received. Metals basis 99.9\% Li foil was used as received from Alfa Aesar company. Upon receipt from the vendor, all these reagents were immediately stored in an MBraun Labmaster 130 argon-filled glovebox with water vapor concentrations maintained below 1 ppm. Electrolyte formulations were carried out in the dry atmosphere glovebox using class B polypropylene volumetric flasks and an APX 153 top loading balance from Denver Instruments.

Cyclic voltammetry experiments were conducted utilizing a PGSTAT30 potentiostat equipped with a scangen module from Ecochemie Inc. A polypropylene jar from Nalgene\textregistered was
employed as the cell container and an in-house fabricated polypropylene lid was put in place to keep the electrolyte solution removed from the ambient room conditions and to hold the electrodes in a stationary fashion, as described previously.\textsuperscript{1,2} The working electrode utilized was a change tip glassy carbon disc of 5 mm diameter held in a Teflon disc holder apparatus all purchased from Pine Instruments. A platinum gauze was utilized as the counter electrode, and an in-house assembled reference electrode made from a silver wire contained in a 100 mM TBAPF\(_6\) 10 mM silver nitrate/CH\(_3\)CN solution in a borosilicate glass sleeve, were affixed in the cell. The reference electrode of the cell was separated from the working cell by a Vycor polymer frit. Oxygen gas was purged into the cell through a solvent reservoir in order to solvate the working gas flow thereby minimizing the evaporation of the electrolyte solvent.

The Ag/Ag\(^+\) reference cell was routinely calibrated in separate cyclic voltammetry experiments conducted in tenth molar TBAPF\(_6\) CH\(_3\)CN electrolytes with the addition of 1 mM ferrocene. The measured potential scale was then adjusted to the Li/Li\(^+\) scale for plotting purposes based on the ferrocene/ferricenium experimental data.

\textbf{2.2.2 Post Voltammetry Scanning Electron Microscopy Analysis}

Images were gathered using the secondary electron signal generated in a Hitachi S-4900 FSEM instrument. The disc electrode was carefully removed from the Teflon disc holder, rinsed in 1,2 dimethoxyethane to remove residual electrolyte, and then mounted to a carbon adhesive on an aluminum stub for imaging.

\textbf{2.3 Results and Discussion}

\textbf{2.3.1 Comparison of Li\(^+\) and TBA\(^+\) Cation by CV and SEM Analysis}

The influence of cation acidity introduced above on the oxygen electrode voltammetry is depicted below in Figure 2.2.
Figure 2.2. Scanning electron micrographs of a glassy carbon working electrode magnified 150x10^3 times after holding at the cathodic peak in two different electrolytes separately, (a) 0.1 M TBAPF$_6$ in CH$_3$CN and (b) 0.1 M LiPF$_6$ in CH$_3$CN.

The soft Lewis acid TBA$^+$-based electrolyte facilitates nearly an order of magnitude larger oxygen reduction wave magnitude for the voltammogram than does the Li$^+$-based electrolyte. This result is explained as an effect of the insoluble Li$_2$O$_2$ formation at the disc interface in the Li$^+$-based electrolyte which begins to take place via equation [2] as soon as the dissolved oxygen begins to be reduced to superoxide. The passivation film is imaged in the micrograph shown in Figure 2.2, which was collected from the disc after holding the disc potential at the O$_2$ $\rightarrow$ O$_2^-$ wave peak on the second sweep. The buildup of the insoluble product at the electrode surface prevents the reduction wave magnitude from reaching its diffusion controlled limit as it does in
case (a) and also results in the decrease in reduction peak magnitudes on subsequent cycles. Comparison of these two voltammograms also shows the change in free energy brought forth by the charge transfer reaction is greater (i.e. higher onset potential vs. Li/Li$^+$ reference) in the Li$^+$-based electrolyte than it is in the TBA$^+$-based electrolyte as indicated by the positive shift in potential for the Li$^+$-based electrolyte.

2.3.2 The Reduction of Superoxide to Peroxide

As shown below in Figure 2.3a the $O_2^-\text{TBA}^+$ ion pair complex is so stable that it cannot be reduced electrochemically until the disc potential is biased below 1 Volt vs. Li/Li$^+$. As indicated by the EpC2 label in Figure 2.3a, a second reduction of the superoxide can be forced electrochemically, but only after biasing the working electrode potential beyond the working limit (as measured in the absence of oxygen) of the electrolyte. Following this second reduction the return anodic sweep shows lesser magnitudes (decrease from 3.9 mA cm$^{-2}$ to 2.4 mA cm$^{-2}$) of current, corresponding to the oxidation of superoxide (EpA1) as the concentration of the superoxide has been partially depleted. It is remarkable that there is still a considerable quantity of the superoxide present even after biasing the electrode to such extreme overpotentials. The superoxide stability over such an extended potential range usually does not exist in the Li-based electrolytes as will be elaborated in Chapter 3. Correlated to Epc2 is a second oxidation peak labeled EpA2 which corresponds to the oxidation of the $O_2^{2-}\text{TBA}^+$ ion pair.
Figure 2.3 Cyclic voltammograms collected from a glassy carbon working electrode at 100 mV s⁻¹ in (a) dry 0.1 M TBAPF₆ in CH₃CN and (b) water spiked 0.1 M TBAPF₆ in CH₃CN.

Possible solution structures of the O₂ reduction products formed in TBAPF₆ through EpC1 and EpC2 are displayed in Figure 2.4a and 2.4b, respectively.
2.3.3 Influence of Water in the Soft Acid TBA$^+$ -based Electrolyte

Figure 2.3b reports further insight into the behavior of the O$_2$/O$_2^-$ couple in the TBA$^+$-based electrolyte by studying the electrode response after additions of H$_2$O to the electrolyte. The water concentrations presented in Figure 2.3b are 10 mM, 300 mM, and 3 M which correspond to water mole fractions ($\chi_{H_2O}$) of 0.06 %, 1.6 % and 16 % respectively. Mixtures of acetonitrile and water have been studied in the past in order to evaluate molecular associations which occur in solutions of various molar ratios using thermodynamic measurements to evaluate the Kamlet and Taft solvatochromic parameters, ATR mode infrared measurements to calculate the molar polarizability spectra, molecular dynamic simulations to study radial distribution functions and NMR data to confirm these simulations, and XRD and transmission IR were used to directly determine solution structures. All these studies consistently report that in acetonitrile-water mixtures of $\chi_{H_2O} < 20\%$, all of the water is associated with acetonitrile in a 1:1 CH$_3$CN:H$_2$O complex via a hydrogen bond with the acetonitrile nitrogen atom, CH$_3$CN---H-O-H. Each of
these discrete complexes exists as solutes in the abundance of acetonitrile. Clusters of water molecules containing hydronium ions do not exist unless the $\chi_{H_2O}$ fraction is $> 20\%$. As discussed below, the hydrogen bonded complex found in solutions with a low mole fraction of water molecules is believed to function as a charge transfer mediator promoting the outer sphere electro-reduction of the superoxide complex.

The blue curve in Figure 2.3b is a measurement of the superoxide couple after the addition of 10 mM H$_2$O. At this concentration a mild change in the response is observable as a suppression of the magnitude of the superoxide oxidation signal labeled EpA1. In the case of the dry electrolyte (Figure 2.3a), the superoxide oxidation peak current magnitude is approximately 4 mA cm$^{-2}$, while after the 10mM addition the magnitude is lowered to 2.5 mA cm$^{-2}$. This decrease in the EpA1 signal is correlated with the onset of the reduction wave shown at 1.75 V vs. Li/Li$^+$, which is the electrochemical reduction of the superoxide to peroxide. This process, in the presence of 10 mM CH$_3$CN-H$_2$O, has been shifted to lesser over potentials compared to the dry electrolyte voltammogram in Figure 2.3a where such process is not initiated until 1.1 V vs. Li/Li$^+$. The hydrogen bonded complex with its positive dipole oriented toward the electrode surface probably facilitates the reduction of the superoxide as a charge transfer mediator, allowing the electrochemical process to occur at lesser over-potentials. An illustration of this occurrence is provided in Figure 2.5.
Increasing the CH$_3$CN-H$_2$O charge transfer mediator concentration from 10 mM to 300 mM (χ$_{H2O}$ = 1.6%) shifts the onset of the Epc2 process further to 2.0 V vs. Li/Li$^+$ and also decreases the EpA1 signal magnitude further as a more substantial quantity of the superoxide has been electrochemically reduced.

At 3 M H$_2$O ($\chi_{H2O} = 16\%$) two additional changes in the oxygen voltammogram are observable. First the EpA1 signal is almost completely absent, only a relatively small magnitude signal which is shifted to greater anodic over-potential remains. This change is consistent with a near complete depletion of the superoxide concentration. However, comparing the magnitude of EpC2 signals for the 300 mM H$_2$O and 3 M H$_2$O there is no increase in the amount of
electrochemically formed peroxide as a result of increasing the charge transfer mediator concentration. Therefore, the almost complete absence of the EpA1 signal cannot be explained solely as an effect of the electrochemical reduction of the superoxide to peroxide as it was in the 300 mM circumstance. Considering that water clusters containing hydronium cations are expected to be present in acetonitrile-water mixtures at approximately $\chi_{H2O} = 20\%$ in conjunction with the aforementioned observation leads to the conclusion that the electrochemically formed superoxide must also be consumed in a chemical reaction in addition to the measured electrochemical reduction (EpC2). This chemical reaction is presumably a reaction involving the hydronium ion present in solution as an effect of the water cluster formations which occur in the $\chi_{H2O} = 16\%$ solution. A possible reaction sequence is shown in equations [4] and [5] below

$$
TBA^+ O_2^- + H_3O^+ \rightarrow TBA^+ + HO_2 + H_2O \quad [4]
$$

$$
2 HO_2 \rightarrow H_2O_2 + O_2 \quad [5]
$$

The second major change observed at the 3 M concentration is a shift to greater anodic over-potential required to induce the peroxide oxidation process labeled as EpA2. The peroxide reduction product is a harder base than is the superoxide product and since the hydronium ion is a harder acid (due to its smaller ionic radius) than the TBA cation, the peroxide reduction product will preferentially pair in solution with the hydronium ions present in the 3 M H$_2$O solution. Therefore, in this solution the peroxide is more stable in accordance to Pearson’s HSAB theory as it is paired with the harder acid hydronium cation and requires more electrochemical force to drive the oxidation process depicted in equation [5].

$$
TBA^+ \cdots O_2^\cdots H_3O^+ \rightarrow TBA^+ \cdots O_2^- + H_3O^+ + e^- \quad [5]
$$
Although the presence of the hydrogen bonded water-acetonitrile complex in the electrolyte certainly is shown to lower the stability of the \( O_2^- \text{TBA}^+ \) complex by facilitating a mediated outer sphere reduction, the effect is not as drastic as that observed in the Li\(^+\)-based electrolytes. First, the magnitudes of the reduction waves corresponding to superoxide formation are still on the same order as measured in dry electrolyte voltammogram of Figure 2.3a (this is in contrast to the response in the Li\(^+\)-based electrolyte shown in Figure 2.2b). This shows that the peroxide species formed in the water-spiked electrolytes (at all three concentrations) is likely soluble in the solution and not forming an insulating barrier film on the electrode. Secondly, the presence of the hydronium ion in solution does not cause the large shift in oxygen reduction onset as it does in the Li\(^+\)-based electrolyte.

Although the Lewis acidity of the Li\(^+\) cation in organic electrolytes is harder than the TBA\(^+\) acidity, it was found that in organic solvents of high donor number the Li\(^+\) cation is effectively softened by the strong donicity of the solvent.\(^{10}\) This finding has also been vital to the understanding of the oxygen electrode in the Li/O2 development and has been cited 152 times thus far.\(^{2}\) It was revealed that the superoxide intermediate has a significantly longer lifetime in the Li\(^+\)-(DMSO)\(_n\) than it does in other lower donor number electrolytes. Again this outcome is predicted by the HSAB theory as the Li\(^+\) is a softer acid in the high donor number electrolyte than it is in lower donor number electrolytes. This concept will be elaborated in chapter 3 with a study of oxygen redox reactions in dimethyl sulfoxide (DMSO)-based electrolytes.

### 2.4 References

2. Google Scholar Citations


Chapter 3:

Studies of Li-air Cells Utilizing Dimethyl Sulfoxide-Based Electrolyte

3.1 Introduction

Recent investigations of the non-aqueous Li/O\textsubscript{2} battery, popularly known as the lithium-air battery, universally acknowledge that the passivation of the porous cathode is a central challenge toward the development of a rechargeable system.\textsuperscript{1-4} As the cell discharges, passivation of the cathode occurs via the formation of insoluble, electrically insulating ORR products, of which the predominant material is Li\textsubscript{2}O\textsubscript{2}. Some studies have shown suppression of this problematic occurrence by limiting the depth of discharge, which allows the battery to undergo multiple charge/discharge cycles.\textsuperscript{5,6} The challenge of achieving multiple full discharge/charge cycles while maintaining high Coulombic efficiency without the use of catalyzed electrodes remains unsolved.

Our previous study of the oxygen reduction reactions (ORR) in non-aqueous electrolytes\textsuperscript{7} has led to the realization that Li\textsuperscript{+}-conducting electrolytes in dimethyl sulfoxide (CH\textsubscript{3}SOCH\textsubscript{3}) (DMSO), a solvent with very high Lewis basicity as measured by its Gutmann donor number of 29.8, are good media to fully elucidate ORR and oxygen evolution reaction (OER) mechanisms, and ultimately to utilize in Li-air cells. A major reason for this is their ability to stabilize oxygen reduction reaction intermediates and products, and facilitate the reverse (recharge) reactions. The fundamental concepts understood from these half-cell experiments lead us to continue investigating the DMSO-based electrolyte, evolving into full cell galvanostatic studies, preliminary results of which we first reported at the Electrochemical Society meeting in Boston.\textsuperscript{8} A full account of our work is presented here. A recent paper has shown that the DMSO
electrolyte is promising for repeated galvanostatic cycling of Li-O₂ cells with a porous gold electrode.⁹

Included in this chapter is a detailed study of the rechargeability of the oxygen electrode via half-cell voltammetry in DMSO-LiPF₆ electrolytes and Li/O₂ cell performance evaluation. With respect to the latter we report on the Li/O₂ cell reaction products, and elucidation of the factors affecting its rechargeability. We demonstrate here that the ORR reduction products in DMSO-LiPF₆ electrolytes can be fully recharged. Importantly, we have found that a Li/O₂ cell with DMSO-LiPF₆ electrolyte and no cathode catalyst can be recharged at lower charge potentials than cells utilizing other non-aqueous electrolytes such as electrolytes in organic ethers and carbonates.

### 3.2 Experimental Methods

#### 3.2.1 Material Source and Purity

All solvents utilized in electrolyte media were anhydrous grade purity purchased from Sigma Aldrich and used as received. Specifically, anhydrous grade DMSO certified to contain less than 50 ppm water was used as received after performing Karl Fischer titrations as described below. The DMSO solvent was found to contain 20.5 ppm H₂O. Purolyte® LiPF₆ certified to contain less than 20.0 ppm water was purchased from Novolyte Technologies and used as received. Metals basis 99.9% Li foil was used as received from Alfa Aesar Company. Upon receipt from the vendor, all these reagents were immediately stored in an MBraun Labmaster 130 argon-filled glovebox with water vapor concentrations maintained below 1 ppm.

#### 3.2.2 Water Content by Karl Fischer Analysis

Coulometric Karl Fischer titrations were performed via a compact Mettler Toledo C20 Coulometric titration apparatus in conjunction with a Mettler Toledo XP56 microbalance. All
measurements were made only after the titration drift value had settled to 1 µg/min or less. Hydranal water standards of 100 ppm were analyzed before and after samples of interest were measured. All measurements were made utilizing a 3 ml aliquot of the solution of interest delivered via a Whatman gas tight syringe.

