INVESTIGATIONS OF OXYGEN REDUCTION REACTIONS IN NON-AQUEOUS ELECTROLYTES AND THE LITHIUM-AIR BATTERY

A Dissertation Presented

by

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ABSTRACT OF DISSERTATION

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Abstract

Unlocking the true energy capabilities of the lithium metal negative electrode in a lithium battery has until now been limited by the low capacity intercalation and conversion reactions at the positive electrodes. This is overcome by removing these electrodes and allowing lithium to react directly with oxygen in the atmosphere forming the Li-air battery. The Li/O$_2$ battery redox couple has a theoretical specific energy of 5200Wh/Kg and represents the ultimate energy density, environmentally friendly battery.

Chapter 2 discusses the intimate role of electrolyte, in particular the role of ion conducting salts on the mechanism and kinetics of oxygen reduction in non-aqueous electrolytes designed for such applications and in determining the reversibility of the electrode reactions. Such fundamental understanding of this high energy density battery is crucial to harnessing its full energy potential. The kinetics and mechanisms of O$_2$ reduction in solutions of hexafluorophosphate salts of the general formula $X^+ PF_6^-$, where, $X = $ tetra butyl ammonium (TBA), K, Na and Li, in acetonitrile have been studied on glassy carbon electrodes using cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques. Our results show that cation choice strongly influences the reduction mechanism of O$_2$. Large cations such as TBA facilitate reversible O$_2$ reduction involving the one electron reduction product, O$_2^-$ which is stabilized by the large TBA cation. In contrast small cations like Li (and other alkali metals), promote an irreversible electrochemical reaction. The initial reaction again is one-electron reduction of O$_2$ to LiO$_2$ or other alkali metal superoxides. The LiO$_2$
formed initially either decomposes to Li₂O₂ or undergoes further reduction to Li₂O₂ and Li₂O. Electrochemical data supports the view that alkali metal oxides formed via electrochemical and chemical reactions passivate the electrode surface inhibiting the kinetics and reversibility of the processes. The O₂ reduction mechanisms in the presence of the different cations have been supplemented by kinetic parameters determined from detailed analyses of the CV and RDE data. The Lewis acid characteristics of the cation appear to be crucial in determining the reversibility of the system. The organic solvent present in the Li⁺-conducting electrolyte has a major role on the reversibility of each of the O₂ reduction products as found from the work discussed in the next chapter.

A fundamental study of the influence of solvents on the oxygen reduction reaction (ORR) in a variety of non-aqueous electrolytes was conducted in chapter 4. In this work special attention was paid to elucidate the mechanism of the oxygen electrode processes in the rechargeable Li-air battery. Towards this end, using either tetrabutylammonium hexafluorophosphate (TBAPF₆) or lithium hexafluorophosphate (LiPF₆) electrolyte solutions in four different solvents, namely, dimethyl sulfoxide (DMSO), acetonitrile (MeCN), dimethoxyethane (DME), and tetraethylene glycol dimethyl ether (TEGDME), possessing a range of properties, we have determined that the solvent and the supporting electrolyte cations in the solution act in concert to influence the nature of reduction products and their rechargeability. In solutions containing TBA⁺, O₂ reduction is a highly reversible one-electron process involving the O₂/O₂⁻ couple in all of the electrolytes examined with little effect on the nature of the solvent. On the other hand, in Li⁺-containing electrolytes relevant to the Li-air
battery, O₂ reduction proceeds in a stepwise fashion to form O₂⁻, O₂²⁻ and O³⁻ as products. These reactions in presence of Li⁺ are irreversible or quasi-reversible electrochemical processes and the solvents have significant influence on the kinetics, and reversibility or lack thereof, of the different reduction products. The stabilization of the one-electron reduction product, superoxide (O₂⁻) in TBA⁺ solutions in all of the solvents examined can be explained using Pearson’s Hard Soft Acid Base (HSAB) theory involving the formation of the TBA⁺---O₂⁻ complex. The HSAB theory coupled with the relative stabilities of the Li⁺-(solvent)ₙ complexes existing in the different solvents also provide an explanation for the different O₂ reduction products formed in Li⁺-conducting electrolyte solutions. Reversible reduction of O₂ to long-lived superoxide in a Li⁺-conducting electrolyte in DMSO has been shown for the first time here.

Chapter 5 is the culmination of the thesis where the practical application of the work is demonstrated. We designed electrolytes that facilitate Li-Air rechargeability, by applying the knowledge gained from chapters 2-4. A rechargeable Li-air cell utilizing an electrolyte composed of a solution of LiPF₆ in tetraethylene glycol dimethyl ether, CH₃O(CH₂CH₂O)₄CH₃ was designed, built and its performance studied. It was shown that the cell yields high capacity and can be recharged in spite the absence of catalyst in the carbon cathode. From the X-ray diffraction patterns of the discharged carbon electrodes, the discharge product of the cell was identified to be Li₂O₂ during normal discharge to 1.5 V. Discharging the cell to 1.0 V produces Li₂O as well. The application of X-ray diffraction to identify these products formed in a porous carbon electrode is shown here for the first time. The rechargeability of
the cell was investigated by repeated charge/discharge cycling of the cell, and the factors limiting the cycle life of the cell were studied using AC impedance spectra of the cells as a function of cycle number.

In conclusion, the work carried out in this research has shown that the O$_2$ electrochemistry in organic electrolytes is substantially different from that in aqueous electrolytes. Our work has uncovered the key roles the ion conducting salts and the organic solvents play in determining the nature of the reduction products and their reversibility. The results presented here for the first time provide a rational approach to the design and selection of organic electrolyte solutions for use in the rechargeable Li-air battery. Factors affecting the cycle life limitations of the Li-air cell have been identified from the cycling performance and the associated impedance changes of Li/air laboratory test cells. Our work is expected to contribute to the rapid development of the rechargeable Li-air battery.
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I would like to thank Dr K.M Abraham, for his mentorship and guidance during the last six years of my graduate career. It is a great honor to be his first graduate student and the first of what I am sure will be a long line of students. I’m grateful for K.M taking me under his wing and selflessly imparting decades of scientific and life advice. His uncanny knack of turning lemons into lemonade is inspiration to all his students and serves as a life lesson to us all.

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To my wonderful parents Denis and Eucharia you can start cashing in all those IOU’s. Hopefully it goes without saying how much I appreciate all your love. Thank you for enabling me to pursue my dream and supporting me during the highs and lows. I want you to know this is your PhD too.
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For the family member funerals I missed Damien O Callaghan and Ben Healy may you all rest in peace.
# Table of Contents

Abstract 4  
Acknowledgements 8  
Table of Contents 11  
List of Tables 14  
List of Figures 16  
List of Illustrations 22  
List of Abbreviations and Symbols 23

## Chapter 1 Introduction 25

1.1 Energy Challenge 25  
1.2 Batteries 27  
1.3 Fundamentals of the Lithium –Air Battery 34  
1.4 Lithium-Air Today 37  
1.5 Non-Aqueous Electrolytes 40  
1.6 Non Aqueous Oxygen Reduction Reaction (ORR) 45  
1.7 Scope of Dissertation 47  
1.8 References 48

## Chapter 2 Electrochemical Studies of Ferrocene in a Lithium Ion Conducting Organic Carbonate Electrolyte 51

2.1 Introduction 51  
2.2 Experimental 53  
2.2.1 Chemical Reagents 53  
2.2.2 Instrumentation 54  
2.3 Results and Discussion 55  
2.3.1 Cyclic Voltammetry 55  
2.3.2 Rotating Disk Electrode 62  
2.4 Conclusions 66
Chapter 3  Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Application

3.1  Introduction 70
3.2  Experimental 73
3.2.1  Chemical Reagents 73
3.2.2  Instrumentation 73
3.3  Results and Discussion 74
3.3.1  Oxygen Reduction in Tetrabutylammonium hexafluorophosphate (TBA⁺PF₆⁻)-Based Electrolytes 76
3.3.2  Oxygen Reduction in Alkali Metal-Hexafluorophosphate (X⁺PF₆⁻)-Based Electrolytes 87
3.4  Conclusions 99
3.5  References 100

Chapter 4  Influence of Non-aqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air battery

4.1  Introduction 102
4.2  Experimental 106
4.2.1  Materials 106
4.2.2  Electrochemical Experiments 106
4.3  Results and Discussion 108
4.3.1  ORR in Selected Non-Aqueous Electrolytes 108
4.3.2  ORR in TBAPF₆ solutions in DMSO, DME and MeCN 110
4.3.3  ORR in LiPF₆ solutions in DMSO, DME, MeCN, and TEGDME 117
4.3.4 Impedance spectroscopy to determine O₂ reduction kinetics 128
4.3.5 Understanding ORR in non-aqueous electrolytes using Pearson’s HSAB Theory
4.4 Conclusions 136
4.5 References 137

Chapter 5 A Rechargeable Lithium/TEGDME-LiPF₆/O₂ Battery 140

5.1 Introduction 141
5.2 Experimental 141
5.2.1 Materials 141
5.2.2 Li/O₂ Cells 142
5.3 Results and Discussion 143
5.3.1 Li/O₂ Cell Discharge and Charge Behavior 146
5.3.2 Factors affecting the Cycle Life of the Li/O₂ Cell 154
5.4 Conclusions 160
5.5 References 161

Chapter 6 Thesis Summary and Future Directions 163

6.1 Summary 163
6.2 Salt Effects on ORR 163
6.3 Solvent Effects on ORR 164
6.4 Experimental Li-Air Cells 165
6.5 Future Directions for Li-Air Research 165

Biographical Information 167
List of Tables

Chapter 1

Table 1.1. Standard Electrode Potentials in Aqueous Solutions at 25°C in V vs. SHE.

Table 1.2. Practical and Theoretical Energy Capacity.

Table 1.3. Physical and Chemical properties.

Chapter 2

Table 2.1. Voltammetric properties of Fe/Fc$^+$.

Chapter 3

Table 3.1. Physical properties of Acetonitrile.

Table 3.2. Conductivity and Viscosity of the Electrolyte Solutions in acetonitrile.

Table 3.3. Electrochemical Charge area under the peaks. Scan rate 100mV/s. Error ± 0.002C.

Table 3.4. Voltammetric properties of 0.1MTBAPF$_6$ & TBACIO$_4$ in oxygen saturated acetonitrile. Scan rate 100mV/s. Potential error ±0.002V.

Table 3.5. Voltammetric properties of O$_2$/O$_2^-$ redox couple in 0.1MTBAPF$_6$ & TBACIO$_4$/MeCN.

Table 3.6. Voltammetric properties of 0.1M Li, Na &KPF$_6$ in oxygen saturated acetonitrile. Scan rate 25mV/s.
Chapter 4

**Table 4.1.** Conductivity of the Electrolyte Solutions.

**Table 4.2.** Solvent Properties.

**Table 4.3.** Voltammetric properties of oxygen saturated electrolytes. Scan rate 100mV/s.

**Table 4.4.** Oxygen Diffusion coefficient in electrolytes.

**Table 4.5.** $O_2/O_2^-$ kinetic parameters of 0.1M Li & TBAPF$_6$.

Chapter 5

**Table 5.1.** Tetraethylene glycol dimethyl ether Properties.
List of Figures

Chapter 1

Figure 1.1. Electrochemical operation of a battery during (a) charging &
(b) discharging.

Figure 1.2. Lithium-ion cell schematic.

Figure 1.3. Lithium-ion cell material costs.

Figure 1.4. Ragone plot showing energy density vs. power density for various
energy devices.

Figure 1.5. Lithium air cell schematic.

Figure 1.6. Electrolyte salts.

Chapter 2

Figure 2.1. Purpose built air tights electrochemical cell.

Figure 2.2. Cyclic voltammograms for the oxidation of 3.3mM Ferrocene in
1M LiPF$_6$/1:1 EC: EMC on a glassy carbon working electrode at a scan rate of
100mVs$^{-1}$.

Figure 2.3. (A) Cyclic Voltammograms for Fc/Fc$^+$ in 1M LiPF$_6$/1:1 EC: EMC
on a GC electrode at sweep rates between 5mVs$^{-1}$ and 300 mVs$^{-1}$. (B)
Randles-Sevcik plot of peak current vs. square root of the scan rate for the
curves in 2.3(A).
Figure 2.4. (A) Disk currents on a RDE obtained in 1M LiPF<sub>6</sub>/1:1EC: EMC in the anodic sweep at room temperature by various rotation rates. (B) Levich plot of limiting current vs. square root of rotation for the data in fig 2.3(A) at scan rate = 10 mVs<sup>-1</sup>.

Figure 2.5. Tafel plots for ferrocene oxidation at room temperature on a glassy carbon electrode at 2500 rpm for anodic sweep from 3.145V to 3.35V at 10mVs<sup>-1</sup> (OCP 3.145V vs Li/Li<sup>+</sup>).

Chapter 3

Figure 3.1. A) iR corrected voltammograms for the reduction of oxygen in 0.1M TBAPF<sub>6</sub> (Black), 0.1M TBAClO<sub>4</sub> (Blue) and the argon background (dotted) in MeCN. B) CVs in the –2 to +0.5 V range. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.

Figure 3.2. (A) Cyclic Voltammograms for the reduction of oxygen saturated 0.1M TBAPF<sub>6</sub>/MeCN on GC electrode at sweep rates 0.1V/s (solid), 0.1V/s (long dash) and 0.025V/s (short dash), (B) Randles-Sevcik plot of peak current vs. square root of the scan rate for the curves in 0.1 M TBAPF<sub>6</sub> & 0.1 M TBAClO<sub>4</sub>/MeCN.

Figure 3.3. (A) Disk currents obtained in 0.1 M TBAPF<sub>6</sub> MeCN during ORR in the anodic sweep at room temperature by various rotation rates at 100mV/s. (B) Levich plot of limiting current vs. square root of rotation in 0.1 M TBAPF<sub>6</sub> & 0.1 M TBAClO<sub>4</sub> in MeCN vs. Ag/AgCl at scan rate =100mVs<sup>-1</sup>.

Figure 3.4. Tafel plots for ORR at room temperature on a glassy carbon electrode at 2500 rpm for cathodic sweep 0.1V to -0. /s. (OCP: TBAPF<sub>6</sub> - 0.25V & TBAClO<sub>4</sub> -0.34 vs Ag/AgCl).
Figure 3.5. (A) Cyclic voltammograms of oxygen reduction in 0.1M LiPF$_6$ (dashed line), 0.1M NaPF$_6$ (Solid) in MeCN. Scan rate of 100mV/s (-3V to 3V vs. Ag/AgCl). (B) Oxygen reduction voltammograms in 0.1M LiPF$_6$ /MeCN on GC electrode at various sweep rates.

Figure 3.6. Semi-log plot of potential versus log $\frac{I_d - I}{I}$ for the reduction of oxygen in 0.1M LiPF$_6$ (red), 0.1M NaPF$_6$ (Black) and 0.1MKPF$_6$ (Blue) in MeCN obtained at a scan rate of 25mV/s versus Ag/AgCl.

Figure 3.7. Experimental and theoretical (n=1) $\sqrt{v}$ vs. Ip plots for in 0.1M LiPF$_6$, NaPF$_6$, and KPF6 & 1M KPF$_6$ in MeCN.

Figure 3.8. Cyclic Voltammograms for the reduction of oxygen saturated 1M XPF$_6$ (X= Li$^+$, Na$^+$, K$^+$) in MeCN on GC electrode at 500mV/s.

Figure 3.9. Steady voltammograms for the reduction of oxygen in 0.1M LiPF$_6$ & NaPF$_6$ in MeCN at various rotation rates at 100mV/s.

Chapter 4

Figure 4.1. Solvent Structures.

Figure 4.2. A) Cyclic voltammograms for the reduction of oxygen in 0.1M TBAPF$_6$ (Red, iR corrected) and the argon background (dotted) in DMSO. B) Cyclic voltammograms (iR un-corrected) for the reduction of oxygen in 0.1M TBAPF$_6$/MeCN (Black), DME (Blue). Scan rate 100mV/s.

Figure 4.3. Randles-Sevcik plot of peak current vs. square root of the scan rate in 0.1 M TBAPF$_6$/DMSO.
Figure 4.4. Levich plot of limiting current vs. square root of rotation in 0.1 M TBAPF$_6$/DMSO scan rate=100mVs$^{-1}$ (Inset Tafel plot).

Figure 4.5. Current-voltage curves measured at 100 mV/s on a GC rotating disk electrode (400-3600rpm) for oxygen reduction in (A) 0.1M TBAPF$_6$/DMSO (B) 0.1M TBAPF$_6$/MeCN. Insets: Koutecky- Levich plot at different potentials in kinetic-diffusion region of the polarization curve.

Figure 4.6. Cyclic voltammograms (iR corrected) for the reduction of oxygen in 0.1M LiPF$_6$/DMSO at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.

Figure 4.7. (A) Peak current vs. square root of the scan rate in 0.1 M LiPF$_6$/DMSO. (B) Cathodic Tafel plot obtained in 0.1 M LiPF$_6$/DMSO during ORR. Scan rate = 10mV/s.

Figure 4.8. Cyclic voltammograms (iR corrected) for the reduction of oxygen in 0.1M LiPF$_6$/MeCN at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.

Figure 4.9. Cyclic voltammograms (iR corrected) for the reduction of oxygen in (A) 0.1M LiPF$_6$/DME & (B) 0.1M LiPF$_6$/TEGDME at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.

Figure 4.10. Peak current vs. square root of the scan rate plots for the reduction of oxygen in (A) 0.1 M TBAPF$_6$ & 0.1 M LiPF$_6$/MeCN. n = number of e$^-$ (B) 0.1M TBA$^+$ & LiPF$_6$/DME and 0.1M LiPF$_6$/TEGDME on GC electrode.
**Figure 4.11.** Real impedance versus inverse square root of frequency in 0.1 M LiPF$_6$ DMSO (grey), DME (blue), TEGDME (red) and MeCN (black).

**Chapter 5**

**Figure 5.1.** Li-air cell.

**Figure 5.2.** Cyclic voltammograms for the reduction of oxygen in 0.1M LiPF$_6$/TEGDME (Blue) and the argon background (Black). Scan rate 100mV/s.

**Figure 5.3.** Li/air cell discharge curves at 0.25 (blue) & 0.16 (black) mA/cm$^2$ in 1M LiPF$_6$/TEGDME. Capacities are expressed per gram of carbon in the electrode.

**Figure 5.4.** XRD pattern of fully discharged air cathode in 1M LiPF$_6$/TEGDME.

**Figure 5.5.** Full Discharge of Li/air cell discharge at 0.16mA/cm$^2$ in 1M LiPF$_6$/TEGDME. Following discharge the cell was charged to 4.5V.

**Figure 5.6.** A) The cycling data for a 1M LiPF$_6$/TEGDME electrolyte oxygen cell at room temperature. The cell was discharged and charged for 2 hours at 0.13 mA/cm$^2$. Capacities are expressed per gram of Black Pearls 2000 carbon + PVDF in the electrode. B) Discharge/Charge capacities as a function of cycle number for the same cell.

**Figure 5.7.** A) The cycling data for a 1M LiPF$_6$/TEGDME electrolyte oxygen cell at room temperature. The cell was discharged and charged for 2 hours at 0.13 mA/cm$^2$. Capacities are expressed per gram of Black Pearls 2000 carbon
+ PVDF in the electrode. B) Discharge/Charge capacities as a function of cycle number for the same cell.

**Figure 5.8.** Discharge curves of the lithium air cell at various current densities in 1M LiPF6/TEGDME oxygen cell at room temperature. Capacities are expressed per gram of carbon in the electrode. (Red) 0.25mA/cm², (Blue) 0.13mA/cm², (Black) 0.07mA/cm².

**Figure 5.9.** Nyquist impedance plots of the Li-air battery for both (9a) 2h (9b) 14h Discharge states (9c) 2h charge states at various cycles. (9)The data is fitted by using a RC equivalent-circuit model.

**Figure 5.10.** Rechargeable Lithium anode.

**Figure 5.11.** SEM micrographs of the air cathode (11a) fresh (11b) discharged. Scale bar is 1 μm. Energy-dispersive X-ray spectroscopy (EDAX) (11c) fresh (11d) discharged at 0.13 mA/cm² in oxygen.

**Figure 5.12.** (a) Full discharge of Li/air cell in 1M LiPF6/TEGDME (-0.13mA/cm²). (b) Nyquist plot
List of Illustrations

Chapter 4

**Structure I**  Ion pair between TBA$^+$ and O$_2^-$ . Nitrogen is blue, carbon is gray and O is red. (Alkyl hydrogens are omitted in the structure)

**Structure II**  Ion pair between solvated Li$^+$ and O$_2^-$. (The methyl hydrogens are omitted in the structure)
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Electron transfer coefficient</td>
</tr>
<tr>
<td>$\Delta E_p$</td>
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</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
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<td>$\Delta G^0$</td>
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<td>$E^0$</td>
<td>Standard potential</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron spin resonance</td>
</tr>
<tr>
<td>F</td>
<td>Faradays Constant</td>
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\( i \)   \( i \)\( ^0 \)   \( i_k \)   \( i_{\text{lim}} \)   \( i_{\text{pc}} \)   \( k^0 \)   \( n_e \)   \( N \)   \( O \)   \( \text{OCP} \)   \( \text{ORR} \)   \( R \)   \( R \)   \( \text{RDE} \)   \( T \)   \( t \)   \( \text{UHP} \)   \( \text{UHV} \)   \( V \)   \( \text{WE} \)

Current density
Exchange current density
Kinetic current density
Diffusion limiting current
Cathodic peak current density
Standard rate constant
Number of electrons
Coordination number
Oxidized reactant
Open circuit potential
Oxygen reduction reaction
Reduced reactant
Gas constant
Rotating disk electrode
Temperature
Time
Ultra-high purity
Ultra-high vacuum
Volts
Working electrode
Chapter 1

Introduction

1.1 Energy Challenge

In mid 2009, just after taking office as Secretary of Energy, Steven Chu addressed a clean energy forum and urged the scientific community to take on what he called "the energy challenge." Put simply the challenge is for humans to develop alternative energy resources that run in harmony with nature, a difficult yet not impossible task for our highly skilled scientific community.

The search for renewable energy sources is driven by humanity's appetite for energy. By 1800s the industrial revolution was in full flight, machines were able to replace humans resulting in higher output at lower cost. Interestingly, prior to the industrial revolution, renewable energy resources such as wind, water and wood supplied human energy needs. The industrial revolution led to an increase in food production, clothing and housing resulting in unprecedented population growth. This new society could now educate more individuals leading to developments in technology and medicine in turn making life longer and more comfortable for the masses. According to the U.N Department of Economic and Social Affairs census, the world population has grown by 600% since the onset of the industrial revolution and a further 200% increase is expected by 2025. Human population explosion is inextricably linked with energy. Future population growth will drain the earth’s resources and energy demand will increase. Renewable energy is generally an
inexhaustible source and typically undeveloped due to the overall reliance on fossil fuels over the last century. Viable renewable energy sources are listed below.