3.2.3 Air Cell Assembly Procedures

Air cell cathodes were fabricated by curing slurries of Ketjen300 JD carbon black powder from AkzoNobel dispersed in 1-methyl-2-pyrrolidone with 10% Kynar 2801 binder onto 1 inch diameter Panex30® carbon cloth substrates. Typical cathode loadings were between 5 and 10 mg carbon powder per cathode substrate, which had an area of 5.1 cm². Anodes were cut from lithium foil as received from Alfa Aesar and pressed onto copper mesh current collectors in between two polypropylene blocks. A standard polypropylene separator was used after it was soaked in electrolyte for 12 hours. Air cell components were assembled into custom-designed air cell containers fabricated from polypropylene. All assembly procedures were conducted in the argon-filled glovebox described above. Prior to cell assembly the dried cathodes were submerged in electrolyte solution while vacuum impregnated in the antechamber of the glove box for approximately 30 minutes. The mass change of the electrode as a consequence of the impregnation was measured roughly to be 250 mg. Assembled cells were transferred to 3 mil thick multilayered aluminized polyethylene bags and heat impulse sealed. Sealed bags were transferred to a Labconco dry atmosphere glove box where moisture levels are maintained below 0.5 ppm. Once in the glove box cells were installed to a discharge chamber which was custom modified from a gasket-sealed polycarbonate transport carrier from Nalgene. The discharge chamber was purged with dry grade oxygen gas that had first passed through a sieve moisture trap. After sealed in the oxygen environment, galvanostatic discharge/charge experiments were
conducted via an Arbin BT-2000 4 channel instrument which was connected to the discharge chamber through electrode posts installed through the glovebox wall. All galvanostatic studies were conducted at a current density of 0.1 mA per square centimeter of geometric area unless noted otherwise.

### 3.2.4 Discharge Product Characterization by X-ray Diffraction Analysis

Post discharge X-ray diffraction analysis was conducted on air cell cathodes via a Bragg-Brentano para-focusing UltimaIV powder diffractometer utilizing a Cu K$_\alpha$ radiation source from Rigaku. Sample preparation was conducted in the dry glove box. Cathodes were cut to fit the dimension of the quartz sample holder apparatus and then sealed in the sample holder by a film of 2.5 mil thick Kapton® polyimide tape.

### 3.2.5 Half Cell Voltammetry Experiments

Cyclic voltammetry (CV) experiments were conducted within the dry glove box atmosphere described above via a PGSTAT30 bipotentiostat equipped with a scangen module from Ecochemie Inc. A polypropylene screw-cap container from Nalgene was employed as the cell container and an in-house fabricated polypropylene lid was in place to hold the electrodes in a stationary fashion while maintaining a controllable headspace atmosphere above the electrolyte. Platinum gauze was utilized as the counter electrode and, a glassy carbon disc of 0.196 cm$^2$ was used as the working electrode. A reference electrode was made from a silver wire contained in a glass jacket filled with the working electrolyte plus a 10mM addition of silver nitrate salt. The reference electrode was separated from the working electrode by a Vycor polymer frit purchased from BASi. The reference cell was routinely calibrated in separate cyclic voltammetry experiments conducted in 0.1M TBAPF$_6$/acetonitrile electrolytes with the addition of 7 mM ferrocene. The silver reference cell couple was found to be approximately 88 mV below the
formal reduction potential of the standard ferrocene/ferrocenium couple. The silver reference electrode potential from the Li/Li$^+$ was evaluated experimentally by submerging the jacketed reference electrode in a 1M LiPF$_6$/DMSO solution containing a clean lithium electrode and monitoring the potential between the silver reference wire and the lithium foil. All voltammograms reported herein are referenced to this potential difference which is 3.60 V.

3.2.6 Rotating Ring Disc Electrode (RRDE) Voltammetry

Additional CV experiments were conducted utilizing the half-cell equipments described above with the inclusion of a ring-disc working electrode. The ring-disc electrode consists of two electrically insulated electrodes, one a glassy carbon disc of 0.247 cm$^2$ and the other a gold ring of 0.187 cm$^2$ located immediately outside the disc circumference. Generally the ring electrode is held at a constant potential from the reference electrode while the disc electrode potential is scanned linearly. While the two electrodes are rotated (RRDE) the electrochemical products produced at the disc have the opportunity to be detected at the ring.

3.3 Results and Discussion

3.3.1 Voltammetric Investigations

Previous cyclic voltammetry studies of the oxygen redox couple in 0.1 M LiPF$_6$/DMSO electrolyte show that by carefully limiting the cathodic voltage, it is possible to detect superoxide O$_2^-$, oxidation current on the return anodic sweep. This is an atypical result for lithium and other alkali metal cation-containing electrolytes and is explained on the basis of the ability of the Li$^+$, solvated by DMSO in this electrolyte, to stabilize the superoxide in accordance with the hard soft acid base (HSAB) concept we have discussed. The high Gutmann donor number of DMSO lowers the Lewis acidity of the solvated lithium cation, Li$^+$ (DMSO)$_n$ making it a softer Lewis acid than it would be if it were dissolved in lower donor number solvents. This
softening of the Lewis acidity of Li$^+$ makes the $O_2^-\cdot$Li$^+$\(\text{DMSO})_n\) ion pair complex more stable by suppressing its tendency to disproportionate via the reaction described in equation [2] below. A consequence of this unique property of DMSO is the electrochemical detection of all of the oxygen reduction products, namely LiO$_2$, Li$_2$O$_2$ and Li$_2$O, formed according to the reactions in equations [1-4]

\[
\begin{align*}
O_2 + e^- + Li^+ & \rightarrow LiO_2 & [1] \\
2 LiO_2 & \rightarrow Li_2O_2 + O_2 & [2] \\
LiO_2 + e^- + Li^+ & \rightarrow Li_2O_2 & [3] \\
Li_2O_2 + 2 e^- + 2 Li^+ & \rightarrow 2 Li_2O & [4]
\end{align*}
\]

In other electrolytes the initially formed superoxide is short-lived in the presence of Li$^+$ and will undergo relatively fast decomposition to Li$_2$O$_2$ (equation [2]) resulting in negligible or no superoxide detection on the anodic sweep of a cyclic voltammogram.$^7$

The results presented herein show evidence that the DMSO solvent medium facilitates the full reversal of the ORR process throughout the multiple reactions described in equations [1-4], involving four electrons per O$_2$. Figure 3.1 presents cyclic voltammograms collected separately on a planar glassy carbon disc in four different oxygen saturated organic electrolytes.
Figure 3.1. Consecutively collected voltammograms of a glassy carbon disc working electrode at 100 mV s$^{-1}$ in oxygenated 0.1M LiPF$_6$ (a) DMSO (b) MeCN (c) TEGDME (d) PC. The voltammogram for each de-oxygenated electrolyte is presented in dashed line.

The voltammograms collected after purging the electrolytes with argon have been overlaid to show the voltage widow for each electrolyte. The aforementioned passivation associated with ORR in Li$^+$-containing electrolytes is manifested as a continually decreasing reduction current magnitude obtained on consecutive voltammetric sweeps as shown for cases b, c, and d in Figure 3.1. For these cases the deposition of the insoluble reduction products on the surface of the disc electrode fouls reaction sites available to subsequent reaction and is apparently not removable via electrochemical cycling. This results in a continuously decreasing magnitude of reduction current over multiple cycles. The voltammograms collected in the DMSO-based electrolyte
display a remarkable exception in this regard showing virtually no decrease in the reduction peak current magnitude even after fifty voltammetric sweeps.

The reduction peak currents corresponding to superoxide formation in 0.1 M LiPF₆/DMSO at various sweep rates are presented in Figure 3.2.

![Figure 3.2](image-url)

**Figure 3.2.** (a.) Voltammograms of a glassy carbon disc working electrode in oxygenated 0.1M LiPF₆ in DMSO collected at six different scan rates. (b) Nicholson Shain theoretical peak currents overlaid with experimental peak currents obtained from (a).
A linear regression coefficient of 0.997 was obtained for the experimental data signifying that the reduction process is a diffusion-controlled electrochemical reaction. Further analysis of the data was conducted by fitting the linear regression to the Nicholson and Shain equation.\[^{10}\]

\[
i_{p,c} = (2.99 \times 10^5) n (n^* \alpha)^{1/2} D_o^{1/2} C_o^* \nu^{1/2}
\]

The theoretical slope is comparable to the experimental data if the number of electrons transferred, \(n\), and the number of electrons transferred in the rate-determining step, \(n^*\), are both set equal to 1 and the transfer coefficient, \(\alpha\), is set to 0.69. The fit utilized already established values for the diffusion coefficient, \(D\), and oxygen solubility, \(C\), \(1.67 \times 10^{-5}\) cm\(^2\) s\(^{-1}\) and 2.1 mM, respectively\[^7,11\]. These results are consistent with a one-electron electrochemical reduction of molecular oxygen to superoxide as described in more detail below.

The cycleability of the oxygen electrode in 0.1 M LiPF\(_6\)/DMSO was investigated further as a function of the voltage limits utilized in the cycle. Figure 3.3a shows a mild passivation effect induced by repeated cycling in the narrow voltage limits corresponding to the one-electron redox process of equation [1] which is associated with the oxygen/superoxide couple as described in the preceding paragraph. The peak corresponding to the reduction of oxygen has been labeled \(E_{pc}\) and that corresponding to the oxidation of superoxide has been labeled \(E_{pa}\).
Figure 3.3. Consecutively collected voltammograms of a glassy carbon disc working electrode at 100 mV s\(^{-1}\) in oxygenated 0.1M LiPF\(_6\) in DMSO with potential sweep ranges (a) 2.15 V to 2.8 V (b) 2.05 V to 4.1 V  (c) 1.95 V to 3.45 V  (d) 1.95 V to 4.1 Voverlayed with sweeps 1-10 from range (c) in grayscale. All plots overlayed with voltammogram collected over the full voltage range represented by the dashed line.
The data in Figure 3.3b indeed support our view that the superoxide chemically decomposes to Li$_2$O$_2$ as in equation [2] since two distinct oxidation peaks are seen when the anodic sweep limit is extended to the full range of 4 V. The peak $E_{pa2}$ corresponds to Li$_2$O$_2$ oxidation and its presence in the voltage window (which does not extend low enough to include $E_{pc2}$) of Figure 3.3b provides evidence to support that the superoxide undergoes chemical decomposition to form lithium peroxide. Interestingly, in these latter cyclic sweeps the reduction peak currents remain steady upon repeated cycling unlike in Figure 3.3a. It appears from Figures 3.3a and 3.3b that by allowing the disc electrode potential to reach higher anodic limits the superoxide decomposition products are oxidized fully and removed from the ORR active sites thus alleviating the passivation effect seen in Figure 3.3a. Figure 3.3c reinforces the necessity of sweeping through the full anodic voltage range to avoid passivation even after sweeping to lower cathodic limits. In Figure 3.3c the superoxide OER (reverse of equation [1]) peak is absent as all of it has been reduced to Li$_2$O$_2$ (as in equation 3) as a result of the lower cathodic limit. The electrochemical reduction of superoxide to peroxide is a broader peak in the voltammogram as it is close in potential to, and thus convoluted with, the initial reduction process. We have labeled its approximate peak position as the shoulder above $E_{pc2}$. We conclude from the anodic portion of Figure 3.3c that Li$_2$O$_2$ is directly oxidized to oxygen without going through the superoxide intermediate and will reiterate this in the discussion of the RRDE data. However, without biasing the electrode to the anodic 4 Volt limit, current magnitudes decrease on subsequent cycles, supporting the notion that electrode passivation is experienced with incomplete removal of Li$_2$O$_2$ from the electrode reaction sites. Interestingly, in the voltammograms of Figure 3.3d, collected immediately after the twentieth sweep in Figure 3.3c, the peak currents are restored to the initial magnitudes when the anodic limit is extended to 4 V. The extension of the anodic limit
in Figure 3.3d produces a broad oxidative response which is centered near the potential labeled by $E_{pa3}$. Although the current magnitude of this oxidation peak is not large, it is essential to removal of the electrode passivation material, and without sweeping the electrode through this region of the voltammogram it is not possible to measure consistent reduction peak current magnitudes.

We infer from these results that the oxygen is first reduced to the superoxide and upon further cathodic bias it is reduced further to peroxide and finally to monoxide upon reaching the full cathodic limit. Simultaneously, it is clear that the superoxide undergoes a chemical decomposition side reaction which also leads to the formation of the peroxide film. Additionally, these results suggest the DMSO medium allows for the electrochemical removal of passivating reduction products which is not realized in other electrolyte media displayed in Figure 3.1. Such a behavior of the oxygen electrode in non-aqueous Li$^+$-conducting electrolytes to our knowledge has been observed for the first time here. The OER processes involving the oxidation of Li$_2$O appear to proceed through Li$_2$O$_2$ with no evidence for the superoxide intermediate formation step.

Further investigation of the reduction process was conducted via rotating disc electrode (RDE) voltammetry displayed in Figure 3.4a.
Figure 3.4. (a) Rotating Disc Electrode voltammograms collected at 100 mV s\(^{-1}\) in oxygenated 0.1 M LiPF\(_6\) / DMSO electrolyte at various rotation rates. (b) Theoretical Levich plots for the one and two electrochemical reduction of oxygen in 0.1M LiPF\(_6\) in DMSO overlaid with the experimentally obtained limiting currents in (a)

These experiments were conducted at a potential sweep rate of 100 mV s\(^{-1}\). Fast sweep rates of this magnitude, due to the lower amounts of electrochemical charge associated with them, are preferred to study this system as they allow voltammetric scanning without the excessive
deposition of the insulating product film associated with slower sweep rates. The limiting peak
currents obtained from the RDE voltammetry profile were analyzed using the Levich equation\(^{10}\)

\[
i_{l,c} = 0.62 n F A D_o^{2/3} \nu^{-1/6} C_o^{+} \omega^{1/2}
\]

By plotting the angular velocity, \(\omega\), of the various rotation rates as a function of the
experimentally obtained limiting currents as shown in Figure 3.4b a nearly linear correlation is
apparent with a linear correlation value of 0.997, indicating that the maximum in the cathodic
current magnitude is a consequence of the laminar flow controlled supply of dissolved oxygen to
the electrochemical interface. The slope for the experimental line of best fit is approximately
27% higher than the theoretical fit for a one-electron process. This is explainable by the large
applied over-potential required to reach the limiting regime of the RDE curve which allows for
the facilitation of a multi electron reduction process. The lack of a plateau feature, replaced
instead by a broad peak, in the RDE curve can be understood by consideration of Figure 3.5,
which shows an overlay with the voltammogram from a disc electrode in quiescent electrolyte.

**Figure 3.5.** Glassy Carbon disc voltammograms collected at 100 mV s\(^{-1}\) in oxygenated
0.1M LiPF\(_6\) in DMSO electrolyte in both quiescent and laminar flow medium.
The potential where reduction current magnitude begins to decrease in the RDE voltammogram is correlated with the potential at which a second reduction process is initiated in the quiescent solution voltammogram. As noted earlier this potential corresponds to the deposition of an insoluble electrically insulating reduction product ($\text{Li}_2\text{O}_2$) which begins to block the availability of the oxygen to reach the electrochemical interface and thereby prevents the realization of a plateau limiting current in such an experiment.

Additional insight of the RDE voltammetric profile was gained by including a gold ring electrode in a RRDE experiment. Prior to conducting the RRDE experiment, quiescent voltammograms displayed in Figure 3.6 were collected on a gold disc electrode in order to understand the potential dependence of the various Faradaic processes as they occur on a gold surface.

**Figure 3.6.** Gold disc voltammograms collected at 100 mV s$^{-1}$ in oxygenated 0.1M LiPF$_6$ in DMSO electrolyte at various cathodic sweep limits. The solid line marks the potential where superoxide oxidation on a gold surface is apparent.
The voltammograms were again collected with various cathodic sweep limits as conducted previously on a glassy carbon disc electrode. A nearly identical response was measured from both the glassy carbon and the gold electrodes. Most importantly it was shown that if the cathodic limit of the gold electrode is limited to 2.43 V or less, then the following anodic sweep will show an additional oxidative response which peaks at approximately 2.93 V. This initial anodic process is not detected in voltammograms in which the disc is scanned below 2.33 V as the superoxide species is further reduced at such high cathodic over-potential. Biasing the gold ring electrode to a potential of 2.93 V in the RRDE experiment allows for the selective oxidation of superoxide species generated at the disc interface as shown in Figure 3.7.

![Graph showing RRDE response at 500 rotations per minute collected in oxygenated 0.1M LiPF₆ in DMSO electrolyte at 40 mV s⁻¹ while the gold ring electrode was biased to 2.93 V. The ring response is plotted in dash-dot line style on the right hand current scale while the disc response is shown in solid line style on the left hand current scale.](image)

**Figure 3.7.** RRDE response at 500 rotations per minute collected in oxygenated 0.1M LiPF₆ in DMSO electrolyte at 40 mV s⁻¹ while the gold ring electrode was biased to 2.93 V. The ring response is plotted in dash-dot line style on the right hand current scale while the disc response is shown in solid line style on the left hand current scale.

These data unambiguously demonstrate the generation of a solution stabilized superoxide species which is transported to the ring interface and oxidized.
After correcting the ring electrode response according to the ring collection efficiency measured for the ferrocene/ferrocenium couple in a ferrocene solution, a comparison was made between the charge area under the reduction curve and the charge area under the oxidation response for both the disc and ring electrodes. The results of this analysis show that 92% of the charge from reduction is reversed through the sum of the oxidations at the ring and disc electrodes for one sweep cycle. This is close to unity, with the small deviation from unity explained by the differences in the kinetics between the superoxide oxidation and the ferrocenium oxidation.

We would like to note that that the oxidation of the peroxide film at the disc which appears as an anodic peak above 3.5 V does not simultaneously show any change in the current response at the gold ring held at 2.93 V. This result leads us to conclude that the peroxide oxidation does not proceed through the formation of superoxide intermediate; instead, it is directly oxidized to oxygen.

To our knowledge this is the first report of the detection of superoxide in an RRDE experiment utilizing a non-aqueous lithium cation electrolyte. In order to demonstrate the solvent medium’s role in facilitating these redox processes, the same RRDE experiment was also conducted in a 0.1 M LiPF$_6$ in acetonitrile electrolyte and is displayed in Figure 3.8.
Clearly there does not exist any soluble reduction intermediates in the acetonitrile medium in contrast to the DMSO medium.

3.3.2 Li/O₂ Full Cell Galvanostatic Studies

The preceding results in conjunction with the low volatility and high ionic conductivity of DMSO-based electrolytes prompt consideration of DMSO as a practical solvent for a rechargeable non-aqueous lithium air battery. Although there seems to be an opinion established
regarding the instability of a lithium foil in contact with the DMSO solvent, we have found no such evidence of instability. This holds true for both the pure DMSO solvent, the 0.1 M LiPF$_6$ in DMSO solution, and also for the 1M LiPF$_6$ in DMSO solution. This finding is also consistent with earlier investigations of organic chemistry “Lithium wire did not react with neat DMSO at temperatures up to 80 [°C].”\textsuperscript{12} However, there is one circumstance where the authors indeed noted a substantial extent of a gas-evolving chemical reaction occurring on the surface of a lithium foil upon contact with the DMSO solvent. Specifically, when a DMSO-wetted lithium foil is brought into a room atmosphere without any moisture barrier it will react quite readily. We believe this is a consequence of the high polarity of the DMSO solvent making it more miscible with water than many other organic solvents. Ultimately, we believe it is the water mixed in the DMSO that reacts with a lithium foil, not the DMSO itself.

A series of galvanostatic discharge and charge studies of full cells are discussed below. Figure 3.9 shows the galvanostatic charge/discharge profile obtained from a cell devoid of oxygen.
Figure 3.9. Galvanostatic charge discharge profile of a Lithium / 1M LiPF$_6$ in DMSO / Ketjen300 cell collected in an inert gas atmosphere. Both charging and discharging current magnitudes were fixed at 0.1 mA cm$^{-2}$. Capacity is expressed per gram of Ketjen carbon powder.

These results are important to affirm that the discharge behavior in the oxygen environment is indeed a consequence of the ORR product formation and also to establish the upper voltage limit that can be reached in cells without inducing the oxidation of the electrolyte itself. A substantial charging plateau is observed at 4.40 V indicating electrolyte oxidation and that the full cell should not be charged above 4.2 V in order to avoid the decomposition of the electrolyte medium itself. This charging plateau occurs at a potential slightly lower than the upper voltage limit of the 0.1M LiPF$_6$/DMSO cyclic voltammetry at a glassy carbon disc. This shift in the onset of the electrolyte oxidation is a consequence of the large magnitude of surface area of the Ketjen300 electrode in contrast to the glassy carbon disc electrode. This straightforward screening technique is essential to all investigations of novel electrolytes in the lithium air battery since oxidation of the electrolyte has been a common problematic occurrence with many media.
As mentioned in the Introduction, we have observed that DMSO-based Li/O\textsubscript{2} cells can be recharged with significantly less over-potential than cells utilizing other organic non-aqueous electrolytes. In order to exemplify this, Figure 3.10 displays the first cycle of two Li/O\textsubscript{2} cells one was assembled utilizing a TEGDME electrolyte, the other a DMSO electrolyte.

![Graph showing discharge capacity and cell voltage over time for DMSO and TEGDME electrolytes.](image)

**Figure 3.10.** Galvanostatic discharge of a Li / 1 M LiPF\textsubscript{6} in DMSO / O\textsubscript{2} cell and a Li / 1 M LiPF\textsubscript{6} in TEGDME / O\textsubscript{2} conducted at 0.1 mA cm\textsuperscript{-2}. Discharge capacity is normalized by the mass of the Ketjen300 carbon powder.

Clearly, a significant voltage advantage is present on both the discharge and charging steps of the cycling experiment, characteristic of enhanced energy efficiency for the DMSO cell. In terms of Coulombic efficiency it is noteworthy to mention that the TEGDME cell shown in Figure 3.10 is showing greater apparent Coulombic efficiency than the DMSO cell. This is not extremely surprising though considering the discharge capacity per carbon mass is twice as large for the DMSO cell, which corresponds to twice the amount of insulating discharge product being
deposited into the pores of the carbon electrode. It has been established\textsuperscript{5} that the electrochemical removal of the discharge products becomes more difficult as its deposition becomes more extensive in terms of the specific capacity of the cell in mAh per gram of carbon. We schematically illustrate this in Figure 3.16, which will be discussed further.

Figure 3.11a displays the full discharge to 2 V for a DMSO lithium oxygen cell. The majority of the discharge capacity occurs at a cell voltage of 2.76 V, which is markedly higher than discharge voltages reported in other non-aqueous electrolyte media. This higher discharge voltage can be directly translated to higher power delivery from a Li/O\textsubscript{2} cell with DMSO-based electrolytes. Even in the event that a secondary Li-O\textsubscript{2} battery with long cycle life is not developed, the DMSO electrolytes still offer a performance enhancement over the tetraglyme and carbonate electrolyte solvents for primary cells, and would likely facilitate higher rate capabilities as a consequence of its higher ionic conductivity.
Figure 3.11. (a) Galvanostatic discharge of a Li / 1 M LiPF$_6$ in DMSO / O$_2$ cell conducted at 0.1 mA cm$^{-2}$. Discharge capacity is normalized by the mass of the Ketjen300 carbon powder. (b) Cu$_{\text{K} \alpha}$ X-radiation diffraction pattern from the cathode after the discharge cycle shown in (a). Experimental background was collected from a sample of the substrate and Kapton seal only. Inset shows an expansion of the pattern between 2-theta values of 30 and 40 degrees.
Figure 3.11b shows the X-ray diffraction pattern obtained from the carbon cathode at the end of the discharge. In addition to two amorphous peaks generated from the carbon cloth substrate at 2-theta values of 43 and 78, degrees there clearly exists a substantial amount of crystalline material. Database matching of the experimental pattern confirmed that the two different crystalline phases are Li$_2$O$_2$ and LiOH.

Realizing that a substantial amount of lithium hydroxide material was being deposited on the cathode, a rigorous determination of the water content in the electrolyte was conducted by means of the Karl Fischer titration method. The Karl Fischer titration of the 1M LiPF$_6$/DMSO electrolyte solution had an average of 41.4 ppm H$_2$O with a standard deviation of 0.85. Assuming that the electrolyte contained 41 ppm H$_2$O, we calculate that the maximum amount of lithium hydroxide possibly formed by water contamination is approximately 13 $\mu$g. We then confirmed experimentally that 13 $\mu$g of lithium hydroxide mixed with 7 mg of Ketjen300 carbon black does not generate any measurable X-ray diffraction signal.

We propose that the lithium hydroxide is formed by a chemical reaction of the superoxide with DMSO. Prior investigations of the organic chemistry of DMSO have shown that bases like potassium t-butoxide will chemically react with DMSO, forming the methylsulfinyl carbanion CH$_3$SOCH$_2^-$, which can remain in the electrolyte as the Li salt CH$_3$SOCH$_2$Li.$^{12,13}$ It is reasonable to consider that the superoxide has a significant probability to be protonated by the weakly acidic DMSO via an acid base chemical reaction yielding a protonated superoxide intermediate, which subsequently undergoes further reduction to LiOH. Possible reactions between DMSO and superoxide to form LiOH are depicted in equations [7-8]

\[
\text{CH}_3\text{SOCH}_3 + O_2 \rightarrow \text{CH}_3\text{SOCH}_2^- + \text{HO}_2 \quad [7]
\]

\[
\text{HO}_2^- + e^- + \text{Li}^+ \rightarrow \text{LiOH} + \frac{1}{2} \text{O}_2^- \quad [8]
\]
The Li\(^{+}\)-containing DMSO electrolyte medium stabilizes and increases the lifetime of the superoxide as \(O_2^-\text{--}Li^+(\text{DMSO})_n\) as we described previously.\(^7\) The first consequence of this is the higher cell voltage as the initial one-electron reduction step of superoxide becomes the rate-determining step for the Li/O\(_2\) cell. Secondly, the stabilized superoxide has ample opportunity to undergo additional chemical reactions with DMSO leading to the formation of not only Li\(_2\)O\(_2\) but also LiOH. It is possible that the methylsulfinyl carbanion undergoes further reactions with the DMSO to form organic products. We have not investigated that in this study.

Figure 3.12 shows the discharge/charge cycles of a Li/O\(_2\) cell. The first charge at cell activation was conducted in order to confirm that charging capacity measured after a discharge in fact corresponds to the oxidation of the discharge products. Negligible charge capacity is measured in the cell when it was activated with a first charge. Following the full discharge to 2 V 48% of the discharge capacity was recharged on the subsequent charge step. Again the cathode was removed from the cell and scanned by X-rays for the presence of crystalline material. As shown in Figure 3.12b, only faint signals from crystalline material are present in the diffraction pattern. This result supports the notion that the charge capacity measured is due to the oxidation of the crystalline materials deposited during the discharge cycle.
Figure 3.12 (a) Galvanostatic charge/discharge/charge schedule of a Li / 1 M LiPF$_6$ in DMSO / O$_2$ cell conducted at 0.1 mA cm$^{-2}$. Discharge capacity is normalized by the mass of the Ketjen300 carbon powder. (b) Cu$_{\text{K\alpha}}$ X-radiation diffraction pattern from the cathode after the final charge cycle shown in (a). Experimental background was collected from a sample of the substrate and Kapton seal only.
Figure 3.13 shows the repeated cycling of a Li/O\textsubscript{2} cell between the voltage limits of 2 V and 4.35 V.

![Graph showing cell voltage over time](image)

**Figure 3.13.** Galvanostatic cycling of a Li / 1 M LiPF\textsubscript{6} in DMSO / O\textsubscript{2} cell conducted at 0.1 mA cm\textsuperscript{-2} between 2 and 4.35 Volts.

The first charge efficiency is only about 50% of the discharge. The capacity measured in the second discharge is nearly equal to the capacity realized in the first charge. The cell capacity quickly faded in subsequent cycles. Although this capacity fading is in contrast to the cycleability measured in the half cell voltammetry experiments discussed earlier, it is a reasonable finding upon consideration of the inherent differences between the two techniques. In the half cell voltammetry, the carbon electrode potential is controlled to sweep in a relatively fast manner, resulting in the deposition of only a thin film of reduction products. Even if the reduction products are insulating and may passivate the electrode surface, since the film is thin they could
be fully reduced. This explains the full reduction of oxygen to Li$_2$O in the CV experiments. In contrast, the full galvanostatic experiments will draw a constant current between the two electrodes for a long duration of time causing the following two vastly different effects. Firstly, the deposition of product is significantly more substantial than in the CV half-cell, and secondly, the potential of the Li/O2 cell remains relatively constant at the first oxygen reduction reaction since there is a continuous supply of oxygen reagent. Therefore, in the full cell experiment only one electrochemical charge transfer process will continue to occur, which facilitates the formation of Li$_2$O$_2$.

To further emphasize the factors limiting the rechargeability of the cell at full depth of discharge, two other cells were cycled at low depths of discharge and charged as depicted in Figures 3.14 and 3.15.
Figure 3.14. (a) Galvanostatic cycling of a Li / 1 M LiPF$_6$ in DMSO / O$_2$ cell discharged to 10% depth of discharge at 0.1 mA cm$^{-2}$ and charged to 4.35 V. (b) Discharge capacity is normalized by the mass of the Ketjen300 carbon powder. Cumulative discharge capacity is the sum of all the consecutive discharge steps excluding the last step.

Such low depth of discharge/charge cycles yields a significantly greater number of cycles with many nearly of 100% Coulombic efficiency in contrast to the cells discharged fully. Furthermore, decreasing the charging current enhanced the cumulative discharge capacity
significantly, suggesting the Coulombic efficiency of the charging process is being limited by the kinetics of the electrochemical OER process.

![Diagram](image)

**Figure 3.15.** (a) Galvanostatic cycling of a Li / 1 M LiPF$_6$ in DMSO / O$_2$ cell discharged at 0.1 mA cm$^{-2}$ to 10% depth of discharge and charged at 0.05 mA cm$^{-2}$ to 4.35 Volts. (b) Discharge capacity is normalized by the mass of the Ketjen300 carbon powder. Cumulative discharge capacity is the sum of all the consecutive discharge steps excluding the last step.

Previously, we described that the end of discharge of the Li-air cell occurs when the insoluble discharge products (Li$_2$O$_2$ and LiOH in this case) deposited in the carbon electrode
pores chokes this porous cathode and disables it from further facilitation of the discharge process. Remarkably, as noticed in the cell in Figure 3.13, a portion of the discharge capacity can be recharged and a few additional low capacity cycles can be obtained. This can be understood by considering that during charge the discharge product deposited very near to the carbon particle surface gets oxidized first. After a certain fraction of the discharge product has been removed from the carbon surface in the charge, the remaining material is separated from the surface and loses electronic contact with the carbon and is therefore not electrochemically oxidized. This is schematically depicted in Figure 3.16.

![Illustration of the porous carbon electrode](image)

**Figure 3.16.** Illustration of the porous carbon electrode (a) prior to cycling (b) after full depth of discharge (c) after completion of a charge cycle. Isolation of discharge products in the void of the carbon pores prevents full Coulombic efficiency.