- Bioenergy
- **Electric Power**
- Fusion
- Geothermal
- Hydrogen
- Hydropower
- Nuclear
- Renewables
- Solar
- Wind

The sun delivers 800 terawatts (tW) of energy continually, of this only 18 tW are required by a 9 billion-person planet\(^3\). A small percentage of this energy was captured by earth and stored as non-renewable in the form of fossil fuels. We do not have billions of years to wait for fossil fuels to be replenished. Solar energy will likely be the game changer or a combination of these technologies. The energy challenge at its core consists of two entwined issues. Firstly, that of energy generation, which encompasses fossil fuels, nuclear, hydropower, wind, electric power and so on. Secondly, once we have generated energy how do we store it? Energy can be stored as heat in thermal storage, or as chemical energy in batteries and capacitors. In the mid nineties Dr K.M Abraham and his colleague developed the non-aqueous lithium air battery (Li-air)\(^4\) which addresses both these issues simultaneously. The lithium air battery can act as both an energy source and energy storage device. I found this energy system to be most intriguing and decided to devote my graduate career to it.
1.2 Batteries

A battery allows a controlled oxidation-reduction (redox) reaction to occur to generate electricity. Chemically, energy trapped in active materials on polar electrodes in the battery is converted to electrical energy. Electrons travel from the negative to the positive electrode through an external circuit to power the load and complete the discharge reaction in combination with the ions that flow between the electrodes inside. A battery cell consists of three key components:

1) Anode (negative electrode) gives up electrons (or undergoes oxidation reaction) during discharge.

2) Cathode (positive electrode) accepts electrons (or undergoes reduction reaction) during discharge.

3) Electrolyte facilitates the flow of ions between the electrodes and ultimately decides the kinetics of the reaction. The electrolyte together with an ion-conducting separator keeps the electrodes isolated electronically from one another to prevent short circuit.

In a rechargeable battery, the opposite processes occur during recharge (Figure 1.1).
The theoretical voltage of a reaction is determined by the difference between the Gibbs free energy of reactants and products.

\[
\Delta G^o_{\text{reaction}} = \sum \Delta G^o_f (\text{products}) - \sum \Delta G^o_f (\text{reactants}) \quad (\text{Equation 1.1})
\]

\[
\Delta G^o = nFE \quad (\text{Equation 1.2})
\]

Where \( E \) is the cell voltage, \( n \) number of electrons consumed in the reaction, and \( F \) is Faraday's constant, the charge on one mole of electrons (96500C). The capacity of a cell is the total quantity of charge involved in a reaction defined as coulombs or ampere-hours. Usually capacities are normalized by the mass of the material and reported as gravimetric specific capacities, milliampere-hours per gram (mAh/g).
The specific energy, $S_E$, of batteries is given in Wh/kg and is calculated by multiplying the specific capacity by the voltage of the system.

$$S_E \text{ (Specific Energy)} = \text{Voltage (E)} \times \text{ampere-hour (Ah)} \quad (Equation \ 1.3)$$

Battery power is a function of current measured in C rates. The 1C rate is defined as the amount of current needed to fully discharge the battery in one hour.

The lightest anode and cathode materials with the highest cell voltages lead to the greatest energy. Table 1.1 shows standard redox potentials for various redox couples versus a standard hydrogen electrode (SHE). Lithium is the strongest reducing agent displaying the highest negative potential. Fluorine is the strongest oxidizing agent with the largest positive potential. A Lithium-Fluorine redox couple yields the highest theoretical voltage; unfortunately these elements react quite violently.

Today’s battery research is focused on those based on lithium metal as it is the most electropositive element known (-3.04V vs. SHE) and also the lightest metal (6.94 gram per mole). Consequently, lithium based battery systems have extremely high energy densities.
Table 1.1 Standard Electrode Potentials in Aqueous Solutions at 25°C in V vs. SHE.

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>E° /V</th>
<th>Electrode reaction</th>
<th>E° /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺ + e⁻ → Li</td>
<td>- 3.045</td>
<td>AgI + e⁻ → Ag + I⁻</td>
<td>- 0.152</td>
</tr>
<tr>
<td>K⁺ + e⁻ → K</td>
<td>- 2.925</td>
<td>Sn²⁺ + 2e⁻ → Sn</td>
<td>- 0.136</td>
</tr>
<tr>
<td>Ca²⁺ + 2e⁻ → Ca</td>
<td>- 2.84</td>
<td>Pb²⁺ + 2e⁻ → Pb</td>
<td>- 0.125</td>
</tr>
<tr>
<td>Na⁺ + e⁻ → Na</td>
<td>- 2.714</td>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>0 exactly</td>
</tr>
<tr>
<td>Mg²⁺ + 2e⁻ → Mg</td>
<td>- 2.56</td>
<td>Sn⁴⁺ + 2e⁻ → Sn²⁺</td>
<td>0.15</td>
</tr>
<tr>
<td>Sc³⁺ + 3e⁻ → Sc</td>
<td>- 2.03</td>
<td>AgCl¹⁻ + e⁻ → Ag + Cl⁻</td>
<td>0.2223</td>
</tr>
<tr>
<td>Be²⁺ + 2e⁻ → Be</td>
<td>- 1.97</td>
<td>½O₂ + H₂O + 2e⁻ → 2OH⁻</td>
<td>0.40</td>
</tr>
<tr>
<td>Al³⁺ + 3e⁻ → Al</td>
<td>- 1.67</td>
<td>Cu²⁺ + e⁻ → Cu</td>
<td>0.520</td>
</tr>
<tr>
<td>Ti²⁺ + 2e⁻ → Ti</td>
<td>- 1.63</td>
<td>Fe²⁺ + e⁻ → Fe²⁺</td>
<td>0.771</td>
</tr>
<tr>
<td>Mn²⁺ + 2e⁻ → Mn</td>
<td>- 1.18</td>
<td>Ag⁺ + e⁻ → Ag</td>
<td>0.799</td>
</tr>
<tr>
<td>Zn²⁺ + 2e⁻ → Zn</td>
<td>- 0.763</td>
<td>Pd²⁺ + 2e⁻ → Pd</td>
<td>0.915</td>
</tr>
<tr>
<td>Fe²⁺ + 2e⁻ → Fe</td>
<td>- 0.44</td>
<td>O₂ + 4H⁺ + 4e⁻ → 2H₂O</td>
<td>1.229</td>
</tr>
</tbody>
</table>

Lithium’s unique properties high voltage, high capacity (3.86 Wh/kg) and the ability to operate over a wide temperature range make it an ideal material for both primary and secondary cells. Lithium anodes are quite safe for primary cells; however safety is an issue in their rechargeable or secondary analogues. During the charge process in a secondary lithium battery, metallic lithium is electroplated onto the anode surface forming a porous deposit with a larger surface area than the original metallic electrode. As the surface area increases with repeated charging and
discharging of the battery, metallic lithium is less thermally stable. The formation of the high surface area lithium dendrites on the anode surface can also lead to the shorting of cells when it grows through the separator and touches the cathode.

Removing metallic lithium and replacing it with ionic lithium (Li$^+$) solves many of these problems. The Lithium ion (Li-ion) concept involves replacing metallic lithium anodes with intercalation compounds such as graphite. Carbon-based anodes materials stabilize the electrode/electrolyte interface and can operate at voltages outside lithium metal. Typical cathode intercalation compounds are transition metal oxides (LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$), which incorporate lithium in their lattices and undergo oxidation to higher valences when Li is removed during charge and vice versa when Li is inserted during discharge. Figure 1.2 shows a schematic of a rechargeable Li-ion battery.$^7$

![Figure 1.2 Lithium-ion schematic]$^8$. 

Throughout the charging process lithium migrates from the cathode (for example a lithium metal dioxide such as LiCoO$_2$) through the electrolyte and is intercalated into the graphite anode (Li$_x$C$_6$). During discharge lithium is extracted from the anode and intercalated into the cathode.

\[
\text{LiMO}_2 \quad \xrightarrow{\text{Charge}} \quad \text{Li}_1 - x \text{MO}_2 + x\text{Li}^+ + xe^- \quad \text{Cathode}
\]

\[
6\text{C} + x\text{Li}^+ \quad \xrightarrow{\text{Charge}} \quad \text{Li}_x\text{C}_6 \quad \text{Anode}
\]

\[
6\text{C} + \text{LiMO}_2 \quad \xrightarrow{\text{Discharge}} \quad \text{LiC}_6 + \text{Li}_{1-x}\text{MO}_2 \quad \text{Overall}
\]

Cathode intercalation electrode materials contain transition metals (M) such as (Co, Mn, Ni, Fe) and the prominent examples include, LiCoO$_2$, LiNiO$_2$, LiNi$_{0.8}$Co$_{0.2}$O$_2$, LiMn$_2$O$_4$ and LiFePO$_4$. Lithium ion batteries are the state-of-the-art although they are not without their problems. At full charge graphite can only incorporate one lithium per hexagon (LiC$_6$). As a result anode capacity drops from 3861Ah/g in the case of elemental Li to 372mAh/g for graphite almost a 90% decrease$^9$. Internal resistance increases throughout the cycle life of the cell due to reactions between the electrolyte and electrodes which inhibit lithium ion transport and reduce cell capacity$^{10,11}$. Battery lifetime is drastically reduced at high temperatures as a result of increased chemical reactions at the electrode-electrolyte interfaces$^{12,13}$. Long-term storage is an issue as chemicals and materials are prone to
aging. In 2006 a series of fires associated with Dell laptops prompted an unprecedented recall\textsuperscript{14} of Dell Li-ion batteries. Such incidents have highlighted the need for safer Li-ion batteries.

Battery price is a concern especially for large batteries for electric vehicle propulsion. One kg of oil gives about 20Wh/kg practical energy at a cost of $0.53/kg, which is miniscule when compared to the costs of Li-ion batteries. Figure 1.3 shows the results of a study conducted by Argonne National Lab, which found the cost of a Li-ion battery to be around $158 per 100Ah cell having an energy density of 100Wh/kg.

![Figure 1.3 Lithium-ion cell material costs\textsuperscript{15}.](image)

Expensive cathodes are about 50\% of the cost for these cells, twice as much as other components. Research efforts are focused on the development of low cost long life materials, particularly electrode materials, and the key to lowering the price of rechargeable Li batteries. In this respect Li-air battery is highly promising as the electroactive element $O_2$ is free and environmentally friendly.
1.3 Fundamental of the Lithium-Air Battery

The Lithium-air battery is one of the most energy dense electrochemical power sources. Table 1.2 compares theoretical energy capacities of metal air batteries to well established systems.

<table>
<thead>
<tr>
<th>System</th>
<th>OCV, V</th>
<th>Theoretical Specific Capacity, Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li/O₂</td>
<td>2.91</td>
<td>5200 (including oxygen) 11140 (excluding oxygen)</td>
</tr>
<tr>
<td>Na/O₂</td>
<td>1.94</td>
<td>1677</td>
</tr>
<tr>
<td>Ca/O₂</td>
<td>3.12</td>
<td>2990</td>
</tr>
<tr>
<td>Mg/O₂</td>
<td>2.93</td>
<td>2789</td>
</tr>
<tr>
<td>Zn/O₂</td>
<td>1.65</td>
<td>1090</td>
</tr>
</tbody>
</table>

Theoretical Practical

<table>
<thead>
<tr>
<th>System</th>
<th>OCV, V</th>
<th>Theoretical Specific Capacity, Wh/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-ion</td>
<td>4.1</td>
<td>500-1000</td>
</tr>
<tr>
<td>Lead Acid</td>
<td>1.6</td>
<td>252</td>
</tr>
<tr>
<td>Ni-Cd</td>
<td>1.35</td>
<td>244</td>
</tr>
<tr>
<td>Na-S</td>
<td>2.1</td>
<td>791</td>
</tr>
<tr>
<td>Ni-MH</td>
<td>1.35</td>
<td>278</td>
</tr>
<tr>
<td>Gasoline</td>
<td></td>
<td>12000</td>
</tr>
</tbody>
</table>

Table 1.2 Practical and Theoretical Energy Capacities.
Figure 1.4 Ragone plot showing energy density vs. power density for various energy devices.

The Ragone plot (fig 1.4) shows Li-air has both high energy and power densities. Oxygen the cathode active material is not stored in the battery but is accessed from the environment, and in turn significantly reduces the battery’s total mass. The Li/O₂ redox couple has the highest theoretical energy density of any known viable redox couple and has the potential to significantly increase the energy density of practical batteries. Fully developed and optimally packaged Li-air batteries could exceed specific energies of 2000 Wh/kg, table 1.2 shows only gasoline has a higher theoretical energy density. However at only 20% efficiency its practical energy density pales in comparison to the Li-air battery. Specific energies for the metal-air cells were calculated using Gibbs energies of formation according to

\[ \Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{\text{f (products)}} - \sum \Delta G^\circ_{\text{f (reactants)}} \]
In practice, oxygen is not stored in the battery, which increases the theoretical specific capacity of the cell to 11,140 Wh/kg although the battery weight would increase as battery is discharged. Figure 1.5 shows a schematic of a Li-air cell. Lithium metal is oxidized at the anode to form Li$^+$ ions, which migrate towards the cathode. The electrons from the oxidation reaction at the anode are passed through an external circuit to perform work in the load, and are returned to the cell at the cathode to complete the electrochemical reaction in combination with the Li ions that migrate to it from the anode. Oxygen is reduced at the cathode in the presence of the supplied electrons and Li$^+$ ions to one or more of following products, LiO$_2$, Li$_2$O$_2$ and Li$_2$O.

Figure 1.5 Lithium air cell schematic.
The possible reactions of the Li-air cell at the cathode and anode are:

**Cathode**

(1) \( \text{O}_2(g) + \text{Li}^+ + e^- \rightarrow \text{LiO}_2(s) \Delta G^o = -70 \text{ kcal} \quad (E^o = 3.0 \text{ V}) \)

(2) \( \text{O}_2(g) + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{O}_2(s) \Delta G^o = -145 \text{ kcal} \quad (E^o = 3.1 \text{ V}) \)

(3) \( 2\text{O}_2(g) + 4\text{Li}^+ + 4e^- \rightarrow 2\text{Li}_2\text{O}(s) \Delta G^o = -268 \text{ kcal} \quad (E^o = 2.91 \text{ V}) \)

**Anode**

\( \text{Li}(s) \rightarrow \text{Li}^+ + e^- \quad (E^o = 0.00 \text{ V}) \)

Recently, we have shown\(^{16}\) that the first product of the reduction of oxygen in non-aqueous electrolytes is superoxide, \( \text{O}_2^- \), involving a one-electron process. We also found that the half-life of the superoxide depends on the cation present in the electrolyte solution. The most prominent product in Li-air cell as discussed in Chapters 3-5 is Li\(_2\)O\(_2\).

**1.4 Lithium-Air Today**

The non-aqueous Lithium air battery is a relatively new technology. It all began in 1996\(^4\) when a battery technician accidentally introduced a little oxygen to a Li/graphite half-cell of a Li-ion battery. Slightly bemused by the large increase in cell voltage, he showed his results to his boss (Dr K.M Abraham). He quickly recognized the importance of this accidental observation and put it together by devising a series of experiments which led to his seminal paper and the introduction of the non-aqueous organic Li-air battery. In the 15 years since, Li-air has emerged as major candidate
for alternative energy in the future. This first paper was quite bold in that it addressed the major drawbacks of the Li-air battery listed below.

a) Oxygen Solubility  
b) Lithium Oxide dissolution  
c) Stability of Lithium anode  
d) Catalyst Development for rechargeability

Rechargeability is the most significant obstacle that has to be overcome before full capability of the battery is realized as a renewable energy storage system. Oxidation of the reduction products is thermodynamically unfavorable and suffers from poor kinetics. The first Li-air cell was composed of a Li anode, a polyacrylonitrile-based gel polymer electrolyte and a porous carbon cathode. In the absence of a catalyst the oxidation reaction occurs near 4V, and a large hysteresis between charge and discharge voltages was observed. The hysteresis was reduced by employing a cobalt phthalocyanine (CoPc) - based oxidation catalyst which also improved charge/discharge efficiency. Recent investigations have employed manganese oxide (MnO2) catalysts although the charge voltages in these cells are similar to the uncatalyzed cells. Through Raman spectroscopy Lithium peroxide (Li2O2) was identified as the chief discharge product. The formation of Lithium peroxide is consistent with the open circuit voltage (OCV) of about 2.9V measured for the cell and the theoretical voltages calculated for the reactions in equations 1-3. Li-air cells shares similar drawbacks relevant to both Li-ion and fuel cell technologies, therefore teething problems were surmounted by applying known
solutions. An avenue of investigation is applying existing electrolytes from conventional Li-ion batteries to Li-air. Initially Jeffery Read investigated possible electrolytes, by drawing on his experience with Li-ion electrolytes\textsuperscript{20-22}. The results of his studies found electrolyte formulation has a large influence on cell performance. Kuboki et al\textsuperscript{23} studied the performance of hydrophobic ionic liquids in an ambient environment as electrolytes. Ionic liquids demonstrated high lithium stability and high discharge capacities. A number of groups are interested incorporating solid electrolytes in Li-air batteries. Protected lithium electrodes (PLE) such as Lisicon\textsuperscript{24} have been applied successfully in both aqueous and non-aqueous Lithium batteries. Such coating protect against moisture permeation into the cell especially to the anode. Low carbon loading on nickel foam\textsuperscript{25} has demonstrated the highest discharge capacity thus far (5,000mAh/g).

Li-air discharge products are fairly insoluble in contemporary Li-ion organic electrolytes. Rechargeability maybe enhanced by suitable organic solvents. Electrode structure is crucial as it sets the stage for the oxygen reduction reaction (ORR). Appropriate electrode morphology, surface structure, pore volume and surface area can enhance the rechargeability of the Li-air cell. Our recent studies have revealed that the Li/O\textsubscript{2} cell can be recharged with high efficiency without a catalyst by using appropriate porous carbon electrodes. Interestingly charge voltages of these uncatalyzed cells are similar to those of the MnO\textsubscript{2} catalyzed cells with both of these cell exhibiting higher charge voltages than the cobalt-catalyzed cells. Studies discussed in Chapter 5 have uncovered factors limiting the rechargeability of the Li-air battery.
1.5 Non-Aqueous Electrolytes

The majority of electrochemical reactions are carried out in solution. A liquid medium allows control of reaction conditions, i.e., temperature, pressure, rate of mass transfer and reactant concentration. Water is the most popular solvent, its high polarity (78 \( \varepsilon \) (dielectric constant)) make it ideal for dissolving a wide variety of salts. In certain circumstances water maybe an undesirable medium for the following reasons:

1) Water is a source of protons, which are highly reactive with electrode materials and alkali earth metals, which undergo fast hydrolysis.

2) The electrochemical window of water is too narrow (1.299V). Hydrogen and oxygen evolution occurs at cathode and anode, respectively. Numerous electrochemical reactions of high energy density batteries occur beyond these voltage limits.

3) Many chemical compounds are insoluble in water

4) Aqueous electrolytes are limited by temperature, i.e. the boiling point of water of 100\(^\circ\)C, which is too low for many practical uses in conversion and energy storage.

Solvents other than water are generally called non-aqueous solvents. Appropriate non-aqueous solvents can dissolve substances that are insoluble in water, stabilize substances that are unstable in water, and facilitate electrochemical reactions that are otherwise impossible. The electrochemical window of non-aqueous solvents is much larger than in water. As a result the field of non-aqueous electrochemistry has
attracted increasing interest for energy storage. Electrolyte consists of solvents such as molecular liquids or ionic liquids that dissolve solutes, which can be solid, liquid or gaseous. Electrolytes can be liquid solutions based on organic and inorganic solvents or molten salts. Solid electrolytes such as ionically conducting polymers and conducting solids such as doped oxides and glasses have a whole host of applications.

Non-aqueous liquid electrolytes may be divided into protic or polar aprotic solvents. Protic solvents donate protons (H\(^+\)), solvents containing amine or hydroxyl groups are protic. These solvents generally have low dielectric constants and low polarity and are reactive toward electrode materials, particularly Li. Aprotic solvents do not contain acidic hydrogen’s. In this work our attention will be devoted to polar aprotic solvents as they are the most important and useful with respect to the Li-air battery. Common organic carbonates, esters and ethers used as solvents in lithium chemistry are shown in table 1.3.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>M. Wt</th>
<th>T_m/°C</th>
<th>T_v/°C</th>
<th>νcP 25 °C</th>
<th>ε 25 °C</th>
<th>Dipole Moment/debye</th>
<th>T_f/°C</th>
<th>d/gcm³, 25'</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td><img src="image" alt="Structure EC" /></td>
<td>88</td>
<td>36.4</td>
<td>248</td>
<td>1.90</td>
<td>89.78</td>
<td>4.61</td>
<td>160</td>
<td>1.321</td>
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<td>PC</td>
<td><img src="image" alt="Structure PC" /></td>
<td>102</td>
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<td>242</td>
<td>2.53</td>
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<td>240</td>
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<td>53</td>
<td>4.23</td>
<td>97</td>
<td>1.199</td>
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<tr>
<td>γBL</td>
<td><img src="image" alt="Structure γBL" /></td>
<td>86</td>
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<td>204</td>
<td>1.73</td>
<td>39</td>
<td>4.23</td>
<td>97</td>
<td>1.199</td>
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<tr>
<td>γVL</td>
<td><img src="image" alt="Structure γVL" /></td>
<td>100</td>
<td>-31</td>
<td>208</td>
<td>2.0</td>
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<td>81</td>
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<td><img src="image" alt="Structure NMO" /></td>
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<td>78</td>
<td>4.52</td>
<td>110</td>
<td>1.17</td>
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<tr>
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<td>90</td>
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<td>91</td>
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<td>1.063</td>
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<tr>
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<td>121</td>
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<td>0.47</td>
<td>6.2</td>
<td>1.6</td>
<td>-11</td>
<td>0.85</td>
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<td>-95</td>
<td>78</td>
<td>0.59</td>
<td>7.1</td>
<td>1.25</td>
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<td>1.06</td>
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<td>4-Me-1,3-DL</td>
<td><img src="image" alt="Structure 4-Me-1,3-DL" /></td>
<td>88</td>
<td>-125</td>
<td>85</td>
<td>0.60</td>
<td>6.8</td>
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<td></td>
<td>0.54</td>
<td>4.39</td>
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</tr>
</tbody>
</table>

Table 1.3 Physical and chemical properties\(^{26}\)
These solvents are useful for lithium battery applications for the following reasons;

1) Wide electrochemical window
2) Low volatility
3) Low reactivity towards electroactive species and electrode materials
4) High polarity (Ability to dissolve salts especially Li salts)

Formulating the ideal electrolyte is about finding the right blend of both physical and chemical properties. The boiling point of the solvent is crucial to an electrochemical experiment conducted at both low and high temperatures. Solvent viscosity strongly influences mass transport of electroactive species hence determining kinetics of the reaction. The dielectric constant ($\varepsilon_r$) is measure of polarity of the solvent to enable salt dissociations into ions. Polar solvents separate charged particles, by weakening their respective electrostatic forces. The ideal electrolyte for the Lithium air battery requires solvents of low viscosity, high dielectric constant, high oxygen solubility and low water solubility.

**Lithium salt criteria:**

1) Lithium salts should be able to completely dissolve and dissociate in the non-aqueous solvent.
2) The anion should be inert and stable to the cathode potential.
3) Anion and cations should be inert to cell components such as electrode material and separators.
4) Remain thermally stable
Although the availability of non-aqueous solvents is large, the choice of lithium salts is quite limited. Ions of low charge density usually lead to good charge solubility and separation if paired with bulky anions and or cations. Lithium is often paired with bulky anions such as $\Gamma^-$, $\text{Br}^-$, $\text{ClO}_4^-$, $\text{PF}_6^-$, $\text{BF}_4^-$, $\text{RCO}_2^-$. Most Lithium salts are rather difficult to dissolve due to the small ionic radius of $\text{Li}^+$. Eligible candidates are usually based on large anions such as $\text{PF}_6^-$ where essentially $\text{F}^-$ is stabilized by $\text{PF}_5$ by distributing the charge throughout the ion. The corresponding lithium salts ($\text{LiPF}_6$) usually are better dissociated and solvated in low dielectric solvents. For fundamental electrochemistry using a large like Tetra butyl ammonium ($\text{TBA}^+$) eliminates complications associated with $\text{Li}^+$ such as insoluble salt precipitates. The solvating power of solvent is complex especially in electrochemistry. Although dielectric constant is the primary measure of polarity other factors such as acidity, basicity and structure are crucial.

To understand the solvation of metal cations one must understand acid base chemistry. According to this theory metal cations act as Lewis acids and solvent molecules act as Lewis bases. Lewis acids act as electron pair acceptors and Lewis bases electron donors. Gutmann\textsuperscript{27} developed the acceptor number (AN) and the donor number (DN) model as a measure of a solvents Lewis acidity and Lewis basicity respectively. The higher the DN or AN of a solvent the stronger its basic or acidic character.
1.6  Non-Aqueous Oxygen Reduction Reaction (ORR)

Oxygen is the essence of all life; and we are only beginning to understand its role in nature. In biological terms oxygen is reduced by cellular respiration, enzyme reaction and photochemistry to produce oxygen radicals known as superoxides ($O_2^-$). In its free radical state this ion can be detrimental to tissue and DNA. However harmful these free radicals may be biologically, their chemistry is proving very attractive as energy sources. The electrochemical reduction of oxygen to superoxide can be taken advantage of as the superoxide ion can behave as a Lewis base, nucleophile, as well as both an oxidizing and reducing agents.

$$O_2 + e^- \rightleftharpoons O_2^-$$

These traits make the reduction of oxygen ideal for energy production and storage. Unfortunately superoxide has a relatively short lifetime in aqueous media due to the presence of protons, which result in the direct $2e^-$ reduction of oxygen to hydrogen peroxide.

$$O_2 + 2e^- + 2H^+ \rightleftharpoons H_2O_2$$

Nonaqueous solvents free of proton interference are an ideal environment for stable oxygen reduction. Electrochemical studies in non-aqueous oxygen reduction reaction (ORR) begun in the early 1960’s. The original research utilized aprotic organic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile (MeCN) and bulky salts like tetraalkylammonium perchlorate ($NR_4^+ClO_4$) for the reasons listed above. This early work demonstrated for the first time a reversible oxygen redox couple stable in aprotic solvents based on quaternary
ammonia salts. More recently stability of ionic liquids towards superoxide has been examined\textsuperscript{33-35}. We seek to expand our understanding of the electrochemical behavior of oxygen in aprotic media in presence of Li salts, as they are relevant to the Li-air battery.

The work as discussed in this thesis shows that the electrochemistry of oxygen in non-aqueous electrolytes in presence of alkali metal salts is markedly different from that in the presence of the alkyl ammonium salts and that in aqueous media. We are interested in using small cations of lithium (Li), sodium (Na) and potassium (K) in an effort to apply oxygen chemistry towards metal-air batteries. We carried out this study in a series of electrolyte solutions of hexafluorophosphate salts (X\textsuperscript{+} PF\textsubscript{6}\textsuperscript{-}), (X = TBA, K, Na, Li) shown in figure 1.6.

![Electrolyte salts](image)

**Figure 1.6:** Electrolyte salts.

This thesis reports our fundamental studies aimed at rationally designing electrolytes for the Li-air battery.
1.7 Scope of Dissertation

At the outset of this work we sought to fully elucidate the oxygen reduction reactions (ORR) in the non-aqueous environment. These studies of ORR were performed using standard electrochemical techniques such as cyclic voltammetry (CV), rotating disk electrode (RDE) and electrochemical impedance spectroscopy. The studies of Li-air cell charge and discharge were combined with standard analytical techniques such as X-ray diffractometry to analyze discharge products.

The focus of chapter 2 is two-fold. First we wished to evaluate and validate our experimental techniques for the ORR studies using a well-known redox couple for which the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple is a prominent one for use in non-aqueous electrolytes. Coincident with this was the second aspect of the studies involving the Fc/Fc$^+$ couple as a redox reagent for the overcharge protection of rechargeable Li batteries. Such reagents are necessary for building high voltage batteries from single Li-cells by connecting them in series.

In Chapter 3 we investigate the effects of conducting salts (anion and cation) on the ORR in acetonitrile. We found that the conducting salt significantly affected the reversibility and kinetics of oxygen reduction in non-aqueous electrolytes. The effects of organic solvents on ORR are examined in chapter 4. The results of this study show that the solvent and the supporting electrolyte act collectively to influence the nature of reduction products and their rechargeability. In chapter 5 we pool all the knowledge collected throughout these ORR studies to construct and discharge and charge the first uncatalyzed Li-air battery.
The significance of this thesis is the insight gained into non-aqueous ORR which can be directly applied to the Li-air battery. The legacy of this work is to provide a methodology for rationally designing and selecting appropriate electrolytes for Li-air batteries and developing a fundamental mechanism for ORR in non-aqueous electrolytes.

1.8 Chapter 1 References


(14) Dell In Battery Recall 2006.


(27) Gutmann, V. Coordination Chemistry Reviews 1976, 18, 225-255.


Chapter 2

Electrochemical Studies of Ferrocene in a Lithium Ion Conducting Organic Carbonate Electrolyte

2.1 Introduction

Interest in non-aqueous solvents for electrochemical research and practical applications such as lithium batteries has increased significantly over the past four decades.

Ferrocene (Fc\textsuperscript{0}) is a useful reference material for non-aqueous electrochemistry as it demonstrates good solubility, invariant redox potentials and excellent chemical and electrochemical reversibility in organic electrolytes\textsuperscript{1}. The reversibility of the (Fc\textsuperscript{0}/Fc\textsuperscript{+}) redox couple was established from polarographic studies\textsuperscript{2} soon after the discovery of this organo-iron compound in 1951 by Kealy and Pauson\textsuperscript{3}. Previous studies\textsuperscript{4} of the electrochemistry of ferrocene in various non-aqueous solvents revealed a reversible one-electron process.

The diffusion coefficient (D) of ferrocene in different solvents was found to be inversely dependent on the viscosity of the solvent medium. Weaver et al\textsuperscript{5} conducted a study of the thermodynamic effects of solvent dynamics on various metalloocene redox couples by both theoretical and experimental methods. Their results indicated that solvent viscosity contributed to the high energy barrier, which influenced the kinetics of outer-sphere reactions. Mass transfer of the electroactive species to the electrode surface is a major factor in the rate of an electrochemical
oxidation or reduction reaction. If the electron transfer step is not hindered kinetically, movement of the electroactive species through the solution becomes the rate-limiting step in this case. As a result, electrochemical measurements are frequently used to determine diffusion coefficients of electroactive species and kinetics of electrode reactions. The process of diffusion is important in a wide variety of chemical scenarios, including kinetics of rapid reactions, chromatographic and electrophoretic separations, and battery electrode reactions.

A literature review revealed some prior studies of ferrocene electrochemistry in propylene carbonate (PC) solutions containing lithium salts. In the first of these studies, Abraham et al. investigated the electrochemical properties of Fc in a polyacrylonitrile-based gel polymer electrolyte (PAN)-EC/PC-LiClO₄) and established that the oxidation of ferrocene is electrochemically reversible. They found that the diffusion coefficient of Fc decreased by an order of magnitude in the gel polymer electrolyte compared with liquid electrolytes having similar Li salt concentrations.

To the best of our knowledge, few studies concentrating on ferrocene oxidation kinetics in highly concentrated solutions of Li salts in organic carbonates of the types used in Li-ion batteries have been performed. Such studies are relevant in view of the fact that ferrocene and its derivatives have been shown to be potentially useful redox reagents for the chemical overcharge protection of rechargeable lithium and lithium-ion (Li-ion) batteries. In this application, ferrocene added to the electrolyte in a rechargeable Li or Li-ion battery cell is oxidized at a potential slightly positive of the oxidation potential of the positive electrode in the cell and the
ferrocenium ions ($\text{Fc}^+$) thus produced diffuse to its negative electrode and gets reduced to regenerate ferrocene. Consequently, the electrode potential remains locked at the oxidation potential of ferrocene and prevents the cell from overcharge. This type of chemical shuttles for overcharge protection is highly desirable to protect individual cells in a battery having two or more cells connected in series from overcharge during recharge with the result of improving cell performance and mitigating safety hazards.

In this work, we investigated ferrocene redox chemistry in 1M LiPF$_6$/1:1 EC:EMC which is a typical liquid electrolyte used in Li-ion batteries. Another motivation for our study is that these ferrocene experiments can serve as models for investigating the redox chemistry of other chemical shuttle reagents used for overcharge protection of rechargeable Li-ion batteries\textsuperscript{16-19}. We report the mass transport and kinetic parameters of the Fc$^0$/Fc$^+$ couple in this prototypical Li-ion battery electrolyte. The results of this study should further our ability to design and develop redox shuttles in non-aqueous electrolytes leading to improved performance and safety in Li-ion and Li–air batteries\textsuperscript{20}. A comparison of the results obtained from CV and RDE experiments is useful in understanding the role of mass transport on the kinetic parameters of redox reagents for Li-ion batteries.

### 2.2 Experimental

#### 2.2.1 Chemical Reagents

All reagents were electrochemical grade unless stated otherwise stated. Battery grade solvents, Ethylene Carbonate (EC) and Ethyl Methyl Carbonate (EMC) and Lithium
hexafluorophosphate (LiPF₆) (battery grade, >99.9%, H₂O< 20ppm) were obtained from Ferro Corporation, Cleveland, Ohio. Ferrocene was purchased from Sigma-Aldrich, Allentown, PA.

2.2.2 Instrumentation

The electrochemical experiments were performed with a VoltaLab (Radiometer Analytical Inc, model-VoltaLab 10) potentiostat in an air-tight electrochemical cell. Figure 2.1 show’s the electrochemical cell which was designed and built in-house. It consisted of a traditional 3-electrode system utilizing Li/Li⁺ as the reference electrode and platinum wire as the counter electrode.

![Figure 2.1: Purpose built air tight electrochemical cell](image)

A glassy carbon working electrode (3mm diameter) was employed for the cyclic voltammetry experiments. The electrodes were polished with 0.5 and 0.05 mm
alumina paste prior to the experiments. For RDE experiments, the glassy carbon electrode was rotated with an Autolab RDE rotor. Scan rate analyses were performed using 3.3mM solutions of ferrocene in a 1MLiPF₆/1:1 (by volume) EC: EMC electrolyte, and scan rates were varied between 5mV/s and 300mV/s. All of the cyclic voltammetry experiments were initially performed in an argon (Ar)-atmosphere glove box where H₂O and O₂ concentrations were kept below 5ppm and temperature was held at 22 ± 2°C. RDE experiments were conducted outside the glove box in a glove bag purged with argon.

The conductivities of the solutions were measured using a 4-electrode conductivity cell with a Thermo Scientific Orion Model 550A Multiparameter Meter. Electrolyte viscosities were measured with a size 1 Ubbelohde Viscometer. Measurements and calibration were performed according to ASTM protocol as described by the manufacturer. Efflux time between the upper and lower fiducial marks on the apparatus were monitored with a stopwatch. Average times for four runs were recorded, with all results averaged together. The viscosities were measured at room temperature, 22± 2°C.

2.3 Results and Discussion

2.3.1 Cyclic voltammetry

The redox chemistry of ferrocene was studied using cyclic and rotating disc voltammetric techniques and the results are compared. The electrolyte solution used for these studies was characterized by determining its conductivity and dynamic viscosity with values of 8.8 mS/cm and 4.66cP, respectively at room temperature. Figure 2.2 shows the cyclic voltammograms (CVs) of the ferrocene redox couple on a
glassy carbon (GC) electrode in 1MLiPF$_6$/1:1EC:EMC solution (hereafter referred to also as the carbonate electrolyte) at a sweep rate of 100 mVs$^{-1}$.

**Figure 2.2:** Cyclic voltammograms for the oxidation of 3.3mM Ferrocene in 1MLiPF$_6$/1:1 EC: EMC on a glassy carbon working electrode at a scan rate of 100mVs$^{-1}$.

Our study was restricted to glassy carbon electrodes, since surface adsorption effects on platinum electrodes are well documented$^{21}$. Also, glassy carbon electrodes are practically more relevant to Li-ion batteries as one or another form of carbon is present in the electrodes of the battery. At low concentrations, ferrocene oxidation in many organic electrolyte solutions does not precipitate surface films on glassy carbon electrodes and, thus, would serve as a good standard for non-aqueous electrochemistry. The CV data were corrected for Ohmic (iR) losses using the well established semi-integral technique$^{22}$, (see fig 2.2). Equilibrium is established
quickly between the active species as the voltammetric responses of ferrocene appear between 3.22 and 3.28V vs. Li/Li⁺. The peak potential separation ΔEₚ between the anodic and cathodic peak potentials ranged from 60-67mV with an average of 63 ± 0.002 mV. These values are close to the theoretical value of 59mV for a one-electron reaction. For a reversible process the peak width is given by the following relationship.

\[
E_{p2} - E_p = 2.2 \left( \frac{RT}{nF} \right)
\]

*(Equation 2.1)*

Where \(E_{p2}\) is the half-peak potential at the half value of the peak current, \(E_p\), is the peak potential, \(F\) is the Faraday constant and \(n\) is the number of electrons in the reaction. From the data obtained at the sweep rate of 5mV/s, the number of electrons \(n\) was calculated to be 1.05 (see Table 2.1).

<table>
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<tr>
<th>Scan Rate(V) mV/s</th>
<th>Eₚₑ₀.₀₀₂V</th>
<th>Eᵦₑ₀.₀₀₂V</th>
<th>ΔEₚ</th>
<th>Charge Ratio, Qₑ/Qₑ</th>
<th>Number of e⁻, n</th>
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</thead>
<tbody>
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<tr>
<td>50</td>
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<td>0.91</td>
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<td>1.125</td>
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<tr>
<td>300</td>
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<td>3.221</td>
<td>0.063</td>
<td>0.91</td>
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Analysis of the CVs over the whole sweep ranges (see Table 2.1) gave \( n \) values close to this indicating that the number of electrons transferred in the reaction is one. We found the electrochemical charge ratio \( (Q_c/Q_a) \) determined from the area under the oxidation \( (i_{pa}) \) and reduction \( (i_{pc}) \) peaks to be over 91%.

Cyclic voltammetry is a useful technique for discerning kinetics, rates, and mechanisms in addition to thermodynamic parameters. The magnitude of the current, \( I \), in a cyclic voltammogram is a function of temperature, concentration, \( C_{\text{analyte}} \), electrode area, \( A \), the number of electrons transferred, \( n \), the diffusion coefficient, \( D \), and the speed at which the potential is scanned, \( v \), related by the Randles-Sevcik equation (Equation 2.2).

\[
I_{pa} = (2.69 \times 10^5)n^{3/2}AD^{1/2}v^{1/2}C
\]  
\textbf{(Equation 2.2)}

Figure 2.3a shows both the cathodic and anodic peak potential variations with sweep rates. The dependence of \( I_{pa} \) on sweep rate is evident at both low and high scan rates. The little variation in both the reduction and oxidation peak positions with increase in sweep rates reflects the reversibility of the system. The Randles–Sevick plot (Fig 2.3b) shows a linear relationship between \( I_p \) vs. \( v^{1/2} \) passing through the origin. Assuming \( n=1 \) we calculated the theoretical Randles-Sevick plots, which agree with the experimental data. This infers that ferrocene is a reversible redox couple in this media and follows scheme 2.1.

\[
\text{Fe}^{2+}\left(C_{3}H_{7}\right)_{2} \rightleftharpoons \text{Fe}^{3+}\left(C_{3}H_{7}\right)_{2} + e^{-}
\]  
\textbf{(Scheme 2.1)}
Figure 2.3: (A) Cyclic Voltammograms for Fc/Fc⁺ in 1M LiPF₆/1:1 EC: EMC on a GC electrode at sweep rates between 5mVs⁻¹ and 300 mVs⁻¹. (B) Randles-Sevcik plot of peak current vs. square root of the scan rate for the curves in 2.3(A).
The voltammetric parameters for 3.3mM Fc in the carbonate electrolyte are summarized in Table 2.1. All potential values are reported versus the Li/Li\textsuperscript{+} reference electrode. From the dependence of current on scan rate, the diffusion coefficients of ferrocene and ferrocenium ion in solution were calculated as \(2.03 \times 10^{-6} \pm 0.02 \text{ cm}^2 \text{ sec}^{-1}\) and \(1.38 \times 10^{-6} \pm 0.01 \text{ cm}^2 \text{ sec}^{-1}\), respectively. The lower diffusion coefficient of ferrocenium ion is understood as arising from interactions between the ferrocenium cation and the PF\textsubscript{6}\textsuperscript{-} anion as well as solvent molecules. The diffusion coefficient of ferrocene we found is an order of magnitude lower than that reported for PC/0.1M LiClO\textsubscript{4}.\textsuperscript{6} The lower value obtained in the present work is attributed to higher viscosity of the concentrated solution. This points out the importance of the present work.

The diffusion coefficient of a species in solution is inversely proportional to the viscosity of the solution according to Walden’s Rule. The theoretical diffusion coefficient of this system can be determined by the relationship between diffusion coefficient and solution viscosity given by the Stokes Einstein equation (Equation 2.3).

\[
D = \frac{kT}{6\pi\eta a}
\]

(Equation 2.3)

In this equation \(k\) is the Boltzmann constant, \(T\) is temperature, \(\eta\) is dynamic viscosity and \(a\) is the effective hydrodynamic radius of ferrocene. The hydrodynamic radius is influenced by a number factors such as solubility of analyte, solvent molecule size and polarity of the solvents. In this case we decided to use the crystallographic radius of ferrocene (0.32nm)\textsuperscript{23}. The dynamic viscosity (4.65cP) was calculated from the solution’s kinematic viscosity (0.0372 cm\textsuperscript{2}s\textsuperscript{-1}) and density (1.25gcm\textsuperscript{-3}) are measured.
Figure 2.4: (A) Disk currents on a RDE obtained in 1M LiPF₆/1:1EC: EMC in the anodic sweep at room temperature by various rotation rates. (B) Levich plot of limiting current vs. square root of rotation for the data in fig 2.3(A) at scan rate = 10 mVs⁻¹.
The theoretical diffusion coefficient is \( D = 1.50 \times 10^{-6} \, \text{cm}^2\text{s}^{-1} \), very close to the measured value.

### 2.3.2 Rotating Disk Electrode

Rotating disk electrode is a hydrodynamic electrode technique which utilizes convection as the mode of mass transport as opposed to CV which is governed by diffusion. Convection is more efficient and is not diffusion limited with the result that the analytical data is more reproducible and precise. Thus a comparison of the kinetic parameters obtained from CV and RDE experiments is informative to elucidate the role of mass transport on electrode reaction kinetics. Figure 2.4a shows RDE voltammograms for ferrocene at a series of rotation rates. It is evident from the data that the current generated by the RDE method is much larger than that generated under diffusion control (Figure 2.1a). The much larger current obtained using RDE reflects the efficiency of this method. Also notice that there is significant increase in anodic current (i.e. \( \text{Fc}^0 \) to \( \text{Fc}^+ \)) while the amount of cathodic current (i.e. \( \text{Fc}^+ \) to \( \text{Fc}^0 \)) is negligible, essentially making the cyclic voltammogram anodic. This is due to the vast difference in concentration between the \( \text{Fc}^+ \) and \( \text{Fc}^0 \). The bulk solution contains \( \text{Fc} \), which provides a constant supply to the rotating electrode while the concentration of \( \text{Fc}^+ \) ions at the electrode is so minuscule that little anodic current is produced. The Levich equation (equation 4.4) establishes relationship between current at the RDE and concentration of the analyte.

\[
I_{\text{lim}} = (0.620)n\text{FAD}^{3/2} \omega^{1/2}v^{-1/6}C
\]  

(Equation 4.4)
where $I_{\text{lim}}$ is the limiting current density (Acm$^{-2}$), $n$ is the number of electrons for the reaction, $F$ is the Faraday constant (96,500 Cmol$^{-1}$), $D$ is the diffusion coefficient of ferrocene in the solution, $\nu$ is the experimentally determined kinematic viscosity of the solution (0.0372cm$^2$s$^{-1}$), $C$ is the concentration of ferrocene in the solution (3.3mM) and $\omega$ is the angular frequency ($\frac{2\pi f}{60}$). Furthermore, the Levich equation allows us to construct a plot of $I_{\text{lim}}$ versus $\omega^{1/2}$ to determine a value of $D$ which was found to be $2.35 \times 10^{-6} \pm 0.2$ cm$^2$ sec$^{-1}$. This value is slightly higher that determined from the aforementioned CV experiments. RDE provides insight into the number of electrons transferred in the electrochemical reaction by comparing the limiting currents to the rotation rate of the electrode. These Levich plots, shown in figure 2.3b, display well defined linear plots indicating a simple mass transfer controlled electrode process. The slope of the Levich plot for the experimental data closely parallels the theoretical line for a one electron reaction ($n=1$).

We can apply the Tafel equation (equation 2.5) which relates the rate of an electrochemical reaction to the overpotential, according to

$$\log i = \log i_0 + \left(\frac{1-anF}{RT}\right)\eta$$

(Equation 2.5)

In this equation $\eta$ is overpotential for the anodic reaction and the other symbols have their usual meaning. The Tafel plot is corrected for diffusion. In order to correct the measured currents for diffusion, the kinetic current in the mixed activation-diffusion region is calculated from equation (2.6).  


\[ i_k = \frac{i_{\text{lim}} \cdot i}{i_{\text{lim}} - i} \]  \hspace{1cm} (Equation 2.6)

A plot of \( \log i_k \) against overpotential, \( \eta \), should be linear, leading to the Tafel slope \( b \), from which the transfer coefficient, \( \alpha \), can be determined. As already stated (Fig 2.4) the RDE experiments are related exclusively to the oxidation of ferrocene. Figure 2.5 shows the Tafel plot from the anodic region of the voltammogram beginning with the open circuit potential (OCV) of 3.145. In this plot, the Tafel region starting at about 60 mV positive of the OCP is clearly delineated from the Butler Volmer region below that. A single Tafel slope of c.a. 79mV/decade was obtained in the entire potential range for all rotation rates. This slope is analogous that obtained by Petrocelli for the oxidation of Potassium Ferricyanide in NaOH on platinum. This implies that the initial electron transfer is the rate-limiting step of this reaction.
Figure 2.5: Tafel plots for ferrocene oxidation at room temperature on a glassy carbon electrode at 2500 rpm for anodic sweep from 3.145V to 3.35V at 10mVs⁻¹ (OCP 3.145V vs Li/Li⁺).

The heterogeneous kinetics of this reaction is so rapid that over a wide range of sweep rates, the reaction is reversible. From this data we calculated the transfer coefficient α = 0.3, which is comparable to previous ferrocene experiments in aprotic solvents. The observed values of Tafel slope and α are indicative of strong interactions between the ferrocenium ions and PF₆⁻ as well as the solvents. The low α also suggests that the structure of the activated complex for the oxidation reaction is closer to that of the oxidized specie. As we noted earlier about 8% of ferrocenium ions are not available for reduction back to ferrocene. This together with the kinetic information suggest a chemical step, following the one electron rate determining
oxidation reaction, in which the ferrocenium ion formed is stabilized by the solvent as well as some of it being transformed into products. This is not unreasonable considering the dipolar nature of the organic carbonate solvents. Extrapolating the Tafel line to equilibrium potential provides the exchange current density ($I_o$) of $2.0 \times 10^{-6}$ Acm$^{-2}$. The rate constant of the electron transfer (anodic oxidation in this case), $k^o$, is proportional to $I_o$ according to.

$$I_o = nF A k_o C \quad \text{ (Equation 2.8)}$$

We obtained a rate constant of $k^o = 1.4 \times 10^{-3}$ cm.s$^{-1}$ from the exchange current density using equation 2.8. Our results show that RDE technique can be successfully applied to highly concentrated electrolyte solutions. The data revealed defined limiting currents from which the kinetics of the system can be deciphered.