The buildup of these isolated deposits of discharge products inhibits the transport of additional reagent to the electrochemical interface and leads to a permanent choking of the carbon’s capacity in a very few cycles. This is in large part overcome when the discharge is limited to lower amounts of discharge capacity per carbon electrode surface and the result is improved recharge efficiency. Although theoretical DFT calculations have presumed that the Li$_2$O$_2$ electrochemical oxidation initiates at the outermost surface of the Li$_2$O$_2$ crystallites,$^{14}$ a recent report shows experimental evidence confirming that the electrochemical charging process
actually occurs at the carbon-Li$_2$O$_2$ interface\textsuperscript{15} as we have reported. A thorough understanding of the charging process will be critical to the development of a secondary Li/O$_2$ battery technology.

The data presented here thus provides important information relevant to the eventual engineering design of Li-air cells, confirming that a lithium foil electrode is indeed stable in DMSO electrolytes as previously found in neat DMSO.\textsuperscript{12} Harvesting the full potential of the Li-O$_2$ electrochemistry in the DMSO medium will be an ongoing effort.

3.4 Conclusion

In conclusion, the cyclic voltammetry results presented herein support the notion that the DMSO-based electrolyte medium offers a unique ability to facilitate the full reversible reduction of the oxygen electrode in the non-aqueous Li-air cell over multiple cycles. For the first time, full galvanostatic cycles of the oxygen electrode in a Li-air cell with a DMSO-LiPF$_6$ electrolyte has been demonstrated. The discharge plateau voltage of such a cell is markedly higher than cells discharged in TEGDME or organic carbonate-based electrolytes under comparable conditions. We conclude that the stabilization of the superoxide intermediate by solvated Li$^+$ leads to a lowering of the activation energy barrier for the reduction process, and the initial one-electron reduction reaction of oxygen to form superoxide becomes the rate-determining step in Li-air cells. This explains the higher discharge voltage of the DMSO based cell which certainly represents an advantageous Li/O$_2$ battery electrolyte. The presence of a stable and soluble superoxide intermediate is confirmed via the ring electrode response in an RRDE experiment. The superoxide stabilization however lends opportunity for secondary reaction pathways involving DMSO which accounts for additional discharge products in the Li/O$_2$ cell. This notion is confirmed by the X-ray diffraction analysis of a cathode after a full discharge showing the
presence of both the Li$_2$O$_2$ and LiOH. Discharge/charge cycling data obtained from the Li-air cells provide information on the factors affecting its rechargeability.

3.5 Acknowledgement

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3.6 References


Chapter 4

Cobalt Phthalocyanine Catalyzed Lithium-Air Batteries

4.1 Introduction

As discussed in the previous chapters, our recent investigations of oxygen reduction reactions (ORR) in non-aqueous electrolytes have revealed that the reduction mechanism is influenced by the Lewis acidity of the cation of the supporting electrolyte (ion-conducting electrolyte salt) and the donor number (DN) (or the Lewis basicity) of the solvent medium.\(^1\) The overall reaction in a Li/O\(_2\) battery cell is now recognized to be the two-electron process shown in equation [1] below. The four-electron reduction of O\(_2\) converting it to Li\(_2\)O as depicted in equation [2] is not generally achieved in Li-O\(_2\) battery cells due to kinetic factors.\(^5\)

\[
2 \text{Li} + O_2 \rightarrow \text{Li}_2O_2 \quad \text{[1]}
\]

\[
4 \text{Li} + O_2 \rightarrow 2 \text{Li}_2O \quad \text{[2]}
\]

The theoretical specific energy of the Li-air battery with the discharge reaction shown in equation [1] is 3505 Wh kg\(^{-1}\), which is 33% less than when the reaction is that displayed in equation [2] with a specific energy of 5200 Wh kg\(^{-1}\). It is believed that the use of appropriate catalysts in the carbon cathodes of Li-air cells could promote full reduction of O\(_2\) to Li\(_2\)O, although most of the studies reported to date utilizing a variety of catalysts have not demonstrated the cell discharge reaction depicted in equation [2].\(^6\)\(^22\) An effective ORR catalyst will also lower the activation energy for O\(_2\) reduction and raise the load voltage of the Li-air cell, thereby contributing to an additional increase in the practical energy density of Li-air batteries. A review of catalysis in non-aqueous Li/O\(_2\) battery was recently published.\(^23\)
Cobalt phthalocyanine (CoPC) has been investigated as a non-precious metal catalyst for the ORR in aqueous PEM fuel cells.\textsuperscript{24-29} The structure of this macrocycle is shown below in Figure 4.1.

\textbf{Figure 4.1.} Molecular structure of Cobalt (II) phthalocyanine

These investigations show that heat treatment of the CoPC-containing carbon yields a catalytically active electrode material in both alkaline and acidic electrolyte environments. In their original work on the non-aqueous Li-air battery, Abraham et al showed\textsuperscript{4} that a catalyzed cathode composed of carbon black and CoPC pyrolyzed at temperatures between 600 and 800 °C exhibited catalytic activity for the oxygen reduction reaction, manifested as an increase in the discharge load voltage of the Li-air cell and improved rechargeability of the discharged cell. Mechanistic details of the observed ORR catalysis by CoPC in the non-aqueous Li-air cell have not yet been studied and are the focus of this work.

Here, we report on the preparation and characterization of the CoPC-containing carbon black electrode which results upon pyrolysis of the carbon black/CoPC mixture at 600 °C,
referred to as Co600 electrode throughout this Chapter. A detailed understanding of the changes in oxygen reduction reactivity brought forth by the Co600 reaction center in the porous carbon electrode is obtained from O$_2$ half-cell voltammetry in conjunction with the X-ray Absorption Spectroscopy (XAS), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) analysis of discharged Li-O$_2$ cell cathodes.

It is shown that the rate-determining step in the ORR of the CoPC catalyzed Li-air cell is the formation of the catalyst-stabilized superoxide, O$_2^{-}$, formed from the one electron reduction of oxygen. The stabilization of O$_2^{-}$ by the CoPC catalyst lowers the activation energy for O$_2$ reduction and increases the load voltage of the cell. The X-ray diffraction data obtained from discharged cathodes of Li-O$_2$ cells show that the catalyst also promotes the full reduction of O$_2$ to O$^{2-}$, and improves the rechargeability of the Li-air battery as demonstrated by lower charging voltage. These results are reported here.

4.2 Experimental Methods

4.2.1 Preparation of Co-catalyzed high surface area carbon powders

Carbon black samples containing cobalt catalyst were prepared as previously described$^{27}$. Briefly, purum grade cobalt phthalocyanine as received from SigmaAldrich was dissolved in a concentrated sulfuric acid solution after which carbon black was added under stirring until a homogenous paste was formed. The mass of the high surface area carbon added was set so that the solid phase of the slurry contained 2 wt.% cobalt(II). The paste was then instantaneously diluted via directly transferring into a large volume of deionized water, forcing CoPC to precipitate out of solution and deposit onto the carbon black. Aliquots of the Co600 catalyst powder were separately synthesized with both the Vulcan XC72R and Ketjen300 carbon black powders. The particulate suspension was then separated via vacuum filtration and the resulting
powder was dried under vacuum at 70°C. Dried powder samples were then loaded into an argon purged quartz furnace tube and sintered at 600 Celsius for four hours.

4.2.2 Preparation of dispersions for thin film analysis

High surface area carbon ink suspensions for thin film voltammetry experiments were created by dissolving a polyvinylidene fluoride (PVDF) Kynar® 2801 binder material into a N-methyl-2-pyrrolidone solvent. Catalyzed or uncatalyzed carbon powder was then added (90:10 powder:binder by mass) to the binder solution and sonicated until a homogenous ink suspension resulted. Microliter aliquots of the ink suspension were cured onto a 0.196 cm$^2$ glassy carbon working electrode substrate at 80°C under vacuum, creating carbon/catalysts films of 100 μg cm$^{-2}$.

4.2.3 Half-cell voltammetry measurements

Anhydrous grade ≥99.8% acetonitrile (CH$_3$CN), purum grade ≥98.0% tetraethylene glycol dimethyl ether (TEGDME) anhydrous grade ≥99.5%, 1,2-dimethoxyethane (DME), and electrochemical grade tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were purchased from SigmaAldrich and used as received. Electrochemical grade ethylene carbonate (EC) was purchased from Ferro Corporation and used as received. Purolite® lithium hexafluorophosphate (LiPF$_6$) certified to contain less than 20.0 ppm water was purchased from Novolyte Technologies and used as received. Metals basis 99.9% Li foil was used as received from Alfa Aesar company. Upon receipt from the vendor, all these reagents were immediately stored in an MBraun Labmaster 130 argon-filled glovebox with water vapor concentrations maintained below 1 ppm. Electrolyte formulations were carried out in the dry atmosphere glovebox using class B polypropylene volumetric flasks and an APX 153 top loading balance from Denver Instruments.
Cyclic voltammetry experiments were conducted utilizing a PGSTAT30 potentiostat equipped with a scangen module from Ecochemie Inc. A polypropylene jar from Nalgene® was employed as the cell container and an in-house fabricated polypropylene lid was put in place to keep the electrolyte solution removed from the ambient room conditions and to hold the electrodes in a stationary fashion, as described previously\textsuperscript{1,2}. A platinum gauze was utilized as the counter electrode, the working electrode prepared as described above, and an in-house assembled reference electrode made from a silver wire contained in a 100 mM TBAPF\textsubscript{6} 10 mM silver nitrate/CH\textsubscript{3}CN solution in a borosilicate glass sleeve, were affixed in the cell. The reference electrode of the cell was separated from the working cell by a Vycor polymer frit. Oxygen gas was purged into the cell through a solvent reservoir in order to solvate the working gas flow thereby minimizing the evaporation of the electrolyte solvent.

The Ag/Ag\textsuperscript{+} reference cell was routinely calibrated in separate cyclic voltammetry experiments conducted in tenth molar TBAPF\textsubscript{6} CH\textsubscript{3}CN electrolytes with the addition of 1 mM Ferrocene. The measured potential scale was then adjusted to the Li/Li\textsuperscript{+} scale for plotting purposes based on the ferrocene/ferricenium experimental data.

\textbf{4.2.4 In-situ X-ray absorption spectroscopic measurement}

A Teflon fluorescence cell container previously described\textsuperscript{30} was used to house a sandwich style electrode assembly for simultaneous collection of voltammetric and spectroscopic data for the Co-catalyzed air cell cathodes. The cathode wetted with 1M LiPF\textsubscript{6} in TEGDME was separated from the lithium anode via a Celgard® polypropylene Li\textsuperscript{+}-ion conducting membrane. A gas purge line was plumbed into the side-wall of the cell container so as to flow through the cathode window with the gas of choice (either argon or oxygen). The cell was installed to the
beam-line experimental table with the cathode window at a 45° relative to the fluorescence X-ray detector, allowing for measurement of both transmission and fluorescence mode signals.

4.2.5 X-ray absorption data processing

All the experimental XAS data were processed utilizing the IFFEFIT suite\textsuperscript{31} version 1.2.11. Each datum is calibrated to the same energy scale by carefully aligning each scan of a cobalt reference foil which had been collected simultaneously during each sample scan. The Athena software was utilized to achieve the background subtraction and normalization via the AUTOBK\textsuperscript{32} algorithm. Processed data was imported into the Artemis software for the purpose of fitting the Fourier transform.

4.2.6 Fabrication of Li/O\textsubscript{2} cell cathodes

Powder dispersions were formulated in 1-methyl-2-pyrolidinone solutions containing already dissolved kynar 2801 binder material. The powder to binder ratios of these inks were fixed at 90:10 by mass. The inks were delivered via pipette to one inch diameter precut Panex® conductive carbon cloth substrates and cured under vacuum at 80 Celsius. Typical mass loadings were between 2-4 mg cm\textsuperscript{-2}.

4.2.7 Li/O\textsubscript{2} cell assembly procedures

All assembly procedures were carried out in an MBraun Labmaster 130 Argon dry atmosphere glove box with H\textsubscript{2}O vapor levels maintained below 1 ppm. The cathodes were saturated with electrolyte under vacuum in the glove box’s antechamber at approximately 1 Bar below atmosphere. A 32 mm diameter lithium foil disc was cut with a steel di-cut apparatus from a 1.5 mm thick ribbon as received from AlfaAesar. A 50 mesh copper current collector was pressed into the lithium foil between two polypropylene sheets. The copper current collector was screwed into the stainless steel electrode terminal via a stainless steel bolt and nut mounting hardware. A circular cut out of Celgard® polypropylene Li\textsuperscript{+}-ion conducting membrane was
placed on top of the anode. The cathode was then removed from the antechamber vacuum and placed onto a paper Kimwipe, drained of excess electrolyte, weighed (approximately 150-200 mg of electrolyte per cathode), and placed on top of the Celgard® membrane with the high surface area carbon material faced inward to the lithium foil. An aluminum Dexmet cut out was placed on top of the cathode to supply a uniform compressing force between the electrode areas and allow for current collection through the cathode cell terminal.

4.2.8 Post discharge X-ray diffraction analysis

Analysis was conducted via a Bragg-Brentano para-focusing UltimaIV powder diffractometer utilizing a Cu K$_\alpha$ radiation source from Rigaku. Sample preparation was conducted in the dry atmosphere glove box. Cathodes were cut to fit the dimension of the quartz sample holder and then sealed in the sample holder by a film of 2.5 mil thick Kapton® polyimide tape.

4.2.9 Post discharge Scanning Electron Microscopy analysis

Images were gathered using the secondary electron signal generated in a Hitachi S-4900 FSEM instrument. The inner face of both the anode and cathodes were imaged separately with an accelerating voltage of 3.0 keV. Sample preparation involved rinsing the electrode in 1,2 dimethoxyethane to remove residual electrolyte and then evaporating the solvent in the glovebox antechamber. Samples were then carefully mounted on a carbon adhesive stub and brought to the SEM affixed to the sample holder in a sealed aluminized bag. The sample holder was then quickly locked to the specimen rod of the SEM and brought into the SEM vacuum atmosphere. Each sample is exposed to the room atmosphere for approximately 30 seconds while affixing the sample holder to the specimen rod.
4.3 Results and Discussions

4.3.1 Structural identity of the Co600 catalyst material
Structural changes produced from the pyrolysis of CoPC dispersed on high surface area carbon have been documented previously.\textsuperscript{26-28,33} Through a study of the thermogravimetric analysis conducted by Abraham et al it was shown that the macrocycle dispersed on a high surface area carbon remains intact upon heat treatment up to 600 °C.\textsuperscript{33} It should also be noted that pyrolysis of CoPC (C\textsubscript{33.3}H\textsubscript{15.3}N\textsubscript{8.3}Co) (without carbon) at 600 °C results in small structural changes, primarily involving the removal of some hydrogens, leaving a residue with the composition of C\textsubscript{33.9}H\textsubscript{11.4}N\textsubscript{9.1}Co. These results together with the IR spectra of the residues indicate that in the Co-600 carbon catalyst powder the CoPC chemical structure mostly remains intact. The CoPC acquires an amorphous morphology with some loss of hydrogen in the process of chemically attaching itself to the carbon black. We have confirmed this catalyst structure in this study using X-ray absorption spectroscopy (XAS) and X-ray diffraction analysis (XRD). A comparison of the X-ray Absorption Near Edge Spectra (XANES) for the as-received CoPC material, the Co600 material, as well as three cobalt standard materials (having a cobalt oxidation state of zero, two, and three) is shown in Figure 4.2.


Figure 4.2. Overlay of XANES spectra from Cobalt metal foil, Co-800, Co-600, CoPC, and CoF₃. The arrow indicates the shift to higher ionization energy as the cobalt atoms oxidation state increases.

Specifically, the edge peak feature, a spectroscopic signature of the planar Co-N₄ geometry, which peaks at 7716 eV remains intact after pyrolysis at 600 °C, confirming that the thermal treatment is mild enough to avoid degradation of the macrocycle. The XANES data were Fourier transformed to R-Space and a very reasonable first and second shell fit of the data to the cobalt phthalocyanine model was achieved as shown in Figure 4.3 and reported in Table 4.1.
Figure 4.3. (a) Near edge X-ray absorption spectra for neat CoPC and Co600 on Vulcan carbon. (b) The $k^3$-weighted Fourier Transform of the Co600 spectrum and its fit overlaid with the three photoelectron scattering paths of the first and second shell. Inset shows the macrocycle model with the various neighbor scattering atoms coordinate with the fitting profiles in color.