### 2.4 Conclusions

A detailed study of the kinetics of the oxidation of ferrocene in a concentrated lithium ion conducting electrolyte was carried out using cyclic and rotating disc electrode voltammetry. The results obtained show that the ferrocene-ferrocenium redox couple is reversible in this medium. The values for ferrocene and ferrocenium ion diffusion coefficients were determined from these data. In addition, the electron transfer rate constant ($k^o$) and the exchange current density ($I_o$) for the oxidation of ferrocene were calculated. A comparison of the kinetic data obtained from the two electrochemical techniques appears to show that the data from the RDE experiments
are perhaps more reliable, because they are collected under strict mass transport control. A Tafel slope of c.a. 79mV/decade and a transfer coefficient $\alpha$ of 0.3 obtained from analysis of the RDE data suggest that the structure of activated complex in the oxidation reaction of ferrocene is closer to that of the oxidized specie, probably due to strong interactions with PF$_6^-$ and carbonate solvents. Strong interactions between the ferrocenium ion and the carbonate solvent is consistent with the highly dipolar nature of the organic carbonates.

Our results indicate that useful electrochemical kinetic data for soluble redox species in highly concentrated electrolyte solutions relevant to Li-ion batteries can be obtained using the complementary CV and RDE techniques. Such kinetic data are relevant to the studies of redox reagents for overcharge protection of Li-ion batteries, particularly in simulation studies aimed at understanding their performance in practical batteries, and in the development of improved materials.
2.5 References


Chapter 3

Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Applications

3.1. Introduction

The Lithium-air battery is one of the most energy dense, and environmentally friendly, electrochemical power sources. Fully developed and optimally packaged Li-air batteries could exceed specific energies of 2000 Wh/kg, versus a theoretical value of 5200 Wh/kg, which is more than twice as much as any battery, primary or secondary, presently known. The Li-air battery is composed of a Li metal anode and an air cathode in which the cathode active material, oxygen, is accessed from the environment. The first non-aqueous, rechargeable, Li-air battery\(^1\) used Li\(^+\)-conducting gel polymer electrolytes based on polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF). In that battery Li\(_2\)O\(_2\) was identified as a product of the discharge reaction, which in presence of catalysts could be oxidized (recharged), albeit at high overvoltages to oxygen and lithium metal. Later studies of Li-air batteries utilized organic carbonate- and ether-based electrolytes of the types used in Li metal and Li-ion batteries\(^2\). In a recent study Bruce and co-workers\(^3\) demonstrated possibility of using Li\(_2\)O\(_2\) as a positive electrode material in a Li/air battery which was activated by initially charging (oxidizing) the peroxide to oxygen and lithium metal. The electrochemical reduction of oxygen to superoxide and other oxides can be taken advantage of practically as they can behave as Lewis bases, nucleophiles, as a well as both oxidizing and reducing agents. These traits make the reduction of
oxygen desirable for energy production and storage. Previous electrochemical studies of the oxygen reduction reaction (ORR) in organic solvents\textsuperscript{4-7} demonstrated that it is possible to reduce molecular oxygen to superoxide (O\textsubscript{2}\textsuperscript{-}) in a non-aqueous environment. An identified distinction between the use of non-aqueous and aqueous electrolytes is that in aqueous electrolytes the preferred reduction product is water or hydrogen peroxide corresponding to a four or two-electron reduction of O\textsubscript{2} respectively, as opposed to the formation of superoxide in organic electrolytes. Almost all of the prior research in organic electrolytes utilized quaternary ammonium cation (NR\textsubscript{4}\textsuperscript{+} where, R= ethyl, butyl etc.)-based salts as supporting electrolytes for ion conduction. We are interested in understanding the electrochemistry of oxygen in organic electrolytes in presence of alkali metal cations such as Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+} in an effort to apply oxygen chemistry towards non-aqueous metal-air batteries, particularly Li and Na batteries. These results together with the early investigations of oxygen electrochemistry in non-aqueous electrolytes suggest that more than one product is possible in the electrochemical reduction of non-aqueous Li-air batteries and that a good understanding of the mechanism of oxygen reduction in organic electrolyte is lacking. An in-dept study of the electrochemical redox behavior of O\textsubscript{2}, including the kinetics and transport properties of the reduction and oxidation products in the electrolyte, is important in further developing the Li-air battery. To this end, we have initiated studies of the redox reactions of oxygen in non-aqueous electrolytes with the objective of elucidating the roles of ion conducting salts and organic solvents on the mechanisms of the corresponding reactions. We present a full account of our work in acetonitrile. This solvent is not practically useful in a Li-air battery because its reacts
with Li metal. Despite this we chose it for this initial study because of previous electrochemical studies of oxygen in this solvent and because of some initial surprising results we obtained when a Li salt was used as the conducting salt. Most of the early electrochemistry of molecular oxygen in organic solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile, utilized tetra alkyl ammonium perchlorate (NR₄⁺ClO₄⁻) as the ion conducting salts leading to similar overall results. We show here that there are significant differences in the reduction mechanism and products when alkali metal salts are used. (Our results in other practically more relevant organic electrolytes for the Li-air battery will be published in the future). Using cyclic voltammetry (CV) and rotating disc electrode (RDE) voltammetry we first studied O₂ reduction in acetonitrile electrolyte solutions containing both TBAClO₄ and TBAPF₆ to assess the influence of anion on oxygen reduction. We then studied oxygen redox reactions in hexafluorophosphate-based electrolytes of the formula A⁺PF₆⁻ where A = TBA, K, Na, Li. We have discovered that the electrochemistry of oxygen is strongly influenced by the nature of the cation and very little by the anion in the conducting salt. Also our RDE studies reported here represent the first application of this technique to elucidate the mechanism of oxygen reduction in non-aqueous electrolytes and the results for the first time provided detailed information on the influence of supporting electrolytes on the kinetics and mechanisms of oxygen reduction in non-aqueous electrolytes.
3.2 **Experimental**

3.2.1 **Chemical reagents.**

All reagents were electrochemical grade unless stated otherwise stated. Battery grade solvents and Lithium hexafluorophosphate (LiPF$_6$) ((battery grade, $>$99.9%, $\text{H}_2\text{O}<$ 20ppm) were obtained from Ferro Corporation Cleveland, Ohio. Tetrabutylammoniumhexafluorophosphate (TBAPF$_6$), anhydrous acetonitrile (MeCN), tetrabutylammonium perchlorate (TBAClO$_4$), Potassium hexafluorophosphate (KPF$_6$), and Sodium hexafluorophosphate (NaPF$_6$) were purchased from Sigma-Aldrich, Allentown, PA.

3.2.2 **Instrumentation.**

The electrochemical experiments were performed with an Autolab (Ecochemie Inc., model-PGSTAT 30) potentiostat equipped with a bi-potentiostat interface in an airtight electrochemical cell. The electrochemical cell designed and built in-house consisted of a traditional 3-electrode system utilizing Ag/AgCl as the reference electrode and platinum wire as the counter electrode. This reference electrode was used instead of the Li foil electrode typically used in Li$^+$ conducting electrolytes because of its instability as a reference electrode in this electrolyte. The Ag/AgCl gives a voltage of 2.93 V versus Li/Li$^+$, as measured using a Li foil reference electrode in a LiPF$_6$ solution in organic carbonates. The cell also had inlet and outlet valves for oxygen or argon purging. The cell was entirely airtight with exception of the gas outlets, which were kept under pressure with the working gas. The glassy carbon (3 mm diameter) working electrode employed for the cyclic voltammetry experiments was polished with 0.5 and 0.05 mm alumina paste prior to the
experiments. For RDE experiments, the glassy carbon electrode was rotated with an Autolab RDE rotor. All of the cyclic voltammetry experiments were initially performed in an Ar-atmosphere glove box where H₂O and O₂ concentrations were kept below 5ppm and temperature was held at 22 ± 2°C. For RDE experiments the cell was brought outside of the glove box and placed in a glove bag purged with Argon. The electrolyte solutions were first purged with argon, and the electrode was cycled continuously until reproducible cyclic voltammetric profile was obtained. The solutions were then purged with O₂ for ORR measurements. All solutions were prepared in the glove box. Conductivity measurements of all samples were carried out using a 4-probe Thermo Orion conductivity cell from Thermo Fisher Scientific Inc Waltham MA. Viscosity was measured using Ubbelohde viscometer purchased from Technical Glass Products Inc NJ.

3.3 Results and Discussion

The roles of the TBA and alkali metal salts on the reduction properties of molecular oxygen (O₂) in acetonitrile were studied using cyclic (CV) and rotating disk electrode (RDE) voltammetry. Cyclic voltammetry is a useful technique for discerning kinetics, and mechanisms of electrochemical reactions. It is an electrochemical potential sweep reversal method wherein a certain potential range is swept at a known scan rate (measured in volt per second) in both the negative and positive directions and the change in current is recorded. By applying appropriate equations, the CV data can tell whether the reaction is nernstian (reversible), quasi-reversible or irreversible. The RDE technique can be used in a complementary fashion to discern the mechanistic details of the electrochemical processes. The same
disk electrode can be used to run both CV and RDE scans. The rotating disk, hydrodynamic, technique utilizes convection as the mode of mass transport as opposed to CV, which is governed by diffusion. Convection is a more efficient means of mass transport with the result that the analytical data are more reproducible and precise. In Table 3.1 we list the physical properties of the acetonitrile. In Table 3.2 the conductivities and viscosities of the electrolyte solutions used in this study are presented.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Mw(g)</th>
<th>D(g/ml)</th>
<th>Viscosity, η(cm²/s)</th>
<th>Oxygen Solubility, (M/cm³)</th>
<th>Donor Number (kcal/mol)</th>
<th>Dipole Moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>41.05</td>
<td>0.786</td>
<td>0.0228</td>
<td>0.0081</td>
<td>14.1</td>
<td>3.92</td>
</tr>
</tbody>
</table>

**Table 3.1: Physical properties of Acetonitrile**

Some of these physical properties are used in calculating kinetic parameters discussed below.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Kinematic Viscosity ν (cm²/s)</th>
<th>Conductivity, σ(mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>± .003 cm²/g</td>
<td>------------------------</td>
</tr>
<tr>
<td>0.1MTBAPF₆/Acetonitrile</td>
<td>0.00440</td>
<td>------------------------</td>
</tr>
<tr>
<td>0.1MLiPF₆/Acetonitrile</td>
<td>0.00442</td>
<td>14.39</td>
</tr>
<tr>
<td>0.1MNPF₆/Acetonitrile</td>
<td>0.00461</td>
<td>10.85</td>
</tr>
<tr>
<td>0.1MKPF₆/Acetonitrile</td>
<td>0.00456</td>
<td>12.50</td>
</tr>
<tr>
<td></td>
<td>0.00451</td>
<td>14.02</td>
</tr>
</tbody>
</table>

**Table 3.2: Conductivity and Viscosity of the Electrolyte Solutions in acetonitrile**
3.3.1 Oxygen Reduction in Tetrabutylammonium hexafluorophosphate (TBA$^+\text{PF}_6$)-Based Electrolytes

The full-range cyclic voltammograms (CV) scanned from -3V to 1V, for the reduction of oxygen in 0.1M TBAPF$_6$ and TBACIO$_4$/MeCN are presented in fig 3.1a.

![Cyclic Voltammograms](image)

**Figure 3.1:** A) iR corrected voltammograms for the reduction of oxygen in 0.1M TBAPF$_6$ (Black), 0.1M TBACIO$_4$ (Blue) and the argon background (dotted) in MeCN. B) CVs in the –2 to +0.5 V range. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.
CVs were first run under an inert atmosphere of argon to provide a background voltammogram. As shown no appreciable current was observed under argon over the full potential range of which oxygen redox reactions were investigated confirming that the electrolyte contained no other electroactive species. The similarity of the voltammograms is quite evident, the first reduction peak ($E_{p1}$) at c.a (−0.9 V) is present in both CV’s with little difference in peak position. Polarizing the electrode to further negative potentials a second reduction peak ($E_{p2}$) emerges at c.a (−2.2V) also present in both electrolytes. The oxidation peak ($E_{p3}$) peak is very similar in shape and size to that of $E_{p1}$ and only slightly separated in the ClO$_4^-$ case. This can only be attributed to the subsequent oxidation of $E_{p1}$ reduction products. $E_{p4}$ is separated from $E_{p2}$ by almost 2V highlighting an irreversible reaction. In fact $E_{p2}$ ‘s reduction products are oxidized only at these high overpotentials. By integrating the area under each peak we find the charge area. The charge area under $E_{p1}$ and $E_{p3}$ peaks are similar. However expanding the electrochemical window to encompass $E_{p2}$ we see a distinct loss in charge area under the anodic peak ($E_{p3}$). Comparing this loss of charge to the area under $E_{p2}$ we find this area is proportional to that of the loss (Table 3.3).

<table>
<thead>
<tr>
<th></th>
<th>$E_{p1}$</th>
<th>$E_{p2}$</th>
<th>$E_{p3}$</th>
<th>$E_{p1}$ - IR</th>
<th>$E_{p2}$ - IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO$_4^-$</td>
<td>4.98</td>
<td>1.45</td>
<td>3.47</td>
<td>4.91</td>
<td>4.30</td>
</tr>
<tr>
<td>PF$_6^-$</td>
<td>4.72</td>
<td>1.31</td>
<td>3.30</td>
<td>3.7</td>
<td>3.3</td>
</tr>
</tbody>
</table>

**Table 3.3**: Electrochemical Charge area under the peaks. Scan rate 100mV/s. Error ± 0.002C.

Thus implying a portion of the first reduction product formed on the electrode undergoes a secondary irreversible reduction. The peak $E_{p4}$ appears if the second
reduction peak $E_{p2}$ is formed and hence we associate it with the oxidation of the material generated at the electrode during this process. This can be clearly discerned from CV in figure 3.1b, where the scan region is restricted to avoid $E_{p2}$. Generally speaking these voltammograms are identical except for peak positions, which maybe attributed to ohmic losses. This weak but noticeable oxygen reduction dependence on the counter ion is evident by these shifts. ORR in perchlorate solution is slightly positive by a 100mV indicating that oxygen reduction in the presence of hexafluorophosphate is to some extent slightly polarized. This may be due in part to the less coordinating nature of the PF$_6^-$, allowing the larger tetra butyl ammonium ion to interact with dissolved oxygen. Generally the electrolyte/electrode interface is affected by the nature of the counter ion. A summary of voltammetric results is provided in Table 3.4.

<table>
<thead>
<tr>
<th>Scan Rate(V) mV/s</th>
<th>$E_{p1}$=0.002V ClO$_4^-$ (PF$_6^-$)</th>
<th>$E_{p1}$=0.002V ClO$_4^-$ (PF$_6^-$)</th>
<th>$\Delta E_{p}$ ClO$_4^-$ (PF$_6^-$)</th>
<th>Charge Ratio, $Q_a/Q_c$ ClO$_4^-$ (PF$_6^-$)</th>
<th>Number of e$^-$, n ClO$_4^-$ (PF$_6^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-0.801 (-0.837)</td>
<td>-0.863 (-0.903)</td>
<td>-0.062 (-0.066)</td>
<td>0.87 (0.87)</td>
<td>1.04 (1.10)</td>
</tr>
<tr>
<td>25</td>
<td>-0.780 (-0.846)</td>
<td>-0.847 (-0.898)</td>
<td>-0.067 (-0.062)</td>
<td>0.85 (0.88)</td>
<td>1.12 (1.04)</td>
</tr>
<tr>
<td>50</td>
<td>-0.771 (-0.840)</td>
<td>-0.852 (-0.904)</td>
<td>-0.068 (-0.064)</td>
<td>0.87 (0.89)</td>
<td>1.11 (1.07)</td>
</tr>
<tr>
<td>75</td>
<td>-0.760 (-0.836)</td>
<td>-0.822 (-0.901)</td>
<td>-0.062 (-0.065)</td>
<td>0.88 (0.89)</td>
<td>1.04 (1.09)</td>
</tr>
<tr>
<td>100</td>
<td>-0.745 (-0.837)</td>
<td>-0.807 (-0.893)</td>
<td>-0.062 (-0.067)</td>
<td>0.87 (0.89)</td>
<td>1.04 (1.12)</td>
</tr>
<tr>
<td>20</td>
<td>-0.720 (-0.826)</td>
<td>-0.786 (-0.883)</td>
<td>-0.066 (-0.067)</td>
<td>0.87 (0.88)</td>
<td>1.10 (1.12)</td>
</tr>
<tr>
<td>300</td>
<td>-0.718 (-0.815)</td>
<td>-0.785 (-0.871)</td>
<td>-0.067 (-0.068)</td>
<td>0.86 (0.88)</td>
<td>1.12 (1.14)</td>
</tr>
</tbody>
</table>

**Table 3.4:** Voltammetric properties of O$_2$/O$_2^-$ redox couple in 0.1MTBAPF$_6$ & TBAClO$_4$/MeCN

These results indicate that the solvent/salt interactions are well coordinated in the case of TBAClO$_4$ leading to a structured double layer region, which is coupled to the ion diffusion coefficients. We found the charge area ratio $(Q_a/Q_c)$ under the peaks to
be over $89 \pm 0.02\%$ for the CVs portrayed in Figure 3.1b. The peak potential separation $\Delta E_p$ between the anodic and cathodic peak potentials for $\text{ClO}_4^-$ and $\text{PF}_6^-$ are presented in Table 3.4. These values are close to the theoretical value of 59mV for a one-electron reaction. For a reversible process the peak width is given by the following relationship.

$$E_{p/2} - E_p = 2.2 \left( \frac{R T}{n F} \right)$$  \hspace{1cm} \textit{Equation 3.1}$$

Where $E_{p/2}$ is the half-peak potential at the half value of the peak current $i_p$ is the peak potential, $F$ is the Faraday constant and $n$ is the number of electrons in the reaction. Analysis of the CVs over the whole sweep ranges gave $n$ values close to unity (see Table 3.4) indicating that the number of electrons transferred in the reaction is one. Possible reasons $\Delta E_p$ is slightly larger than the theoretical value are sluggish kinetics due to Ohmic ($iR$) contributions ($E_{\text{true}} = E_{\text{actual}} - iR$) at high scan rates. The magnitude of the current ($I$) in a cyclic voltammetry is a function of temperature, concentration $C$, electrode area $A$, the number of electrons transferred $n$, the diffusion coefficient $D$, and the speed at which the potential is scanned $V$, all related by the Randles-Sevcik equation (Eq 2).

$$I_{pa} = (2.69 \times 10^5)n^{3/2}AD^{1/2}V^{1/2}C$$  \hspace{1cm} \textit{Equation 3.2}
Figure 3.2: (A) Cyclic Voltammograms for the reduction of oxygen saturated 0.1M TBAPF$_6$ /MeCN on GC electrode at sweep rates 0.1V/s (solid), 0.1V/s (long dash) and 0.025V/s (short dash), (B) Randles-Sevcik plot of peak current vs. square root of the scan rate for the curves in 0.1 M TBAPF$_6$ & 0.1 M TBAClO$_4$/MeCN.
Figure 3.2a displays the cyclic voltammograms for the reduction of oxygen saturated TBAPF$_6$/MeCN at different sweep rates. The reduction is reversible at all sweep rates and there is only a slight shift in the peak position. The Randles-Sevcik plots presented in Fig. 3.2b are linear and pass through the origin as per theory, indicating a fast, diffusion controlled electrochemical process. The theoretical plots of $n=1$ in figure 3.2b parallels the one-electron experimental plot implying that $n=1$ and that the first reduction involves the formation of superoxide ($O_2^-$). The presence of superoxide in solution was confirmed qualitatively by adding Nitrotetrazolium Blue Chloride tablet, which produced the characteristic purple color.

Figure 3.3(a) shows the typical steady-state voltammograms for $O_2$ reduction on a RDE in oxygen saturated 0.1 M TBAPF$_6$ solution at various rotation rates. This figure demonstrates that the current generated by this hydrodynamic method is much larger than that generated in the CV under diffusion control. The much larger current obtained using RDE reflects the efficiency of this method. We can easily determine the limiting current, $i_{\text{lim}}$, from these voltammograms. Also notice in the figure that there is significant increase in cathodic current (i.e. $O_2$ to $O_2^-$) while the amount of anodic current (i.e. $O_2^-$ to $O_2$) is negligible essentially making the voltammogram cathodic. This is due to the vast difference in the concentrations of $O_2$ and the $O_2^-$ ions. The bulk solution contains $O_2$, which is constantly supplied to the rotating electrode while the superoxide ion’s concentration at the electrode is so minuscule that little anodic current is produced. The Levich equation (3.3) establishes relationship between current at the RDE and concentration of the analyte.
Figure 3.3: (A) Disk currents obtained in 0.1 M TBAPF$_6$ MeCN during ORR in the anodic sweep at room temperature by various rotation rates at 100mV/s. (B) Levich plot of limiting current vs. square root of rotation in 0.1 M TBAPF$_6$ & 0.1 M TBAClO$_4$ in MeCN vs. Ag/AgCl at scan rate =100mVs$^{-1}$. 
In the Levich equation

\[ i_{\text{lim}} = (0.620) n F A D^{2/3} \omega^{1/2} v^{-1/6} C \]  

*Equation 3.3*

\( i_{\text{lim}} \) is the limiting current density (A cm\(^{-2}\)), \( n \) is the number of electrons involved in the reaction, \( F \) is the Faraday constant (96,500 C mol\(^{-1}\)), \( D \) is the diffusion coefficient of oxygen in the solution, \( v \) is the kinematic viscosity of the solution (4.4 x 10\(^{-3}\) cm\(^2\)s\(^{-1}\)), \( C \) is the concentration of oxygen in solution (8.1mM)\(^{8,9}\) and \( \omega \) is the angular frequency (\( \frac{2\pi f}{60} \)). The RDE data provide insight into the number of electrons transferred to the analyte by comparing the limiting currents to the rotation rate of the electrode. Figure 3.3b displays the Levich plot for the reduction of oxygen from the RDE data presented in figure 3a. A linear Levich plot passing through the origin indicates that mass transfer of oxygen from the bulk solution to the electrode surface controls the limiting current. The experimental Levich parallels the theoretical line when \( n = 1 \), where \( n \) is the number of electrons, indicating that the reduction of oxygen at this electrode is a one electron process to form superoxide. These CV and the RDE data are consistent with the reaction Scheme 1 for the reduction of O\(_2\) in acetonitrile.

**Scheme 3.1**

**Step1.** \( O_2 + TBA^+ + e^- = TBAO_2 \)

**Step2.** \( TBAO_2 + TBA^+ + e^- = TBA_2O_2 \)
The peak $E_{p1}$ in the CV corresponds to step 1 and $E_{p2}$ to step 2. We calculated the diffusion coefficient of $O_2$ from the dependency of $I_{pc}$ on $V^{1/2}$ (from the Randles-Sevcik equation). The diffusion coefficient for $O_2$ ($D_{O2}$) is found to be $2.2 \times 10^{-5}$ cm$^2$ sec$^{-1}$ in 0.1M TBAClO$_4$ and $2.1 \times 10^{-5}$ cm$^2$ sec$^{-1}$ in 0.1M TBAPF$_6$. These values are very close to the previously reported values of $4.87 \times 10^{-5}$ cm$^2$ sec$^{-1}$ in 0.9 M TEABF$_4$ and $2.07 \times 10^{-5}$ cm$^2$ sec$^{-1}$ in acetonitrile containing 0.1M TEAP$^{10,11}$. We also calculated the diffusion coefficients of oxygen using the Levich method for ClO$_4^-$ ($2.3 \times 10^{-5}$ cm$^2$ sec$^{-1}$) and PF$_6^-$ ($2.1 \times 10^{-5}$ cm$^2$ sec$^{-1}$). Again the small difference in the diffusion coefficient values between both the Randles–Sevcik and the Levich equations maybe ascribed to the fact that the Randles-Sevcik equation does not contain the term for mass transport control. Deviation from linearity at the lower rotation rates in figure 3a is attributed to poor mass transport or slow kinetics. The data presented above indicate that the most likely pathway for oxygen reduction is by an initial one-electron transfer to $O_2$ to form $O_2^-$. We can utilize the Stokes-Einstein equation to calculate the theoretical diffusion coefficient for $O_2$ in this electrolyte and account for the small differences in the diffusion coefficients. The relationship between diffusion coefficient and solution viscosity is given by the Stokes-Einstein equation (3.4).

$$D = \frac{kT}{6\pi\eta a} \quad \text{(Equation 3.4)}$$

Where $a$ is the effective hydrodynamic radius of oxygen, $k$ is the Boltzmann constant, and $T$ is the temperature and $\mu$ is the dynamic viscosity. The latter was
calculated from the aforementioned kinematic viscosity and the solution density and was found to be 0.384 cP. Using Stokes-Einstein relationship we calculated $D_{O_2} = 2.6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. The $O_2$ hydrodynamic radius used for this calculation was $2.16 \AA^{12}$. Randles-Sevcik can also be applied to obtain the diffusion coefficient of the superoxide ($D_{O_2^\cdot}$) generated, values obtained were $8.4 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ in 0.1M TBAClO$_4$ and $9. \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ for 0.1M TBAPF$_6$, approximately an order of magnitude lower than that of $O_2$. The diffusion coefficients of $O_2$ and $O_2^\cdot$ are of particular interest to understand and model mass transport of these species in the Li-air battery. We investigated the nature of the reduction further using the Tafel equation, which relates the rate of electrochemical reaction to overpotential according to

$$\log i = \log i_0 + \left( \frac{1-anF}{RT} \right) \eta$$

(Equation 3.5)

A plot of log $i$ versus overpotential ($\eta$) should be linear, from which the transfer coefficient $\alpha$, and the exchange current density $i_0$ can be determined. Figure 3.4 shows cathodic Tafel plots obtained after the measured current is corrected for mass transport to give the kinetic current. The kinetic current is calculated from the equation,

$$i_k = \frac{i_{\text{lim}}}{i_{\text{lim}} - i}$$

(Equation 3.6)

where $i_k$ is the kinetic current density, $i$ is the measured current density during $O_2$ reduction, and $i_{\text{lim}}$ is the diffusion limited current density.
Figure 3.4: Tafel plots for ORR at room temperature on a glassy carbon electrode at 2500 rpm for cathodic sweep 0V to -1.0V. (OCP: TBAPF$_6$ -0.25V & TBAClO$_4$ -0.34 vs Ag/AgCl). The Tafel region is indicated in red.

The Tafel slope is consistent with a reversible one-electron reduction to superoxide (step 1), as the slope is very close to 120mVdec$^{-1}$. This indicates that step 1 is rate determining. The reversibility of this step is evident from the kinetic data listed in Table 3.5.

<table>
<thead>
<tr>
<th>Anions</th>
<th>(η): ClO$_4^-$</th>
<th>(η): PF$_6^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope (mV/dec)</td>
<td>115</td>
<td>111</td>
</tr>
<tr>
<td>Exchange Current Density ($i_0$) (Acm$^{-2}$)</td>
<td>4.33 x10$^{-5}$</td>
<td>4.44x10$^{-5}$</td>
</tr>
<tr>
<td>Rate Constant ($k^o$) (em.s$^{-1}$)</td>
<td>2.82 x10$^{-4}$</td>
<td>2.89x10$^{-4}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.45</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 3.5: $O_2$/O$_2^-$ kinetic parameters in 0.1M TBAPF$_6$ & TBAClO$_4$/MeCN
The exchange current, \( \log i_0 \) is defined as the intersection of the Tafel line and the y-axis (\( \log I_b \)). The standard rate constant \( k^0 \) is calculated from \( i_0 \) using equation.

\[
I_0 = nF A k^0 C \quad (Equation 3.7)
\]

We established that the anion has very little effect on the mechanism of reduction in this media. Both perchlorate and hexafluorophosphate solutions exhibit very similar electrochemical behavior.

### 3.3.2 Oxygen Reduction in Alkali Metal-Hexafluorophosphate (\( X^+PF_6^- \)) Based Electrolytes

The electrochemical behavior of oxygen in the presence of alkali metal cations differed from that observed in the TBA-based electrolytes. Figure 3.5a, illustrates the considerable difference in electrochemistry, when the TBA cation is substituted with alkali metal cations such as lithium (Li), sodium (Na) and potassium (K). Reversibility or lack thereof is a major difference between the TBA based electrolytes and the alkali solutions. Reversible systems correspond to a half-wave potential \( E_{1/2} \) that is near the peak potential \( E_p \). Figure 3.5a (inset) illustrates the irreversible nature of these systems. The reduction wave is broadened by the sluggish kinetics, leading to a displacement in potential between \( E_{1/2} \) and \( E_p \). The relevant voltammetric properties are listed in Table 3.6. Although the CVs appear relatively mundane these systems are a lot more complex upon closer inspection. The cathodic peak is shifted from -0.84V as in the case of the TBA cation to ca. -0.7V at the scan rate of 25mV/s respectively. The peak shifts are possibly the result of the relative
Lewis acidities of the cations. Both sodium and lithium cations are recognized as hard Lewis acids due to their small ionic radii Li$^+$ (0.90 Å) and Na$^+$ (1.16 Å) and low oxidation states. Hard Lewis acids have high charge densities on their surface and tend to form ionic bonds with hard bases such as superoxide. The appearance of a second cathodic peak, which is characterized by the plateau region at -1.5V, was a distinct feature of the LiPF$_6$ case. Investigation of the plateau region was conducted by varying the scan rate (Fig. 3.5b).
Figure 3.5: (A) Cyclic voltammograms of oxygen reduction in 0.1M LiPF$_6$ (dashed line), 0.1M NaPF$_6$ (Solid) in MeCN. Scan rate of 100mV/s (-3V to 3V vs. Ag/AgCl). (B) Oxygen reduction voltammograms in 0.1M LiPF$_6$/MeCN on GC electrode at various sweep rates.
Ep$_2$ is associated with the successive reduction of lithium superoxide to lithium peroxide through the reaction in Step 2. Note that the appearance of the peak Ep$_2$ corresponding to lithium superoxide reduction is scan rate dependent. The lack of this feature at low scan rates reveals that the kinetics of this process is extremely rapid. On the reverse sweep to positive potentials this peroxide reduction product is oxidized at high overpotentials via the reaction in step 3 (Ep$_3$=1.3V). This peak is analogous to peroxide oxidation observed in TBA salt solutions. This oxidation peak is absent in the sodium CV probably as a result of the decomposition of sodium superoxide to sodium peroxide via reaction in step 2 (scheme 3). Lithium peroxide decomposes slightly in a similar manner to sodium peroxide but not to the same extent. This explains the absence of the peak corresponding to the reduction of LiO$_2$ at slow scan rates. The electrochemical reduction of oxygen in these solutions is irreversible. The cathodic peak current is directly proportional to the square root of scan rate (inset 5b), indicating a fast diffusion controlled reaction. The initial electrode processes can be described by similar reactions for O$_2$ reduction in presence of both Li$^+$ and Na$^+$ as depicted in Scheme 3.2 and Scheme 3.3, respectively

**Scheme 2:**

<table>
<thead>
<tr>
<th>Step</th>
<th>($E_p$)</th>
<th>Reaction</th>
<th>Product</th>
<th>$E^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>($E_{p1}$)</td>
<td>O$_2$ + Li$^+$ + e$^-$ = LiO$_2$</td>
<td>E$^0$ = 3.0V(Li/Li$^+$)</td>
<td></td>
</tr>
<tr>
<td>Step 2</td>
<td></td>
<td>2 LiO$_2$ = Li$_2$O$_2$ + O$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 3</td>
<td>($E_{p2}$)</td>
<td>LiO$_2$ + Li$^+$ + e$^-$ = Li$_2$O$_2$</td>
<td>E$^0$ = 3.1V</td>
<td></td>
</tr>
<tr>
<td>Step 4</td>
<td>($E_{p3}$)</td>
<td>Li$_2$O$_2$ = O$_2$ + 2Li$^+$ + 2e$^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scheme 3:

Step 1 \( (E_{p1}) \): \( O_2 + Na^+ + e^- = NaO_2 \)

Step 2 \( 2NaO_2 = Na_2O_2 + O_2 \)

Oxygen is reduced to lithium superoxide via reaction Step 1\( (E_{p1}) \). Knowing the thermodynamic quantity \( \Delta G \) (Gibbs free energy) the cell potential may be obtained from the equation,

\[-\Delta G = nFE^o\]  \(\text{(Equation 3.8)}\)

The calculated \( E^o \) is presented in scheme 3.2 for the lithium case.

According to equation (9)\(^{13}\) the transfer coefficient maybe approximated from the difference between the peak potential and the half wave peak potential see table 3.6. The low \( \alpha_n \) values, which are not in the typical region of 0.5, suggest sluggish kinetics due to formation of a passive oxide layer on the surface of the electrode.

\[E_{p} - E_{p/2} = \frac{1.857RT}{\alpha_n} \frac{47.7}{\alpha} \, \text{mV} \]  \(\text{(Equation 3.9)}\)

The rate constant may also be calculated if the diffusion coefficient is known. According to Nicholson\(^{14,15}\) an irreversible cathodic reaction modeled through the relationship between \( I_p \) and \( V^{1/2} \) is linear, and is described by equation (3.10).

\[I_p = (2.99 \times 10^5)n(\alpha)^{1/2}ACD^{1/2}V^{1/2} \]  \(\text{(Equation 3.10)}\)
The diffusion coefficient of oxygen in these alkali metal-based salts can be estimated using this equation along with the calculated \( \alpha \) values. In equation (10) \( I_p \) is the peak current, \( A \) is the area of the electrode, \( C \) is the concentration of oxygen, and \( V \) is the scan rate. A plot of \( V^{1/2} \) vs. \( I_p \) shown in Figure 3.6 contains both the experimental plots using data collected and the simulated plots for \( n \) equal to 1. From these plots the number of electrons involved in the first reduction process is determined to be one.

![Figure 3.6](image-url)

**Figure 3.6**: Experimental and theoretical \((n=1) \sqrt{v}\) vs. \(I_p\) plots for in 0.1M LiPF\(_6\), NaPF\(_6\), and KPF\(_6\) in MeCN.

This confirms that the overall reduction of oxygen in these salts is a one-electron process to form an alkali metal superoxide. The diffusion coefficients of the alkali salts are presented in Table 3.6.
These are an order of magnitude lower than their TBA counterparts. The standard rate constants of these reactions are calculated from the y-intercepts in figure 3.6. The $k^o$ values show that $O_2$ reduction kinetics in sodium salt solutions are a compared to lithium and potassium based electrolytes. The irreversibility of these systems obvious from the lack of oxidation peaks in the sodium data even at high scans rates points to the chemical decomposition of the first reduction product. In order to understand the system in further detail we examined oxygen reduction as a function of concentration. Figure 3.7 shows voltammograms for 1M APF$_6$ (A= Li$^+$, Na$^+$ & 0.5M K$^+$) in MeCN, scanned at 100mV/s. For the cases of sodium and lithium results are similar to those in 0.1M solutions although there was a shift in the anodic peak position in the lithium case.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$E_{p1}$ (V)</th>
<th>$E_{p2}$ (V)</th>
<th>$E_{p3}$ (V)</th>
<th>$E^o$ (V)</th>
<th>$\alpha n$</th>
<th>$k^o$ (cm$^{-1}$)</th>
<th>Diffusion coefficient (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>-0.71</td>
<td>-1.30</td>
<td>1.8</td>
<td>-0.580</td>
<td>0.225</td>
<td>8.10e$^{-5}$</td>
<td>3.77e$^{-7}$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>-0.76</td>
<td>-</td>
<td>-</td>
<td>-0.730</td>
<td>0.190</td>
<td>6.97e$^{-4}$</td>
<td>1.03e$^{-6}$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-0.78</td>
<td>-</td>
<td>1.2</td>
<td>-0.677</td>
<td>0.230</td>
<td>1.97e$^{-4}$</td>
<td>2.30e$^{-7}$</td>
</tr>
</tbody>
</table>

**Table 3.6:** Voltammetric properties of 0.1M Li, Na & KPF$_6$ in oxygen saturated acetonitrile. Scan rate 25mV/s.
Figure 3.7: Cyclic Voltammograms for the reduction of oxygen saturated 1M XPF$_6$ (X=Li$^+$, Na$^+$ & 0.5M K$^+$) in MeCN on GC electrode at 100mV/s.

Increasing the concentration of alkali salts facilitates oxidation of the reduction products. Increased concentrations of cations stabilize the superoxide and peroxide products. The electrochemistry of oxygen is influenced by the cation size, increasing the cation size from lithium to potassium alters the cyclic voltammogram. Potassium is a larger alkali metal ($r=2.20$ Å). The CV in 0.1M KPF$_6$ it is comparable to Li and Na salt solutions. At high concentrations it is reminiscent of the TBA electrolytes; notice two reduction peaks followed by two subsequent oxidation peaks observed on the return sweep in the range. Applying RDE voltammetry to these systems was unsuccessful. This is illustrated in Figure 3.8 where it is interesting to note that there is little increase in current density as the electrode is rotated, in fact the
current decreases. It appears that the reduction product passivates the electrode and as the rotation rate increases so does the passivation rate. The electrode appears to passivate quicker than mass transport limit can be reached. The same behavior is observed for NaPF₆ although it occurs much faster. Thus the RDE data provide additional support to the notion that the reduction products of oxygen passivate the electrode. Figure 3.9 shows the typical steady-state voltammograms obtained on the RDE in O₂-saturated solution containing 0.1 & 1M KPF₆. These voltammograms do not show a clear limiting current due to mass transport limitations. However, the formation of a slight horizontal current plateau during oxygen reduction is observed. The formation of this plateau at potentials less negative than -1V is indicative of a competitive secondary reduction at the electrode. This maybe the reason behind the overlapping oxygen reduction peaks especially in the 1M solution.
Figure 3.8: Steady voltammograms for the reduction of oxygen in 0.1M LiPF$_6$ & NaPF$_6$ in MeCN at various rotation rates at 100mV/s.
Figure 3.9: Disk currents obtained in 0.1 & 1M KPF₆ MeCN during ORR in the anodic sweep at room temperature at various rotation rates. All scans used a glassy carbon working electrode at a scan rate of 100 mV.
In summary, the data we obtained in TBAClO\textsubscript{4} and TBAPF\textsubscript{6} based electrolytes reveals that the anion has little or no effect on the redox processes. In TBA salt solutions the first reduction process is a one-electron reversible reduction of oxygen to form the superoxide. The superoxide can be reduced to the peroxide irreversibly at lower potentials. Alkali metal hexafluorophosphate APF\textsubscript{6} (where A is Li\textsuperscript{+}, Na\textsuperscript{+} and K\textsuperscript{+}) solutions were investigated to establish the effect of cations on oxygen electrochemistry. By replacing the larger TBA\textsuperscript{+} with alkali metal cations the reversible nature of oxygen reduction is severely suppressed. The reduction reaction in solutions containing the smaller cations Li\textsuperscript{+} and Na\textsuperscript{+} is irreversible. In LiPF\textsubscript{6} solutions O\textsubscript{2} is irreversibly reduced first by a one-electron process to form LiO\textsubscript{2}, followed by a second one-electron reduction to Li\textsubscript{2}O\textsubscript{2} which appears to passivate the electrode surface making the reaction irreversible. It also appeared that the LiO\textsubscript{2} formed on the electrode surface chemically decomposes to Li\textsubscript{2}O\textsubscript{2}. However, there is a finite lifetime for the LiO\textsubscript{2} on the electrode surface with the result that at high scan rates the reduction of LiO\textsubscript{2} to Li\textsubscript{2}O\textsubscript{2} can be observed. Both LiO\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2} can be oxidized at high overvoltages to oxygen and lithium. Oxygen reduction in NaPF\textsubscript{6} is also a one-electron first step to form NaO\textsubscript{2}, which appears to passivate the surface as well as decomposing rapidly to Na\textsubscript{2}O\textsubscript{2} hence the complete lack of oxidation.

The sodium oxides cannot be oxidized even at high overvoltages, except in highly concentrated electrolyte solutions. Potassium a slightly larger alkali metal (radius =2.2 Å) and displays a voltammogram that is somewhat quasi reversible as verified by the increase of anodic current in comparison to lithium and sodium. Although the oxygen reduction is not as reversible as that in the tetra alkyl
ammonium salt solutions the reduction of $O_2$ to $KO_2$ and $KO_2$ to $K_2O_2$ is observed as two distinct peak as opposed to the mix potential regions of lithium and sodium at 1m concentration. Both of these oxides are electrochemically oxidized at significant overpotentials.

These results maybe explained in terms of the charge density on the surfaces of the cations. The smallest of the cations $Li^+$ is a good Lewis acid capable of forming a very strong ionic bond with the superoxide ion. Increasing the cation size from $Li^+$ to $TBA^+$ ($TBA^+<K^+<Na^+<Li^+$) the positive charge density (charge per unit volume) on the ion decreases, as does the relative Lewis acidity, leading to weaker interactions with the superoxide ion. This has several consequences: The $TBAO_2$ is soluble in the electrolyte and the redox reaction is reversible. The $KO_2$ formed appears to have partial solubility in the electrolyte with the result that the redox processes are somewhat reminiscent of that in the TBA solutions. The smaller $Li$ and $Na$ cations are stronger Lewis acids and they form ionic bonds with oxides leading to their precipitation on the electrode surfaces. This surface coverage of the electrode by the $O_2$ reduction products passivates the electrode, shuts down the reduction and renders the reaction irreversible.

3.4 Conclusions

Our results show that the reduction and subsequent oxidation of $O_2$ in acetonitrile-based electrolytes is strongly influenced by the cation of the conducting salt used. A practical outcome of the results from this work to the lithium-air battery is that it would be advantageous to use a mixture of $Li$ and $K$ and/ or TBA salts as supporting electrolytes in order to dissolve the oxygen reduction products. This in
turn would increase the amount of oxygen that can be reduced to deliver higher capacity. Dissolving the reduction products would also promote reversibility of O₂ reduction, which would increase the battery’s rechargeability. Our results also show that useful electrochemical kinetic data for soluble redox species in highly concentrated electrolyte solutions relevant to Li batteries can be obtained using the complementary CV and RDE techniques. Such kinetic data are relevant to the studies of the Li-air battery as well as others containing soluble electrode materials especially for battery simulation studies aimed at understanding the performance of practical batteries, and generally for the development of improved materials.

### 3.5 References


Chapter 4

Influence of Non-aqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air battery

4.1 Introduction

The non-aqueous, rechargeable Li-air battery, introduced in 1996\(^1\) has emerged as a major candidate for future alternative energy source. It is actively being developed worldwide because of its potential to deliver ultrahigh energy density in a battery that is low cost and environmentally friendly. In the first rechargeable Li-air cell reported by Abraham\(^1\), composed of a Li metal anode, a polyacrylonitrile-based gel polymer electrolyte\(^2,3\) and a porous carbon cathode, Li\(_2\)O\(_2\) was identified as the discharge product. The formation of Li\(_2\)O\(_2\) is consistent with the open circuit voltage (OCV) of about 2.9 V measured for the cell (1) and the theoretical voltages calculated for possible Li-air cell reactions depicted in equations 1-3.

\[
\begin{align*}
2Li + O_2 &= Li_2O_2; \Delta G^0 = -145 \text{ kCal} \quad (E^0 = 3.1 \text{ V}) \quad (1) \\
4Li + O_2 &= 2Li_2O; \Delta G^0 = -268 \text{ kCal} \quad (E^0 = 2.91) \quad (2) \\
Li + O_2 &= LiO_2; \Delta G^0 = -70 \text{ kcal} \quad (E^0 = 3.0 \text{ V}) \quad (3)
\end{align*}
\]

Equations 1-3 reveal that two other products besides Li\(_2\)O\(_2\) can be formed from the reduction of oxygen. Recently, we have shown\(^3\) that the first product of the reduction
of oxygen in non-aqueous electrolytes is superoxide, $O_2^-$, involving a one-electron process. We also found that the half-life of the superoxide depends on the nature of the supporting electrolyte cation present in the electrolyte solution. In presence of tetra butyl ammonium cations ($\text{Bu}_4\text{N}^+$) in acetonitrile solutions, the superoxide, $\text{Bu}_4\text{NO}_2^-$, is extremely stable and resists further reduction to $\text{O}_2^{2-}$ or $\text{O}_2^2-$. On the other hand, in presence of $\text{Li}^+$ ions, the superoxide, $\text{LiO}_2^-$, is unstable with very short half-life and decomposes to $\text{Li}_2\text{O}_2$ and $\text{O}_2$. The $\text{LiO}_2$ that survives decomposition can be reduced to $\text{Li}_2\text{O}_2$.

The electrochemistry of $\text{O}_2$ in presence of $\text{Na}^+$ is somewhat similar to that in presence of $\text{Li}^+$, except that the $\text{NaO}_2$ first formed appears to decompose very rapidly to $\text{Na}_2\text{O}_2$. Recent data\textsuperscript{5} suggest that $\text{Li}_2\text{O}$ is probably formed in some $\text{Li}/\text{O}_2$ cells from the reduction of $\text{Li}_2\text{O}_2$. The rechargeable Lithium-air battery research is in its infancy and a lot of further work remains to be done to fully elucidate the cell chemistry involved in discharge/charge cycling, and to bring this technology to practicability. A number of research groups have heeded the call and investigated various aspects of this battery. The work so far can be divided into three major categories; 1) Li-air cells with liquid and solid electrolytes, 2) porous electrode materials and structures, and cell performance evaluation, and 3) catalysis of cell reactions

Jeffery Read has contributed to liquid electrolytes\textsuperscript{6-8} for Li-air batteries. Having conducted an exhaustive review of solvent properties he found electrolyte formulation as having the largest influence on cell performance including the nature of the reduction products. Discharge capacity is dependent on $\text{O}_2$ solubility, which
led him to suggest ether-based electrolytes for improved cell performance. Abraham et al\textsuperscript{2} studied low volatile organic liquid and polymer electrolytes for the Li-air battery. Hydrophobic ionic liquids\textsuperscript{9,10} have been studied as electrolytes demonstrating good lithium stability and high cell discharge capacities. Another avenue of investigation involved applying existing electrolytes from conventional Li-ion batteries to the Li-air\textsuperscript{11} battery. Recently, the usefulness of solid electrolytes for Li-air batteries has been demonstrated with an all-solid-state rechargeable Li-air battery\textsuperscript{12}. Protected lithium electrodes (PLE) stabilized by lithium ion conductors\textsuperscript{13} have been applied successfully in both aqueous and non-aqueous Lithium batteries. Finally, low loading of a very high surface area carbon on nickel foam\textsuperscript{14} has demonstrated the highest discharge capacity thus far. Since the discharge products of the Li-air battery are insoluble in most organic electrolytes, a porous electrode structure with appropriate morphology, surface structure, pore volume and surface area is crucial for the oxygen reduction reaction (ORR) and rechargeability of the Li-air cell.