<table>
<thead>
<tr>
<th></th>
<th>CoN</th>
<th>CoC</th>
<th>CoN (3\textsuperscript{rd} shell)</th>
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<tbody>
<tr>
<td>CN</td>
<td>R (Å)</td>
<td>CN</td>
<td>R(Å)</td>
<td>CN</td>
</tr>
<tr>
<td>Co600</td>
<td>4.2(±0.4)</td>
<td>1.89(±0.01)</td>
<td>7.5 (±2.3)</td>
<td>2.93(±0.01)</td>
</tr>
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</table>

Table 4.1. EXAFS fitting results for the pristine Co600 cathode. $S^2$ fixed at 0.76 as obtained by fitting the reference foils. Fits were done in $R$-space, $k^3$ weighting. $0.9 < R < 3.17$ Å and $\Delta k = 2.82 – 13.15$ Å\textsuperscript{-1} were used.
Additionally, the XRD patterns measured from the Co600 and Co800 powder samples are compared in Figure 4.4.

![X-ray diffraction pattern](image)

**Figure 4.4.** X-ray diffraction pattern measured from the CoPC on Vulcan powder samples heat treated at 600°C and 800°C. The lowest plot shows the database pattern corresponding to metallic cobalt.

Although there is a metallic cobalt signal present in the powder that was processed at 800°C, the absence of this signal in the sample processed at 600°C further confirms that the macrocycle remains intact in the CoN₄ configuration. These results clearly elucidate the local chemical structure of the Co600 catalyst material.

**4.3.2 Catalyst-superoxide complex formation revealed by cyclic voltammetry**

A comparison of the voltammetric response from a porous film of the high surface area carbon with and without the Co600 catalyst is shown in Figure 4.5.
Figure 4.5. (a) Cyclic Voltammograms of the high surface area Vulcan carbon, planar vitreous carbon disc, Co600 catalyzed carbon film, all collected at 100 mV s\(^{-1}\) in oxygenated 0.1M LiPF\(_6\) CH\(_3\)CN. The current scale of the high surface area carbon is shown on the right hand scale for comparison. (b) Cyclic Voltammograms of the Co600 film collected at different sweep rates. Peak markers distinguish the two cathodic waves. (c) Peak current density values for each of the two cathodic waves plotted as a function of the square root of the sweep rate. Error bars indicate the standard deviation for each peak current average. The solid lines represent the line of best fit for each of the two experimental waves. The theoretical Nicholson Shain model for a one and two electron transfer process are shown as dashed lines in black and red respectively.
These voltammograms were collected from an oxygen-saturated solution of 0.1M LiPF$_6$ in acetonitrile (CH$_3$CN). This electrolyte medium was chosen for the initial studies because of its high ionic conductivity, wide electrochemical window, and the previously generated baseline ORR data$^2$, which allowed for a judicious and thorough analysis of the current-voltage response. The voltammogram from the Co600 catalyst clearly shows a substantial positive shift in the onset of the ORR potential and a stepwise sequence of two convoluted, but resolved, reduction waves. This response is markedly different from the response of the uncatalyzed working electrode, which shows only one reductive wave. The un-catalyzed electrode response is similar for both the planar vitreous carbon disc and for the catalyst-free high surface area Vulcan carbon films. The current density for the high surface area carbon film is greater than that for the planar carbon and the CoPC-treated carbon due to the larger surface areas of the pristine carbons.

Further details of the Co600 catalyst carbon film response were discerned from studying the effect of sweep rate on the reduction peak magnitudes for each of the two waves. Figure 4.5b shows the response of the film at the sweep rates of 10, 50, 100 mVs$^{-1}$ separately. As highlighted by the peak markers in Figure 4.5b, the relation between sweep rate and peak current magnitudes is different for each of the two cathodic processes. In Figure 4.5c we plot the peak current magnitudes as a function of the square root of the sweep rate for each cathodic process measured from the Co600 catalyst film at four different sweep rates. Linear regression analysis of the experimental peak currents indicate a strong linear correlation for both waves and are included as solid lines overlaid in Figure 4.5c. The regression for the first reduction wave intercepts the origin perfectly, indicative of a process controlled by diffusion forces. The regression for the second wave intercepts the ordinate of the plot above the origin, suggesting the experimental magnitudes are being controlled not only by pure diffusion forces. This finding is
consistent with the previously established\textsuperscript{2} notion that the interface is passivated by the O\textsubscript{2} reduction products, forming an insulating Li\textsubscript{x}O\textsubscript{x} film, which begins to foul the interface as the electrode potential is swept cathodically. The passivation effect was described at length in Chapters 2 and 3.

The Nicholson-Shain equation \cite{3} for an irreversible electrode process was utilized by applying already established properties for ORR in CH\textsubscript{3}CN-based electrolyte.\textsuperscript{2,35}

\[
i_{p,c} = (2.99 \times 10^{-5}) n (n^* \alpha)^{1/2} D_o^{1/2} C_a^{1/2} \nu^{1/2}
\]

\[\text{[3]}\]

A close fit of the data to the Nicholson Shain equation was achieved by keeping the transfer coefficient, alpha equal to 0.6, and the number of electrons transferred in the rate determining step, n*, equal to 1 for the first process in the voltammogram. The slope of the linear regression for the second reduction wave is slightly more than twice as large as the regression for the first wave, which strongly suggests the first process is a one electron reduction while the second wave more closely resembles a two electron process.

These voltammetric data on the catalyzed electrode together with the XANES data discussed below support the view that the first reduction reaction of O\textsubscript{2} is the formation of superoxide (O\textsubscript{2}•⁻) in a one-electron reduction reaction, which is complexed by the CoPC catalyst. Further reduction of the catalyst-O\textsubscript{2}•⁻ complex is achieved through chemical and electrochemical processes to form, as discussed below, ultimately, Li\textsubscript{2}O, the four electron reduction product of O\textsubscript{2}.

Although the CH\textsubscript{3}CN medium was effective in the half-cell studies, it cannot be utilized in the full cell due to its reactivity with the lithium foil. Therefore, we conducted our full cell evaluation utilizing an EC:DME and a TEGDME-based electrolyte. Figure 4.6a shows the half-
cell voltammetric response of the different electrodes measured in EC:DME is similar to the response measured in the CH$_3$CN medium with respect to the presence of both cathodic waves.

**Figure 4.6.** (a) Cyclic Voltammograms of the high surface area Vulcan carbon, planar vitreous carbon disc, Co600 catalyzed carbon film all collected at 100 mV s$^{-1}$ in oxygenated 0.1M LiPF$_6$ in 1:1 EC:DME. The current scale of the high surface area carbon is shown on the right hand scale for comparison. (b) Galvanostatic discharge curves for both an uncatalyzed Vulcan carbon and a Co600 on Vulcan carbon cathodes measured at 0.1 mA cm$^{-2}$ in 1M LiPF$_6$ in 1:1 EC:DME.

It is noteworthy to mention that the overpotentials required for the oxygen reduction process in the EC:DME-based electrolyte are greater than those found in the CH$_3$CN-based electrolyte. The oxygen reduction peak potential of the glassy carbon disc shown in Figure 4.6a is consistent with that found by others in DME-based electrolytes.$^{2,36}$ This shift to lower onset potentials is indicative of the previously established instability of the superoxide intermediate and its propensity to undergo side reactions with DME. The strong influence of the catalyst on the ORR activity is demonstrated in the Li/O$_2$ cells in Figure 4.6b. The discharge curve collected in an EC:DME-LiPF$_6$ electrolyte clearly shows the Co600-containing carbon provides a 200mV higher
voltage advantage during the discharge process. These data in conjunction with the aforementioned voltammetric data provide evidence that the Co600 electrode is lowering the activation energy for the initial one electron reduction of O₂. The superoxide intermediate thus formed is stabilized through an acceptor/donor complex formation involving interactions between the partially filled Co²⁺ 3d orbitals and the superoxide 2p molecular orbitals. Both these orbitals have a lone unpaired electron in their valence shell as shown in Figure 4.7.

![Molecular orbitals configurations of O₂⁻ and Co²⁺.](image)

**Figure 4.7.** Molecular orbitals configurations of O₂⁻ and Co²⁺. Electrons native to the Co²⁺ atom are represented by arrows whereas the electrons shared with the nitrogen ligands are represented by dots. Unpaired electrons are highlighted in red font style.

A pairing of the lone electron in the superoxide valence shell with the lone electron in the Co 3d band leads to a catalyst-stabilized superoxide complex.

**4.3.3. In-situ XANES Spectra for Co600 Carbon Catalyst**

The XANES spectral features of the Co600 catalyst were followed during a voltammetric sweep in a tetraglyme-based electrolyte which has very low solvent evaporation rates while the cell is being discharged with exposure to O₂. The potential range was 1.5 to 3.5 V as indicated by the voltammetric response from the spectro-electrochemical cell provided in Figure 4.8b. Data were collected for O₂ reduction on a Co600 cathode in-situ, separately under argon flow and oxygen gas flow.
Figure 4.8.(a) Theoretical and experimental $\Delta \mu$ curves for the Co600 macrocycle. Experimental spectra were collected during the cathodic sweep in-situ with and without oxygen dissolved in the 1M LiPF$_6$ in TEGDME electrolyte. The spectrum collected from the cell prior to gas flow or application of potential bias was utilized as the subtraction reference. The two models shown above the plot were used as the inputs to the FEFF 8.0 code to generate the theoretical signature. (b) Typical Voltammetric response of a Ketjen300 carbon working electrode in the two electrode in-situ fluorescence cell with and without oxygen gas flowing through the cathode compartment. The electrolyte was 1M LiPF$_6$ in TEGDME and the sweep rate is 10 mV s$^{-1}$.

Although only small changes to the XAS signal were apparent, comparisons of difference spectra from the cathode using the initial open circuit spectrum as the subtraction reference proved insightful. Shown in Figure 4.8a is the experimental difference spectra with and without the oxygen in the electrolyte overlaid with the difference spectra ($\Delta \mu$) generated from FEFF 8.0$^{37}$ calculations simulating the presence of an oxygen atom in an atop position. This delta Mu (
Δµ) analysis for studying the role of catalysts on ORR is well recognized as being sensitive to the detection of surface adsorbates.\textsuperscript{38-41} The strong similarity in the line shape of the theoretical and experimental curves is indicative of an oxygen adsorbate on the cobalt center. This finding is consistent with the Co600 catalyst being involved in the facilitation of the ORR but without undergoing structural changes to the local coordination chemistry of the macrocycle around the Co atom. Figure 4.9 provides an illustration of this effect. We conclude from these findings that the Co moiety participates in ORR catalysis by lowering the activation energy barrier for the electron transfer to convert the oxygen reactant to the superoxide intermediate.

![Figure 4.9](image.png)

**Figure 4.9.** Graphical illustration of the chemisorption of dissolved oxygen to the Co600 structure and subsequent one electron reduction of oxygen to form Co-$O_2^-$ complex which is stabilized within the inner Helmholtz plane of the cathode double layer.

A study of the changes in the XANES spectrum as a consequence of the galvanostatic discharge process is shown in Figure 4.10.
Figure 4.10. (a) Galvanostatic discharge curve of a Co600 cathode conducted at 0.1 mA cm$^{-2}$ in oxygenated 1M LiPF$_6$ in 1:1 EC:DME electrolyte. (b) X-ray absorption spectra of the pristine and discharged cathode. (c) The $k^2$-weighted Fourier transform of the discharged cathode and the corresponding first shell fit overlaid with the first shell photoelectron scattering paths.
The discharge process has the effect of suppressing the intensity of the edge peak feature at 7716 eV. This is caused by the establishment of an axial ligand interaction between the Co atom and the oxygen molecule which partially occupies the 4p\textsubscript{z} orbital of the Co. Simultaneously, the transition to the 4p\textsubscript{xy} orbital is enhanced after the discharge which is explained by the electron withdrawing effects of the oxygen species which borrows electron density from the cobalt’s ligand-nitrogen.

These changes to the XAS spectrum of the Co600 material were further analyzed by fitting the experimental data of the discharged cathode in Fourier Transformed R-space as shown in Figure 4.10c. The most notable feature of the discharged cathode’s spectrum in R-space is the prominence of the peak at approximately 1.7 Å which still represents the most intense signal of cobalt’s first shell. This confirms that the discharge process does not destroy the Co-N\textsubscript{4} local chemical environment as shown in the result in Table 2 below. The Co-N coordination number is close to 4 for both the pristine and discharged Co600 electrodes. The increase in the magnitude of the Fourier transform at 2 Å after discharge is consistent with the presence of a Co-O bond in the first shell of the cobalt. This can be modeled by a fit which includes the photoelectron scattering paths of both the CoPC material and also the scattering Co-O path of a Co(II)O oxide material.

<table>
<thead>
<tr>
<th></th>
<th>CoN</th>
<th>CoO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN R (Å)</td>
<td>CN R (Å)</td>
<td>σ\textsuperscript{2} \times 10\textsuperscript{-5}</td>
</tr>
<tr>
<td>Discharged Co600</td>
<td>4.2(±1.2) 1.89 (±0.02)</td>
<td>2.3(±0.5) 2.08 (±0.02)</td>
</tr>
</tbody>
</table>

Table 4.2. EXAFS fitting results for the fully discharged Co600 cathode. S\textsuperscript{2} fixed at 0.76 as obtained by fitting the reference foils. Fits were done in R-space, k\textsuperscript{2} weighting. 1.0 < R < 3.0 Å and \( \Delta k = 2.47 - 11.64 \text{ Å}^{-1} \) were used.
4.3.4 Mechanistic support from XRD analysis of Li/O₂ cell discharge products

Analysis of the XRD patterns of the Li/O₂ cell discharge products provide further insights on Co600 catalysis. Figure 4.11a shows the voltage versus capacity profiles of two cells discharged to 2V; one with a Co600 catalyzed Ketjen black carbon cathode the other an uncatalyzed Ketjen black carbon cathode.
Figure 4.11. (a) Galvanostatic discharge curves for both an uncatalyzed Ketjen300 carbon and a Co600 on Ketjen carbon cathodes. Inset shows an expansion of the voltage scale between 1.75 and 3.0 V. (b) X-ray diffraction pattern collected from both cathodes after the discharge shown in (a). Bar plots show the database RIR patterns for the LiOH, Li₂O₂, and Li₂O phases. Inset shows an expansion of the plot between 30 and 40 two-theta. (c) The X-ray diffraction patterns collected from the same (as in b.) Co600 cathode over time consecutively, while the electrode is sealed from the atmosphere in polyimide tape. Control scans are also overlaid to show the effect of the radiation on the electrolyte in the absence of a discharge process.
The Figure 4.11b displays XRD patterns measured from each cathode at the end of discharge. The uncatalyzed cathode clearly has a significant quantity of crystalline lithium peroxide product, a result consistent with our previous findings, and of others. In the case of the catalyzed cell the diffraction signal from the peroxide product is significantly less intense than the aforementioned uncatalyzed electrode albeit after comparable discharge capacity. The peroxide phase is still present in the catalyzed cathode, however the pattern also shows an additional diffraction signal centered at a Bragg angle of 33.6 degree two theta. The presence of this signal can be explained as a reflection from the (1,1,1) plane of an Fm3m Li$_2$O. Previous studies have suggested that heat-treated CuFe PC cathodes could facilitate the conversion of Li$_2$O$_2$ to Li$_2$O. However, only one other study has actually shown detection of the Li$_2$O reduction product in a Li/O$_2$ cell utilizing a palladium catalyzed cathode. The full XRD pattern of Li$_2$O is comprised of 3 major diffraction signals at 33.6, 56.4, and 67.3 two theta angles with a reference intensity ratio (RIR) of 100, 40, and 16 respectively. The line at 33.6° is the most intense line which explains its sole presence in the cathode XRD pattern, whilst the reflection intensity from the other two planes would expectedly be less than the background of the sealed cathode based on the RIR of the crystallographic database entry. An alternative explanation of the other reflection’s absence in the experimental data is the preferential orientation of the electrochemically formed Li$_2$O crystals.

Further confirmation of the Li$_2$O phase is obtained by studying this signal’s dependence on time as shown in Figure 4.11c which is composed of the same initial XRD pattern from the Co600 cathode of Figure 4.11b and an overlay of the measurements repeated subsequently over time. It is apparent from this overlay that the signal at 33.6 degree two theta is decreasing over time, while two new signals characteristic of the XRD peaks for LiOH emerge. These changes
are consistent with a chemical conversion of the Li$_2$O phase to a lithium hydroxide phase, which is an expected consequence of the reaction of Li$_2$O with ambient water vapor$^{46}$ which slowly diffuses through the polyimide film protecting the cathode sample for XRD analysis. Also overlaid in Figure 4.11c is the data from a control experiment where a cathode was treated identically except for the galvanostatic discharge. Absolutely no crystalline diffraction peak is observed from any of the subsequently collected control scans ruling out the possibility that the X-ray radiation and/or atmospheric exposure alone induce crystalline product forming chemical reactions in the electrolyte medium itself. From these results we propose that the Co-N$_4$ moiety of the Co600 cathode stabilizes the superoxide reduction intermediate as a surface adsorbate, which is further reduced ultimately to Li$_2$O involving an overall four electron reduction of oxygen. A possible sequence of reactions on the catalyzed electrodes is those in equations [3] – [5]:

$$\text{Co600} + \text{O}_2 + e^- + \text{Li}^+ \rightarrow \text{Co600} - \text{O}_2\text{Li}^+ \quad [3]$$

$$2 \text{Co600} - \text{O}_2\text{Li}^+ \rightarrow \text{Co600} - \text{O}_2\text{Li}_2 + \text{O}_2 \quad [4]$$

$$\text{Co600} - \text{O}_2\text{Li}_2 + 2 \text{Li}^+ + 2 e^- \rightarrow 2 \text{Li}_2\text{O} + \text{Co600} \quad [5]$$

The presence of the Li$_2$O$_2$ as a co-product in the catalyzed cathode is possibly the result of two causes. First, it is possible that a portion of the carbon surface is not covered with the catalyst material and in those regions the ORR would proceed as it would on the uncatalyzed carbon to produce Li$_2$O$_2$. Secondly, as the discharge proceeds, the insoluble oxide products begin to inhibit the flow of electrons throughout the carbon support, causing the electrode to be “choked out” to terminate the discharge. This would prevent the reduction of all of the Li$_2$O$_2$ to Li$_2$O, leaving a mixture of both lithium peroxide and monoxide in the discharged cathodes.
4.3.5 SEM analysis of Li/O₂ cell discharge products morphology and elemental composition

Shown in Figure 4.12 are the surface morphologies imaged from the inside face of both an uncatalyzed Ketjen black carbon cathode (images (a) and (b)) and a Co600 catalyzed Ketjen black carbon cathode (images (c) and (d)).

![SEM images of cathode surfaces](image)

**Figure 4.12.** Scanning electron micrographs of the cathode surface collected after a galvanostatic discharge in 1M LiPF₆ in TEGDME. Image (a) and (b) are from an uncatalyzed Ketjen cathode magnified at ten and twenty thousand times respectively while (c) and (d) are from a Co600 on Ketjen black cathode at the same magnifications.

The images in each case were collected after a galvanostatic discharge to 2 V in the 1M LiPF₆ in TEGDME. For both electrodes there is an abundance of reduction products imbedded amongst the carbon particles. In the case of the uncatalyzed electrode these morphologies appear as
needle like strands and also toroidal agglomerates characteristic of the Li$_2$O$_2$ material.\textsuperscript{47-51} In the case of the Co600 surface there exist two different surface morphologies. Some of the cathode area is made up of large concentrically oriented sheets which appear as a rose-like morphology at lower magnifications (image (c)). The regions in-between these large rose-like structures have toroidal and needle like morphologies comparable to those observed throughout the uncatalyzed electrode surface. Elemental mapping of the fluorescence X-ray emissions (see Figure 4.13) from the Co600 cathode shows that the rose-like morphologies are high in oxygen concentration and depleted of carbon atoms.
Figure 4.13. (a) Secondary electron image of the Co600 cathode morphology after galvanostatic discharge to 2.0 V. (b) X-ray Fluorescence emission map of the Carbon-K$_\alpha$ signal collected from the same raster area shown in (a). (c) X-ray Fluorescence emission map of the Oxygen-K$_\alpha$ signal collected from the same raster area shown in (a). (d) Composite overlay of both the Carbon -K$_\alpha$ and Oxygen-K$_\alpha$. The accelerating voltage utilized was 5.0 KeV and the magnification is 2x10$^3$ times.

SEM images of carbon electrodes collected prior to discharge show a uniform distribution of carbon particles approximately 50 nm in diameter for both electrodes. These findings from the SEM analysis are consistent with results from the X-ray diffraction data discussed above where two different lithium oxide phases of reduction products were identified in the Co600 cathode, namely Li$_2$O$_2$ and Li$_2$O.
4.3.6 Partial depth of discharge cycling of the Co600 cathode

The effect of the Co600 catalyst on the cell cycleability is shown in Figure 4.14.

![Figure 4.14](image)

**Figure 4.14.** Galvanostatic cycling at 500 mA h g$^{-1}$ depth of discharge with a 0.1 mA cm$^{-2}$ current magnitude in 1 M LiPF$_6$ in TEGDME under oxygen flow for (a) Co600 catalyzed Ketjen black cathode and (b) uncatalyzed Ketjen black cathode.

There is clearly an advantage of higher energy efficiency for the catalyzed cell throughout the experiment as it includes relatively large charging capacities below 4 Volts. The Co600 catalyst-carbon material outperforms the uncatalyzed carbons showing greater cycle numbers and higher Coulombic efficiency.

Figure 4.15 shows SEM images collected from a lithium anode following the galvanostatic cycling of the Li/O$_2$ cell.
Figure 4.15. Scanning electron micrographs captured from the lithium anode of a Li/O₂ cell after a galvanostatic cycling experiment. Pit like morphologies are found across the majority of the surface area.

The lower magnification (100X and 150X) images show an abundance of “pit” like morphologies across most of the anode surface, whilst the higher magnification image shows the dendritic morphology of the surface imaged on the inside wall of a “pit”. The pitting of the anode surface is consistent with the uneven stripping of lithium foil as the anode reaction proceeds via the electrochemical oxidation (equation [6]) of the lithium as shown (Figure 6)\(^{52}\) in a recent review.

\[
\text{Li}^0 + e^- \rightarrow \text{Li}^+ 
\]

Pitting of the anode can cause regions of the interface between the cathode and anode to become disconnected from the ionic transport necessary to support electrochemical charge transfer. We
believe this issue with the lithium electrode is likely impacting the cycleability and total discharge capacity of the tetraglyme based cells reported herein.

4.4 Conclusions

The data presented in this work demonstrate that the Co-N_4 entity of the cobalt phthalocyanine macrocycle incorporated into a high surface area carbon cathode is actively participating in the ORR catalysis of Li-air batteries. The Co-N_4 moiety in the catalytic electrode provides a site for chemisorption of the O_2 reactant. This conclusion is supported by the changes in the XANES Δμ signature measured in situ under potential control. The direct adsorption of O_2 to the electrode surface lowers the activation energy of the charge transfer process, resulting in a lowering of the over-potential for the reduction of O_2 in the Li-air battery. This effect is directly observable in the response of the porous electrode in a half cell potential sweep experiment that clearly shows the resolution of two separate charge transfer steps throughout the cathodic sweep, first for O_2^- formation, and the second for the reduction of O_2^- to Li_2O. The presence of these two peaks in the cathodic response is indicative of the stabilization of the one electron reduction product superoxide (O_2^-) through an interaction of its unpaired electron with the Co^{2+} d-orbitals. The Co^{2+} functions as a relatively soft acid and is capable of forming a stabilized ion pair with the soft base superoxide. The Lewis acidity of Co^{2+} is less than that of Li^+ as seen from the following relative Lewis acidity strengths for a series of metal cations,^{53} H^+ > Li^+ > Fe^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+} > Ru^{2+} > Pb^{2+} > Cu^+ > Cd^{2+} > Au^+, which supports the view of the softer acid Co^{2+} exerting a stronger affinity for the softer base O_2^- forming a relatively stable, complex, in conformity with hard-soft acid base concept we previously advanced to explain ORR in non-aqueous electrolytes.^{2,5}
In full cell galvanostatic experiments this stabilization is manifested by an increase in the potential of the discharge plateau voltage in conjunction with a strong influence on the disproportionation pathway to crystalline ORR products. The initially-formed superoxide disproportionates into Li$_2$O$_2$ and O$_2$. The Li$_2$O$_2$ formed is further reduced catalytically to Li$_2$O with the assistance of the CoPC catalyst. The reduction of Li$_2$O$_2$ to Li$_2$O is not ubiquitous due to the presence of a significant amount of un-catalyzed reaction sites on the porous electrode and due to the passivation of the electrode by Li$_2$O$_2$. The full reduction of O$_2$ to Li$_2$O reported here with further development could lead to the realization of achieving the full potential of the Li-air battery as a super-high-energy-density rechargeable battery.

4.5 Acknowledgement
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4.6 References


Chapter 5

Homogeneous versus Heterogeneous ORR Catalysis in Non-Aqueous Electrolytes for Li-air Batteries

5.1. Introduction

Recent investigations\(^1\)-\(^3\) of oxygen reduction reactions (ORR) in non-aqueous electrolytes for Li-air batteries have revealed that the ion-conducting salt cations and the organic solvents play important roles on the ORR mechanism and the stability of the ORR products formed. This dominant coupling of ORR to the nature of the electrolyte has been explained using the Hard Soft Acid base (HSAB) concept, which states that hard Lewis acids ions wants to combine with hard Lewis bases while soft Lewis acids like to be associated with soft Lewis bases.\(^1\),\(^4\),\(^5\) The relevance of the HSAB concept to ORR in non-aqueous electrolytes is that the Lewis acid properties of the electrolyte salt cations are modulated by their solvation (or acid-base complex formation) with the solvents, which lead to strong correlations between the ORR mechanism and the solvent’s Lewis basicity. Solvents with high Guttmann donor numbers are strong Lewis bases that make Li\(^+\) cations softer Lewis acids by forming solvates of the type Li\(^+\)\((\text{solvent})_n\). Depending on the donor number of the solvent used to prepare electrolytes, the Li\(^+\) cation acquires a range of hard-soft Lewis acidity which in turn controls the mechanism and products of ORR. In this chapter, we wish to report that ORR catalyst activity in non-aqueous electrolytes is coupled to the Lewis basicity of the solvent as measured by its donor number (DN). This makes the ORR process in non-aqueous electrolytes unique and different from that generally observed in aqueous electrolytes in which the nature of the solvent (H\(_2\)O) remains invariant with the presence of the strongest Lewis acid cation, H\(^+\). In aqueous electrolytes the ORR pathway and the stability of the ORR intermediate are influenced by the pH scale and it has been found that the peroxide intermediate is more prevalent as pH increases.\(^6\),\(^7\) The variable Lewis acidity of the
Li$^+$ cation in non-aqueous electrolytes is vital to the development of appropriate catalysts for the non-aqueous Li-air battery for which the choice of electrolytes is potentially large. While we acknowledge the many recent studies demonstrating the influence of catalysts on the discharge and rechargeability of the Li-air battery, the present work using the CoPC-based catalyst suggests that the knowledge gained from fuel cell catalysis may be insufficient to explain the ORR pathways and products formed in non-aqueous Li-air batteries. On the other hand, the data presented in this chapter indicate that ORR catalysis can proceed either via a homogeneous (outer Helmholtz sphere reaction) or a heterogeneous (inner Helmholtz sphere reaction) pathway. This information is expected to satisfactorily explain and unify the results of the various ORR catalysis studies pertaining to non-aqueous Li-air batteries.

5.2. Experimental

5.2.1 Catalyst Preparation

Cobalt catalyst powder samples were prepared as previously described. Briefly cobalt phthalocyanine (CoPC) was dissolved in a concentrated sulfuric acid solution after which high surface carbon (either Vulcan XC72R for thin film studies or Ketjen300 for full cell studies) was added under stirring until a homogenous paste was formulated. The quantity of carbon black added was fixed to achieve a 2 wt% Co concentration of the solid phase components. The paste was then instantaneously diluted via directly transferring into a large volume of deionized water forcing CoPC to precipitate out of solution and deposit onto the carbon black. The particulate suspension was then separated via vacuum filtration and the resulting powder was dried under vacuum at 70°C. Dried powder samples were then loaded into an argon purged quartz tube and sintered in a furnace at either 600°C or 800 °C.
The two catalyzed carbons thus prepared are designated as Co-600 and Co-800. Uncatalyzed Vulcan samples were also prepared via the same procedure described above. The resulting carbon powder products were analyzed by powder X-ray diffraction using a Rigaku Ultima IV Bragg-Brentano para-focusing diffractometer with a Cu $k_\alpha$ radiation source.

5.2.2 Voltammetric Measurements

High surface area carbon ink suspensions for thin film voltammetry experiments were created by dissolving a polyvinylidene fluoride (PVDF) (Kynar® 2801) binder material into a N-methyl-2-pyrrolidone solvent. Catalyzed or uncatalyzed carbon powder was then added (90:10 powder:binder by mass) to the binder solution and sonicated until a homogenous ink suspension resulted. Microliter aliquots of the ink suspension were cured onto a 0.196 cm$^2$ glassy carbon change tip disc working electrode from Pine Instrument Company at 80°C under vacuum creating carbon/catalysts films of 100 µg cm$^{-2}$ on the disc electrode. Additional experiments were conducted with both a platinum and gold change tip disc electrode of the same diameter.

All electrochemical experiments were carried out in the absence of air and moisture in an Argon-filled Labmaster 130 glove box. The test cells for electrochemical experiments were airtight and were handled using techniques employed in the manipulation of air-sensitive compounds. Anhydrous grade $\geq$ 99.8% acetonitrile (CH$_3$CN), purum grade $\geq$98.0% tetraethylene glycol dimethyl ether (TEGDME), and anhydrous grade DMSO certified to contain less than 50 ppm water, were purchased from Sigma Aldrich and stored in the dry atmosphere glove box upon receipt.

Cyclic voltammetry experiments were conducted utilizing a PGSTAT30 bipotentiastat equipped with a scangen module from Ecochemie Inc. Electrolytes were prepared in the glovebox using polypropylene class B volumetric flasks. A polypropylene screw cap container
from Nalgene® was employed as the cell container and an in-house fabricated polypropylene lid was in place to keep the electrolyte solution removed from the ambient room conditions and to hold the electrodes in a stationary fashion, as described previously\textsuperscript{4,5}. Oxygen gas was purged into the cell through a solvent reservoir in order to solvate the gas flow thereby minimizing the evaporation of the electrolyte solvent. Platinum gauze was utilized as the counter electrode, the working electrode prepared as described above, and an in house assembled reference electrode made from a silver wire contained in a 100 mM TBAPF$_6$, 10 mM silver nitrate acetonitrile solution in a glass tube, was used. For the DMSO and TEGDME based electrolytes the Li/Li$^+$ scale was directly measured by monitoring the potential of the reference electrode from an actual lithium ribbon submerged in the electrolyte solution.

For the CH$_3$CN-based electrolyte the reference cell was routinely calibrated in separate cyclic voltammetry experiments conducted in tenth molar TBAPF$_6$ acetonitrile electrolytes with the addition of 1 mM Ferrocene. Steady state scans collected at 50 mV s$^{-1}$ with a planar glassy carbon disc working electrode were utilized to determine the potential of the reference cell from the ferrocene/ferricenium couple. The silver reference cell couple was consistently found to be approximately 88 mV below the formal reduction potential of the standard ferrocene/ferricenium couple. The data plots shown here in are shifted to the Li/Li$^+$ scale after measuring the potential of the ferrocene/ferricenium versus a Li foil immersed in the electrolyte.

\textbf{5.2.3 Rotating Ring Disc Electrode (RRDE)}

The ring-disc electrode consists of two electrically insulated electrodes, one a glassy carbon disc of 0.247 cm$^2$, the other a gold ring of 0.187 cm$^2$, located immediately outside the disc circumference. For the rotating electrode experiments the ring electrode was held at a constant potential from the Ag/Ag+ reference electrode. This potential value was determined separately.
for each electrolyte by measuring the voltammetric response of a gold electrode in the oxygenated electrolyte to determine a potential where superoxide was expected to be oxidized in the voltage window of the electrolyte

5.2.4 Fabrication of Li/O$_2$ cell cathodes

Powder dispersions were formulated in 1-methyl-2-pyrrolidinone solutions containing already dissolved kynar 2801 binder material. The powder to binder ratios of these inks were fixed at 90:10 by mass. The inks were delivered via pipette to one inch diameter precut Panex® conductive carbon cloth substrates and cured under vacuum at 80 °C. Typical mass loadings were between 2-4 mg cm$^{-2}$.

5.2.5 Li/O$_2$ Cell Assembly Procedures

All assembly procedures were carried out in an MBraun Labmaster 130 Argon dry atmosphere glove box with H$_2$O vapor levels maintained below 1 ppm. The cathodes were saturated with electrolyte under vacuum in the glove box’s antechamber at approximately 1 Barr below atmosphere. A 32 mm diameter lithium foil disc was cut with a steel di-cut apparatus from a 1.5 mm thick ribbon as received from AlfaAesar. A 50 mesh copper current collector was pressed into the lithium foil between two polypropylene sheets. The copper current collector was screwed into the stainless steel electrode terminal via a stainless steel bolt and nut mounting hardware. A circular cut out of polypropylene Li$^+$-ion conducting membrane was placed on top of the anode. The cathode was then removed from the antechamber vacuum and placed onto a paper Kimwipe, drained of excess electrolyte, massed (approximately 150-200 mg of electrolyte per cathode), and placed on top of the polypropylene membrane with the high surface area carbon material faced inward to the lithium foil. An aluminum Dexmet cut out was placed on top of the cathode to supply a uniform compressing force between the electrode areas and allow for current collection through the cathode cell terminal.
5.3 Results and Discussions

5.3.1 Influence of Donor Number on Superoxide Stability

Non-aqueous electrolytes are composed of a continuum of solvents having a range of electron donor properties (basicities) defined by the Guttmann donor numbers (DN). The DN is the enthalpy of reaction in kcal/mole for the reaction between the solvent and antimony pentachloride chloride (SbCl$_5$) in dichloroethane (CH$_2$ClCH$_2$Cl).$^{40}$ The higher the DN of the solvent, the stronger is its tendency to donate electrons, forming electron donor complexes with Lewis acids such as Li$^+$. Recently we have shown$^1$ using $^{13}$C NMR that the Li$^+$ ions in Li salt solutions in non-aqueous electrolytes are solvated, typically by four solvent molecules per Li$^+$, to form the complexes Li$^+$-(solvent)$_4$. Recent results for oxygen reduction reactions (ORR) in non-aqueous electrolytes have unequivocally shown that the basicity of the solvent strongly influences the relative stabilities of the ORR products, superoxide (O$_2^-$) and peroxide (O$_2^{2-}$).$^{1-5}$ In high donor number solvents such as dimethyl sulfoxide (DMSO, DN= 29.8), the one-electron ORR product superoxide (O$_2^-$) (equation 1) is stabilized in solution with longer lifetimes, whereas in low donor solvents such as acetonitrile (CH$_3$CN, DN= 14.1) and tetraethylene glycol dimethyl ether (TEGDME; DN= 16), the superoxide has very short lifetimes and decomposes into the stable two-electron reduction product, peroxide (O$_2^{2-}$), in an overall two-electron reaction (sum of equations [1] and [2]). The peroxide can also be formed by further electrochemical reduction of the superoxide as depicted in equation [3].

\[
\begin{align*}
O_2 + e^- + Li^+ \rightarrow LiO_2 & \quad [1] \\
LiO_2 \rightarrow 1/2 Li_2O_2 + 1/2 \ O_2 & \quad [2] \\
LiO_2 + e^- + Li^+ \rightarrow Li_2O_2 & \quad [3]
\end{align*}
\]
This ability of the solvents to stabilize different ORR products in Li\(^+\)-conducting electrolytes has been explained on the basis of the hard-soft-acid-base (HSAB) concept\(^{41}\). In non-aqueous Li\(^+\)-conducting electrolytes, the Li\(^+\) acquire a range of Lewis acidities by forming complexes with solvents having varying donor numbers which modulates the acidity of Li\(^+\) to the extent determined by the solvent’s basicity. The Li\(^+\) which form complexes with high donor number solvents acquire softer acidity than those which form complexes with low donor solvents. Thus, the Li\(^+\) in different non-aqueous electrolytes promote different ORR mechanisms and products determined by the donor number of the solvents.

Reported here our recent ORR results on catalyzed electrodes in non-aqueous electrolytes have revealed that there is a striking influence of the solvents’ donor number (or basicity) on the ORR catalysis process. We have found that ORR on carbon electrodes in electrolytes based on high donor number solvents prefers to take place in the outer Helmholtz plane of the electrical double layer (outer sphere ORR) regardless of the presence of a catalysts, whereas in electrolytes utilizing low donor number solvents, the ORR on a catalyzed electrode is facilitated in the inner Helmholtz layer of the electrical double layer (inner sphere ORR), making the ORR process both catalyst and solvent dependent in non-aqueous electrolytes. In low donor number solvent-based electrolytes such as LiPF\(_6\) in TEGDME, an outer sphere ORR is seen as well, although the superoxide formed in the first electron transfer to O\(_2\) is not stabilized in solution by the Li\(^+\)(TEGDME)$_n$ as it is a harder Lewis acid. The superoxide decomposes to peroxide as the overall oxygen reduction product.
5.3.2 Inner Sphere and Outer Sphere Electrochemical Processes Affected by Catalyst Surfaces In Low Donor Electrolytes

A way to differentiate the inner sphere ORR process from the outer sphere process is by careful analysis of the voltammetric response from three different working electrode surfaces in oxygenated electrolytes in both low and high donor number solvents as shown in Figures 5.1 and 5.5, respectively. Some properties of the electrolytes used in this study are given in Table 5.1.

<table>
<thead>
<tr>
<th>0.1M LiPF&lt;sub&gt;6&lt;/sub&gt; in</th>
<th>Solvent Donor Number / kcal mol&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Conductivity / mS cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; Solubility / mol ml&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>29.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.11&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.1&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>TEGDME</td>
<td>16.6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.43&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CN</td>
<td>14.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14.39&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.1&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Gutmann<sup>40</sup>; <sup>b</sup> Mamanotov<sup>42</sup>; <sup>c</sup> Ó’laoire<sup>43</sup>, <sup>d</sup> Sawyer et. al.<sup>44</sup>; <sup>e</sup> Zhang et. al.<sup>45</sup>

Table 5.1. Properties of solvents and their Li salt solutions.

For the experiment in Figure 5.1, the solvent is CH<sub>3</sub>CN while in Figure 5.5, it is DMSO. The disc working electrodes utilized were the noble metals gold and platinum, and vitreous carbon. Additional studies of voltammograms with and without a cast film of CoPC catalyst on vitreous carbon are included in Figures 5.3 and 5.7 for the low and high donor number electrolytes, respectively. In Figures 5.1 and 5.5, the carbon disc electrode does not contain CoPC catalyst film. One important difference in the voltammograms on these three electrode disc interfaces is found in the current response measured just prior to the onset of the Faradaic ORR process. This region of the voltammogram is expanded in Figure 5.1a for the electrolyte in the low donor number CH<sub>3</sub>CN and Figure 5.5a for the electrolyte in high donor number DMSO.
In Figure 5.1a at approximately 2.9 Volts, there is a distinctive pre-peak feature present in the current response of the noble metal electrodes in contrast to the carbon disc, which has no such pre-peak feature. This region is highlighted with a yellow ellipse.

Figure 5.1. First sweep voltammograms measured at 100 mV s\(^{-1}\) in oxygenated 0.1 M LiPF\(_6\) CH\(_3\)CN with three separate working electrode discs plotted at a current range of (a) -0.1 mA cm\(^{-2}\) to 0.05 mA cm\(^{-2}\) and (b) -1.5 mA cm\(^{-2}\) to 1.0 mA cm\(^{-2}\).

I interpret this pre-peak feature in the reductive wave to be indicative of the direct adsorption of the oxygen from the outer Helmholtz plane to the inner Helmholtz plane of the double layer onto the noble metal surface. This occurrence does not precede the faradaic ORR at the carbon.
interface, indicating that the charge transfer proceeds via an outer sphere electron transfer at the carbon interface. This adsorption is probably facilitated on the noble metals because of their favorable electronic structures, which provide energetically advantageous adsorption sites that are not present on the surface of the carbon electrode. Similar features in the voltammograms of noble metal electrodes have been observed in low donor solvent based electrolytes previously (Figure 5)\textsuperscript{10}, although the implication of that finding was not discussed in great detail. One consequence of this adsorption is apparent in Figure 5.1b where the reduction peak currents for the three electrodes can be directly compared. Clearly the two noble metal surfaces, which facilitate the direct adsorption of the oxygen at the inner Helmholtz plane prior to reduction, experience more severe passivation than the carbon electrode as evident by the peak current magnitudes. This can be explained by the notion that at the inner Helmholtz plane, a charge transfer process would result in the deposition of the ORR product more tightly bound to the electrode surface and therefore more effectively fouling the electrode interface than an outer Helmholtz plane process. This is supported further by the comparison of the platinum electrode response with that of gold: the platinum pre-peak feature starts at lower over-potential than on gold, and consequently, shows more peak current suppression than on gold. This shift in adsorption onset has been predicted by DFT calculations of the metal-oxygen bond energy for platinum (4.2 eV) compared to gold (2.7 eV)\textsuperscript{46} and it is telling that the oxygen is more closely bound (shorter bond distance) to the platinum than it is to the gold. Therefore, the change in free energy for the adsorption on platinum is more effective in lowering the activation energy for the overall charge transfer process. This trend also further affirms that the pre-edge current signal does correspond to oxygen adsorption to the metal surface.
In addition to the gold and platinum surfaces, there also is a pre-peak feature in the current response of the cobalt phthalocyanine catalyzed high surface carbon black electrode which we studied under the same conditions. As shown in Figure 5.3a for ORR in 0.1 M LiPF$_6$ /CH$_3$CN, the CV on both the Co800 and the Co600 displays a pre-peak adsorption signature prior to the onset of faradaic current flow, which is comparable to that measured from the noble metal electrodes shown in Figure 5.1a. For these high surface area carbon catalyst-containing films, the pre-edge feature is not as sharply defined as it was for the noble metal discs shown in Figure 5.1a due to the film surface being comprised of a mixture of both carbon surface and cobalt catalyst surfaces. Figure 5.3b indicates the presence of the Co800 (metallic cobalt) material in the high surface area carbon network causes a 400 mV positive shift in the onset of the ORR. This shift is a result in a lowering of the activation energy for the superoxide product formation. The electronic structure of the superoxide product and the Co metal surface is shown below in Figure 5.2.

![Figure 5.2. Electronic Structure diagram of the superoxide intermediate and the metallic cobalt. Unpaired electrons are highlighted by the red font.](image-url)
Figure 5.3. First sweep voltammograms measured at 100 mV s$^{-1}$ in oxygenated 0.1 M LiPF$_6$ CH$_3$CN with three separate working electrode surfaces plotted at a current range of (a) 0.05 mA cm$^{-2}$ to 0.2 mA cm$^{-2}$ and (b) -4 mA cm$^{-2}$ to 2.0 mA cm$^{-2}$.

In this low donor number solvent-based electrolyte, the gold, platinum, cobalt metal, and cobalt-N$_4$ electrode surfaces appear to lower the activation energy for ORR by facilitating oxygen adsorption and stabilization of the ORR product intermediate through a direct surface adsorption. A graphical display of this difference between outer (region A) and inner (region B) Helmholtz plane electron transfer processes is shown in Figure 5.4 for the double layer structure in low donor number solvent-based electrolytes.
Figure 5.4. Electrochemical double layer at the interface of a Co600 catalyzed carbon electrode in a Li$^+$-(CH$_3$CN)$_n$ electrolyte. Highlighted section A shows the outer sphere one electron charge transfer as it occurs on an uncatalyzed surface. Highlighted section B shows inner sphere charge transfer process facilitated by the presence of a catalyzed surface.

As will be shown below these same electrode materials exhibit little effect on the reduction potentials in the electrolyte based on the high donor number DMSO solvent. In the high donor number electrolyte an outer Helmholtz sphere homogenous catalysis is able to stabilize the ORR intermediate and product regardless of the presence of catalyst in the electrode.
5.3.3 Inner Sphere and Outer Sphere Electrochemical Processes Affected by Catalyst Surfaces In High Donor Electrolytes

The influence of the solvent donor number on the ORR mechanism and products can be understood by considering the change in the electrode double layer structure of the same working electrodes in DMSO-based electrolytes. Figure 5.5a shows an expansion of the same current range displayed in the CH$_3$CN voltammograms of Figure 5.1a for the same three disc electrodes now in this high donor number electrolyte.
Figure 5.5. Third sweep voltammograms measured at 100 mV s\(^{-1}\) in oxygenated 0.1 M LiPF\(_6\) in DMSO with three separate working electrode discs plotted at a current range of (a) -0.1 mA cm\(^{-2}\) to 0.05 mA cm\(^{-2}\) and (b) -1.0 mA cm\(^{-2}\) to 0.6 mA cm\(^{-2}\) (c) voltammograms measured at 10 mV s\(^{-1}\).
In contrast to the voltammograms measured in CH$_3$CN-based electrolytes, neither of the noble metal electrodes or the vitreous carbon electrode shows any pre-peak response in the DMSO solution. The unique feature in this electrolyte is the current peak at 2.5 V on the vitreous carbon electrode, assigned to the formation of the one-electron reduction product superoxide ($O_2^-$) which is stable in this electrolyte as we already reported. The superoxide reduction intermediate is stabilized by the Li$^+$(DMSO)$_n$ solvate and the charge transfer proceeds via an outer Helmholtz plane pathway (outer sphere process). A visual description of this homogenous catalysis is depicted in Figure 5.6 (part A displays the outer sphere electron transfer) which shows the double layer interface structure for the high donor number-based Li$^+$-electrolyte.

Figure 5.6. Electrochemical double layer at the interface of a Co600 catalyzed carbon electrode and a Li$^+$-DMSO electrolyte. Highlighted section A shows the outer sphere one electron charge transfer. Highlighted section B shows the one electron product superoxide chemisorbed to the Cobalt catalyst promoting further electrochemical reduction of the oxygen radical.
Because of the dominance of the high donor number DMSO medium in promoting the outer sphere ORR process, there is no additional increase in the ORR voltage due to the CoPC catalyst in this electrolyte. However, a close examination of the results in Figures 5.1 and Figure 5.5 indicates that the nature of the catalyst has a role on its catalytic activity in high donor number solvents. First of all the limiting ORR peak currents measured on Pt, Au and vitreous carbon in the DMSO medium are much closer in magnitude than those observed in the CH$_3$CN electrolyte. This indicates that the electrode fouling is occurring more rapidly in the CH$_3$CN based electrolyte, especially for the noble metal surfaces, as a result of the direct adsorption of the oxygen to the metal surface. For the DMSO based electrolyte the three disc electrodes have nearly identical onset potentials for ORR and the noble metals do not appear to be facilitating catalysis of the first step in the reduction process. Further understanding of the differences caused by the chemistry of the disc material can be gained by analysis of the reduction wave measured at slower sweep rates. Figure 5.5c shows the response of the three electrodes at 10 mV s$^{-1}$ allowing direct comparison of the relative peak current magnitudes of the first and second waves in the reduction process for the three electrode materials. As a reminder, the first peak in the diffusion controlled reduction corresponds to the one electron reduction of oxygen to superoxide. The broad shoulder observable upon further cathodic over-potential corresponds to the further electrochemical reduction of the superoxide to form insoluble materials which lead to disc passivation. Some noteworthy observations regarding Figure 5.5a and 5.5c are that the carbon disc shows this distinctive broad peak even at the faster sweep rate (Figure 5.5a), whilst this feature is not as pronounced on the noble metal electrodes unless slower sweep rates are utilized. Furthermore, the slower sweep rate voltammogram for the carbon disc actually shows a
greater peak current for the second cathodic process. These observations suggest that the superoxide formed initially in the OHP has a greater propensity to adsorb to the noble metal surfaces than to the carbon, resulting in two effects. First, the superoxide is stabilized on the noble metal inhibiting possible side reactions with solvent molecules. Secondly, the direct adsorption of the $\text{O}_2^-$ intermediate promotes its further reduction to $\text{O}_2^{2-}$ and perhaps $\text{O}^{2-}$.

Additionally, the CVs of cobalt catalyzed carbon electrodes were also measured in the DMSO as shown in Figure 5.7.

![Graph showing the first sweep voltammograms measured at 100 mV s$^{-1}$ in oxygenated 0.1 M LiPF$_6$ DMSO with three separate working electrode surfaces plotted at a current range of (a) 0.12 mA cm$^{-2}$ to 0.1 mA cm$^{-2}$ and (b) -4 mA cm$^{-2}$ to 2.0 mA cm$^{-2}$.

Figure 5.7 First sweep voltammograms measured at 100 mV s$^{-1}$ in oxygenated 0.1 M LiPF$_6$ DMSO with three separate working electrode surfaces plotted at a current range of (a) 0.12 mA cm$^{-2}$ to 0.1 mA cm$^{-2}$ and (b) -4 mA cm$^{-2}$ to 2.0 mA cm$^{-2}$.
These voltammograms indicate that neither the Co800 nor the Co600 electrode is effective at lowering the overpotential required for oxygen reduction beyond that of DMSO itself on the vitreous carbon electrode. These various results in DMSO are consistent with the notion that the Li\(^+\)-containing electrolyte in DMSO functions as a homogenous catalyst through an outer sphere ORR process by stabilizing the one-electron ORR intermediate superoxide. The stabilization of the superoxide ORR product by the high donor number DMSO supersedes the adsorption of oxygen by the cobalt catalysts with the result that a homogeneous outer sphere catalysis path persists in these electrolytes. Note that we have identified both \(\text{O}_2^2^-\) and \(\text{O}^2^-\) in Li-air cells with CoPC catalyzed electrodes.\(^{47}\) This superoxide intermediate adsorption is shown schematically in region B of Figure 5.6 for a CoPC-based catalyst. The vitreous carbon electrode surface does not have the electronic features to adsorb the superoxide to the electrode and therefore it remains solvated in the OHP where it can either undergo chemical decomposition to Li\(_2\)O\(_2\) or take part in possible side reactions with the solvent.

5.3.4 Stability of the Solution Soluble Superoxide Influenced by Donor Number

Evidence for the electrolyte’s role in facilitating the outer or inner sphere ORR charge transfer process can be gathered by measuring the current response from the ring electrode of a rotating ring disc electrode assembly in electrolytes prepared in different solvents. In this technique, materials which are generated at the working electrode interface can be detected if they are released into the bulk electrolyte and transported to the ring electrode. As shown in Figure 5.8 there is a strong correlation between the solvent donor number in Li\(^+\)-electrolytes and the quantity of solution-stabilized superoxide ORR intermediate generated at the disc.
Figure 5.8. RRDE response of a glassy carbon disc measured in three aprotic Li$^+$-electrolytes of varying donor number. (a) Disc response (b) Ring response (c) charge ratio as a function of donor number. The ring electrode is biased to 3.6 V, 3.2 V, 2.9 V vs Li/Li$^+$ for the CH$_3$CN, TEGDME, DMSO experiments, respectively.
Clearly, the ring response measured in the DMSO-based electrolyte is significantly larger than that measured in the TEGDME-based electrolyte. This effect is further quantified by plotting the integrated charge area corresponding to the ring’s oxidation process (after collection efficiency adjustment) normalized by the integrated charge area corresponding to the disc’s reductive wave as a function of donor number as shown in Figure 5.8c. This finding emphasizes that the superoxide intermediate is not stable in the low donor number electrolytes as it is prone to undergo rapid chemical reaction with the harder acid Li$^+$ cation. For these low donor number electrolytes the presence of a heterogeneous electrode catalyst can effectively lower the activation energy required to reach full reduction of oxygen via stabilizing the intermediate and therefore provide an advantage in cell voltage and coulombic capacity.

The RRDE voltammetry was also applied to the same cobalt catalyzed high surface area films discussed above in the DMSO electrolyte and their response is shown in Figure 5.9.
Figure 5.9. RRDE response collected at 500 rpm from three separate working electrode surfaces measured at 100 mV s\(^{-1}\) in oxygenated 0.1 M LiPF\(_6\) in DMSO. (a) shows the disc response (b) shows the response of the gold ring while biased at 2.93 V vs Li/Li\(^+\).

Again, there is no advantage in the ORR onset for either of the two films as compared to the uncoated planar disc in this high donor number electrolyte. Interestingly, small changes in the ring current response (both in regards to peak magnitude and onset potential) can be detected as shown in Figure 5.9 b. The glassy carbon working electrode shows the greatest peak in ring
current response and also the earliest onset of oxidative current flow, followed by the Co600 film and then the Co800 film, which has the lowest ring current peak magnitude and the latest onset of the oxidative current flow. We interpret this trend to be indicative of an increase in the rate that the superoxide reduction product is further reduced electrochemically as it passes along the working electrode interface on the way to the ring electrode. We have included a visual description of this process in the Figure 5.6 B graphic of the high donor number electrolyte double layer. This second charge transfer process also explains the slight increase in the limiting current measured at the disc in the following order Glassy Carbon < Co600 < Co800. The same trend in the ring response (both in regard to the magnitude and also the time delay) was observed in the TEGDME-based electrolyte as shown in Figure 5.10.

![Figure 5.10](image)

**Figure 5.10.** RRDE response collected at 500 rpm from three separate working electrode surfaces measured at 100 mV s⁻¹ in oxygenated 0.1 M LiPF₆ in TEGDME. The disc response is plotted in solid line style on the left hand current scale while the ring response is in dashed line style on the right hand current scale.

The magnitude of the superoxide detection at the ring electrode from the Co800 film is less than half of that detected from the planar carbon disc (albeit after larger limiting current magnitudes from the film), again suggesting that the superoxide intermediate is more prone to be reduced
further as it travels along the Co800 electrode interface than it does in the case of the Co600 or the planar carbon electrode. The observed shifts in onset of ring current flow are much larger in the TEGDME-based electrolyte than those observed in the DMSO-based electrolyte. For the former electrolyte the ring current response is nearly an order of magnitude lower than those measured in the DMSO-based electrolyte. Both of these observations support the prolonged stability of the superoxide in the DMSO-based Li$^+$ electrolyte.

5.3.5 Full Cell Performance of the Co Catalyst Material in High and Low Donor Number Based Electrolytes

In order to provide further support to the homogeneous catalysis and the stability of the ORR intermediate $O_2^-$ in electrolytes based on high donor number solvents, we have studied the discharge behavior of Li/O$_2$ cells filled with DMSO-1M LiPF$_6$ electrolyte and both catalyzed and uncatalyzed Ketjen black carbon cathodes. Shown in Figure 5.11 is an overlay of the discharge curves for both the uncatalyzed Ketjen300 and the Co600 catalyzed Ketjen black electrodes assembled in DMSO based cells.
Figure 5.11.: Galvanostatic Discharge of a Co600 catalyzed Ketjen cathode and an uncatalyzed Ketjen cathode measured in 1M LiPF$_6$ in DMSO at a rate of 0.1 mA cm$^{-2}$. Inset shows an expansion of the voltage range from 2.5 to 3.0 Volts.

Although the voltage of the catalyzed cell is initially higher for a brief duration (see inset Figure 5.11), the catalyzed cell quickly steps down to the same voltage plateau as the uncatalyzed cathode for the remaining cell discharge capacity. This discharge performance is markedly different than the discharge voltage of cells assembled with low donor number solvents such as TEGDME. As shown below in Figure 5.12, we observed that the Co600 catalyzed electrodes discharge at about 200 mV higher than the uncatalyzed Ketjen300 electrode in the low donor number electrolytes. These observations are consistent with our half-cell voltammetry results, which prove that the higher donor number electrolytes negate the advantage of having a catalyzed cathode material.
5.12. Galvanostatic Discharge of a Co600 catalyzed Ketjen cathode and an uncatalyzed Ketjen cathode measured in 1M LiPF₆ in TEGDME at a rate of 0.1 mA cm⁻². Inset shows an expansion of the voltage range from 2.0 to 3.0 Volts.

5.4 Conclusions

Cyclic and ring-disc voltammetry data obtained in this work have revealed that oxygen reduction reactions on vitreous carbon electrodes occur via an outer Helmholtz sphere mechanism. The donor number of the electrolyte solvent plays a dominant role on the stability of the initial one electron reduction product $O_2^-$, and hence the mechanism of the reaction. In electrolytes based on high donor solvents such as DMSO, the $O_2^-$ is stabilized by the solvated Li⁺ so that the activation energy for electron transfer is lowered to provide a higher voltage for the Li-air cell. Thus, high donor number solvents homogeneously catalyze the reduction of oxygen. In low donor solvents there appears to be no homogeneous catalysis despite an outer sphere ORR process. The homogeneous catalysis of the high donor number solvent is so dominant that cathode catalysts
such as CoPC showed little catalytic effect in electrolytes in DMSO. Catalysts such as CoPC, Pt and Au promote ORR in low donor number solvents via inner Helmholtz sphere process due to the strong adsorption of O\(_2\) as well as the ORR intermediates O\(_2^-\) and O\(_2^{2-}\). The adsorption of these intermediate reduction products on the catalysts surface lowers the the propensity for these materials to react with the solvents and to be fully reduced to O\(^{2-}\).

5.5 Acknowledgment

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5.6 References


Chapter 6: Conclusions and Future Direction

6.1 Conclusions

Conducting research of the Li/O\textsubscript{2} battery technology over the last three years has proven to be a most exciting endeavor. The understanding of the redox reactions pertinent to the cell operation has been a dynamic process as the cell emerges from its infancy. I consider myself most fortunate to follow the road paved by my former colleague Dr. Cormac Ó’Laoire who made significant advancements in pin-pointing the influence of electrolyte properties on the oxygen electrode behavior. Following his lead my research has been focused on understanding the influence of catalytic materials on the oxygen redox processes and further developing electrolyte solutions for full Li/O\textsubscript{2} cell operation. Presented below is a highlight of contributions brought forth through my research.

My first publication presented the developments made on the dimethyl sulfoxide solvent based electrolytes as a medium for the oxygen reduction reactions. I was intrigued by my initial study of the oxygen electrode response in DMSO based electrolytes via half-cell cyclic voltammetry experiments, as remarkably the carbon disc electrode does not show the detrimental passivation effect observed in acetonitrile electrolytes. Since the passivation effect is believed to be the main cause of the limited cycle life in the full cell performance, it was hypothesized that the DMSO medium may provide a means to enhance the cycle life of the full cell. My presentation at the ECS Boston meeting in October 2011 regarding our DMSO (both voltammetric and galvanostatic results presented) studies was the first submission publicized of a DMSO based electrolyte for Li/O\textsubscript{2} batteries and prompted immediate investigation by both the IBM group and also the researchers at St. Andrews University in Scotland. Advancing this development was challenging (in fact many people still don’t believe a lithium anode is stable in DMSO) and required careful observations before multiple galvanostatic cycles were achieved.
K.M’s encouragement insisting it was possible was a paramount influence. As mentioned in the introductory chapter, “the jury is still out” regarding the stability of this medium over prolonged cycling, regardless the discharge performance of primary DMSO cells is superior to many of the alternative options to date.

The main focus of my research was toward understanding in greater detail how incorporating a catalyst material into the carbon current collector influences the ORR processes. Abraham was first to observe that the discharge voltage of a catalyzed cell was higher than that of an uncatalyzed cell in his 1996 publication. As discussed in chapter 4 we used cyclic voltammetry to study the ORR process on the catalyzed high surface carbon and found evidence that the CoN₄ center in cobalt phthalocyanine facilitates a multistep faradaic reduction in contrast to uncatalyzed carbon surfaces which show only one reduction wave. We successfully interpreted these steps to be: first the one electron inner sphere reduction of the surface adsorbed oxygen, followed by a two electron reduction of the surface bound peroxide to monoxide. The surface bound superoxide is believed to be stabilized through its interaction with the Co²⁺ macrocycle. This finding was also consistent with the product analysis of catalyzed cathodes from full Li/O₂ cell galvanostatic discharge experiments showing the presence of both the peroxide and monoxide reduction products. Additionally the study of the CoN₄ center in-situ via XAS confirmed that the Co atom is involved in the chemisorption of the oxygen reactant further supporting our findings using the other techniques. Furthermore through our ex-situ studies of discharged CoN₄ electrodes we established that the Co²⁺ local chemical environment is stable throughout the full cell discharge to 1.5 V. This confirms that the discharge reaction does not correspond to the reduction of the Co²⁺, but in fact the higher discharge voltage is a consequence of the ORR catalysis in which the activation energy for oxygen reduction is lowered through its
adsorption onto the cobalt ion. Especially considering the specific energy advantage associated with achieving the full reduction of oxygen in a Li/O₂ cell as shown in Table 1.1, these developments are significant. The work presented in this thesis also provided data showing for the first time that the solvent properties influence oxygen reduction reaction catalysis whereby high donor number solvents such as DMSO override the influence of catalysts like CoPC to promote homogeneous ORR catalysis in which the reactions occur on the outer Helmholtz sphere of the electrode surface.

6.2 Future Directions

With the massive amount of interest and research efforts taking place, the Li/O₂ technology is bound to have successful practical applications in the future. Firstly, the U.S. military is interested in developing the technology as a primary battery which would provide the capacity to recharge multiple Li-ion batteries in the field to power communication devices. The system is very attractive toward this end as it is the most lightweight battery capable of providing the necessary energy. The primary cell development avoids all the obstacles associated with a secondary battery and will likely be available very soon.

Regarding the establishment of a secondary Li/O₂ technology there remains further development to be made before this will be possible. One major hurdle is the development of an electrolyte which will facilitate the reversible stripping and plating of the lithium metal at least 500 times without the formation of detrimental pits or dendrites. This is one issue that is rarely addressed in the literature submissions yet will need to be resolved before a lithium anode can be incorporated into the secondary system. Such a development would be epic. Aside from the anode reactions there still needs to be further investigation of the electrolyte’s stability in the presence of the superoxide radical and the peroxide products. I predict that there will be a
discovery in the future of an electrolyte, either liquid polymer or ionic liquid which will provide the stability (and perhaps solubility of the ORR products) toward chemical degradation from the ORR products and at the same time allows for the reversible anode reactions over 1000s of cycles. Once this is established many doors will be opened for applications involving this extremely energy dense rechargeable lithium battery.
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