Abraham et al clearly established in their first paper\textsuperscript{1} that the Li/O\textsubscript{2} cell is rechargeable. They found that in the absence of a catalyst of pyrolyzed cobalt phthalocyanine, (Co-Pc) the recharge occurs at about 4 V, with a large hysteresis between charge and discharge voltages. The hysteresis was reduced and the charge/discharge efficiency increased with the Co-Pc-based catalyst. Recent investigations have employed manganese oxide (MnO\textsubscript{2}) catalysts\textsuperscript{15} although the charge voltages in these cells are similar to the uncatalyzed cells. Our recent studies have revealed that the Li/O\textsubscript{2} cell can be recharged with high efficiency without a
catalyst using an appropriate porous carbon electrode\textsuperscript{3,16}. Interestingly charge voltages of these uncatalyzed cells are similar to those of the MnO\textsubscript{2} catalyzed cells with both of these cell exhibiting higher charge voltages than the cobalt-catalyzed cells. Clearly, a full understanding of the mechanism of the cell discharge reaction mechanism and rechargeability is still lacking.

In this chapter we report on the results of a detailed study of the influence of non-aqueous solvents on O\textsubscript{2} electrochemistry. Our results have shown a relationship between the Lewis basicity of the solvents, measured by their Güttmann donor numbers (DN)\textsuperscript{17}, the Lewis acidity of the cations, and the relative stabilities of the oxygen reduction products in presence of TBA\textsuperscript{+} and Li\textsuperscript{+}, and their rechargeability. These results complementing our recently published results\textsuperscript{3} on the influence of supporting electrolyte cations on O\textsubscript{2} reduction products are expected to provide the ability to systematically design and select new electrolytes for the rechargeable Li-air battery. The structural formulas of the four solvents studied and their acronyms used here are:

\[ \text{EC} \quad \text{TEGDME} \]
\[ \text{DMSO} \quad \text{DME} \]
\[ \text{MeCN} \quad \text{EMC} \]

\textit{Figure 4.1:} Solvent Structures
4.2 Experimental

4.2.1 Materials

Anhydrous acetonitrile (MeCN), Dimethyl sulfoxide (DMSO), 1,2-Dimethoxyethane (DME) and Pursis Tetraethylene glycol dimethyl ether (TEGDME) were purchased from Sigma-Aldrich, Allentown, PA. All chemicals were dried with Lithium and were stored and prepared in an MBraun dry box filled with purified argon where the moisture and oxygen content was less than 1ppm. The dried solvents were stored over 0.3 or 0.4nm molecular sieves and prior to actual measurements all solvents were degassed under vacuum.

Tetrabutylammonium hexafluorophosphate (TBAPF₆) electrochemical grade, ≥99.0% (Fluka, puriss grade) from Sigma-Aldrich, Allentown, PA was dried under reduced pressure at room temperature. Lithium hexafluorophosphate (LiPF₆) (battery grade, >99.9%, H₂O< 20ppm) was obtained from Ferro Corporation Cleveland, Ohio.

4.2.2 Electrochemical Experiments

The electrochemical experiments were performed with an Autolab (Ecochemie Inc., model-PGSTAT 30) potentiostat equipped with a bi-potentiostat interface in an airtight electrochemical cell. The electrochemical cell designed and built in-house consisted of a traditional 3-electrode system utilizing Platinum (Pt) mesh as the reference electrode and Pt mesh as the counter electrode. This reference electrode was used because of the instability of Li foil typically used in Li⁺ conducting electrolytes as a reference electrode because of its reaction in acetonitrile. The Pt reference electrode provided stable potentials and was calibrated with
reference to the ferrocenium ion/ferrocene couple (Fe+/Fc) in each electrolyte studied, which in turn was calibrated to Li/Li+ in a stable ethylene carbonate/dimethyl carbonate-based electrolyte. The cell also had inlet and outlet valves for oxygen or argon purging. The cell was entirely airtight with exception of the gas outlets, which were kept under pressure with the working gas. The glassy carbon (5 mm diameter) working electrode employed for the cyclic voltammetry experiments was polished with 0.5 and 0.05 mm alumina paste prior to the experiments. For RDE experiments, the glassy carbon electrode was rotated with a Pine AFCPRB RDE rotor. All of the cyclic voltammetry experiments were initially performed in an argon-atmosphere glove box where H2O and O2 concentrations were kept below 1ppm and temperature was held at 22 ± 2°C. For RDE experiments the cell was brought outside of the glove box and placed in a glove bag purged with Argon.

The electrolyte solutions were first purged with argon, and the electrode was cycled continuously until reproducible cyclic voltammetric profile was obtained. The solutions were then purged with O2 for ORR measurements. The electrochemical impedance measurements were performed with the Autolab PG 30 supplied with a FRA 2 module for impedance measurements. The impedance spectra were measured in the frequency range from 100 mHz to 100 kHz at open circuit potential with an AC voltage amplitude of 5mV. Conductivity measurements of all samples were carried out using a 4-probe Thermo Orion conductivity cell from Thermo Fisher Scientific Inc Waltham MA. Conductivity data for the solutions of 0.1M NBu4PF6 and LiPF6 in dimethyl sulfoxide (DMSO), acetonitrile (MeCN), 1,2 Dimethoxyethane (DME),
tetraethylene glycol dimethyl ether (TEGDME) are summarized in Table 4.1. All measurements were carried out at room temperature (22±2).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conductivity, $\sigma$(mS/cm) Li$^+$</th>
<th>Conductivity, $\sigma$(mS/cm) TBA$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>2.11</td>
<td>2.08</td>
</tr>
<tr>
<td>MeCN</td>
<td>14.39</td>
<td>10.85</td>
</tr>
<tr>
<td>DME</td>
<td>1.16</td>
<td>1.42</td>
</tr>
<tr>
<td>TEGDME</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 4.1**: Conductivity of the Electrolyte Solutions

4.3 **Results and Discussion**

4.3.1 **ORR in Selected Non-Aqueous Electrolytes.**

Electrolytes based on aprotic non-aqueous solvents are the ideal medium to investigate the oxygen reduction reactions (ORR) relevant to the Li-air battery. An environment free of protons could enable the full reduction of oxygen, essential to realize the full energy density of the Li-air cell without interference from protonated intermediates or products. Our previous work$^3$ revealed that the three possible O$_2$ reduction products in the Li-air battery, LiO$_2$, Li$_2$O$_2$ and Li$_2$O are highly polar. Therefore, appropriate polar solvents are required to dissolve these products in order to avoid their precipitation and passivation of the electrode surface. However, there is no metric currently existing to select the optimum non-aqueous solvent for the rechargeable Li-air battery.
Polar solvents such as sulfoxides (R₂S=O), ethers (R–O–R) and nitriles (RC≡N) are potentially useful candidates as they may dissolve O₂ reduction products at least partially to promote rechargeability, but there is no guiding principle presently available to select the best solvent or family of solvents Table 4.2 lists the four solvents with widely varying properties, particularly donor numbers (DN) that are a measure of solvent basicity, investigated in this work. We have purposely chosen these solvents with the goal of identifying a fundamental property or properties that can be used as the metric to select solvents with optimum properties for the Li-air battery.

Table 4.2. Solvents Properties.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε 25°C</th>
<th>DN (Kcal/mol)</th>
<th>Viscosity η(P)</th>
<th>Oxygen Solubility (mM/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfoxide -DMSO</td>
<td>48.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>29.8&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.948&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2.10&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>Acetonitrile-ACN</td>
<td>36.64&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.361&lt;sup&gt;e&lt;/sup&gt;</td>
<td>8.1&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>Tetraethylene glycol dimethyl ether</td>
<td>7.79&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16.6&lt;sup&gt;d&lt;/sup&gt;</td>
<td>4.05&lt;sup&gt;f&lt;/sup&gt;</td>
<td>4.43&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
<tr>
<td>1,2-dimethoxyethane -DME</td>
<td>7.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>20.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.46&lt;sup&gt;d&lt;/sup&gt;</td>
<td>9.57&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Goldfarb et al., Ref.<sup>28</sup>  
<sup>b</sup> Rivas et al., Ref.<sup>29</sup>  
<sup>c</sup> Lago et al., Ref.<sup>30</sup>  
<sup>d</sup> Chemistry of Non aqueous Solutions., Ref.<sup>31</sup>  
<sup>e</sup> Aminabhavi et al., Ref.<sup>32</sup>  
<sup>f</sup> Marcus Properties of Solvents., Ref.<sup>33</sup>  
<sup>g</sup> Sawyer et al., Ref.<sup>18</sup>  
<sup>h</sup> Read., Ref.<sup>5</sup>
4.3.2 ORR in TBAPF$_6$ solutions in DMSO, DME and MeCN

Dimethyl sulfoxide (DMSO) is a highly polar versatile solvent, which displays high salt solubility to produce well-conducting solutions with a wide electrochemical window (Figure 4.2A). This figure also displays a cyclic voltammogram (CV) for the reduction of oxygen in a 0.1M TBAPF$_6$/DMSO electrolyte. The peak potential separation $\Delta E_p$ between the anodic ($E_{pa} = 2.40\text{V}$) and cathodic ($E_{pc} = 2.34 \text{ V}$) peaks is 60mV and the charge area ratio $\left(\frac{Q_a}{Q_c}\right)$ under the peaks is close to unity. These results indicate that $O_2$ reduction in the presence of TBA$^+$ ions is reversible.
Figure 4.2: A) Cyclic voltammograms for the reduction of oxygen in 0.1M TBAPF$_6$ (Red, iR corrected) and the argon background (dotted) in DMSO. B) Cyclic voltammograms (iR un-corrected) for the reduction of oxygen in 0.1M TBAPF$_6$/MeCN (Black), DME (Blue). Scan rate 100mV/s.
Figure 4.3 portrays a Randles-Sevcik (RS) plot of this ORR. The Randles-Sevcik equation (1) describes the relationship between the current and scan rate of a reversible electrochemical reaction. The magnitude of the current (I) is a function of temperature, T, the oxygen concentration in solution, C, \((2.1 \text{ mM})^{18}\), electrode area A, the number of electrons transferred n, the diffusion coefficient D, and the rate, V, at which the potential is scanned (scan rate).

\[
I_p = (2.69 \times 10^5) n^{3/2} AD^{1/2}V^{1/2}C
\]  
\textit{(Equation 4.1)}

![Randles-Sevcik Plot](image)

\textit{Figure 4.3:} Randles-Sevcik plot of peak current vs. square root of the scan rate in 0.1 M TBAPF₆/DMSO.

The plot of experimental data versus a theoretical Randles-Sevcik plot shows that it is in close agreement with the \(n = 1\) theoretical plot, thereby indicating that \(E_{pc}\) is a one-
electron reduction process. The plot linearity also suggests that this is a mass transport limited process. This behavior is identical to that we previously found in TBAPF$_6$/acetonitrile$^3$ and by others in TBAClO$_4$ solutions$^{18}$. The reduction of O$_2$ in DME/TBAPF$_6$ and MeCN/TBAPF$_6$ exhibits similar behavior as shown in figure 4.2B indicating the general nature of the mechanism of O$_2$ reduction in TBA$^+$-containing solutions. The O$_2$ reduction potential and the associated current varied slightly in the different electrolytes probably due to the different O$_2$ solubilities and reduction kinetics. The voltammograms obtained from the RDE experiments were analyzed using the Levich equation (2) which defines the relationship between current at a rotating disk electrode RDE and the angular frequency ($\omega$) of rotation of the electrode.

$$i_{\text{lim}} = \left(0.620\right)nFAD^{2/3}\omega^{1/2}v^{-1/6}$$  \hspace{0.5cm} (Equation 4.2)

In equation 4.2 $i_{\text{lim}}$ is the limiting current density (amps), $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant (96,500 C mol$^{-1}$), $D$ is the diffusion coefficient of oxygen in the solution, $v$ is the kinematic viscosity of the solution ($1.9 \times 10^{-3}$ cm$^2$s$^{-1}$)$^{19}$. In RDE voltammetry, steady state is reached quickly eliminating double layer charging. Also mass transfer affects are eliminated, as mass transfer rates are much larger than diffusion rates allowing for accurate kinetics calculations. Figure 4.4 displays the Levich plot for the reduction of oxygen in 0.1M TBAPF$_6$/DMSO; its linearity indicates that mass transfer of oxygen from the bulk solution to the electrode surface controls the limiting current. The experimental Levich plot parallels the theoretical line.
Figure 4.4: Levich plot of limiting current vs. square root of rotation in 0.1 M TBAPF$_6$/DMSO scan rate=100mVs$^{-1}$ (Inset Tafel plot).

When $n = 1$, which is consistent with the CV data. The kinetic nature of the reaction can be further investigated using the Tafel equation,

$$\log i_k = \log i_0 + \left(\frac{1-\alpha nF}{RT}\right)\eta$$  \hspace{1cm} (Equation 4.3)

A plot of $\log i_k$ versus overpotential ($\eta$) should be linear, from which the transfer coefficient $\alpha$, and the exchange current density $i_0$ can be determined. The inset in figure 4.4 shows cathodic Tafel plots obtained after the measured current is corrected for mass transport to give the kinetic current. The kinetic current is calculated from the equation,

$$i_k = \frac{i_{\text{lim.}}}{i_{\text{lim-}} i}$$  \hspace{1cm} (Equation 4.4)
where \( i_k \) is the kinetic current density, \( i \) is the measured current density during \( O_2 \) reduction, and \( i_{\text{lim}} \) is the diffusion limited current density from the Levich plot. The Tafel slope is consistent with a reversible one-electron reduction to superoxide, as the slope is very close to 120mVdec\(^{-1}\). This indicates that \( E_{p_c} \) is the rate-determining step (rds). The reversibility of this step is evident from the kinetic data listed in Table 4.5.

The kinetic current density, \( i_k \), the diffusion-limited current \( i_{\text{lim}} \) density, and the measured current density, \( i \), are related through the Koutecky-Levich equation

\[
\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{\text{lim}}} = \frac{1}{i_k} + \frac{1}{0.62nFAD_o^{2/3} \omega^{1/2} V^{-1/6} C_o} \tag{Equation 4.5}
\]

The inverse kinetic current density, \( 1/i_k \), can be obtained from the intercept of Koutecky-Levich plot Fig 4.5. Reasonably linear plots are obtained (see the insets) at all measured potentials where ORR is expected to be under the mixed kinetics/diffusion control, and the linear plot under the pure diffusion control intercepts close to zero. Determination of \( i_k \) at different values of \( E \) allows determination of the standard rate constant \( k^\circ \) at different potentials where the rate of electron transfer is sufficiently slow (equilibrium) to act as a limiting factor and when the electron transfer is rapid in the limiting-current region. Standard rate constants varied from \( 3.8 \times 10^{-2} \) to \( 4 \times 10^{-3} \)cm\(^{-1}\) and \( 3 \times 10^{-3} \) to \( 6 \times 10^{-4} \)cm\(^{-1}\) for DMSO and MeCN respectively.
Figure 4.5. Current-voltage curves measured at 100 mV/s on a GC rotating disk electrode (400-3600rpm) for oxygen reduction in (A) 0.1M TBAPF₆/DMSO (B) 0.1M TBAPF₆/MeCN. Insets: Koutecky- Levich plot at different potentials in kinetic-diffusion region of the polarization curve.
We can describe the ORR mechanism in TBAPF$_6$ solutions according to the reactions in Scheme 1, involving a

**Scheme 4.1:**

Cathodic ($E_{pc}$). \[ O_2 + TBA^+ + e^- = TBAO_2 \] \( (6) \)

Anodic ($E_{pa}$). \[ TBAO_2 - e^- = TBA^+ + O_2 \] \( (7) \)

one electron reduction of oxygen to superoxide ($O_2^-$) and subsequent reoxidation of superoxide to oxygen. An explanation for the reversible $O_2$ reduction process in TBA salt solutions and the superior stability of the superoxide, $O_2^-$, in presence of TBA$^+$ in the various solvents is presented later in this chapter.

### 4.3.3 ORR in LiPF$_6$ solutions in DMSO, DME, MeCN, and TEGDME.

The ORR results obtained in these electrolytes will show clearly that the $O_2$ reduction mechanism in Li$^+$-containing electrolytes is different from that seen in presence of TBA$^+$. In addition, these results will demonstrate the subtle influence of the solvent on the mechanistic details of the $O_2$ reduction reactions in Li$^+$-containing electrolyte solutions as well as the rechargeability of the reduction products. We have found that the voltammetric data in DMSO is especially instructive to unambiguously map the $O_2$ reduction mechanism in Li$^+$-containing organic electrolytes relevant to the rechargeable Li-air battery.
Figure 4.6 illustrates \( \text{O}_2 \) reduction in 0.1M LiPF\(_6\)/DMSO. This figure comprises four separate CV’s overlaid. Each CV corresponds to a defined electrochemical window over which the voltammogram was scanned.

![Cyclic voltammograms (iR corrected) for the reduction of oxygen in 0.1M LiPF\(_6\)/DMSO at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.](image)

**Figure 4.6**: Cyclic voltammograms (iR corrected) for the reduction of oxygen in 0.1M LiPF\(_6\)/DMSO at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.

The shortest window is shown in dark yellow (2.57- 4.5 V) in which the scan was reversed at the half-peak potential \( E_{pc1/2} \) (2.57V) of the first cathodic peak in order to examine the associated anodic features. Reversing the sweep at \( E_{pc1/2} \) resulted in two clear anodic peaks, \( E_{pa1} \) at 2.75V followed by a broad peak (\( E_{pa2} \)) at 3V. Expanding the cathodic scan to the peak potential \( E_{pc1} \) (2.45V) produces an increase of the current in the following anodic \( E_{pa1} \) & \( E_{pa2} \) peaks becoming similar in magnitude.
Two anodic peaks resulting from a single cathodic peak suggests a dual step reduction mechanism from the very beginning. A one-electron reversible process is characterized by 56mV difference between the cathodic peak and half-peak potential. For this system the potentials ($|E_{pc1} - E_{pc1/2}|$) are separated by 100mV, demonstrating the complexity of this process. Upon scanning cathodically further, the current slope changes at 2.12V, $E_{pc2}$ (blue), signifying another electrochemical event. Reversing the scan subsequently in the positive direction results in the disappearance of $E_{pa1}$ and increase in $E_{pa2}$ peak current. This suggests that the first reduction product is consumed and converted to the second reduction product, which is oxidized at $E_{pa2}$.

Finally the cathodic sweep was allowed to continue towards 1.35V (Red line) where it was reversed. The corresponding anodic scan consists of two broad overlapping peaks. Similar to the blue scan $E_{pa1}$ is absent and the magnitude of $E_{pa2}$ decreased. The new anodic peak $E_{pa3}$ that emerged is believed to be due to the oxidation of the product formed from the reduction at $E_{pc2}$.

As these reactions are irreversible Randles Sevcik & Levich treatments cannot be applied to these CV data. We have deconvoluted the data using the Nicholson & Shain relationship\textsuperscript{20} (equation (8)) developed for irreversible electrochemical reactions,

$$I_p = (2.99 \times 10^5)n(n\alpha)^{1/2} ACD^{1/2} V^{1/2} \quad (Equation 4.8)$$

The symbols in equation 4.8 have their usual meaning. Figure 4.7a clearly shows that the number ($n$) of electrons transferred in the first reduction reaction is one since the theoretical $n=1$, plot follows the experimental data.
Figure 4.7: (A) Peak current vs. square root of the scan rate in 0.1 M LiPF₆/DMSO. (B) Cathodic Tafel plot obtained in 0.1 M LiPF₆/DMSO during ORR. Scan rate = 10mV/s.
The best theoretical fit was obtained using a transfer coefficient $\alpha = 0.5$ which is a typical value for reversible reactions. This suggests that the first one-electron reduction of $O_2$ in DMSO/LiPF$_6$ is substantially reversible. Tafel analysis can also be used to obtain further insight. Tafel plots for ORR in 0.1MLiPF$_6$/DMSO (from the CV data from figure 4.6) are depicted in figure 4.7b. At low overpotentials between about 50 and 150 mV from OCP, the Tafel slope is close to 120 mV/dec. On the other hand, at high overpotentials, the value is approximately 220 mV/dec. A 120mV/dec Tafel slope is typical of a one-electron process. The subsequent 220mV/dec Tafel slope is due to a second reduction step. The observations in DMSO/LiPF$_6$ can be summarized by the reactions in Scheme 4.2 involving first the formation of superoxide $O_2^-$ first (eq 9) which decomposes (eq 10), or is reduced further (eq 11), to form $O_2^{2-}$. Finally, $O_2^{2-}$ is formed (eq 12) as the final reduction product $O_2$.

**Scheme 4.2:**

**Cathodic**

\[
\begin{align*}
O_2 + Li^+ + e^- & = LiO_2 \quad (E_{pc1}) \quad (9) \\
2LiO_2 & = Li_2O_2 + O_2 \quad \text{(chemical)} \quad (10) \\
LiO_2 + Li^+ + e & = Li_2O_2 \quad (E_{pc2}) \quad (11) \\
Li_2O_2 + 2Li^+ + 2 e^- & = 2Li_2O \quad (E_{pc3}) \quad (12)
\end{align*}
\]

**Anodic**

\[
\begin{align*}
LiO_2 & = O_2 + Li^+ + e^- \quad (E_{pa1}) \quad (13) \\
Li_2O_2 & = O_2 + 2Li^+ + 2 e^- \quad (E_{pa2}) \quad (14) \\
Li_2O & = \frac{1}{2}O_2 + 2Li^+ + 2e^- \quad (E_{pa3}) \quad (15)
\end{align*}
\]
Li$_2$O$_2$ as a discharge product of the Li-air battery is well recognized from Raman spectral analysis of discharged cathodes. Our recent unpublished X-ray diffraction data for discharged cathodes indicate that Li$_2$O$_2$ and probably Li$_2$O are discharge products of the Li-air battery. The anodic Tafel slope for $E_{pa1}$ was calculated to be 128mV/dec, which is quite similar to $E_{pc1}$ illustrating the reversibility of the first one-electron process. The corresponding apparent transfer coefficients ($\alpha$) can be calculated from the Tafel slopes. The sum of $\alpha_c + \alpha_a = 1$ indicating that the number of electrons transferred between $E_{pc1}$ and $E_{pa1}$ is one. The kinetic parameters, the cathodic Tafel slope, the cathodic transfer coefficient ($\alpha_c$), the number of electron transferred ($n$), and the exchange current density ($i_o$) are listed in Table 4.5.

We note here that a reversible reduction of O$_2$ in a Li$^+$-containing electrolyte is reported here for the first time. The cyclic voltammetric parameters for the solutions of 0.1M NBu$_4$PF$_6$ and LiPF$_6$ in dimethyl sulfoxide (DMSO), acetonitrile (MeCN), 1,2 Dimethoxyethane (DME), tetraethylene glycol dimethyl ether (TEGDME) are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$E_{pc}$(V)</th>
<th>$E_{pa}$(V)</th>
<th>$E_{pa2}$(V)</th>
<th>$\Delta E_p$(V)</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO$^{\text{Li}^+}$</td>
<td>2.54</td>
<td>2.77</td>
<td>3.17</td>
<td>0.23</td>
<td>2.65</td>
</tr>
<tr>
<td>DMSO$^{\text{TBA}^+}$</td>
<td>2.34</td>
<td>2.40</td>
<td>-----</td>
<td>0.06</td>
<td>2.37</td>
</tr>
<tr>
<td>MeCN $^{\text{Li}^+}$</td>
<td>2.32</td>
<td>3.33</td>
<td>-----</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>DME $^{\text{Li}^+}$</td>
<td>2.05</td>
<td>3.26</td>
<td>-----</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>TEGDME$^{\text{Li}^+}$</td>
<td>1.76</td>
<td>2.98</td>
<td>-----</td>
<td>1.22</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.3:** Voltammetric properties of oxygen saturated electrolytes. Scan rate 100mV/s
A key difference between O\textsubscript{2} reduction in LiPF\textsubscript{6}-containing DME, MeCN or TEGDME solution and that in DMSO is the absence of E\textsubscript{pc1} and the corresponding Ep\textsubscript{a1}. Single broad reduction and oxidation peaks are observed in the DME, MeCN or TEGDME solutions, indicating multiple processes are occurring. We found E\textsubscript{pc} shifts toward more negative potentials according to the order TEGDME<DME<MeCN<DMSO indicating that the reduction of oxygen is hindered going from DMSO to TEGDME. The reduction of O\textsubscript{2} in acetonitrile/LiPF\textsubscript{6} is shown in figure 4.8.

**Figure 4.8:** Cyclic voltammograms (IR corrected) for the reduction of oxygen in 0.1M LiPF\textsubscript{6}/MeCN at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.
The cathodic peak and half-peak potential are separated (|\(E_{pc} - E_{pc/2}\)|) by 220mV indicating a complex reduction mechanism. Examining the complete CV we notice a large broad oxidation peak at 3.33V. We studied anodic processes as a function of cathodic sweep reversal potentials. The CV is first scanned to 2.5V, which is just after the reduction onset potential. There is little anodic activity at this potential. The lack of anodic activity indicates that the initial reduction step is irreversible or that the product undergoes a secondary reaction like that eq.4.10 in scheme 4.2. Increasing the electrochemical window to 2.37V the half-wave potential (\(E_{pc/2}\)) produces an anodic response \(E_{pa2}\) at 3.25V (grey line), which based on the DMSO data and our previous results in acetonitrile is believed to be the oxidation of \(\text{Li}_2\text{O}_2\). This suggests that \(\text{Li}_2\text{O}_2\) is formed at \(E_{pc}\) via the reactions in eq.4.10 and eq.4.11. Anodic peak capacity increases as the electrode is swept cathodically, closer to the peak potential of 2.27V (\(E_{pc}\)). Maximum anodic activity is reached after sweep reversal at 2.10V a potential just after \(E_{pc}\). \(E_{pa2}\) begins to broaden and second anodic peak \(E_{pa3}\) emerges as the potential is scanned cathodically to 1.65V. The presence of this second anodic peak suggests a third reduction process occurs as the electrode is cathodically polarized to low potentials, possibly the reduction of \(\text{Li}_2\text{O}_2\) to \(\text{Li}_2\text{O}\), eq. 12. Scanning the electrode to 0.65V, results in disappearance of \(E_{pa2}\) in the following anodic scan.

Oxygen reduction CVs in LiPF\(_6\)/DME and LiPF\(_6\)/TEGDME are illustrated in figure 4.9a & 9b, respectively. The cathodic peaks are shifted negatively relative to MeCN, attributed to increase solution resistance and the associated iR polarization. Little anodic activity is visible prior to arriving at the half wave reduction peak.
potential $E_{pc/2}$. The anodic peaks continue to broaden as the CV is scanned towards $E_{pc}$.

Figure 4.9: Cyclic voltammograms (iR corrected) for the reduction of oxygen in (A) 0.1M LiPF$_6$/DME & (B) 0.1M LiPF$_6$/TEGDME at various potential windows. All scans used a glassy carbon working electrode. Scan rate of 100mV/s.
The broadness of the anodic peak with increasing cathodic potentials indicates that more than one reduction reaction occurs. The oxidations of these reduction products occur at $E_{pa1}$, $E_{pa2}$ and $E_{pa3}$. We see that DME & TEGDME differ in that $E_{pa2}$ in DME is the predominant peak, while $E_{pa3}$ manifests itself as the dominant anodic peak in TEGDME, once the electrode is polarized below $E_p$. We interpret these results to mean that the LiO$_2$ formed in the ether electrolytes decompose rapidly to Li$_2$O as we observed in MeCN, and that the Li$_2$O is readily reduced to Li$_2$O.

Figure 4.10a shows both a Randles Sevcik plot for a reversible redox couple (for TBAPF$_6$) and Nicholson plot for an irreversible couple (for LiPF$_6$) in MeCN. Note the large difference in current for ORR in this electrolyte. A combination of electrode passivation, oxygen solubility and transfer coefficient contribute to the decrease of current. The diffusion coefficients of oxygen in both electrolytes are presented in Table 4.4.

Figure 4.10b shows the scan rate dependence of ORR in both DME and TEGDME based electrolytes. These plots display an obvious linear relationship between peak current and scan rate. Both plots clearly obey the Nicholson equation demonstrating that the oxygen reduction process is totally irreversible in these electrolytes. This is consistent with the rather small exchange current values derived below. Cathodic current generated by ORR in the presence of TBA$^+$ is an order of magnitude larger than the Li$^+$ based electrolyte. Plots of experimental data follow theoretical n=1 plots quite well although not to the same extent as in DMSO. The Tafel slopes are much higher as is the case for MeCN (484mv/dec). As the mixed potential region dominates it is difficult to extract precise kinetic values from these
Tafel plots. In such cases it is useful to apply electrochemical impedance spectroscopy (EIS).

Figure 4.10: Peak current vs. square root of the scan rate plots for the reduction of oxygen in (A) 0.1 M TBAPF$_6$ & 0.1 M LiPF$_6$/MeCN. n = number of e$^-$ (B) 0.1M TBA$^+$ & LiPF$_6$/DME and 0.1M LiPF$_6$/TEGDME on GC electrode.
Table 4.4: Oxygen Diffusion coefficient in electrolytes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diffusion coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO^{Li⁺}</td>
<td>1.67 x10⁻⁵</td>
</tr>
<tr>
<td>DMSO^{TBA⁺}</td>
<td>9.75 x10⁻⁵</td>
</tr>
<tr>
<td>MeCN^{Li⁺}</td>
<td>4.64 x10⁻⁵</td>
</tr>
<tr>
<td>MeCN^{TBA⁺}</td>
<td>2.45 x10⁻⁵</td>
</tr>
<tr>
<td>DME^{Li⁺}</td>
<td>1.22 x10⁻⁵</td>
</tr>
<tr>
<td>DME^{TBA⁺}</td>
<td>3.88 x10⁻⁵</td>
</tr>
<tr>
<td>TEGDME^{Li⁺}</td>
<td>2.17 x10⁻⁵</td>
</tr>
</tbody>
</table>

4.3.4 Impedance spectroscopy to determine O₂ reduction kinetics

Reaction kinetics can be discerned from faradaic impedance experiments when the working electrode's potential is held at equilibrium. Departure from equilibrium can be characterized by the linearized relationship written in terms of the electronic current as

\[ R_s - \frac{1}{\omega C_s} = R_{ct} = \frac{RT}{F\lambda} \]  \hspace{1cm} (Equation 4.6)

Using this equation the exchange current, and therefore k°, can be evaluated easily (see equation 7) when the charge transfer resistance R_{ct} is known. Extrapolation of kinetic data close to equilibrium potential is accomplished by comparing the calculated data with the experimental results. The data can be analyzed using an equivalent circuit in which the double layer capacitor is in series with the charge transfer resistance R_{ct} \textsuperscript{21}. Plotting Z_{real} versus ω⁻¹/² figure 4.11, where Z_{real} is the real component of impedance series resistance and ω is frequency. The intercept of this
plot is $R_{ct}^{20}$. The exchange current $i_0$ is determined from equation 6 and subsequently the standard rate constant $k^0$ is calculated using equation (7).

$$i_0 = nF\alpha k^0C$$  \hspace{1cm} \textit{(Equation 4.7)}

**Figure 4.11:** Real impedance versus inverse square root of frequency in 0.1 M LiPF$_6$ DMSO (grey), DME (blue), TEGDME (red) and MeCN (black).

The rate constant provides a true measure of reaction kinetics these values are tabulated in table 4.5. Table 4.5 shows that the rate constant decreases as the solvents DN decreases. This dependence implies that the kinetics of the reaction is influenced strongly on solvent.
Table 4.5: $O_2/O_2^-$ kinetic parameters of 0.1M Li & TBAPF_6

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$R_c$</th>
<th>Tafel ($E_p$):($E_{p2}$) mV/dec</th>
<th>Tafel ($E_{pa}$):($E_{pa2}$) mV/dec</th>
<th>$\alpha_{dz}$</th>
<th>$k^*$ (cms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO$^{Li^+}$</td>
<td>308</td>
<td>123:220</td>
<td>129:400</td>
<td>0.5</td>
<td>2.10e-4</td>
</tr>
<tr>
<td>DMSO$^{TBA^+}$</td>
<td>400</td>
<td>120</td>
<td>120</td>
<td>0.5</td>
<td>1.7e-2</td>
</tr>
<tr>
<td>MeCN$^{Li^+}$</td>
<td>75</td>
<td>484:209</td>
<td>331</td>
<td></td>
<td>2.10e-4</td>
</tr>
<tr>
<td>DME$^{Li^+}$</td>
<td>420</td>
<td>360:388</td>
<td>243</td>
<td></td>
<td>1.58e-4</td>
</tr>
<tr>
<td>TEGDME$^{Li^+}$</td>
<td>2300</td>
<td>304:660</td>
<td>243</td>
<td></td>
<td>1.11e-5</td>
</tr>
</tbody>
</table>

4.3.5 Understanding ORR in non-aqueous electrolytes using Pearson’s HSAB Theory

The Hard and Soft Acids and Bases (HSAB) theory states Lewis acids and Bases can be classified into hard and soft sub-categories\textsuperscript{22}. Hard acids interact strongly with hard bases and likewise soft acids interact strongly with soft bases. Hard acids/bases have a relatively small ionic radius and are difficult to polarize, while soft acids/bases unusually have larger radii and are easily polarized. Large differences between hard base solvents and soft-base solvents lead to weaker interactions. Scheme 4.6 shows the order of hardness for both acids and bases.

Scheme 4.3

$H^+ > Li^+ > Fe^{2+} > Co^{2+} > Cu^{2+} > Zn^{2+} > Ru^{2+} > Pb^{2+} > Cu^{+} > Cd^{2+} > Au^+$  

Lewis acids

$O^2-> OH^- > F^- > Cl^- > ClO_4^- > N_2 > NO_2 > SO_3^{2-} > Br^- > R^- > CN^- > I^- > SCN^-$  

Lewis bases
The ions present in the solutions used in this study are the supporting electrolyte ions TBA\(^+\), PF\(_6\)^-, Li\(^+\), and the electrochemically generated ions superoxide (O\(_2^–\)), peroxide (O\(_2^{2–}\)) and monoxide (O\(_2^–\)). The TBA\(^+\) is classified as a soft acid due to its large radius of 0.494 nm (in DMSO)\(^{23}\), and low charge density. It has been shown that tetraalkylammonium ions, NR\(_4^+\), are poorly solvated\(^ {24,25}\) in organic electrolytes due to their large size and the small surface charge. A solvent’s basicity is usually characterized by its donor number (DN) which for the solvents used here follows the order MeCN(14.1) <TEGDME(16.6) <DME(20.0) <DMSO(29.8). Solvent acidity can be characterized by its acceptor number (AN) which in these solvents follow the order DME(10.2) <TEGDME(10.5) <MeCN(18.9) <DMSO(19.3).

In TBA/DMSO electrolytes, although DMSO has a high DN, TBA\(^+\) is weakly solvated. Consequently solvent-TBA\(^+\) interactions are weak in the electrolytes allowing TBA\(^+\) to roam more or less as a naked ion\(^ {26}\). Among the oxides formed from the reduction of oxygen, O\(_2^–\) has a relatively large radius and low charge density; which makes it a moderately soft base. In keeping with the HASB theory, the naked soft acid TBA\(^+\) stabilizes the soft base O\(_2^–\) in the electrolyte with the formation of an ion pair complex of the type, I
Reversibility of the $\text{O}_2/\text{O}_2^-$ redox couple in TBA$^+$ solutions is a result of this stable solution species I. As $\text{O}_2^-$ is strongly coordinated to TBA$^+$ in I, further reduction of superoxide to peroxide ($\text{O}_2^{2-}$) is hindered. The reversibility trend observed in Fig4.1B appears to follow the acceptor number (AN) trend as the AN increases PF$_6^-$-solvent interactions also increase, providing even more TBA$^+$ to interact with $\text{O}_2^-$. Thus, DMSO exhibits excellent electrochemical reversibility for the $\text{O}_2/\text{O}_2^-$ couple. The lower current in the CV of $\text{O}_2$ in DMSO as compared to DME and ACN is probably due to its lower oxygen solubility. Acetonitrile with high oxygen solubility yields
high current for $O_2$ reduction and excellent reversibility in presence of TBA$^+$. In the case of DME TBAPF$_6$ solutions, both the anodic and cathodic peaks in the CV are separated by almost one volt, indicative of slow kinetics.

According to the HSAB theory, alkali metal ions are hard Lewis acids and have a high affinity for hard Lewis bases such as the peroxide and monoxide formed from the reduction of $O_2$. In electrolyte solutions, the hard Lewis acid Li$^+$ ions are solvated by the solvents; usually by about four solvent molecules per Li$^+$ to form solvent separated ion pairs, for example Li$^+$(DMSO)$_4$PF$_6$ in DMSO solutions. The Li$^+$-solvant bond strength in the complexes would follow the solvent DN scale as DMSO>MeCN>DME>TEGDME. Nuclear magnetic resonance studies have revealed that these solvated ion pairs are fluxional complexes even down to $-20$ °C. Although Li$^+$ behaves like a hard acid, its acidity is modulated (or more precisely lowered) by the strength of the coordination bonds in Li$^+$(Solvent)$_n$ formed with the solvent$^{27}$. Since superoxide is a moderately soft base it has low affinity for the hard acid Li$^+$ present in Li$^+$-conducting electrolytes. Consequently, the superoxide formed as the first reduction product of $O_2$ will want either to decompose or undergo a fast second reduction to form the hard base, peroxide ($O_2^{2-}$), as shown in equations 10 and 11.

Peroxide is a strong Lewis base which wants to be associated with the strong base Li$^+$. Similarly, the ultimate reduction product of $O_2$, the monoxide $O_2^-$ is a hard base with a strong affinity for Li$^+$. Consequently, based on the HSAB theory, the stable $O_2$ reduction products in Li ion containing electrolyte solutions are Li$_2$O$_2$ and Li$_2$O.
As mentioned above the formation of the Li$^+$-(solvent)$_n$ complexes would lower the acidity of Li$^+$, roughly in proportion to the donor number of the solvent.

In DMSO solutions of LiPF$_6$, the Li$^+$ Lewis acidity is decreased more than in other solvents due to its higher DN. As a result the superoxide, O$_2^-$, formed as the first O$_2$ reduction product has an increased affinity for these solvated Li$^+$, the O$_2^-$ is stabilized longer in solution, in a structure of the type II, reminiscent of the TBA$^+$--O$_2$ complex I.

**Structure II**  Ion pair between solvated Li$^+$ and O$_2^-$. (The methyl hydrogen's are omitted in the structure)
This explains the distinct $O_2/O_2^-$ couple seen in the DMSO/LiPF$_6$ solutions. Our results suggest that depending on the basicity of the solvent measured by its DN, the superoxide formed as the first reduction product of oxygen will be stabilized to varying degrees before transforming to $O_2^{2-}$ via a chemical or an electrochemical reaction. The multi-step electrochemical reduction of $O_2$ in Li$^+$-containing electrolyte solutions can be schematically represented in the reaction scheme 4.4.

\begin{center}
\textbf{Scheme 4.4}
\end{center}

\[
\text{Li}^+(\text{solvent})_n + O_2 + e^- = [\text{Li}^+(\text{solvent})_n \cdots O_2^-]
\]

\[
\begin{array}{c}
\text{Chemical} \\
\downarrow \\
\frac{1}{2} [\text{Li}_2O_2] + \frac{1}{2} O_2 + n \text{ solvent} \\
\downarrow \\
\text{Li}_2O_2 + n \text{ solvent}
\end{array}
\]

High DN solvents provide increased stability for complex II because of the modulated or more precisely decreased Lewis acidity of the hard acid via complex II. In such electrolytes a distinct $O_2/O_2^-$ reversible couple may be seen in presence of Li$^+$. In solvents with low DN, the general tendency is for the $O_2^-$ to quickly decompose or to undergo fast electrochemical reduction to $O_2^{2-}$ and further to $O^{2-}$.
4.4 Conclusions

Aprotic non-aqueous organic solvents were investigated to determine their influence on the ORR reactions relevant to the rechargeable Li-air battery. We have determined how the supporting electrolyte cations, TBA$^+$ and Li$^+$ together with the solvents comprising the electrolyte solutions influence the nature of reduction products. In solutions containing TBA$^+$, O$_2$ reduction is a highly reversible one-electron process involving the O$_2$/O$_2^-$ couple. On the other hand, in Li$^+$-containing electrolytes relevant to the Li-air battery, O$_2$ reduction proceeds in a stepwise fashion to form O$_2^-$, O$_2^{2-}$ and O$_2^{2-}$ as products. These reactions in the presence of Li$^+$ are kinetically irreversible or quasi-reversible. The stabilization of the one-electron reduction product, super oxide (O$_2^-$) in TBA$^+$ solutions in all of the solvents examined can be explained using Pearson’s Hard Soft Acid Base (HSAB) theory through the formation of the TBA$^+$---O$_2^-$ complex. The HSAB theory coupled with the relative stabilities of the Li$^+$-(solvent)$_n$ complexes existing in the different solvents can also provide a rational explanation for the different O$_2$ reduction products formed in Li$^+$-conducting electrolyte solutions. High DN solvents provide increased stability for the complex [Li$^+$(solvent)$_n$---O$_2^-$] because of the modulated Lewis acidity of the hard acid. In such electrolytes a distinct O$_2$/O$_2^-$ reversible couple may be seen in presence of Li$^+$. In solvents with low DN, the general tendency is for the O$_2^-$ to quickly decompose or to undergo fast electrochemical reduction to O$_2^{2-}$. In Li$^+$ electrolytes prepared in low DN solvents O$_2$ may be fully reduced to O$_2^{2-}$. 
4.5 References


(17) Gutmann, V. *Coordination Chemistry Reviews* 1976, 18, 225-255.


Chapter 5

A Rechargeable Lithium/TEGDME-LiPF$_6$/O$_2$ Battery

5.1 Introduction

Rechargeable Lithium-air batteries are attractive electrochemical power sources because of their potential for ultrahigh energy densities. Despite the considerable recent research and development interest in these batteries\textsuperscript{1}, the full energy density promised by the four-electron reduction of O$_2$ to Li$_2$O has not yet been realized. Furthermore, practically useful electrolytes with low solvent vapor pressures to enable the operation of Li-air batteries with O$_2$ accessed into the cell from open air without losing significant amounts of the solvent in the electrolyte by evaporation has not yet been satisfactorily demonstrated\textsuperscript{2-5}. Recently, we have reported the results of our detailed studies of the oxygen reduction reactions (ORR) in non-aqueous electrolytes showing how the solvent in the electrolyte strongly influences the reduction products and their rechargeability\textsuperscript{6,7}. We have shown from these and earlier investigations\textsuperscript{8} that polyethylene oxide oligomers are potentially useful low volatile solvents to build practical Li/air cells. In order to demonstrate this experimentally and to study the cell chemistry in the absence of catalysts in the cathode, we have built Li/O$_2$ cells utilizing one of these polyethylene oxide oligomer-based electrolytes, namely a solution of LiPF$_6$ in tetraethylene glycol dimethyl ether, CH$_3$O(CH$_2$CH$_2$O)$_4$CH$_3$ (TEGDME) and characterized them. Our principal objectives of this study have been the following:
i) identify the discharge products of the Li/O$_2$ cell in the absence of a catalyst in the cathode, using a commonly available analytical technique such as X-ray diffractometry,

ii) determine if the cell is rechargeable without a catalyst in the carbon cathode, and characterize the relevant cell chemistry, and

iii) elucidate the factors limiting the extended rechargeability of the Li/O$_2$ cell. We have found that the Li/air cell utilizing this electrolyte is rechargeable though with limited cycle life. We have identified the discharge products of these Li/air cells from the X-ray diffraction pattern of the discharged carbon cathodes which is believed to be a first using this technique. We have also made an attempt to determine the factors affecting the rechargeability of the Li/O$_2$ cells from the AC impedance spectra of the discharged charged cathode.

5.2 Experimental

5.2.1 Materials

Pursis Tetraethylene glycol dimethyl ether (TEGDME) and anhydrous N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich, Allentown, PA. All chemicals were dried with Lithium and were stored and prepared in an MBraun dry box filled with purified argon where the moisture and oxygen content was less than 1 ppm. The dried solvents were stored over 0.3-0.4 nm molecular sieves; and prior to actual measurements all solvents were degassed under vacuum. Lithium hexafluorophosphate (LiPF$_6$) (battery grade, >99.9%, H$_2$O< 20ppm) dried under
reduced pressure at room temperature was obtained from Novolyte Corporation Cleveland, Ohio.

5.2.2 Li/O₂ Cells

Porous carbon electrodes were prepared as follows. First, ink slurries were prepared by dissolving a 90 wt% BP2000 carbon black (Cabot Corporation) and 5 wt. % Kynar PVdF (Arkema Corporation) in N-methyl-2-pyrrolidone (NMP). Air electrodes were prepared with a carbon loading of approximately 20.0 mg/cm² by hand-painting the inks onto a carbon cloth (PANEX 35, Zoltek Corporation), which was then dried at 180°C overnight. The total geometric area of the electrodes was 3.14 cm².

The Li/O₂ test cells were assembled in an argon-filled glove box. The cell consists of metallic lithium anode and the aforementioned air electrode as a cathode. A Celgard 2320 separator separated the two electrodes. Both the cathode and the separator were soaked in a TEGDME/1M LiPF₆ solution for a minimum of 24 hours. An in-house built Li/O₂ cell shown in figure 5.1 was used. The cell was placed in an oxygen filled glove bag where oxygen pressure was maintained at 1atm. Cell discharge and charge were carried out with an Arbin battery cycler. The AC impedance was measured on an Autolab PG 30 fitted with a frequency response analyzer (FRA 2 module) in the range of 0.01 to 10⁶ Hz with an amplitude of 5mV. Powder X-ray diffraction (XRD) was carried out using a Rigaku RINT 2500X-ray diffractometer with copper Kα radiation. Scanning electron microscope (SEM) images and Energy dispersive X-ray spectroscopy were measured using Hitachi SEM S-4800. All the tests were carried out at room temperature.
5.3 Results and Discussion

Li air batteries differ from the conventional batteries in that the air electrode in the cell continuously reduces oxygen accessed from the environment. Consequently, the cell is exposed and the loss of solvent from the cell is a concern. Abraham and Jiang\textsuperscript{9} who demonstrated the first non-aqueous rechargeable Li air cell in 1996 employed a cell composed of a Li metal anode, a polyacrylonitrile-based gel polymer electrolyte and a catalyzed carbon cathode. They identified Li$_2$O$_2$ as the main discharge product of that cell with the aid of Raman spectroscopy. Our recent studies have demonstrated\textsuperscript{6,7} that the reduction of O$_2$ can result in Li$_2$O$_2$ and Li$_2$O as stable products following an initial one-electron product LiO$_2$ which is unstable. The Li/O$_2$ cell’s OCVs calculated on the basis of the reactions yielding these three different
products, depicted in equations 1-3, have very similar values indicating that characterization of discharge product(s) is essential to unequivocally establish the discharge reaction in a Li-air cell.

\[ 2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2; \quad \Delta G^\circ = -145 \text{ kCal} \quad (E^\circ = 3.1 \text{ V}) \]
\[ 4\text{Li} + \text{O}_2 \rightleftharpoons 2\text{Li}_2\text{O}; \quad \Delta G^\circ = -268 \text{ kCal} \quad (E^\circ = 2.91) \]
\[ \text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2; \quad \Delta G^\circ = -70 \text{ kcal} \quad (E^\circ = 3.0 \text{ V}) \]

Tetra ethylene glycol dimethyl ether (TEGDME) is a polar versatile solvent, which displays high LiPF$_6$ solubility to produce well-conducting solutions (conductivity equals, 0.2 mS/cm) with a wide electrochemical window Table 5.1 lists the solvent properties of TEGDME.

| Table 5.1. Tetrathylene glycol dimethyl ether Properties. |
|---------------------------------|---------------------------------|-----------------|-----------------|
| ε 25°C | DN (Kcal/mol) | Viscosity η(cP) | Oxygen Solubility (mM/cm$^3$) |
| 7.79$^a$ | 16.6$^b$ | 4.05$^c$ | 4.43$^d$ |

$^a$ Rivas et al., Ref.$^{10}$
$^b$ Chemistry of Non aqueous Solutions., Ref.$^{11}$
$^c$ Marcus Properties of Solvents.,Ref.$^{12}$
$^d$ Read.,Ref.$^{13}$

We first studied the redox electrochemistry of O$_2$ in 1M LiPF$_6$/TEGDME using cyclic voltammetry on a glassy carbon electrode in order to establish the voltage window of the electrolyte and to assess the degree of reversibility of the oxygen reduction reaction. The voltammogram recorded under an atmosphere of argon, shows a nearly
5V wide stability window in which there is very little electrochemical activity. Solvent decomposition is seen as an anodic current at ~4.8V and the onset of lithium plating is seen only near 0.0V. This seemingly good electrolyte stability window led us to use this electrolyte in the Li-air battery. Figure 5.2 shows a cyclic voltammogram (CV) for the reduction of O₂ in a 1M LiPF₆/TEGDME electrolyte saturated with oxygen. The peak potential separation $\Delta E_p$ between the anodic ($E_{pc} = 2.30V$) and cathodic ($E_{pa} = 4.06V$) peaks is almost 1.8V suggesting that O₂ reduction in the presence is only quasi-reversible process.

![Cyclic voltammogram](image)

**Figure 5.2:** Cyclic voltammograms for the reduction of oxygen in 0.1M LiPF₆/TEGDME (Blue) and the argon background (Black). Scan rate 100mV/s.

We recently reported elsewhere on the detailed kinetic analysis of the CV data⁶. The chemical reversibility of the observed O₂ reduction reaction is an impetus
to construct a Li/O$_2$ cell using this electrolyte and study its discharge reaction and rechargeability, and characterize the discharge products formed on the carbon cathode.

5.3.1 \textit{Li/O$_2$ Cell Discharge and Charge Behavior.}

The full discharge curves for two Li/O$_2$ cells obtained with BP 2000 carbon electrodes exposed to a dry oxygen atmosphere are depicted in figure 5.3. The air electrode had loadings between 7-8.5 x 10$^{-4}$ g/cm$^2$, respectively, of the BP 2000 carbon on Panex carbon cloth.

![Discharge Curves](image)

\textbf{Figure 5.3} : Li/O$_2$ cell discharge curves at 0.25 (blue) & 0.16 (black) mA/cm$^2$ in 1M LiPF$_6$/TEGDME. Capacities are expressed per gram of BP 2000 carbon in the electrode.

The open-circuit voltages (OCV) of the cells varied slightly, 3.37 V (black) and 3.18 V (blue) depending on cell setup, oxygen saturation and atmospheric
variables. The working voltages of the cells differed on average by 150mV similar to the difference in the OCVs. The discharge current density affects the specific capacity of the Li-air cell. The discharge capacity at 0.16mA/cm$^2$ is 2,760mAh/g of the BP 2000 carbon in the cathode. Increasing the current to 0.25mA/cm$^2$ decreases the specific capacity to 1452mAh/g of the carbon. These values are very high considering that there is no catalyst in the cathode. It should be noted some discharge of O$_2$ occurs also on the carbon cloth that is used as the current collector but the capacity was small 75-90mAh/gram compared to that on the high surface area carbon. As a result, we have expressed observed the discharge capacity only in terms of capacity per gram of the high surface BP 2000 carbon.

Following full discharge at 0.25 mA/cm$^2$ the cell was disassembled in the glove box and the carbon cathode washed in acetonitrile to remove LiPF$_6$. Figure 5.4 shows the x-ray diffraction pattern of the fully discharged carbon electrode. X-ray diffraction was recorded using Cu K$_\alpha$ radiation with normal ($\theta$ - 2$\theta$) scanning at very slow speed, essential to obtain an assignable pattern. The spectrum can be assigned to that of Li$_2$O$_2$ based on the JCPDS data card (# 7400115). We conclude that the discharge plateau observed at 2.5V is the result of Li$_2$O$_2$ formation confirming the earlier observation made using Raman spectroscopy.
Figure 5.4: XRD pattern of fully discharged O\textsubscript{2} cathode in 1M LiPF\textsubscript{6}/TEGDME. The lines represent the JCPDF pattern for Li\textsubscript{2}O\textsubscript{2}.

Figure 5.5 depicts the full discharge of another cell discharged at 0.25 mA/cm\textsuperscript{2}. Its discharge capacity is 1452mAh/g and a subsequent charge to 4.8 V yields charge capacity of 408mAh/g. In the following discharge a capacity of 488mAh/g is obtained from this cell. The second charge step was shorter with only 200mAh/g capacity before the voltage runs to 4.9V and the cell ultimately fails.
Several cells were cycled at various depths of discharge (DOD), and charge, to follow the impedance of the cell as a function of charge and discharge to ascertain the causes of poor cell rechargeability. These shallow DOD cycles also allowed us to investigate the impact of current density on rechargeability, and to follow cell impedance as a function of cycle life as cycles could be accumulated quickly to provide information on factors affecting cell deterioration.

**Figure 5.5:** Full Discharge of Li/O₂ cell discharge at 0.16 mA/cm² in 1M LiPF₆/TEGDME. Following discharge the cell was charged to 4.5V
Figure 5.6: A) The cycling data for a 1M LiPF$_6$/TEGDME electrolyte oxygen cell at room temperature. The cell was discharged and charged for 2 hours at 0.13 mA/cm$^2$. Capacities are expressed per gram of BP 2000 carbon + PVDF in the electrode. B) Discharge/Charge capacities as a function of cycle number for the same cell.
Figure 5.7: A) The cycling data for a 1M LiPF₆/TEGDME electrolyte oxygen cell at room temperature. The cell was discharged and charged for 14 hours at 0.13 mA/cm². Capacities are expressed per gram of BP 2000 carbon + PVDF in the electrode. B) Discharge/Charge capacities as a function of cycle number for the same cell.

Figure 5.6a illustrates capacity versus cycle number for a cell discharged and charged for 2-hour periods at 0.13mA/cm². The voltage is monitored as a function of time.
The average discharge potential varied between 2.7V for the initial cycles and dropped to 2.45V at the later stages of the cell’s life. The charge plateau steadily increased from 3.2 V initially to 4.7V before cell termination. Figure 5.6b presents the discharge/charge capacity as a function of cycle life. Cycling is demonstrated over 40 cycles during which 100% columbic efficiency is achieved with a capacity utilization of 175mAh/g. The discharge fell below two hours at cycle 41.

High discharge/discharge capacity was maintained after increasing discharge time to 14 hours but the cell exhibited decreasing capacity with increased charge voltage polarization after about 4 cycles (Fig5.7a-b). The discharge profile remains unchanged after the first cycle until sudden cell failure observed during cycle 7, where capacity drops to 400mAh/g. Efficient cycling was observed during the first three charge cycles; however charge profile polarization increases with increasing cycle number further. As polarization increases capacity drops and charge voltage increases. The sudden drop in capacity at the 8th discharge coupled with the impedance data and the physical examination of the Li anode after cycling (see below) led us to believe Li anode failure as a primary contributor to cell failure.

Figure 5.8 illustrates discharge versus capacity utilization of several cells cycled at various current densities. By lowering the current density from 0.25 to 0.13mA/cm$^2$ the charge efficiency of the cell improves to 100% rechargeability. Clearly, rechargeability is affected by the current density. At the highest charge/discharge current density of 0.25 mA/cm$^2$ the cell’s discharge capacity remains steady for the first 6 cycles and drops off sharply thereafter. The recharge on other hand is less than 100 % starting with the first cycle with precipitous loss
occurring in the rest of the cycles. The poor recharge efficiency at the highest current density may be attributed primarily to the inability to oxidize the non-conducting discharge product Li$_2$O$_2$ deposited in the pores of the carbon cathode due perhaps to the increased resistance and the associated over-voltage of the electrode. However, the impedance data discussed below as well as post-test examination of the Li anode revealed that the deterioration of the Li anode is also a major contributing factor for the capacity decline and eventual failure of the Li/air cell.

Figure 5.8: Discharge curves of the lithium air cell at various current densities in 1M LiPF$_6$/TEGDME oxygen cell at room temperature. Capacities are expressed per gram of carbon in the electrode. (Red) 0.25mA/cm$^2$, (Blue) 0.13mA/cm$^2$, (Black) 0.07mA/cm$^2$. 
5.3.2 Factors affecting the Cycle Life of the Li/O\textsubscript{2} Cell

Figure 5.9a shows the complete discharge profile of a Li/O\textsubscript{2} cell to 0.85V. As expected a constant discharge plateau is observed above 2.5V. After 1500mAh/g the cell voltage drops gradually. A second voltage region emerges below about 2 V. Solvent decomposition is not the reason for the small distinct voltage region below 2 V. (fig 5.9). We know from our previous work that Li\textsubscript{2}O\textsubscript{2} is reduced to Li\textsubscript{2}O at potentials below or close to 2V (reaction 3). This decomposition process was discussed in previous chapters. Fig 5.12b shows that there is a significant increase in the cell impedance during the full discharge (R\textsubscript{p} = 250\Omega). This confirms the poor rechargeability of the system after full discharge.
Figure 5.9: (a) Full discharge of Li/air cell in 1M LiPF$_6$/TEGDME (-0.13mA/cm$^2$). (b) Nyquist plot
Figure 5.10: Nyquist impedance plots of the Li-air battery cycled at 2h discharge at the ends of various discharges (9a) and charge (9b). Also for the cell cycled at 14h discharge depths (9c) at the end of different discharges. The data were fitted by using a RC equivalent-circuit model.

Figure 5.10 displays typical AC impedance spectra recorded at various stages in the cycle life of the Li-air cells displayed in figures 5.6 & 5.7. Generally, the spectra displayed show an offset semi-circle at high frequencies. At low frequencies the semi-circle connects with a line inclined at approximately 45° to the x-axis. Initially, the impedance as indicated by the diameter of the semi-circle increases with cycle number (fig 5.10). However, after cycle 4 in the cell in fig 5.10a and after cycle 3 for the cell described the fig 10b impedance drops slowly. Several qualitative changes in the spectra recorded intermittently during the course of the cell discharge are
noticeable. First there is a large increase in the diameter of the semicircle without any significant change in the position of its first intersection with the x-axis. The diameter of the semi-circle reached a maximum at about the fourth (fig 5.10a) and sixth (fig 5.10b) cycles. Contrary to what we believed prior to the experiment there was no significant difference in the impedance between a discharge and the following charge.

Fitting the impedance spectrum to an appropriate equivalent circuit is difficult since the cell does not have a reference electrode which prohibits assigning the contributions of the anode and cathode interfacial reaction impedances to the total cell impedance. A simple equivalent circuit shown in fig 5.10d may describe the observed impedance spectrum at the early stages of the cycling. The circuit consists of an Ohmic resistance \( R_s \) due to electronic resistances of the electrodes and their contacts to the current collectors, and electrolyte resistance, that is in series with a constant phase element that represents the capacitive contributions of the two electrodes in parallel with the polarization (charge transfer) resistances \( R_p \) at the bulk electrodes. Clearly the charge transfer resistances of the reactions at both the anode and cathode contribute to this. Without a reference electrode we can only discuss overall cell polarization impedance and with that in mind the capacitance is represented by a constant phase element \( C_p \). The pre-cycling spectrum of the cell reveals one semicircle with the two intersection \( R_s = 11.50 \) and \( R_p = 14.00 \) Ohm. The linear Warburg element following the semicircle may be attributed to the diffusion of electroactive species to the electrode. The polarization resistance in the 2 hour cycled cell increased after the first discharge to \( R_p = 46.4 \) ohm. Overall impedance of the air
electrode gradually increases with cycle number. However, towards the end of the cycle life of the cell, the initial semi-circle becomes depressed and a second semi-circle emerges. There is little change in the intercept $R_s$ at high frequencies. The impedance increase at the end of discharge is attributed to the deposition of the discharge products in the pores and the surface of the carbon electrode, resulting in sluggish ORR kinetics and diffusion of electroactive species to the electrode surface. As these spectra are of the whole cell, the reactions at the Li electrode, the changing morphology of the plated lithium and the surface films formed on it also contribute to this polarization.

Figure 5.11 displays the photographs of the Li anode before and after cycling. The figure displays the totally changed morphology of the plated Li and shows the granular lithium particles on the surface of the metal after many charge/discharge cycles. The growth results in an increase in overall surface area of the Li anode. This in turn leads to a decrease in the resistance of the surface films on the Li anode and an overall lowering of the anode’s contribution to the total impedance. This would explain the drop in the total cell impedance after several cycles. The evidence suggests that the point where the total cell impedance begins to decrease is a marker of a significant change in the morphology of the Li anode.
SEM micrographs of surface morphology of the O$_2$ cathode electrode are shown in figure 5.12 (a,b). Figure 5.12a shows individual particles of BP2000 carbon on the Panex substrate on the undischarged electrode. Average particle size of BP2000 is 12nm. Figure 5.12b reveals a much different surface after discharging the electrode at a discharge rate at 0.13 mA/cm$^2$ in an oxygen atmosphere. It is clear that the discharge products are evenly deposited on both BP2000 and the Panex substrate resulting in high specific capacity. The deposit as determined (Fig.5.11d) by energy-dispersive X-ray spectroscopy (EDAX) analysis is extremely oxygen rich, which supports the presence of Li$_2$O$_2$ by XRD analysis. The EDAX also reveals the presence of traces of LiPF$_6$ in the electrode.
5.4 Conclusions

The use of the low volatile electrolyte TEGDME-LiPF$_6$ allowed us to study the discharge reaction and rechargeability of the Li/O$_2$ cell substantially without the uncertainties associated with solvent evaporation on cell failure. The cell was fabricated sans electrocatalytic catalyst in the carbon cathode in order to characterize cell chemistry in the baseline Li/O$_2$ cell. From the X-ray diffraction patterns of discharged carbon electrodes we identified Li$_2$O$_2$ in cells discharged to 2.0 V, and, additionally, Li$_2$O in cells discharged to 1.0 V. The rechargeability of the uncatalyzed cell is limited which to a large extent is attributed to the poor cycling
efficiency of the Li anode in addition to the impedance associated with the Li$_2$O$_2$
deposit in the carbon cathode

5.5 References


(7) O'Laoire, C.; Abraham, K. M.; Mukerjee, S. *ECS Meeting Abstracts* 2009, **804**, 404.


Chapter 6

Summary and Future Directions

6.1 Summary

High energy density Li-Air batteries once a laboratory curiosity, are now the focus of serious high-level research. The prospect of cheap high-density energy conversion and storage is irresistible to such industrial giants as Toyota and IBM, both of whom have made a considerable investment in the technology. In the space of three years the number of peer-reviewed articles on the subject has tripled. This thesis endeavors to build upon all previous studies and contribute to furthering the science underlying this battery. Probing electrochemical interfaces using modern electrochemical techniques along with conventional characterization methods yielded a wealth of information regarding the chemical and electrochemical processes in the battery. A highlight of the work is the development of a fundamental mechanistic scheme for oxygen reduction reactions in non-aqueous electrolytes and a methodology for the systematic design of an optimal Li-Air battery electrolyte (chapter 5). In this chapter I summarize the findings and results acquired throughout my research.

6.2 Salt Effects on ORR

We found that the reduction and subsequent oxidation of $O_2$ in acetonitrile-based electrolytes is strongly influenced by the cation of the conducting salt used. Oxygen reduction reactions in Li salt solutions result in irreversible or quasi-
reversible electrochemistry and passivation of the electrodes by the reduction products. On the other hand, ORR in TBA salt solutions exhibits a highly reversible oxygen redox couple. A practical outcome of this observation is that it would be advantageous to use a mixture of Li and K and/or TBA salts as supporting electrolytes in order to dissolve the oxygen reduction products in a Li oxygen battery, at least when the battery is used a primary battery. Increasing the solubility of the reduction products would delay the passivation of the porous electrode that in turn would increase the amount of oxygen that can be reduced to deliver higher capacity. Dissolving the reduction products could also promote reversibility of O$_2$ reduction, which would increase the battery’s rechargeability. Our results also show that vital electrochemical kinetic data provide a platform to quantify catalytic effects on the ORR reaction. Kinetic data are relevant to the studies of the Li-air battery as well as others containing soluble electrode materials, especially for battery simulation studies aimed at understanding the performance of practical batteries, and generally for the development of improved materials.

### 6.3 Solvent Effects on ORR

Chapter 4 examines the electrochemical reduction of oxygen in various TBAPF$_6$ & LiPF$_6$-based organic electrolytes in a series of solvents selected on the basis of their widely varied Donor Numbers.. Stable TBA$^+$--O$_2^-$ complexes are formed in all organic TBA$^+$ electrolytes solutions. This is explained by Pearson’s Hard Soft Acid Base (HSAB) theory. The HSAB theory also provides a rational explanation for the influence of both conducting salts and the organic solvents on the nature of the reduction products. High DN solvents provide increased stability for the
complex $[\text{Li}^+(\text{solvent})n---\text{O}_2]$ because of the modulated decreased Lewis acidity of the hard acid Li$^+$. In such electrolytes a distinct $\text{O}_2/\text{O}_2^-$ reversible couple may be seen in presence of Li$^+$. In solvents with low DN, the general tendency is for the $\text{O}_2^-$ to quickly decompose or to undergo fast electrochemical reduction to $\text{O}_2^{2-}$. In Li$^+$ electrolytes prepared in low DN solvents, $\text{O}_2$ may be fully reduced to $\text{O}^2$.

6.4 **Experimental Li-Air Cells**

The use of the low volatile electrolyte TEGDME-LiPF$_6$ allowed us to study the discharge reaction and rechargeability of the Li/O$_2$ cell substantially without the uncertainties associated with solvent evaporation on cell failure. The cell was fabricated with out an electrocatalytic catalyst in the carbon cathode in order to characterize cell chemistry in the baseline Li/O$_2$ cell. From the X-ray diffraction patterns of discharged carbon electrodes we identified Li$_2$O$_2$ in cells discharged to 2.0 V, and, additionally, Li$_2$O in cells discharged to 1.0 V. The rechargeability of the uncatalyzed cell is limited which to a large extent is attributed to the poor cycling efficiency of the Li anode in addition to the impedance associated with the Li$_2$O$_2$ deposit in the carbon cathode. Our continuing effort to obtain a clear understanding of the roles of conducting salt and the solvent is expected to result in the identification of an optimum electrolyte solution for the non-aqueous Li-air battery.

6.5 **Future Directions for Li-Air Research**

We have only begun to scratch the surface of the fledging Li-Air battery research field. Realization of the Li-Air dream will require a long-term research
initiative. The development of a practical rechargeable Li-air battery will require active research in the fields of catalysis development and electrolyte stability especially towards lithium anode. The prospect for design of electrocatalysts specifically for Li₂O₂ and Li₂O oxidation is challenging. Viable candidates for this work are the macro cycle complexes such as porphyrins, bimetallic porphyrins and phthalocyanines. Nano-porous amorphous manganese oxide is emerging as a promising electrocatalysts in non-aqueous electrolytes. Electrocatalytic activity towards oxide oxidation is imperative to maximizing efficiency. Our electrochemical studies have laid the groundwork for such electrocatalytic studies. Stable electrolytes are crucial to the success of Li-air. As demonstrated in chapter 5 low volatile solvents such TEGDME are possible candidates. However superior solvents blends should be considered which combine beneficial characteristics of multiple solvents such as low volatility, high-oxygen solubility and low viscosity. Possible candidates are room temperature ionic liquids (RTIL). These solvents can be designed to incorporate multiple desirable characteristics of a Li-air electrolyte. Ultimately, packaging of practical cells and batteries would require devoting considerable resources to engineering development.
Biographical Information

Name: Cormac Ó Laoire

Birthplace: Cork, Ireland

Education

Ph.D., Physical Chemistry, May 2010
Northeastern University, Boston, MA
(INVESTIGATIONS OF OXYGEN REDUCTION REACTIONS IN NON-AQUEOUS ELECTROLYTES AND THE LITHIUM-AIR BATTERY)

M.Sc., Materials Science, May 2004
University College Cork, Cork, Ireland
(Thesis: Analysis of Acid Passivation of Stainless Steel)

B.Sc., Chemistry, May 2001
University College Cork, Cork, Ireland
Experience:

Sept 2006-Present

Lithium air batteries are being developed under the direction of Professors K.M. Abraham and Sanjeev Mukerjee. My research focused on elucidating the kinetics and mechanism of the oxygen reduction reaction in the non-aqueous environment with particular emphasis on the roles of ion conducting salts and the non-aqueous solvents. Electrochemical and kinetic characterizations are performed with a wide array of electrochemical and analytical techniques including cyclic voltammetry, rotating disk electrode voltammetry, chronocoulometry and charge/discharge cycling of Li-air cells.

Sept 2004-Sept 2006

Novel non-noble metal chalcogenide clusters development for oxygen reduction reaction in fuel cell applications under the direction of Professor Sanjeev Mukerjee. Also during this time period I investigated carbon-based materials for Li-ion batteries. Structural characterizations were accomplished via in situ EXAFS, XANES and XRD at the National Synchrotron Light Source (Brookhaven National Labs, Upton, NY).
Appointments:

2006-present  Research Assistant
Northeastern University, Boston, MA

2004-2006  Teaching Assistant- General and Physical Chemistry
Northeastern University, Boston, MA

2002-2004  Research Assistant-
University College Cork, Cork, Ireland

Awards: 2009 ECS Battery Division Travel Grant Award (Vienna 2009)
2010 Northeastern University Dissertation completion fellowship

Publications:

“Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air Battery”
O’Laoire, C.; Plichta, E.; Hendrickson, M.; Mukerjee, S.; Abraham, K. M.
(Accepted) J. Phys. Chem. C April 2010

“Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Applications” Cormac O. Laoire, Sanjeev Mukerjee, K. M.
113 (46), 20127-20134


**Skills:**

**Synthetic**

Solid State synthesis of carbon materials for Li-ion batteries.
Electrochemical Instrumentation

Battery Cyclers (Arbin), Potentiostat/Galvanostats (BAS, Autolab, PAR), Rotating Disk Electrodes (Autolab and BAS).

Other Instrumentation

SEM, IR, ESR, NMR, XRF Extended X-Ray Fine Absorption (EXAFS) and High Energy X-ray diffraction.

Computer

Instrument programming skills include C++, and Visual Basic in addition to the following molecular modeling programs: Amber, DLPoly, and BioMedCAChe.

Presentations:
