Investigations of Oxygen Reduction Reactions for Electrochemical Energy Storage and Conversion

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Abstract of Dissertation

High energy density portable power solutions have been of utmost importance for the advancement of modern day necessities such as data and voice communication, vehicular transportation, distributed power generation and storage of energy produced by sustainable power sources. Progress made in fuel cell and lithium-ion battery technologies over the past decade have opened opportunities to power electric and hybrid electric vehicles for long distance transportation. Alkaline membrane fuel cells (AEMFCs) are the new alternatives to proton exchange membrane fuel cells (PEMFCs), which require generous amounts of noble metal-based catalysts on their electrodes. Facile electrode kinetics on non-precious group metal catalysts in alkaline environments is the key factor which has promoted AEMFCs over PEMFCs. While the research on AEMFCs is vastly expanding, high energy density batteries are praiseworthy considering the high cost of hydrogen fuel. The state-of-the-art Li-ion batteries cannot reach the desirable capacity density to power electric vehicles capable of >300 miles on a single charge whereas Li-O₂ batteries with a theoretical capacity more than ten times larger than that of Li-ion have become very promising for this application. Chapter 1 of this thesis provides a discussion of the background behind the fuel cell and battery technologies beyond Li-ion along with the electrochemical and analytical techniques employed throughout this investigation.

The major deterrent to AEMFC technology is its performance decrease by means of carbonate exchange of the membrane when exposed to carbon dioxide. The second Chapter deals with a quantitative determination of the influence of carbonate ions in the alkaline membrane on interfacial electrode reactions and reactant transport through the membrane. A Pt microelectrode investigation conducted on a commercial anion exchange membrane (AEM) (Tokuyama, A201)
showed rather close kinetics for oxygen reduction reaction (ORR) with and without carbonate exchange as well as with a perfluorinated proton exchange membrane analog such as Nafion®. Resolution of the mass transport into constituent components (diffusion coefficient and solubility) showed that the oxygen diffusion coefficient in the AEM exchanged with carbonate ions (CO$_3^{2-}$) is lowered while the solubility remained unaffected. These results show remarkable agreement with polarization corrected fuel cell data, thus enabling a method to better resolve interfacial performance of an AEM fuel cell.

We have also investigated the kinetics of hydrogen oxidation reaction (HOR) and methanol oxidation reaction (MOR) at the Tokuyama (A201/A901) anion exchange membrane/Pt microelectrode interfaces using solid state electrochemical cells. Diffusion of hydrogen molecules through the membrane was not influenced by the carbonate ions due to the smaller size of the gaseous molecule. However, hydrogen concentration in the anion exchange membrane is low in the presence of carbonate ions. Methanol diffusion is facilitated in the anion exchange polymer electrolyte due to its high water content. A change of the diffusion path length in carbonate polymer electrolytes caused methanol permeability to drop significantly. The kinetic parameters obtained for the AEM in the carbonate form suggests that both hydrogen and methanol oxidation reactions proceed through the carbonate pathway. Therefore, the kinetic parameters obtained are significantly lower than what were observed at the AEM in the hydroxide form.

In the third Chapter I demonstrate that a microelectrode can be used as a diagnostic tool to determine O$_2$ transport properties and redox kinetics in dimethyl sulfoxide (DMSO)–based electrolytes for non-aqueous Li-air batteries, and to elucidate the influence of ion-conducting salts on the O$_2$ reduction reaction mechanism. Oxygen reduction/evolution reactions on a carbon
microelectrode have been studied in dimethyl sulfoxide-based electrolytes containing Li$^+$ and tetrabutylammonium ((C$_4$H$_9$)$_4$N$^+$) ions. Analysis of chronoamperometric current-time transients of the oxygen reduction reactions in the series of tetrabutylammonium (TBA) salt-containing electrolytes of TBAPF$_6$, TBACIO$_4$, TBACF$_3$SO$_3$, or TBAN(CF$_3$SO$_2$)$_2$ in DMSO revealed that the anion of the salt exerts little influence on O$_2$ transport. Whereas steady-state ORR currents (with sigmoidal-shaped current-potential curves) were observed in TBA-based electrolytes, peak-shaped current-voltage profiles were seen in the electrolytes containing their Li salt counterparts. The latter response results from the combined effects of the electrostatic repulsion of the superoxide (O$_2^-$) intermediate as it is reduced further to peroxide (O$_2^{2-}$) at low potentials and the formation of passivation films of the O$_2$ reduction products at the electrode. Raman spectroscopic data confirmed the formation of non-conducting Li$_2$O$_2$ and Li$_2$O on the electrode surface at different reduction potentials in Li salt solutions. Out of the four lithium salt-containing electrolytes studied, namely LiPF$_6$, LiClO$_4$, LiCF$_3$SO$_3$, or LiN(CF$_3$SO$_2$)$_2$ in DMSO, the LiCF$_3$SO$_3$/DMSO solution revealed the most favorable ORR kinetics and the least passivation of the electrode by ORR products.

The influence of lithium salts on O$_2$ reduction reactions (ORR) in 1, 2-dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME) has been investigated in Chapter 4. Microelectrode studies in a series of tetrabutylammonium salt (TBA salt)/DME-based electrolytes showed that O$_2$ solubility and diffusion coefficient are not significantly affected by the electrolyte anion. The ORR voltammograms on microelectrodes in these electrolytes exhibited steady-state limiting current behavior. In contrast, peak-shaped voltammograms were observed in Li$^+$-conducting electrolytes suggesting a reduction of the effective electrode area by passivating ORR products as well as migration-diffusion control of the reactants at the
microelectrode as observed in DMSO-based electrolytes. FT-IR spectra have revealed that Li⁺ ions are solvated to form solvent separated ion pairs of the type Li⁺(DME)_nPF₆⁻ and Li⁺(TEGDME)PF₆⁻ in LiPF₆-based electrolytes. On the other hand, the contact ion pairs (DME)_mLi⁺(CF₃SO₃⁻) and (TEGDME)Li⁺(CF₃SO₃⁻) appear to form in LiSO₃CF₃-containing electrolytes. In the LiSO₃CF₃-based electrolytes, the initial ORR product, superoxide (O₂⁻), is stabilized in solution by forming [(DME)_{m-1}(O₂⁻)]Li⁺(CF₃SO₃⁻) and [(TEGDME)(O₂⁻)]Li⁺(CF₃SO₃⁻) complexes. These soluble superoxide complexes are able to diffuse away from the electrode surface reaction sites to the bulk electrolyte in the electrode pores where they decompose to form Li₂O₂. This explains the higher capacity obtained in Li/O₂ cells utilizing LiCF₃SO₃/TEGDME electrolytes.

In Chapter 5 the synthesis of iron(II) phthlaocyanine (FePC)–based catalysts is presented. FePC embedded in a carbon support was heat-treated at a series of temperatures (300°C, 600°C and 800°C) and characterized by means of several spectroscopic and electrochemical techniques. Catalytic oxygen reduction recorded in the low Donor Number acetonitrile (MeCN)–based electrolytes have shown that the oxygen reduction reaction (ORR) mechanism is modified at the catalyst surface. Redox electrochemistry of FePC recorded in argon saturated electrolytes has confirmed that the iron is in the Fe(I) state at the O₂ reduction potential in these electrolytes which is capable of stabilizing the superoxide leading to an inner–Helmholtz plane electron transfer reaction. In high Donor Number DMSO–based electrolytes the ORR was not influenced by the catalyst and this has been attributed to the oxidation state of iron being Fe(II) at the superoxide forming potential. The superoxide formed in such conditions are stabilized by the DMSO solvated softer Lewis acid Li⁺ as the Li⁺(DMSO)_n–O₂⁻ ion pair in solution. The ORR reaction in this electrolyte proceeds through an outer Helmholtz plane
electron transfer process despite the presence of the FePC catalyst in the electrode. Catalyzed carbon electrodes treated at 300 and 600°C were successfully employed in the low Donor Number tetra ethylene glycol dimethyl ether (TEGDME)–based electrolyte-containing Li-O₂ cells. These cells showed significant reduction in the charging overpotentials and a doubling of the cell cycle life compared to uncatalyzed cells.

Chapter 6 sums up the conclusions of the research presented in this thesis and presents future directions for investigations.
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<td>α</td>
<td>Charge transfer coefficient</td>
</tr>
<tr>
<td>η</td>
<td>Overpotential</td>
</tr>
<tr>
<td>λ</td>
<td># of water molecule per exchange site</td>
</tr>
<tr>
<td>ν</td>
<td>Scan rate</td>
</tr>
<tr>
<td>v</td>
<td>Kinematic viscosity</td>
</tr>
<tr>
<td>ω</td>
<td>Rotation speed</td>
</tr>
<tr>
<td>θ</td>
<td>Angle</td>
</tr>
<tr>
<td>ΔH</td>
<td>Change in enthalpy</td>
</tr>
<tr>
<td>A</td>
<td>Ampere/ area</td>
</tr>
<tr>
<td>AEM</td>
<td>Anion exchange membrane</td>
</tr>
<tr>
<td>Ah</td>
<td>Ampere hour</td>
</tr>
<tr>
<td>B-V</td>
<td>Butler-Volmer</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammogram</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DN</td>
<td>Donor number</td>
</tr>
<tr>
<td>E</td>
<td>electrode potential</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>G</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>hcd</td>
<td>High current density</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>HSAB</td>
<td>Hard soft acid base (concept)</td>
</tr>
<tr>
<td>i₀</td>
<td>Limiting current</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>IEC</td>
<td>Ion exchange capacity</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Peak current</td>
</tr>
<tr>
<td>$h$</td>
<td>Hour</td>
</tr>
<tr>
<td>$iR$</td>
<td>Ohmic potential drop</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Heterogeneous rate constant</td>
</tr>
<tr>
<td>KB</td>
<td>Ketjenblack</td>
</tr>
<tr>
<td>lcd</td>
<td>Low current density</td>
</tr>
<tr>
<td>$m$</td>
<td>Meter</td>
</tr>
<tr>
<td>M</td>
<td>Molarity</td>
</tr>
<tr>
<td>$M^+$</td>
<td>Single charged anion</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MeCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>MOR</td>
<td>Methanol oxidation reactions</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons transferred</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>R2</td>
<td>Regression correlation coefficient</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disc electrode</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating ring disc electrode</td>
</tr>
<tr>
<td>RTIL</td>
<td>Room temperature ionic liquid</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>TBA</td>
<td>Tetrabutylammonium</td>
</tr>
<tr>
<td>TEGDME</td>
<td>Tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo gravimetric analysis</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
</tr>
<tr>
<td>VC</td>
<td>Vulcan</td>
</tr>
<tr>
<td>W</td>
<td>Watts</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
Chapter 1
Introduction

1.1. World Energy Demand

In present day the energy economy of the United States and the world is largely dependent on fossil fuels. Close to 44% of the energy consumption in the US is fulfilled by petroleum and coal, and the rest comes from natural gas, nuclear energy, hydropower and renewable energy sources.\(^1\)\(^-\)\(^3\) Heavy dependence on fossil fuel energy is unreliable for a nation due to rapid depletion of these non-renewable energy sources as well as global warming and climate changes associated with the release of large amounts of CO\(_2\) from them to the atmosphere. Energy legislations have created regulations to decrease CO\(_2\) emission from power plants based on fossil fuels.\(^4\) Even though natural gas power plants can provide cleaner energy with half the CO\(_2\) emission of coal power plants, the heavy machinery and hydraulic fractioning process used in the gas extraction can pollute the groundwater system.\(^5\) Nuclear energy is also one of the reliable sources of energy which addresses the concern of greenhouse gas emissions. However, disposal of waste from nuclear power plants and reactor safety issues have impeded the process of building new nuclear power plants\(^6\). As a result of these considerations the current policies of the US government through the department of energy (DOE) is encouraging the development of renewable energy power plants. The resources of renewable energy include solar, wind, geothermal, biomass and hydropower. A key component of widespread adoption of the various renewable sources is the development of energy storage systems in order to store the energy produced from these systems prior to distribution when the demand rises.

Fulfilling the stationary power demand by renewable energy resources is not entirely practical on account of the scarcity of energy storage solutions, the consumption of petroleum for
transportation needs remains unchanged over the years. The best way to address the air pollution caused by petroleum use in transportation is to replace the internal combustion engine vehicles with zero or controlled emission vehicles. Therefore, there is a growing demand for efficient energy conversion and storage systems to produce, store and deliver the energy from renewable power plants to electric and hybrid electric vehicles. Electrochemical energy conversion and storage devices comprising fuel cells and batteries are the two primary candidates to address this demand.

Energy conversion and storage systems with higher energy and power densities are also needed to meet the ever-increasing demands of portable consumer devices such as cellphones, laptop computers, tablets and digital cameras. While lithium ion batteries have played a major role in fulfilling the portable electronics revolution of the past two decades, rechargeable batteries with significantly higher energy densities are needed to meet the continued demand for increasing functionalities of these devices.

In this thesis, the role of electrochemical energy conversion and storage systems to address the aforementioned energy needs are addressed, with a focus on the key challenges associated with anion exchange membrane fuel cells and rechargeable Li-O$_2$ batteries.

1.2. **Electrochemical Energy Conversion and Storage- Fuel Cells and Batteries**

Electrical energy is produced from a fuel cell or battery by means of charge transfer between two chemical reactions, oxidation and reduction, that occur at the anode and cathode, respectively. The reactions are physically separated inside the cell, but when connected externally through a load an electrical current is generated by the electrochemical potential difference between the two electrodes. In a battery the two chemicals are usually stored inside
the battery cell, physically separated by an ion conducting but electronically insulating electrode separator. When it is discharged the battery uses up the stored reactants. The fuel cell, on the other hand, is an energy conversion device and requires a continuous supply of fuel to the electrodes inside the cell to produce electricity.

1.3. Fundamentals of a Fuel Cell

Proton Exchange Membrane Fuel Cells (PEMFC)

A proton exchange membrane fuel cell consists of two electrodes separated by a solid polymer electrolyte that transports protons. Figure 1.1A shows a schematic of a PEM fuel cell. Hydrogen gas supplied to the anode is oxidized, producing protons and electrons. The protons transport to the other side of the cell through the electrolyte membrane and the electrons flow through the external circuit to the cathode, where they are consumed by the oxygen reduction reaction. PEM fuel cells are typically operated at temperatures around 90°C. The hydrogen oxidation reaction (HOR) proceeds at a very fast rate in acidic pHs. Therefore it does not contribute to the activation over-potential in a PEMFC. Therefore, the kinetic over-potentials observed in H2/O2 PEMFCs are mainly the over-potential due to the sluggish oxygen reduction kinetics at the fuel cell cathode.6

The assembled stack of the anode, polymer membrane and the cathode is called the membrane electrode assembly (MEA). PEM fuel cells employ perfluorinated membranes such as Nafion® which contain sulfonic acid anionic sites, as the solid polymer electrolyte. Platinum nanoparticles supported on carbon are used as anode as well as cathode catalysts. Generous amounts of Pt required on the cathode to offset the sluggish ORR kinetics in acidic environments is the biggest challenge in the development of PEM fuel cells.
Figure 1.1: Operation of a A) proton exchange membrane fuel cell, B) alkaline anion exchange membrane fuel cell.

Scheme 1.1: Fuel cell reactions of a proton exchange membrane fuel cell

Anode: \( H_2 \rightarrow 2H^+ + 2e^- \) \( E^0 = 0.0 \text{ V} \) [1.1]

Cathode: \( \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \) \( E^0 = 1.23 \text{ V} \) [1.2]

Full cell reaction: \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) \( E_{\text{cell}} = 1.23 \text{ V} \) [1.3]

Direct Methanol Fuel Cells (DMFC)

In a direct methanol fuel cell (DMFC) an aqueous solution of methanol is supplied as the anode feed or the fuel. The anode catalyst draws hydrogen from the methanol molecules as shown in scheme 1.2. Direct methanol fuel cells have gained attention over hydrogen fuel cells due to many beneficial characteristics of methanol as a fuel, such as ease of storing and handling liquid fuels over gaseous \( H_2 \) and the availability of methanol at low cost. However, the self-poisoning of the platinum surface by methanol oxidation reaction (MOR) products is a major concern associated with DMFCs.
Scheme 1.2: Fuel cell reactions of a direct methanol fuel cell

Anode: \[ CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \] \[ E^0 = 0.02 \text{ V} \] \[ [1.4] \]

Cathode: \[ \frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \] \[ E^0 = 1.23 \text{ V} \] \[ [1.5] \]

Full cell reaction: \[ CH_3OH + \frac{3}{2}O_2 \rightarrow H_2O + CO_2 \] \[ E_{\text{cell}} = 1.21 \text{ V} \] \[ [1.6] \]

Alkaline Anion Exchange Membrane Fuel Cells (AEMFC)

The hydroxide equivalent of the PEM fuel cell is known as alkaline anion exchange membrane fuel cell. The hydroxide ions formed at the cathode during the oxygen reduction reaction are transported to the anode side through the membrane where they combine with the protons to form water.

Fuel cells operated under high pH conditions are currently gaining attention due to many reasons. The beneficial characteristics include: 1) facile oxygen reduction kinetics afforded by non-precious group metals in alkaline conditions,\(^8,9\) 2) favorable hydrodynamics of alkaline membrane fuel cells which translates to better water management in them compared to conventional PEM fuel cells, and 3) improved membrane stability due to the membrane being less prone to attack by peroxide ions in alkaline conditions. In addition, the facile methanol oxidation kinetics in direct methanol fuel cells observed at high pHs\(^8\) is also advantageous.

Figure 1.1B shows a schematic of an anion exchange membrane (AEM) fuel cell (H\(_2\)/O\(_2\)). AEM fuel cells operate at high pHs where the polymer electrolyte employed is a hydroxide ion transport membrane. Scheme 3 and 4 display reactions corresponding to AEMs operating under hydrogen and methanol as anode feed, respectively.
**Scheme 1.3:** Fuel cell reactions of an alkaline hydrogen fuel cell

Anode: \[ H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \] \[ E^0 = -0.83 \text{ V} \] [1.7]

Cathode: \[ \frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^- \] \[ E^0 = 0.40 \text{ V} \] [1.8]

Full cell reaction: \[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \] \[ E_{cell} = 1.23 \text{ V} \] [1.9]

**Scheme 1.4:** Fuel cell reactions of an alkaline methanol fuel cell

Anode: \[ CH_3OH + 6OH^- \rightarrow 5H_2O + 6e^- + CO_2 \] \[ E^0 = -0.81 \text{ V} \] [1.10]

Cathode: \[ \frac{3}{2} O_2 + 3H_2O + 6e^- \rightarrow 6OH^- \] \[ E^0 = 0.40 \text{ V} \] [1.11]

Full cell reaction: \[ CH_3OH + \frac{3}{2} O_2 \rightarrow 2H_2O + CO_2 \] \[ E_{cell} = 1.21 \text{ V} \] [1.12]

**Anion Exchange Membranes (AEM)**

Alkaline anion exchange membranes are solid polymer electrolytes that are capable of conducting \( OH^- \) ions. These polymers contain immobilized quaternary ammonium cation sites which aid in transporting anions. Figure 1.2 shows a typical quaternary ammonium- polysulfone -based anion exchange membrane.

![Structure of a quaternary ammonium polysulfone -based membrane](image)

**Figure 1.2:** Structure of a quaternary ammonium polysulfone -based membrane
Carbonate Poisoning in Alkaline Fuel Cells

Under ideal conditions alkaline anion exchange membranes transport ions through the membrane. However, practically the mobile anion population in the AEM is a mixture of hydroxide, carbonate and bicarbonate ions. The hydroxide ion concentration in the membrane can be decreased by the reaction of the hydroxide ions with the CO$_2$ in the atmospheric air feed or the CO$_2$ produced by methanol oxidation at the DMFC anode. Despite the controversy on the exact composition of the anions inside the membrane, reports suggest that under fuel cell operating conditions CO$_3^{2-}$ enrichment is possible. Selectivity of AEMs for carbonate ions can be explained as follows. Localized cations (quaternary ammonium) will repel ions with the same charge ($\text{H}^+$) out of the membrane which is known as Donnan exclusion principle. When the pore solution pH increases the ion equilibrium shifts in the forward direction as shown in equation 1.13 to increase the CO$_3^{2-}$ concentration.

\[
\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad [1.13]
\]

Prior reports showing that the pore solution becomes rich in multi charged anions$^{10-13}$ are in agreement with this discussion. Consider a H$_2$-Air fuel cell under operation. The carbonate ion concentration is determined by the current density drawn from the cell. The anion composition inside the AEM becomes a mixture of only carbonate/hydroxide ions due to the progressive production of hydroxide ions at the cathode,$^{14}$ towards higher current densities. Watanabe et al. have observed CO$_2$ in the anode exhaust in such conditions, which further suggests the presence of carbonate ions as charge carriers.
1.3.1. Fundamentals of Batteries

Energy balance in a battery system requires matching of the enthalpy of the reactants with the sum of the enthalpies of the products being formed. Consider the reactions that takes place in Daniel cell (Figure 1.3) shown in Scheme 1.5.

![Diagram of Daniell cell]

**Figure 1.3:** Schematic of a Daniell cell

**Scheme 1.5:** Reactions of a Daniell Cell

<table>
<thead>
<tr>
<th>Anode</th>
<th>$Zn \rightarrow Zn^{2+} + 2e^{-}$</th>
<th>$E^0 = -0.76$ V</th>
<th>[1.14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>$Cu^{2+} + 2e^{-} \rightarrow Cu$</td>
<td>$E^0 = 0.34$ V</td>
<td>[1.15]</td>
</tr>
<tr>
<td>Cell</td>
<td>$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$</td>
<td>$E_{cell} = 1.10$ V</td>
<td>[1.16]</td>
</tr>
</tbody>
</table>

The maximum electrochemical work obtained from this system is equal to the standard free energy change for the reaction ($\Delta G^0$) given by equation 1.17.
\[
\Delta G^0 = -nFE^0 \tag{1.17}
\]

where \( n \) is the number of electrons involved in the reaction, \( F \) is the Faraday constant and \( E^0 \) is the electrode potential under standard conditions. The electrode potential for reaction 1.16 under non-standard conditions is given by the Nernst equation (equation 1.18),

\[
E = E^0 - \frac{RT}{nF} \left( \frac{a_{Cu(s)} \times a_{Zn^{2+}(aq)}}{a_{Cu^{2+}(aq)} \times a_{Zn(s)}} \right) \tag{1.18}
\]

In equation 1.18 \( R \) is the gas constant, \( T \) is the temperature in K, \( a_{Cu(s)} \), \( a_{Zn^{2+}(aq)} \) are the activities of the products and \( a_{Cu^{2+}(aq)} \), \( a_{Zn(s)} \) are the activities of the reactants. This equation simplifies to equation 1.19 since the activity of a pure solid is equal to 1.

\[
E = E^0 - \frac{RT}{nF} \left( \frac{a_{Zn^{2+}(aq)}}{a_{Cu^{2+}(aq)}} \right) \tag{1.19}
\]

1.3.2. Voltage Losses Associated with Cells

Typically, the measured cell potential is significantly lower than the thermodynamic equilibrium potential \( (E) \) as depicted in equation 1.20. The voltage losses, also called polarization losses can be broken down to three parameters as shown in this equation, namely ohmic losses, kinetic losses and mass transport losses.\(^{15,16}\) Figure 1.4 shows the quantitative effect of each parameter on cell voltage \( (V_{cell}) \).

\[
V_{cell} = E - \Delta E_{ohmic} - \eta_{kinetic} - \eta_{tx} \tag{1.20}
\]
Ohmic polarization losses ($\Delta E_{\text{ohmic}}$) arise from the resistance of the cell components. Thickness of the electrodes as well as the membrane ion conductivity determines the overall resistance of a battery cell. Voltage drop due to the cell resistance is proportional to the current drawn from the cell as defined by equation 1.21.

$$\Delta E_{\text{ohmic}} = iR \quad [1.21]$$

Kinetic ($\eta_{\text{kinetic}}$) or activation polarization losses which arise due to slow electrochemical reactions are noticeable in the low current region. Activation polarization is given by equation 1.22 where $\alpha$ is charge transfer coefficient, $i$ and $i_o$ are the current density and exchange current density, respectively.

$$\eta_{\text{kinetic}} = \frac{RT}{\alpha n F} \ln \left( \frac{i}{i_o} \right) \quad [1.22]$$

Mass transport ($\eta_{\text{tx}}$) or concentration overpotential losses arise from resistance of reactant diffusion through the gas diffusion layers and the electrodes. These losses are indistinct in the low current region, but become significant in the high current region. In a H$_2$-O$_2$ fuel cell, enhanced mass transport losses at high current densities can be attributed to the flooding of the electrodes from a high rate of water production.
1.4. Lithium Batteries

Lithium has drawn attention as a successful anode material for batteries since the 1960s. This is due to two aspects, lithium being the most electropositive material (-3.04V vs SHE) and the lightest metal (6.94 g mol\(^{-1}\)). These two properties made this unique metal the ideal candidate for high energy density storage applications. The discovery of the stability of lithium metal in organic solvents owing to electronically insulating film with Li ion conductivity formed on the Li metal led to the development of commercial lithium batteries.

A Lithium battery is comprised of an anode made of lithium metal or a lithium-containing compound, an organic liquid or polymer electrolyte, and a cathode. Most common types of primary lithium batteries include Li-SOCl\(_2\), Li-FeS\(_2\) and Li-MnO\(_2\) batteries containing the cathode materials SOCl\(_2\), FeS\(_2\) and MnO\(_2\), respectively. These are not rechargeable once the stored reactants are consumed in the discharge. On the other hand, secondary batteries store energy by means of reversible electrochemical reactions and the products of discharge can be

**Figure 1.4:** Polarization losses in a battery/cell
reversed to their original state by charging the cell. Therefore, these batteries can be recharged and used many times. Early rechargeable Li batteries had safety issues as their continuous charge/discharge cycling led to deposition of dendritic lithium metal on the Li anode.\textsuperscript{18} This raised the serious hazard of needle like lithium formed in the charging process piercing the separator to cause internal short circuits and ensuing thermal runaway reactions with fire hazards.

1.4.1. Non-Aqueous Electrolytes

Since Li is highly reactive towards H\textsubscript{2}O, electrolytes composed of solutions of Li salts dissolved in non-aqueous solvents are used in Li batteries. The frequently used non-aqueous solvents include aprotic organic solvents such as ethers, carbonates and ionic liquids.

The solvent needs to contain polar groups so that it has a sufficiently high dielectric constant to dissolve lithium salts and minimize ion pairing. No matter how strong the solvating ability of the solvent with Li ion is, organic solvents containing active protons are ruled out due to their irreversible reaction with the Li metal anode. In addition, a number of requirements must be fulfilled by a solvent to be a successful candidate in a lithium battery. These include: the ability to dissolve a high concentration of Li\textsuperscript{+}-conducting salts such as LiPF\textsubscript{6}, LiCF\textsubscript{3}SO\textsubscript{3} and LiN(SO\textsubscript{2}CF\textsubscript{3})\textsubscript{2}; high ionic conductivity for the electrolyte prepared; chemical compatibility with the electrode materials in the battery; a high electrochemical stability window within which the electrolyte does not undergo redox reactions when the electrodes are reduced and oxidized during charge/discharge cycling of the battery; good liquid range from -20 to +70\textdegree{}C; and good thermal stability over the entire temperature range of operation of the battery.

Since the discovery of non-aqueous Li-O\textsubscript{2} batteries by Abraham et al.\textsuperscript{19}, a great deal of investigations been carried out with respect to solvent selection and electrolyte formulation for
them. Some of the additional requirements of solvents for these batteries must include the following:

- The solvent must survive in the presence of the nucleophile superoxide, which is an intermediate formed during O₂ reduction at the Li-O₂ cathode. As far as solvent stability is concerned, inactivity towards the Li anode and a high oxidation potential are also required.

- A low viscosity is required for good O₂ and ion transport through the electrolyte. At the same time the solvent should have a low volatility and remain a liquid over a wide range of temperatures.

- The solvent should be able to dissolve the oxygen reduction product Li₂O₂. The overall solubility of Li₂O₂ in the electrolyte is determined by the dissolved Li salt as well.

Aprotic electrolytes over a wide range of properties have been investigated so far and they include Li salt solutions in organic esters, carbonates, ethers and sulfoxides. Another class of electrolytes being investigated for Li-O₂ batteries is room temperature ionic liquids (RTILs). In some instances solvent blends are used incorporated to modulate electrolyte characteristics to meet the aforementioned requirements. Physical properties of a group of aprotic solvents and a RTIL are listed in Table 1.1
Table 1.1: Physical properties of non-aqueous solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting point /°C</th>
<th>Boiling point /°C</th>
<th>Donor number</th>
<th>Dielectric constant (ε)</th>
<th>Viscosity /cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>-109</td>
<td>66</td>
<td>20</td>
<td>7.4</td>
<td>0.46</td>
</tr>
<tr>
<td>DME</td>
<td>-58</td>
<td>84</td>
<td>20</td>
<td>7.2</td>
<td>0.46</td>
</tr>
<tr>
<td>DMC</td>
<td>3</td>
<td>90</td>
<td>17.2</td>
<td>3.1</td>
<td>0.58</td>
</tr>
<tr>
<td>DMSO</td>
<td>18.5</td>
<td>189</td>
<td>29.8</td>
<td>46.7</td>
<td>2.01</td>
</tr>
<tr>
<td>AN</td>
<td>-48</td>
<td>81.6</td>
<td>14.1</td>
<td>37.5</td>
<td>0.34</td>
</tr>
<tr>
<td>PC</td>
<td>-54.5</td>
<td>242</td>
<td>15.1</td>
<td>64.9</td>
<td>2.51</td>
</tr>
<tr>
<td>TEGDME</td>
<td>-30</td>
<td>275</td>
<td>16.6</td>
<td>7.79</td>
<td>4.05</td>
</tr>
<tr>
<td>EC</td>
<td>36.4</td>
<td>238</td>
<td>16.4</td>
<td>95.3</td>
<td>1.9</td>
</tr>
<tr>
<td>EmiTf</td>
<td>-15</td>
<td>-</td>
<td>-</td>
<td>11.5</td>
<td>14</td>
</tr>
</tbody>
</table>
Organic Carbonates

Organic carbonates are the most popular solvents used in state-of-art Li-ion batteries. Formally, dendrite formation on the lithium anode was a drawback of electrolytes based on cyclic carbonates such as propylene carbonate (PC). However, with the invention of carbonaceous Li intercalation anodes leading to the advent of Li-ion batteries, organic carbonate solvents have become popular again with practical electrolytes comprising LiPF₆ dissolved in mixtures of ethylene carbonate (EC) and linear carbonates of dimethyl carbonate (DMC), diethyl carbonate (DEC) and/or ethyl methyl carbonate (EMC).

The high dielectric constants and the wide liquid range of these types of solvents attracted attention of scientists at the beginning of Li-O₂ battery research. Recent experiments of Li-O₂ batteries based on carbonate electrolytes have shown capacity fade with prolonged cycling which has been attributed to stability limitations of these electrolytes under the strongly oxidizing and reducing environments in the Li-O₂ battery. The main discharge product in Li-O₂ batteries utilizing organic carbonate solvents has been found to be Li₂CO₃, suggesting the decomposition of the electrolyte by the reaction with the discharge of the battery lithium peroxide. Therefore, loss of electrolyte and the accumulation of lithium carbonate have been a serious issue which prompted new investigations for alternative solvent systems for the Li-O₂ battery.

Organic Ethers

Organic ethers gained attention as they are less susceptible to reduction at the Li-O₂ cathode compared to carbonate based electrolytes and they are more stable in the presence of the reactive oxygen reduction products formed at the cathode. High boiling point ethers such as tetraethylene glycol dimethyl ether (TEGDME) have been successfully employed in Li-O₂ cells in the past few years. The low cost of the ethers and their wide potential windows have also
been favorable characteristics. Unlike the cells operated in carbonate–based electrolytes, lithium peroxide has been identified as the major discharge product formed at the cathode in Li-O2 cells employing ethereal electrolytes. Inertness towards lithium metal and the oxidative stability up to more than 4.5V vs Li/Li$^+$ of ethers are also attractive properties.

Organic Sulfoxides

High polarity and the fairly low viscosity of dimethyl sulfoxide (DMSO) compared to tetruglymes, have directed Li-O2 battery research towards a new avenue$^{30, 31}$. Current investigations are revealing the importance of the solvation of the Li$^+$ cation in the electrolyte. In this sense DMSO is an important solvent since it combines the properties of ORR product dissolution, modulation of the basicity of lithium ions in solution through the formation of Li$^+$(DMSO)$_n$ solvates and stabilization of the ORR intermediates, high O$_2$ solubility/diffusivity and Li$^+$ conductivity.

Ionic Liquids

The newest candidate to join the non-aqueous electrolyte family is Room Temperature Ionic Liquids (RTILs). Ionic liquids usually consist of large asymmetric organic cations and large anions as depicted in table with the example of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EmiTfsi). They remain liquid at room temperature due to the poor coordination of the ions arising from their asymmetric nature and the charge delocalization. Regardless of high viscosities, RTILs have fairly high ionic conductivities. They are non-volatile due to their ionic nature, and are stable over a wide potential window which makes them excellent electrolytes for Li-O2 batteries. However low oxygen solubility and diffusivity in these high viscous electrolytes have been major challenges for the development of RTIL–based Li-O2 cells.
1.4.2. Lithium-Ion Batteries

In a Li-ion battery both the anode and the cathode serves as host materials for Li ion (Li⁺) intercalation. During discharge, Li⁺ move from the cathode to the anode and the opposite process occurs during charge. A typical Li-ion battery consists of a graphite anode and LiCoO₂ cathode separated by a Li⁺ conducting porous polymer membrane. Lithium ion containing organic electrolyte added to the cell serve as the media for Li⁺ conduction. (Figure 1.5)

![Schematic representation of a Li ion cell.](image)

**Figure 1.5:** Schematic representation of a Li ion cell. Fabricated in the discharged state, the cell is activated by charging, during which the cathode is oxidized (See equation 1.23 for the LiCoO₂ cathode) to produce Li⁺ and electrons (e⁻). The Li⁺ travels through the electrolyte composed of LiPF₆ in organic solvent) and is inserted into the anode (See equation 1.24 for the graphite anode) along with the electrons arriving at it through the external circuit. The opposite processes occur during discharge.
LiCoO$_2$ Cathode  \[ LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^- \]  \[ [1.23] \]

Graphite Anode  \[ xLi^+ + xe^- + xC_6 \rightleftharpoons xLiC_6 \]  \[ [1.24] \]

1.4.3. Lithium-Oxygen Batteries

The various possible reactions in a Li-O$_2$ battery as identified from cyclic voltammetry, chronocoulomtery and product analysis are shown in equations 1.25-1.27. It has been shown that lithium superoxide (LiO$_2$) is formed first by one electron reduction product of oxygen.$^{19, 22, 32}$ The lifetime of the LiO$_2$ is greatly influenced by the nature of the electrolyte. There is a great deal of information on the influence of electrolyte on the O$_2$ reduction reaction (ORR) products formed. It is explained on the basis of the Hard-Soft-Acid-Base concept (HSAB). The superoxide ion being a soft base, its lifetime is influenced by the acidity of Li$^+$ which is modulated by the basicity of the solvents with which it forms solvates in the electrolytes. High electron donor solvents such as DMSO with a Guttmann Donor Number (DN) of 29 kcal/mole decreases the acidity of Li$^+$ enough to form stable ion pairs with O$_2^-$. These ion pairs of the structure (DMSO)$_n$Li$^+$--O$_2$ survive long enough to be observed spectrosopically. Lithium superoxide may be further reduced to lithium peroxide and lithium monoxide. However, it has been found that the major product formed in Li-O$_2$ battery cells is Li$_2$O$_2$.\textsuperscript{19, 30} Figure 1.6 shows a schematic depiction of the Li-O$_2$ cell discharge and charge.
Figure 1.6: Schematic of a Li-O₂ battery a) discharge, and b) charge.

Scheme 1.6: Possible reactions in a Li-O₂ battery and the calculated voltages at standard conditions.

\[
\begin{align*}
Li(s) + O_2(g) \rightarrow LiO_2 &\quad \Delta G^o = -70\text{kcal} \quad (E = 3.0 \text{ V}) \quad [1.25] \\
2Li(s) + O_2(g) \rightarrow Li_2O_2 &\quad \Delta G^o = -145\text{kcal} \quad (E = 3.1 \text{ V}) \quad [1.26] \\
2Li(s) + \frac{1}{2} O_2(g) \rightarrow Li_2O &\quad \Delta G^o = -134\text{kcal} \quad (E = 2.9 \text{ V}) \quad [1.27]
\end{align*}
\]

The specific energy (energy per unit mass) calculated for reaction 1.27 is 5200 Wh kg⁻¹.

The energy densities for the reactions in equations 1.26 is 3500 Wh kg⁻¹, respectively. Figure 1.6 compares the theoretical energy densities of a number of electrochemical couples. The Li-O₂ battery couple provides the highest specific energy after the Li-F₂ couple.
1.5. Microelectrode Diagnostics

The size of an electrode is a critical dimension which determines the electrochemistry at the electrode surface. Microelectrodes have radii in the range of micrometers. While there are different types of microelectrode geometries, disc and hemispherical electrodes are the most widely used.

**Figure 1.7:** Comparison of gravimetric energy densities of some battery systems.

**Figure 1.8:** Diffusion fields around a) macrodisc electrode, b) microdisc electrodes.
1.5.1. Planar vs. Radial Diffusion

The diffusion field around a typical macrodisc electrode is planar where the edge effect is negligible. As the electrode radius becomes smaller, edge effect becomes notable. Figure 1.8 is an illustration of the planar diffusion at a macrodisc electrode and the spherical diffusion at a microdisc electrode.\textsuperscript{33}

The unique mass transport behavior combined with a number of other special characteristics makes a microelectrode powerful tool to analyze electrochemical systems. Following are some advantages of microelectrodes in electrochemistry.

*Mass transport* – Due to the radial diffusion field at a microelectrode surface, transport of species to the microelectrode is extremely fast. This means steady state voltammograms can be obtained even when the electrode is operated at considerably high voltage scan rates. This characteristic is especially useful to analyze flowing electrolyte systems. Rotating techniques have been used with conventional macroelectrodes to promote mass transport to the electrode surface by hydrodynamic forces. Later in this chapter it will be shown that a macrodisc must be rotated at a speed of \( \sim 10^4 \) rpm in order to obtain the rate of mass transport observed at a 11\( \mu \)m diameter microelectrode.

*Double layer effects* – Macroelectrode responses recorded at short time scales are usually complicated, due to double layer capacitance which is proportional to the area of the electrode. The negligible double layer effects experienced by microelectrodes make fast electrochemical measurements possible. This phenomenon is further discussed later.
Small currents – The magnitude of the currents recorded at a microelectrode are considerably small (in the $10^{-9}$–$10^{-10}$ A range) which translates to negligible $iR$ drops associated with their measurements. Therefore microelectrodes can be successfully employed in highly resistive electrolytes such as solid polymer electrolytes and viscous organic electrolytes with very low ion concentrations, without sacrificing the accuracy of the data obtained.

Figure 1.9 is a comparison of voltammetric responses obtained at a microdisc(a) and at a planar macrodisc(b) in a solution of ferrocene in 0.1M Li$^+$/DMSO. The ferrocene oxidation currents obtained at the planar macrodisc is a well-known cyclic voltammogram (CV) and the currents at a microelectrode illustrate a unique sigmoidal shaped voltammogram. The behavior of the latter is due to the fast transport of the ferrocene molecules onto and the efficient removal of the oxidized ferrocenium products from the microelectrode surface by diffusion. Since the oxidation products are efficiently removed, there is no current (ferrocenium oxidation current) observed on the return cathodic sweep on the microelectrode (zero reduction current).
Figure 1.9: Ferrocene oxidation currents obtained at a) an 11µm microdisc electrode at different potential scan rates, b) a glassy carbon macrodisc at different potential scan rates.

1.5.2. Microelectrode Electrochemistry

The current at a microelectrode operating under steady state conditions is given by,

\[ i_t = \frac{4nFADC}{\pi r} = 4nFDCr \]  \hspace{1cm} [1.28]
where \( i_l \) is the diffusion limited current, \( F \) is the Faraday constant, \( D \) is the diffusion coefficient and \( C \) is the solubility of the reactant and \( r \) is the radius of the microdisc electrode and \( n \) is the number of electrons. When the microelectrode potential is stepped from a potential where no reaction occurs to a potential where the reaction is diffusion limited, at small times after polarization, the diffusion limited \( I \) current is given by equation 1.29.\(^{34} \)

\[
I = \frac{nFAD^2C}{\pi^2t^2} + n\pi FDCr
\] \[1.29\]

From the slope and the intercept of \( I \) vs. \( t^{-1/2} \) curve\(^{34} \) (equation 1.29) the diffusion coefficient and solubility of the reactant in the electrolyte can be calculated as shown by equations 1.30 and 1.31 respectively.

\[
D = \frac{\text{intercept}^2 \times r^2}{\text{slope}^2 \times \pi}
\] \[1.30\]

\[
C = \frac{\text{slope}^2}{\text{intercept} \times r^3 \times F \times n}
\] \[1.31\]

Figure 1.10 shows the Cottrell plot calculated for chronoamperometric transitions obtained by stepping the microelectrode potential from 3.62 V to 4.12 V in a solution of ferrocene in 0.1M Li\(^+\)/DMSO. Diffusion coefficient of ferrocene calculated by equation 1.29 is 4.16x10\(^{-6} \) cm\(^2 \) s\(^{-1} \) and concentration of ferrocene is found to be 2.95 mM for an electrode radius of 5.5\( \mu \)m (an 11\( \mu \)m carbon microelectrode was used in this study). This value of diffusion coefficient is in good agreement with the values reported by Janisch et al.\(^{35} \)
1.5.3. Experimental Validation of the Technique

The steady state current on a rotating disc macroelectrode is given by the Levich equation (equation 1.32)

\[ i_l = 0.620 \times nFAD^{\frac{2}{3}}\omega^{\frac{1}{6}}v^{\frac{1}{6}}C \]  

where \( \omega \) is the speed at which the electrode is rotated and \( \nu \) is the kinematic viscosity of the electrolyte. The requirement to obtain a particular limiting current density at a microelectrode and a macroelectrode can be derived using equations 1.28 and 1.32 as follows (equation 1.33).

\[ 4nFDC\pi^{-1}r^{-1} = 0.620 \times nFAD^{\frac{2}{3}}\omega^{\frac{1}{6}}v^{\frac{1}{6}}C \]  

This simplifies to equation 1.34 which shows the relation of a microelectrode radius with the rotating speed of a macrodisc.

\[ 0.620 \times 4\pi D^{\frac{1}{6}}u^{\frac{1}{6}} = \omega^{\frac{1}{6}}r \]  

\[ 1.34 \]
From equation 1.34, it can be shown that the rotation speed of a microdisc corresponding to a microelectrode of 11µm diameter is \( \sim 25000 \text{ rpm} \) (assuming \( D_{O_2, \text{DMSO}} \sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \), \( \nu_{\text{DMSO}} \sim 1.9 \text{ cP} \)). This further confirms the advantage of using a microelectrode for voltammetric measurements related to high resistance electrochemical systems. The maximum rotation speeds that the conventional rotors can operate are limited to \( \sim 3000 \text{ rpm} \). Also the electrode responses obtained at these rotation speeds often suffer from high ohmic voltage drops and needs to carefully corrected using electrochemical impedance spectroscopy. Clearly, a microelectrode is a very useful technique to accurately analyze complicated electrochemical systems.

1.6. **Scope of the Thesis**

The contents of this dissertation are divided into two major parts. The first part presented in detail in Chapter 2 deals with the interfacial kinetics of fuel cell reactions at the membrane/electrode interface and transport characteristics of reactants through alkaline anion exchange membranes. The mass transport losses that occur as result of carbonate exchange of hydroxide ions in alkaline anion exchange membranes are discussed in detail. The qualitative effect of the carbonate exchange on \( O_2 \) reduction, \( H_2 \) oxidation and methanol oxidation under alkaline conditions are also discussed here.

The second part of the dissertation detailed in Chapters 3, 4 and 5 is concerned with the electrochemistry of non-aqueous lithium-oxygen batteries. We show that electrolyte formulation is of utmost importance to overcome the capacity and cycle life limitations associated with these batteries. For the first time microelectrode technique\(^{31, 36}\) has been used to electrochemically characterize and predict \( O_2 \) diffusion and solubility in viscous organic electrolytes relevant to Li-O\(_2\) batteries. The importance of the donor properties of the lithium salt anions, ether and
sulfoxide-based solvents and the significance of the acidity modulation of the Li\(^+\) cation in the electrolytes containing these species are presented.\(^{37}\)

Chapter 5 focuses on the catalysis of the oxygen reduction reaction (ORR) by an iron(II) phthalocyanine–based solid state catalyst. The structure and electrochemistry of iron-based catalysts prepared by heat-treating iron(II) phthalocyanine with high surface area carbon black precursors have been investigated. The pyrolysis temperature of the catalyst determines the ORR mechanism which translates to a better ORR onset potential and the subsequent oxygen evolution reactions (OER). The donor properties of the solvent as well as the salt anion of the electrolyte have a significant effect on the ORR mechanism in the presence of these catalysts. Mechanisms proposed for the catalytic ORR and OER based on the results of electrochemical investigations are discussed, and Raman and FT-IR spectroscopic and X-ray diffraction studies are presented.

The final chapter includes the conclusion of the investigations and a discussion of directions for future work.
Chapter 2

Reactant Transport and Interfacial Kinetics at the Pt/AEM Interface:
Microelectrode Studies on the Effect of Carbonate Exchange in Alkaline Fuel Cells

2.1. Introduction

Development of fuel cell technology requires significant cost reduction which mainly arises from the generous amounts of Pt–based catalysts being used to surmount kinetic overpotentials at the oxygen cathode. Fuel cells operating in alkaline media have possible advantage of facile kinetics of the oxygen reduction reaction (ORR) on non-precious group metals and stability at high pH values. Also, the facile methanol oxidation kinetics observed in direct methanol fuel cells (DMFC) under high pHs\(^8\) have been favorable. In addition, the hydrodynamics of alkaline membrane fuel cells is beneficial considering the problems associated with water management in a conventional PEM fuel cell. Furthermore, highly stable poly(tetrafluoroethylene) (PTFE)-based membranes are not required under alkaline conditions as the membranes are less prone to attack by peroxide ions.

Even though AEMFCs alleviate most of the hurdles associated with PEM fuel cells, state of art performance of \(H_2/O_2\)(air) cells does not exceed half of the performance shown by \(H_2\) fed PEM fuel cells using Pt–based catalysts (compare 700 mW cm\(^{-2}\) for PEMFCs\(^{15}\) at 0.65 V (80°C, 100% RH) with ~40 mW cm\(^{-2}\) for AEMFCs\(^{38}\) at 0.65 Volts (50°C, 85% RH).\(^{38}\) The major concern under atmospheric air feed is carbonate exchange of the hydroxyl ions in the polyelectrolyte due to their complete conversion to carbonate and bicarbonate ions upon exposure.\(^{9,39,40}\) Conversion of the hydroxide ions to \(\text{CO}_3^{2-}/\text{HCO}_3^{-}\) ions can also occur by the CO\(_2\) produced by methanol oxidation at the DMFC anode. In such instances only HCO\(_3^{-}\) and \(\text{CO}_3^{2-}\) are responsible for ionic conduction.\(^{41}\) Donnan exclusion of protons within the membrane and the
fuel cell operating conditions lead to carbonate (\(\text{CO}_3^{2-}\)) ion enrichment\(^{10-14, 42}\) as discussed in Chapter 1. It is well known that conductivities of carbonate ions in aqueous solutions are lower than hydroxyl ions due to larger hydration spheres arising from the size and surface charge densities.\(^{43}\) As reported earlier, relative decrease in ionic conductivity as a function of exchange with carbonate and bicarbonate ions is low.\(^{44, 45}\) Permeation of reactants in the ionomer and membrane thus play an important role in determining the onset of mass transport and hence the power density of the AEM fuel cells. Details of interfacial kinetics and mass transport of dissolved oxygen and the quantitative effect on the performance by carbonate exchange is relatively unknown. The first part of this chapter provides an insight on the relative magnitudes of kinetics of the ORR as well as mass transport of \(\text{O}_2\) in the AEM with and without carbonate exchange. Investigations on the quantitative effect of the carbonate ion contamination in the alkaline membrane on the fuel cell anode (hydrogen and methanol) are discussed later.

A well-known quaternized anion exchange membrane, Tokuyama®A201, (Tokuyama Corp., Tsukuba, Japan) was used in this study in conjunction with a solid state electrochemical cell incorporating a micro-electrode, described in detail elsewhere.\(^ {46, 47}\) The parameters obtained were free from effects typically encountered in liquid electrolytes such as hydroxide ion adsorption effects and presence of mobile cations. Conventional fuel cell electrode kinetics reported on rotating disc electrodes in aqueous electrolytes greatly deviate from the kinetics of the membrane electrode interface.\(^ {48}\) This study for the first time resolves the kinetics from the mass transport contributions (diffusion coefficient and solubility) of fuel cell cathode reactions (ORR) and fuel cell anode reactions (hydrogen and methanol oxidation). Results of this work are used to understand polarization losses at a typical fuel cell interface.
2.2. Experimental

2.2.1. Membranes

Tokuyama-A201-OH\(^-\) and A901-OH\(^-\) membranes were prepared by soaking Tokuyama A201, A901 (Tokuyama Corp., Tsukuba, Japan) membranes in 1 M KOH solutions. Membranes were then rinsed and stored in CO\(_2\) free water (prepared by boiling the water followed by cooling under argon. Membranes in the carbonate form were prepared by soaking as received membranes in 1 M K\(_2\)CO\(_3\) solution. These membranes were then rinsed and stored in milli-q water overnight to leach excess carbonate ions. A solid state cell shown in Figure 2.1a was used to study the oxygen and hydrogen electrode reactions.\(^{13,46,47}\) A liquid feed enabled cell shown in Figure 2.1b was used to study the methanol anode electrochemistry. A 100\(\mu\)m Pt microelectrode (Bio-analytical Systems), 1.6 mm diameter Pt disc counter electrode and a dynamic hydrogen electrode (DHE) made the three electrode system. All electrodes were cleaned using 15 \(\mu\)m, 3 \(\mu\)m, 1 \(\mu\)m diamond polish, respectively, and were sonicated in milli-q water for 10 minutes. The DHE was subsequently platinized prior to use.

2.2.2. Electrochemical Techniques

Voltammetric measurements were taken using a computer controlled potentiostat/galvanostat (Autolab, model PGSTAT30). Measurements of carbonate free membranes were carried out in CO\(_2\) free conditions enabled by an Ar filled glove bag (Atmos-glove bag (Sigma Aldrich)). Cyclic voltammograms were recorded for 100% RH nitrogen saturated membranes to ensure a proper electrochemical interface. Anion exchange membrane exchanged with carbonate ions was studied outside the glove-bag, exposed to air. All measurements were carried out at 293 K temperature and 1 atm pressure.
Potentials were scanned from 0.0 V to 1.3 V in nitrogen saturated membranes at 100 mV s\(^{-1}\), to clean the electrode surface prior to taking readings. All potentials were corrected to the reversible hydrogen electrode (RHE) scale before analysis. Cyclic voltammetry was preceded by measurement of contact impedance changes with variation of contact pressure using a built in micrometer head.\(^{46, 47}\) The relative invariance of contact impedance and the recording of proper Pt features on the CV, were checks to ensure proper interfacial conditions. H\(_\text{UPD}\) areas measured by CV served to determine the active surface area of the microelectrode.

### 2.2.3. Mass Transport Parameters

Using the mathematical model proposed by Aoki and Osteryoung\(^{49}\) to simulate chronoamperometric currents at the microelectrode, Winlove et al.\(^{34}\) have reported that if the time after polarization is small, diffusion limited current at the microelectrode can be given by modified Cottrell equation (equation 2.1).

\[
I = \frac{n F A D^2 C}{\pi^2 t^2} + n \pi F D C r \tag{2.1}
\]

where \(n\) is the number of electrons per reduction of oxygen molecule. \(F\) is the Faraday constant, \(A\) is the geometric area and \(r\) is the electrode radius of the electrode. \(D\) and \(C\) are diffusion coefficient and solubility of the reactant in the AEM. Chronoamperometric measurements were carried out by equilibrating the electrode at potential close to the open circuit potential and stepping to a potential beyond the kinetic region. \(D\) and \(C\) were calculated using the equations involving the slope and the intercept of the Cottrell plot (equations 2.2 and 2.3).\(^{13, 31}\)
D = \frac{\text{intercept}^2 \times r^2}{\text{slope}^2 \times \pi} \quad [2.2]

C = \frac{\text{slope}^2}{\text{intercept} \times r^3 \times F \times n} \quad [2.3]

2.2.4. Oxygen Transport and ORR Kinetics at the Pt/AEM Interface

The membrane was equilibrated for at least two hours with a 100% RH oxygen supply in order to ensure oxygen dissolution. Chronoamperometric measurements were carried out by conditioning the electrode potential at 1.0 V for 10 s and stepping down to 0.4 V for 20 s with respect to RHE. \( D \) and \( C \) were calculated by using the slope and intercept of the current vs. inverse square root plot (equation 2.1). Kinetics of the ORR at the Pt electrode/AEM interface was studied by mass transport corrected Tafel equation (2.4),

\[
\eta = \frac{2.303RT}{\alpha nF} \log i_0 + \frac{-2.303RT}{\alpha nF} \log \left[ \frac{i_0 i}{i_s - i} \right] \quad [2.4]
\]

where \( \eta \) is the overpotential \((E-E^0)\), \( i_o \) is the exchange current density, \( \alpha \) is the transfer coefficient, \( R \) is the gas constant, \( T \) is the absolute temperature, \( i_s \) and \( i \) are limiting current and current, respectively. Transfer coefficient and exchange current densities were calculated using extrapolation of the Tafel slope. Since this extrapolation is over several decades of current, the relative orders of magnitude served as indicators of changes in kinetics. More accurate comparisons were made using currents (mass transport corrected) at 0.9 V vs. RHE.
2.2.5. Hydrogen Transport and HOR Kinetics at the Pt/AEM Interface

The membrane was equilibrated for at least two hours with a 100% RH hydrogen supply in order to ensure proper hydrogen dissolution. Chronoamperometric measurements were carried out by conditioning the electrode potential at 0.0 V for 10 s and stepping up to 0.3 V for 20 s with respect to RHE. $D$ and $C$ were calculated by using the slope and intercept of the current vs. inverse square root plot (equation 2.1). Kinetics at the Pt electrode/AEM interface were studied by mass transport corrected Tafel equation (2.4).

The HOR on platinum electrodes can take place through the following steps (scheme 2.1-2.2).

**Scheme 2.1:** Hydrogen oxidation reaction in acidic environments

\begin{align*}
H_2 + 2Pt & \rightarrow 2(Pt - H) & \text{Tafel} \quad [2.5] \\
H_2 + Pt & \rightarrow Pt - H + H^+ + e & \text{Heyrovsky} \quad [2.6] \\
Pt - H & \rightarrow H^+ + e & \text{Volmer} \quad [2.7]
\end{align*}

**Figure 2.1:** Solid state cells a) For gaseous reactants, b) Liquid feed enabled cell.
Scheme 2.2: Hydrogen oxidation reaction in alkaline environments

\[ H_2 + OH^- + Pt \rightarrow Pt - H + H_2O + e \]  
Heyrovsky  [2.8]

\[ Pt - H + OH^- \rightarrow H_2O + e \]  
Volmer  [2.9]

To interpret the Heyrovky-Volmer reaction with a transfer coefficient of \( \alpha \), Butler–Volmer (B-V) equation can be used.\(^{50}\) Kinetic parameters for HOR were obtained by fitting the polarization data in B-V equation (2.5).\(^{50}\)

\[ i_k = i_o \left\{ \exp \left( \frac{\alpha F}{RT} \eta \right) - \exp \left( \frac{- (1 - \alpha) F}{RT} \eta \right) \right\} \]  
[2.5]

2.2.6. H\(_2\)/Air Fuel Cell Tests

PEM fuel cells and AEM fuel cells were constructed using Pt/C based electrodes (0.5 mg\(_{Pt}\)/cm\(^2\)). A catalyst coated Nafion® membrane (ionomer/carbon ratio of 0.7) was hot pressed to the gas diffusion layer (GDL) at 130°C. Polarization data were recorded for normal air feed at the cathode at 65°C and 100% RH conditions. Catalyst coated Tokuyama-A201 membranes were prepared by hot pressing the membrane between ink coated decal supports (ionomer (AS-4 (Tokuyama Corp.))/carbon ratio of 0.4). Ultra-zero (CO\(_2\) < 1 ppm) air was used at the cathode and polarization curves were recorded at 50°C and 100% RH conditions. Both membrane electrode assemblies (MEAs) were conditioned at series of potentials prior to testing.

2.2.7. Methanol Transport and MOR Kinetics at the Pt/AEM Interface

Equation 2.6 shows possible pathways of the methanol oxidation on a Pt electrode.

\[ CH_3OH \rightarrow \text{Reactive intermediates} \rightarrow HCOO^- \]  
\[ \text{Poisoning species} \rightarrow CO_2 \]  
[2.6]
Methanol oxidation in alkaline conditions proceeds faster than in low pH conditions due to balanced co-adsorption of hydroxyl ions at high pHs. Slow sweep voltammetry cannot be used to obtain diffusion limited currents for the methanol oxidation reaction at a Pt electrode. Therefore, potential step chronoamperometry was applied to obtain steady state methanol oxidation currents for kinetic analysis. For this, starting from 4.0 V the potential of the Pt electrode was increased by 50mV limits and the electrode was held at each potential for 180 seconds.

Methanol transport parameters were evaluated using the Cottrell Plots calculated from the current-time transients obtained by stepping the Pt electrode potential from 0.4 V to 0.8 V.

2.3. Results and Discussion

Cyclic voltammograms (CV) were recorded at the Pt microelectrode for the N₂ saturated alkaline anion exchange membrane, to ensure the proper contact between the AEM and the electrode. All the potentials reported in this chapter are with reference to the RHE. The CVs were recorded under 100% relative humidity (RH) conditions. The electrochemically active area of the platinum microelectrode was calculated using the hydrogen adsorption region of the nitrogen CV. Specific adsorption of hydroxide ions from water leads to Pt-OH formation which is indicated by the peak that appears at 0.8V. Meanwhile in the CO₃²⁻-based AEM, the hydroxide adsorption peak is very low in intensity and it has shifted to a higher voltage (Figure 2.2).⁵¹
Figure 2.2: Cyclic voltammogram recorded on A201 membrane under 100% RH nitrogen saturated conditions, 293K, 1 atm.

The current-voltage behavior observed for A201-OH in Figure 2.2 is similar to the electrochemistry observed at a Pt electrode in an aqueous NaOH solution\textsuperscript{8} that has been reported earlier. Even though some reports suggest that quaternary ammonium ions specifically adsorb on the platinum metal surface affecting Pt-OH formation in solvent electrochemistry,\textsuperscript{3} the quaternary ammonium species tethered to the polymer chain does not seem to have a significant adsorbing effect on the electrode surface.

2.3.1. Oxygen Reduction Kinetics

Linear sweep voltammetry was performed on oxygen saturated alkaline membranes at 100% RH conditions, on a 100µm Pt disc electrode. Cyclic voltammograms recorded with a dynamic hydrogen electrode (DHE) as the reference were corrected using the hydrogen evolution potential recorded under nitrogen saturated conditions. All potentials reported in this chapter are
converted to the RHE unless otherwise stated. Membrane resistance was recorded using electrochemical impedance measurements (frequency response analysis using Autolab model PGSTAT 30 and GPES software). Mass transport corrected Tafel slopes are shown in Figure 2.3a.

Comparison of kinetic currents at 0.9 V, and exchange current at low current density \((lcd)\) region (similar order of magnitude) for Nafion® (112) vs. Tokuyama® (A201) show similar values (Table 2.1). Similar comparison for AEM with and without carbonate exchange did not appear to affect the ORR kinetics significantly (Table 2.1). Slightly lower values for exchange current at high current density region \((hcd)\) for the carbonate exchanged AEM should be considered in the context of their being in the same order of magnitude (especially the extrapolated exchange current density). Invariance of ORR kinetics due to carbonate exchange is in agreement with prior reports by Mustain et al.\(^{52}\) Activity comparison with free electrolytes such as 0.1M HClO\(_4\) vs. Nafion® interface showed the former to be a bit lower.\(^8\) Such differences have been reported earlier;\(^{46, 47}\) combinations of interfacial humidification, electrocatalyst interaction with the ionomer are possible reasons. Notably, while the exchange current density at the \((lcd)\) region and at 0.9 V does not appear to have significant difference between a PEM such as Nafion® and AEM (Tokuyama), the \(hcd\) region activity at the interface with AEM is severely curtailed. The \(lcd\) region represents primarily, the electrocatalytic activity as the effect of other polarization losses are minimal. Difference between 0.1 M HClO\(_4\) and 0.1 M KOH is explained on the basis of specifically adsorbed hydroxyl species\(^6\) in the latter.
Figure 2.3: Kinetics at the Pt/ membrane interface and Mass transport Characteristics, green-Nafion-112, blue-Tokuyama A201-OH, red-A201-CO$_2^-$: a) Mass transport corrected Tafel plots for Oxygen Reduction at the Pt/membrane interface  b) Cottrell plots for the Oxygen reduction at the interface, potential range (1.0 to 0.4 V vs. RHE).
Table 2.1: Comparison of interfacial kinetics of ORR

<table>
<thead>
<tr>
<th>Electrolyte (293K, 1 atm)</th>
<th>$j_0 10^9$ (A cm$^{-2}$) (hcd)</th>
<th>$\alpha_{hcd}$</th>
<th>$j_0 10^{10}$ (A cm$^{-2}$) (lcd)</th>
<th>$\alpha_{lcd}$</th>
<th>$j 10^8$ at 0.9 V (A cm$^{-2}$$_{geo}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM-OH$^+$</td>
<td>8.28</td>
<td>0.79</td>
<td>2.53</td>
<td>1.02</td>
<td>1.0</td>
</tr>
<tr>
<td>AEM-CO$_3^{2-}$</td>
<td>1.03</td>
<td>0.72</td>
<td>0.31</td>
<td>1.09</td>
<td>0.3</td>
</tr>
<tr>
<td>1.0 M NaOH$^8$</td>
<td>--</td>
<td>0.73</td>
<td>0.6</td>
<td>1.32</td>
<td>7.2</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>231</td>
<td>0.50</td>
<td>67.7</td>
<td>0.81</td>
<td>2.3</td>
</tr>
<tr>
<td>0.1 HClO$_4^-$</td>
<td>--</td>
<td>0.57</td>
<td>47</td>
<td>0.83</td>
<td>23</td>
</tr>
</tbody>
</table>

2.3.2. Oxygen Transport Parameters

*Diffusion coefficient*-Chronoamperometric methods were employed to determine diffusion coefficient and solubility of oxygen in the alkaline AEM with and without carbonate exchange. Cottrell plots derived from current–time transients are shown in Figure 2.3b. All three plots exhibit linear behavior with $R^2$ (regression correlation coefficient) values higher than 0.96. Transport parameters were calculated from slopes and intercepts using equations 2.1.

Table 2.2: Comparison of mass transport characteristics

<table>
<thead>
<tr>
<th>Electrolyte (293K, 1 atm)</th>
<th>$D$ $10^6$ (cm$^2$ s$^{-1}$)</th>
<th>$C$ $10^6$ (mol cm$^{-3}$)</th>
<th>$DC$ $10^{12}$ (mol cm$^{-2}$ s$^{-1}$)</th>
<th>IEC (meq g$^{-1}$)</th>
<th>Water uptake (w %)</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM-OH$^+$</td>
<td>4.29</td>
<td>0.93</td>
<td>3.99</td>
<td>1.8</td>
<td>63</td>
<td>18.5</td>
</tr>
<tr>
<td>AEM-CO$_3^{2-}$</td>
<td>0.23</td>
<td>0.90</td>
<td>0.22</td>
<td>1.8</td>
<td>59</td>
<td>18.2</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>0.73</td>
<td>6.5</td>
<td>4.8</td>
<td>0.91</td>
<td>32</td>
<td>19.8</td>
</tr>
<tr>
<td>SPES-40$^{46}$</td>
<td>0.47</td>
<td>4.87</td>
<td>2.30</td>
<td>1.72</td>
<td>60</td>
<td>20.8</td>
</tr>
</tbody>
</table>

The datum in Table 2.2 shows that the A201-OH$^+$ has a higher oxygen diffusion coefficient than the Nafion membrane. Oxygen diffuses mainly through the hydrophilic aqueous phase in hydrated membrane; higher water uptake facilitates such diffusion. Typical ion exchange
capacity of Nafion is 0.91 meq g\(^{-1}\) which when compared with corresponding value of 1.8 meq g\(^{-1}\) for the Tokuyama®A201 membrane indicates a concomitantly higher water content and hence a higher oxygen diffusion coefficient. The higher water content is a bulk property distinct from the \(\lambda\) (\# of water molecule per exchange site), which shows similar values irrespective of the polymer backbone and exchange site (sulfonate vs. quaternary amine). Since diffusion coefficient is directly related to water content and as shown earlier,\(^{53}\) potential window used in this chronoamperometric study provides for sufficient hydration for this not to be a factor in our measured values. Exchange of the AEM with carbonate ions resulted in significant lowering of oxygen diffusion. This is in agreement with oxygen diffusion measurements in aqueous carbonate solutions using rotating disc electrode measurements and comparison of mass transport limited currents.\(^{52}\) Mobility of the molecules inside the pores of the polymer is expected to be low. This in combination with slower steric and electrostatic impedance resulting from the doubly charged carbonate ions result in lower diffusion coefficient of oxygen in carbonate exchanged AEMs.

*Solubility*- Oxygen concentration in the membrane is mainly determined by its solubility in the polymer backbone. Our data (Table 2.2) shows that the solubility of oxygen in the Tokuyama®A201 membrane is much lower than that in Nafion®. This is expected since Nafion® possesses essentially a PTFE backbone which renders very high oxygen solubility \((26.8 \times 10^{-6} \text{ mol cm}^{-3})\) as compared to a typical hydrocarbon backbone such as those in Tokuyama®. Similar comparison for proton exchange membranes has been reported earlier between Nafion® and sulfonated polyether sulfones, with similar results (Table 2.2).\(^{46}\) Since the exact structure of the Tokuyama (A201) membrane is not known, a comparison with the analogous proton exchange membrane (SPES-40) is not possible. It should however be noted for
the record that the solubility of oxygen was significantly lower in the AEM as compared to SPES-40 (Table 2.2). More interestingly the exchange with carbonates had no effect on the solubility of oxygen in the AEM membrane. As mentioned earlier, the oxygen solubility depends primarily on the polymer structure and shows a negative trend based on overall water content, \(^{46,47}\) both of which do not appear to be affected as a result of ion exchange.

*Permeability* - Oxygen permeability, calculated by the product of the diffusion and solubility values is a measure of the overall transport of the gas through the membrane. Permeability is similar in magnitude for Nafion112 and A201 membranes (OH\(^-\)) due to the opposite trends in their diffusivity and solubility values. However, the AEM membrane exchanged with carbonates show much lower permeability, which mainly arises from the hindered diffusivity of the gas molecules within the membrane. Since the water uptake in the AEM in both OH\(^-\) and CO\(_3^{2-}\) forms are similar it does not play a role in lowering the O\(_2\) permeability. It can be concluded that the doubly charged anion in the hydrated region has an electrostatic interaction with the oxygen molecules. Steric factors also play a role in depression of oxygen diffusion. However further investigations need to be done employing molecular modeling techniques to verify this explanation. The lack of literature related to the microstructure of A201 membranes are a disadvantage in this regard.

**2.3.3. Fuel Cell Performance**

Figure 2.4 shows iR-free polarization curves for both AEMFC and PEMFC using CO\(_2\) free and atmospheric air feeds respectively. Polarization curve exhibiting only the kinetic overpotential was obtained by extrapolating the iR-free polarization curve at low current densities, thus eliminating mass transport contributions (dashed lines in Figure 2.4).\(^{15,16}\) This
comparison of polarization curves of the AEMFC (CO₂ free) with Nafion based PEMFCs further reflects that the in AEMFC mass transport of reactants plays a major role in decreasing the fuel cell performance at higher current densities.

![Figure 2.4: iR corrected H₂/Air fuel cell cathode polarization curves for PEMFCs (65°C) and AEMFCs (50°C). Solid curves show mass transport and kinetic overpotentials. Dotted curves show kinetic only overpotential.](image)

2.3.4. Hydrogen Oxidation Kinetics

The inset of Figure 2.5 shows HOR/HER polarization curves at the Pt/AEM interface recorded at a scan rate of 2mV s⁻¹. The blue curve represents the electrochemical data obtained at a membrane in the hydroxide form while the curve in red represents that for a membrane in the carbonate form. Ohmic correction applied to the CVs did not make a significant difference as the currents recorded are in the order of ~nA in magnitude. The hydrogen oxidation current reaches
its limiting region at a potential of 0.2V. The limiting current of 0.16 mA cm$^{-2}$ observed for the A201- OH$^-$ membrane decreases down to 0.05 mA cm$^{-2}$ when the hydroxide ions in the membrane is exchanged with carbonate ions. Figure 2.5 shows the mass transport corrected Tafel plots calculated from the steady state hydrogen oxidation currents shown in the inset of Figure 2.5. Exchange current densities for the HOR at the different AEM interfaces were obtained by fitting the Tafel plots in the region between 0.0V and 0.1V in the Butler–Volmer (equation 2.5, Table 2.3). The exchange current density (ECD) calculated for the HOR at the A201—OH$^-$, 0.63 mA cm$^{-2}$ is in good agreement with 0.69 mA cm$^{-2}$, the ECD reported for the HOR in a 0.1 M aqueous KOH solution.$^{50}$

Table 2.3: Kinetic parameters for hydrogen oxidation reaction in alkaline electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$j_0$ (mA/cm$^2$)</th>
<th>Transfer coefficient - $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M KOH$^{50}$</td>
<td>0.69</td>
<td>0.50</td>
</tr>
<tr>
<td>AEM—OH$^-$</td>
<td>0.63</td>
<td>0.48</td>
</tr>
<tr>
<td>AEM—CO$_3^{2-}$</td>
<td>0.09</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The charge transfer coefficient of 0.48 experimentally obtained for the HOR at the Pt/A201—OH$^-$ interface well agrees with the Heyrovski–Volmer mechanism proposed by DFT calculations.$^4$ The symmetry of the Tafel plot obtained for A201—OH$^-$ suggests a similar mechanism for HER on the Pt/microelectrode interface.$^{50}$

The underlying reason behind the low HOR exchange current density$^8$ at the A201-CO$_3^{2-}$ is probably the mechanism change in the presence of carbonate ions. The hydrogen oxidation in AEM-CO$_3^{2-}$ takes place through the carbonate pathway as shown on equation 2.7.
\[ H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e^- \] [2.7]

As we discussed earlier the pore solution in AEMs becomes acidic due to the Donnon exclusion of H\(^+\) ions from the membrane. However, literature suggests that in aqueous carbonate electrolytes the HOR tends to go through the carbonate pathway rather than reacting with the remaining OH\(^-\) species in the electrolyte. It appears that the HOR mechanism at the Pt/AEM-CO\(_3^{2-}\) interface follows the same trend.

![Figure 2.5](image)

**Figure 2.5:** Mass transport corrected Tafel plots for HOR/HER at the membrane electrode interface.

### 2.3.5. Hydrogen Transport

Transport of gaseous molecules through the membrane is determined by their solubility in the membrane and their diffusion. The experimentally obtained (Figure 2.6) mass transport
parameters for the AEMs are displayed along with the values reported for a PEM by Kucernack et al.\textsuperscript{51} in Table 2.4 for comparison. In water, the diffusion coefficient of hydrogen is $4.5 \times 10^{-5}$ cm$^2$ s$^{-1}$ and the hydrogen solubility is in the order of $\sim 10^{-7}$ mol cm$^{-3}$. The diffusivity of hydrogen molecules in AEM--OH$^-$ is lower than this value regardless of the high water content (or IEC) in the membrane. This implies that the hydrogen molecule diffusion does not take place through the aqueous part of the polymer membrane. Considering the hydrophobicity of non-polar H$_2$ molecules it is practical that the hydrogen molecules dissolve and diffuse through the water–polymer interfacial regions of the membrane.\textsuperscript{54,55}

**Table 2.4:** Mass transport characteristics of hydrogen in the AEM

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Diffusion coefficient (D) 10$^6$ (cm$^2$ s$^{-1}$)</th>
<th>Solubility (C) 10$^6$ (mol cm$^{-3}$)</th>
<th>Permeability (DC) 10$^{12}$ (mol cm$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM --OH$^-$</td>
<td>1.34</td>
<td>2.98</td>
<td>4.00</td>
</tr>
<tr>
<td>AEM --CO$_2$H$_2^-$</td>
<td>1.30</td>
<td>0.52</td>
<td>0.68</td>
</tr>
<tr>
<td>Nafion 117\textsuperscript{51}</td>
<td>7.60</td>
<td>0.51</td>
<td>3.90</td>
</tr>
</tbody>
</table>

**Figure 2.6:** Cottrell plots for the HOR calculated from current-time transients at 0.3V (potential jump from 0V to 0.3 V).
From a study based on proton exchange membranes with different side chain lengths, Tsuo et al\textsuperscript{54} have concluded that extrusion of side chains to the water phase is an important factor which determines the diffusion path of hydrogen molecules. As the aqueous region expands its crystallinity decreases which in turn facilitates the extrusion of the polymer side chains into the water phase. This increases the interfacial path length. Hence the overall H\textsubscript{2} diffusion coefficient decreases. In general it is plausible to say that the diffusion of non-polar molecules in polymer electrolytes with high IEC is low. However it is surprising that the diffusion coefficient of hydrogen gas is not altered when the mobile ion is changed from OH\textsuperscript{−} to CO\textsubscript{3}\textsuperscript{2−}. Ionic species are generally confined to the aqueous part of the membrane. Hence they have a little effect on molecular transport that occurs through the interfacial region. The insignificance of the mobile anion on the diffusivity of the molecular hydrogen further confirms that the hydrogen molecules are diffusing through the interfacial region of the membrane. The effect of carbonate ions on the hydrogen solubility is not very clear. Probably, the interactions of the doubly charged carbonate ions with multiple quaternary ammonium sites leads to a distortion in the polymer micro-channel structure. This may in turn decrease the effective area of interfacial region where H\textsubscript{2} can dissolve. Distortion of the polymer micro-channel system should have a minimal effect on hydrogen diffusivity due to the smaller size of the H\textsubscript{2} molecule. A detailed investigation on the structure of the AEM is required to further explain the trend in H\textsubscript{2} solubility.

2.3.6. Methanol Oxidation Reaction at the Pt/AEM Interface

\textit{Methanol oxidation kinetics:} Cyclic voltammograms (CVs) obtained for the methanol oxidation reaction (MOR) at different Pt/AEM interfaces are shown in Figure 2.7. The CV corresponding to Pt/Nafion interface is superimposed in black dashed curves in the same Figure for better comparison. The MOR begins at a potential of 0.5 V, after the hydrogen desorption region.
Voltammograms shown in Figure 2.7 clearly indicate that the methanol oxidation peak current coincides with the hydroxide layer formation. At potentials above 0.9V, the electrode surface becomes highly covered by hydroxyl species that inhibit methanol adsorption on the electrode. This in turn reduces the MOR current. At both Pt/A201-OH⁻ and Pt/A901-OH⁻ interfaces, the onset potentials of the MOR occur at low potentials compared to that of the Pt/Nafion membrane.

![Cyclic voltammograms for MOR at the membrane/Pt microelectrode interface. 1 M MeOH, 293K.](image)

**Figure 2.7:** Cyclic voltammograms for MOR at the membrane/Pt microelectrode interface. 1 M MeOH, 293K.

The methanol oxidation reaction proceeds through formation of several intermediates and CO is one of the main species formed. As the electrode potential is scanned CO poisoning species are formed which strongly adsorb on the Pt surface. The peak current in the negative going scan becomes low since the effective electrode area is decreased by adsorbed CO species.
formed during the forward scan. Sufficient adsorption of hydroxyl species on the electrode is necessary to regenerate the poisoned electrode surface by oxidation of CO to CO$_2$ (equation 2.8).

$$CO_{ads} + 2OH_{ads} \rightarrow CO_2 + H_2O$$

[2.8]

In alkaline electrolytes the electrode surface is recovered very easily; therefore a shift in reverse peak is not observed. However the reverse peak at the Nafion membrane interface appears at a much lower potential than the forward peak. Tafel plots were calculated for Pt/Membrane interfaces (Figure 2.8) using steady state methanol oxidation currents. These plots shown in Figure 2.8 were used to further evaluate the effect of the pH and the anionic species on the electrode activity towards the MOR. The Tafel slopes of 142 mV dec$^{-1}$ and 122 mV dec$^{-1}$ obtained for Pt/A201-OH$^-$ and Pt/A901-OH$^-$ interfaces respectively agrees well with the MOR kinetic parameters obtained for an aqueous KOH electrolyte\textsuperscript{59} (Table 2.5). The A901 membrane has a better ion conductance than the A201 membrane, which is an indication of the higher surface charge concentration of the former. This is the underlying reason behind the slightly better MOR kinetics observed at the Pt/A901-OH$^-$ interface.

**Table 2.5: Kinetic parameters for methanol oxidation reaction**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>j (at 0.65 V) $10^5$ (A cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A201-OH$^-$</td>
<td>142</td>
<td>4.32</td>
</tr>
<tr>
<td>A201-CO$_3^{2-}$</td>
<td>314</td>
<td>1.00</td>
</tr>
<tr>
<td>A901-OH$^-$</td>
<td>122</td>
<td>15.06</td>
</tr>
<tr>
<td>A901-CO$_3^{2-}$</td>
<td>249</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1M OH solution</td>
<td>113</td>
<td>294.4</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>138</td>
<td>4.12</td>
</tr>
</tbody>
</table>
The cyclic voltammograms obtained at the Pt/AEM-CO$_3^{2-}$ interface shows that the mobile anion in the AEM has a great effect on the MOR kinetics. Effect of anionic species on the MOR in both acid and alkaline aqueous electrolytes has been extensively studied. In an investigation involving electrolytes with HSO$_4^-$, ClO$_4^-$ and H$_2$PO$_4^-$ anions, Wieckowski et al.$^{58}$ reported that the rate of the reaction is highly dependent on the relative strength of a particular anion to adsorb on to the electrode surface. Methanol oxidation reaction is highly dependent on the pH of the solution.$^{60}$ Tripkovic et al.$^{57,60,61}$ has reported that in aqueous alkaline solutions, bicarbonate and carbonate ions affect the adsorption of hydroxide ions on to the electrode in corresponding electrolytes.

The Figure 2.1 that we discussed earlier showed a shift in the OH$_{ad}$ formation region in the carbonate–based electrolyte. Clearly the onset potential of the MOR at the Pt/AEM-CO$_3^{2-}$ appears well below the onset of the Pt-OH formation potential. The Tafel parameters of 314 mV dec$^{-1}$ and 249 mV dec$^{-1}$ obtained for the MOR at Pt/201-CO$_3^{2-}$ and Pt/901-CO$_3^{2-}$ respectively (Figure 2.8), also perfectly reflects that the MOR mechanism in AEM-CO$_3^{2-}$ has changed.

$$CH_3OH + 3CO_3^{2-} \rightarrow 4CO_2 + 2H_2O + 6e$$ [2.9]

Therefore it is safe to say that the MOR proceeds through the carbonate pathway as shown in equation 2.9.

*Methanol transport in the membrane:–* Methanol permeation through alkaline anion exchange membranes have been assessed by several research groups using different strategies. In this study, we have equilibrated the anion exchange membrane with 1M methanol solution at the beginning. Therefore, methanol flow in and out of the solid state cell does not have a significant effect on the local methanol concentration in the membrane.$^{62}$ Chronoamperometric current–time
transients were obtained by stepping the electrode potential from 0.4 V to 0.8 V. In this way the overall methanol permeation through the AEM has been evaluated.

**Figure 2.8:** a) Comparison of kinetic parameters for MOR at the Pt/A201 interface, 293K, 1 M MeOH - Tafel plots, b) Comparison of kinetic parameters for MOR at the Pt/A901 interface, 293K, 1M MeOH - Tafel plots.
It should be noted that this is different from the methanol crossover which is typically been discussed pertaining to direct methanol fuel-cells. Efficient methanol permeation parallel to the electrode is in fact important for the better operation of methanol fuel cells. Methanol permeation calculated here is an intrinsic property which is not determined by the thickness of the membrane.

![Cottrell plots for the MOR calculated from current-time transients at 0.8V (potential jump from 0.4V to 0.8 V).](image)

**Figure 2.9:** Cottrell plots for the MOR calculated from current-time transients at 0.8V (potential jump from 0.4V to 0.8 V).

Transport parameters of methanol shown in Table 2.6 suggest that the methanol solubility is independent of the IEC and the pH of the membrane. The polar methanol molecules are dissolved in the aqueous phase of the membrane. Therefore high ionic capacity of AEMs predicts better methanol solubility. However the absorbed water swells the membrane and increases the overall volume of the membrane which offsets the increased methanol content. This
is consistent of the above observation of the trend in methanol solubility in membranes with different IECs.

**Table 2.6: Mass transport characteristics of Methanol in the AEM**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Diffusion coefficient (D) (10^6) (cm(^2) s(^{-1}))</th>
<th>Solubility (C) (10^6) (mol cm(^{-3}))</th>
<th>Permeability (DC) (10^{12}) (mol cm(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A201-OH(^-)</td>
<td>22.4</td>
<td>1.19</td>
<td>26.7</td>
</tr>
<tr>
<td>A201-CO(_3)^{2-})</td>
<td>0.61</td>
<td>1.22</td>
<td>0.74</td>
</tr>
<tr>
<td>A901-OH(^-)</td>
<td>17.0</td>
<td>1.81</td>
<td>30.8</td>
</tr>
<tr>
<td>A901-CO(_3)^{2-})</td>
<td>0.41</td>
<td>1.93</td>
<td>0.79</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>8.0</td>
<td>1.92</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Table 2.6 shows the calculated methanol diffusion coefficients of the membranes. Diffusion of methanol in the AEM is determined by several factors. Methanol diffusion takes place inside the polymer micro-channels hence the expanded aqueous phase in AEMs is favorable for its diffusivity. This is clearly reflected by better diffusivity of methanol in AEM-OH\(^-\) compared to that in Nafion. Since the ion exchange capacity of the membrane is not influenced by the carbonate exchange the deprived methanol diffusivity in AEM-CO\(_3\)^{2-}\) is surprising.

As we have discussed in the section of hydrogen mass transport, the doubly charged carbonate ions will strongly ion pair with the quaternary ammonium cationic sites. This in turn will create a methanol diffusion path around the bulky ion pairs. Also the carbonate ions would interact with multiple quaternary ammonium sites which will greatly hinder the mobility of the methanol molecules.
2.4. Conclusion

Mass transport and kinetic parameters for the oxygen reduction at a Pt microelectrode/Tokuyama®A201 (AEM) membrane interface was determined using linear sweep voltammetry and chronoamperometry at 298 K and 1 atm for membranes in hydroxide and carbonate forms and compared with corresponding values for a perfluorinated membrane (Nafion®). Compared with Nafion®, the AEM in both the $\text{OH}^-$ as well as those exchanged with $\text{CO}_3^{2-}$ showed similar ORR kinetics at 0.9 V (RHE) and exchange current at the low current density ($\text{lcd}$) region. Comparison of exchange current densities at high current density ($\text{hcd}$) region showed the effects of higher mass transport in the AEMs, especially when exchanged with $\text{CO}_3^{2-}$.

Higher oxygen diffusion in AEM ($\text{OH}^-$ form) compared with Nafion® was explained by the higher ion exchange capacity and hence concomitantly higher water content in the AEM. Exchange with $\text{CO}_3^{2-}$ shows a marked lowering of the $\text{O}_2$ diffusion coefficient, which was ascribed to steric and electrostatic of carbonate exchanged polymer microchannels. Oxygen solubility in AEM is mainly a function of its hydrocarbon backbone chemistry (as opposed to Teflon in the case of Nafion®) and higher water content (higher IEC). Comparison with a similar IEC proton conducting membrane, however, indicated that the solubility value obtained was lower for this AEM than that in an analogous proton exchange membrane containing a hydrocarbon backbone (Table 2.2) with a similar IEC. While no clear explanation is forthcoming at the moment, such differences arise as a result of different phase separation based on the ion exchange site and overall polymer chemistry. The principle effect of carbonate exchange on the oxygen transport was the significant (one order of magnitude) lowering of diffusion coefficient, while the solubility remained unaffected, thus resulting in a concomitant one order of magnitude lowering of the overall permeability.
The presence of carbonate ions (in the aqueous region of the membrane) did not affect the $D_{\text{H}_2}$, as the hydrogen diffusion took place mainly through the hydrophobic interfacial region. However, hydrogen solubility was greatly reduced. Significantly low HOR kinetics were observed at the Pt/AEM-CO$_3^{2-}$, which was attributed to the HOR proceeding through the carbonate pathway.

Methanol transport in AEM-OH$^-$ is better compared to the proton exchange membranes, as the high water content in AEMs increases the pore sizes which facilitate diffusion of molecules in the aqueous region. Decreased methanol diffusion in the anion exchange membrane in the carbonate form is explained by the strong ion pairing between the doubly charged carbonate ions with the quaternary ammonium species: which causes methanol molecules to diffuse around the bulky ion pairs (increasing the diffusion path length). Decrease in methanol oxidation kinetics observed confirmed that the MOR proceeds through the carbonate pathway in the AEM-CO$_3^{2-}$ electrolyte. The effect of such a significant lowering of mass transport in carbonate exchanged membranes is also observed in the fuel cell polarization curves obtained for the AEMFCs (Figure 2.4). The performance of AEMFC cathode side can be improved by means of efficient mass transport through the ionomer in the reaction layer. While avoiding carbonate and to a certain extent even bicarbonate exchange in the membrane cannot be prevented in a practical fuel cell, more careful consideration of solute transport in such varying ion exchanged moieties are needed. In addition, robust polymers enabling higher temperature operation (i.e., up to 80°C) would provide some much needed respite.
Chapter 3
Microelectrode Investigations of the Oxygen Electrode in Dimethyl Sulfoxide-based Electrolytes Lithium-Oxygen Batteries

3.1. Introduction

Li-air batteries, composed of Li metal anodes and oxygen cathodes in combination with non-aqueous electrolytes, have the potential to deliver practical rechargeable batteries with up to ten times more energy density than Li-ion batteries.\textsuperscript{63, 64} However, the reactivity of the oxygen reduction reaction (ORR) products LiO\textsubscript{2} and Li\textsubscript{2}O\textsubscript{2} towards the organic solvents used for electrolytes, and the irreversibility of the ORR processes remain as deterrents to these batteries from becoming practical systems.\textsuperscript{19, 22, 30, 65} Although significant progress has been made in elucidating the redox chemistry of oxygen in non-aqueous Li-air batteries,\textsuperscript{19, 22, 30, 32} a full understanding of the factors affecting the oxygen electrode processes, particularly the ability to delineate mass transport contributions from electron transfer kinetics, is still lacking. In this regard, microelectrodes can provide information that cannot be obtained with the use of the traditional macroelectrodes employed in most ORR investigations.

Electrochemical data gathered using microelectrodes can be used to distinguish reactions controlled by mass transport from those dominated by electrode kinetics. In ideal cases, current-voltage data for an electrochemical process on a microelectrode exhibits limiting currents if there is no inhibition of mass transport. Deviation of the current-voltage response from this behavior is an indication of possible mass transport limitations in the electrode reaction arising from a variety of sources. Poor solubility or high viscosity of the reaction products is a root cause. Another factor is the loss of effective electrode area by passivation films that hinder electrode activity thereby reducing the limiting current even at sufficiently high overpotentials. Finally, if the reaction involves anionic reactants, at voltages sufficiently
negative than the potential of zero charge of the electrode, the electrode can exert an electrostatic repulsion on negatively charged species.\textsuperscript{66} In such cases, the electrode will produce a non-steady state, peak-shaped, response instead of the limiting current behavior.

Charging currents are close to zero on microelectrodes and, as a result, accurate electrode responses can be obtained even at high scan rates which is especially important to investigate fast electrode reactions followed by chemical dissociation of the products as observed in Li-air batteries.\textsuperscript{33} Furthermore, microelectrodes are useful for studying very small volumes of electrolyte and since the reactions occur at homogeneous local physical environments, the current normalized on the electrode can give an accurate picture of the electrolyte/electrode interface behavior. Finally, microelectrode array systems can be used to experimentally characterize the site-dependent electrochemistry of a cathode catalyst which is relevant to ORR in non-aqueous Li-air batteries.

Previous studies\textsuperscript{65} have revealed that many organic carbonate solvents are unstable in the presence of the ORR intermediate superoxide, \( \text{O}_2^- \). Relatively stable solvents for use in Li-air batteries include ethers such as dimethoxy ethane (DME) and tetraethylene glycol dimethyl ether (TEGDME), organic sulfoxides and sulfones typified by dimethyl sulfoxide (DMSO), and ionic liquids exemplified by 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-methyl-1-butyl-pyrrolidinium bis-(trifluoromethanesulfonyl)imide (PYRTFSI)\textsuperscript{67}. In this chapter, we report on a detailed study of the use of microelectrodes for elucidating the influence of a series of ion-conducting salts on ORR in dimethyl sulfoxide-based electrolytes. Our results of the current-voltage response of the microelectrode in DMSO-based electrolytes reveal that the cation of the ion-conducting salt in the electrolyte plays a significant role on the properties of the ORR products. Detailed
analysis of the microelectrode response has also shown that the triflate anion may have a positive influence on the stability and solubility of the ORR products in LiCF$_3$SO$_3$ solutions leading to the most favorable ORR kinetics. We demonstrate that the microelectrode can be used as a diagnostic tool to select and optimize the properties of electrolytes for use in non-aqueous Li-air batteries, and to elucidate the influence of different ion-conducting salts on oxygen redox reaction mechanisms.

3.2. Experimental

3.2.1. Materials

All lithium salts (lithium hexafluorophosphate, lithium perchlorate, lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonyl)imide and tetrabutylammonium salts (tetrabutylammonium hexafluorophosphate, tetrabutylammonium perchlorate, tetrabutylammonium trifluoromethanesulfonate, tetrabutylammonium bis(trifluoromethanesulfonfyl)imide ) and anhydrous grade solvents used in this study were purchased from Sigma-Aldrich and stored in an M-Braun glove box maintained under 1 ppm humidity level. Silver wires and 99.9% lithium foil were purchased from Alfa Aesar. The electrochemical half-cell employed a Pt mesh counter electrode, 11μm diameter glassy carbon working electrode and a Ag/Ag$^+$ reference electrode. This reference electrode was constructed as reported by Wain et al.$^{68}$ The Ag/Ag$^+$ reference electrode potential with respect to the Li/Li$^+$ reference electrode was determined by measuring the potential difference between a clean Li foil and the Ag/Ag$^+$ reference electrode immersed in the same electrolyte. This value was found to be 3.62 V in all electrolytes. All the data gathered on the carbon microelectrode are normalized to its geometric area experimentally determined using the ferrocene oxidation current in DMSO. Potential step chronoamperometric transients for ORR were recorded in
tetrabutylammonium (TBA\(^+\))-based electrolyte solutions at the 11 \(\mu\)m carbon microdisc electrode. Cyclic voltammetric responses were recorded in all Li\(^+\) and TBA-based electrolytes at scan rates up to 1000 mV s\(^{-1}\). Supplementary electrochemical experiments for supporting the microelectrode analyses were carried out on glassy carbon disc electrode (diameter = 0.59 cm). In order to characterize the ORR products, they were electro-deposited on a removable tip glassy carbon disc electrode by holding the electrode at a high enough over-potential for 60 min in O\(_2\) saturated Li\(^+\)/DMSO and TBA\(^+\)/DMSO electrolytes. The products were analyzed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDAX). Raman spectra were obtained for carbon cloth electrodes potentiostated for 5 hr periods at 2.12 V and 2.32 V, respectively, in O\(_2\) purged LiPF\(_6\)/DMSO electrolyte. Conductivities of the electrolytes of interest were measured using a Thermo-Orion™ conductivity cell and a Thermo-Orion™ conductivity meter. Kinematic viscosities of the solutions were recorded at 20ºC using an Ubbelohde Viscometer (C-545). FT-IR spectra were recorded for all four electrolytes on a Bruker ATR Infra-red spectrometer.

3.3. **Results and Discussion**

3.3.1. Validation of the Experimental Approach and Determination of the Microelectrode Radius

Oxidation of ferrocene to ferrocenium ions is a one-electron reaction and the diffusion coefficient (\(D\)) of ferrocene calculated by Janisch et al. for a 0.1-1.5 mM ferrocene solution in DMSO is \(4.4\times10^{-6}\) cm\(^2\) s\(^{-1}\).\(^{35}\) Using this \(D\) and the limiting current in the 2.58 mM ferrocene solution (Figure 1.9), the radius of the carbon microelectrode was calculated from equation 3.1 to be 5.54 \(\mu\)m.
When the microelectrode potential is stepped from a potential where no reaction occurs to a potential where the reaction is diffusion limited, at small times after polarization the diffusion limited current at a microelectrode is given by equation 3.2.\textsuperscript{34,49}

\[ I = \frac{nFAD^2C}{\pi^2t^2} + n\pi FDCr \]  \hspace{1cm} [3.2]

The diffusion coefficient and solubility of a reactive intermediate in the electrolyte can be calculated from the slope and the intercept of \( I \) vs. \( i^{1/2} \) curve.\textsuperscript{34} Chronoamperometric transitions obtained by stepping the electrode potential from 3.62 V to 4.12 V were analyzed by the Cottrell plot (Figure 1.10). Diffusion coefficient of ferrocene in DMSO was calculated to be 4.16×10\(^{-6}\) cm\(^2\) s\(^{-1}\) and ferrocene solubility was found to be 2.95 mM for an electrode radius of 5.5 \(\mu\)m. This calculated diffusion coefficient is in good agreement with the values determined above and those reported by other groups.\textsuperscript{35} This validates the ability of our experimental approach for studying ORR on microelectrodes.

### 3.3.2. Kinetic Equation for the Reaction at the Microelectrode under Steady State Conditions

For a reaction in the form \( O + ne \rightleftharpoons R \), the steady state reversible current at the microelectrode is given by equation 3.3.

\[
  i^r = \left\{ \frac{i_t}{1 + \frac{D_e}{D_R} \exp \left[ \frac{nF(E - E^0)}{RT} \right]} \right\} 
\]  \hspace{1cm} [3.3]

\[
i_t = \frac{4nFADC}{\pi r} = 4nFDCr
\]  \hspace{1cm} [3.1]
This can be simplified to obtain equation 3.4, where \( E \) is the electrode potential, \( E^0 \) is the standard potential and \( i^r \) is the reversible current at the electrode\(^6\). \( D_O \) and \( D_R \) are diffusion coefficient of the oxidized and reduced species, respectively.

\[
E = E^0 + \frac{RT}{nF} \ln \frac{D_R}{D_O} + \frac{RT}{nF} \ln \left[ \frac{(i_t - i^r)}{i^r} \right] \quad [3.4]
\]

At \( i^r = i_t/2 \), the equation takes the form of 3.5, which allows us to calculate the diffusion coefficient of the (reduction) product, given that the \( D_O \) is known.

\[
n(E^0 - E_{1/2}) = \frac{RT}{F} \ln \frac{D_O}{D_R} \quad [3.5]
\]

The diffusion coefficient of ferrocenium ion calculated in this way is \( 3.26 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \).

3.3.3. Oxygen Reduction Reaction in Tetrabutyl Ammonium–based Electrolytes

It is well established in literature that the ORR in non-aqueous electrolytes containing tetrabutyl ammonium(TBA)–based salts is a reversible reaction which stops at the one electron reduction product – superoxide (equation 3.6).

\[
O_2 + TBA^+ + e^- \leftrightarrow TBA^+ - O_2^- \quad [3.6]
\]

Equation 3.7 takes the difference between the experimental system and the reversible system in order to account for any irreversibility in the former. We apply this idea to analyze quasi reversible reactions\(^7\) such as the lithium-oxygen system. The ORR in the TBA-based electrolyte is considered as a reversible system.
\[ E - E^0 = \left[ \frac{RT}{-nF(1 - \alpha)} \right] \ln \left( \frac{4D_R}{\pi k_s r} \right) - \left[ \frac{RT}{-nF(1 - \alpha)} \right] \ln \left( \frac{(i_t - i)}{i} - \frac{(i_t - i^r)}{i^r} \right) \]  

[3.7]

In the above equations \( k_s \) is heterogeneous rate constant and \( \alpha \) is the transfer coefficient of the reaction. Since the ORR electrochemistry in TBA salt/DMSO electrolyte is reversible, the experimental current in this system can be used as \( i^r \). Similarly, the steady state limiting current in TBA salt/DMSO solution can justifiably be taken to be \( i_t \) in the Li-oxygen system. With these assumptions, the slope of the plot of \( E - E^0 \) vs. \( \ln \left( \frac{(i_t - i)}{i} - \frac{(i_t - i^r)}{i^r} \right) \) allows us to calculate the transfer coefficient \( (\alpha) \) for the initial reduction \((n=1)\) of \( O_2 \).

3.3.4. Deviation of Microelectrode response from Classical Diffusion Limited Current

The various factors that can produce a non-steady state current-voltage response on a microelectrode are discussed in this section.

(1) *Passivation film formation:* As expected from equation 3.1, the current-voltage response will deviate from limiting current behavior if one of its parameters changes as the reaction proceeds. For example, insoluble reaction products deposited on the electrode surface will result in a change in the effective geometric radius with time. Furthermore, the diffusion coefficient of electroactive species (oxygen) through the film of insoluble products will be significantly lower. In such cases, the current response when measured as the potential is scanned, would take a peak type (akin to cyclic voltammogram on a macroelectrode) current-voltage profile.

(2) *Migration of charged reactants away from the electrode surface due to electrostatic repulsion:* In some instances, the flux of the electroactive species onto the electrode surface will not be purely diffusion controlled. For example, transport of anionic reactants to a negatively charged electrode will be decreased due to electrostatic repulsion by the negatively
charged electrode. Therefore, the limiting current will be potential dependent. White et al.\textsuperscript{66} described the migration-diffusion limited currents at a spherical microelectrode by taking a new term called “interaction energy” into consideration.

\[
A + e \rightarrow A^- \quad [3.8]
\]

\[
A^- + e \rightarrow A^{2-} \quad [3.9]
\]

For example consider equation 3.8; the neutral reactant giving negatively charged products would give the expected sigmoidal shaped voltammogram. However, as in equation 3.9 for a singly negative reactant giving a doubly negative product, the shape of the voltammogram can deviate from a sigmoidal shape as the electrode potential is scanned towards negative potentials with respect to the potential of zero charge (\(E_{pzc}\)). In our study, the reaction of an oxygen molecule going to superoxide represents the equation 3.8 and the superoxide ion reduction to peroxide ion is similar to the reaction in equation 3.9. In fact as presented below, we consider this behavior as one of the reasons for the non-steady state microelectrode ORR response in Li salt solutions in DMSO.

3.3.5. Oxygen Electrochemistry on Carbon Microelectrodes

We have investigated the ORR current-voltage response at the microelectrode in a series of tetrabutylammonium and lithium salts solutions in DMSO. The salts studied included MPF\textsubscript{6}, MCIO\textsubscript{4}, MCF\textsubscript{3}SO\textsubscript{3}, MN(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2} where M=TBA or Li. Distinct differences in the current-voltage profile attributable to the TBA\textsuperscript{+} and Li\textsuperscript{+} salt solutions were observed, providing valuable insights into the strong influence of cation on the ORR electrochemistry and the mechanism of ORR in these electrolyte solutions.
3.3.6. ORR in Tetrabutylammonium (TBA) Salt-based Electrolytes

Figures 3.1a and 3.1b show the voltammograms recorded on micro and macro electrodes, respectively, in oxygen-saturated solutions of 0.1 M TBAPF$_6$/DMSO. The limiting currents for oxygen reduction obtained for scan rates ranging from 50 to 1000 mV s$^{-1}$ are seen in Figure 3.1a. The ORR is a one-electron reversible reaction in TBAPF$_6$/DMSO electrolyte as determined from detailed analysis of the data in Figure 3.1b using the Randles-Sevcik relationship as done previously$^{22,32}$. As we have recently demonstrated through $^{13}$C NMR chemical shift and spin-lattice relaxation time (T1) data in propylene carbonate solutions, TBA$^+$ is a soft acid due to its low charge density.$^{71}$ Therefore, the TBA$^+$ interaction with the soft base O$_2^-$, the one-electron reduction product of O$_2$, is sufficiently strong to spare it from further reduction$^{22,32}$ at lower potentials. The nearly ideal limiting current behavior displayed in Figure 3.1a for a series of sweep rates indicates that the microelectrode surface is not modified by insoluble ORR products in TBA/DMSO electrolytes. The superoxide reduction product is apparently highly soluble in the electrolyte.
Figure 3.1: Current-voltage behavior observed in O$_2$ purged 0.1 M TBAPF$_6$/DMSO electrolyte at a): carbon microelectrode b): glassy carbon macroelectrode.
Similar ORR limiting currents were observed in 0.1 M TBAPF$_6$, TBAClO$_4$, TBACF$_3$SO$_3$, TBAN(CF$_3$SO$_2$)$_2$ in DMSO (Figure 3.2a). This suggests that the electrode process is primarily controlled by the TBA$^+$ cation with minimal influence of the anion on the ORR mechanism. Current-time transients obtained by stepping the electrode potential from 3.62 V to 1.62 V were analyzed using the Cottrell equation as shown in Figure 3.2b. The oxygen diffusion coefficient and solubility in TBAPF$_6$/DMSO calculated from these data were found to be $2.2 \times 10^{-5}$ cm$^2$ s$^{-1}$ and $2.79 \times 10^{-6}$ mol cm$^{-3}$, respectively.
Figure 3.2: a): Oxygen reduction reaction on the microelectrode in 0.1 M TBA salts in DMSO at 50 mV s\(^{-1}\). b): Cottrell plots calculated for the current time transients obtained by potential jump chronoamperometry experiments on the microelectrode in different TBA salt solutions in DMSO.
Table 3.1: Oxygen transport parameters in TBAX electrolytes

<table>
<thead>
<tr>
<th>Salt</th>
<th>O₂ Diffusion coefficient (cm² s⁻¹)</th>
<th>O₂ Solubility (mol cm⁻³)</th>
<th>O₂ Permeability (mol cm⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAPF₆</td>
<td>2.2 x 10⁻⁵</td>
<td>2.79 x 10⁻⁶</td>
<td>6.14 x 10⁻¹¹</td>
</tr>
<tr>
<td>TBACIO₄</td>
<td>2.3 x 10⁻⁵</td>
<td>2.92 x 10⁻⁶</td>
<td>6.72 x 10⁻¹¹</td>
</tr>
<tr>
<td>TBACF₃SO₃</td>
<td>1.8 x 10⁻⁵</td>
<td>3.89 x 10⁻⁶</td>
<td>7.00 x 10⁻¹¹</td>
</tr>
<tr>
<td>TBAN(CF₃SO₂)₂</td>
<td>4.7 x 10⁻⁵</td>
<td>1.43 x 10⁻⁶</td>
<td>6.72 x 10⁻¹¹</td>
</tr>
</tbody>
</table>

Table 3.2: Superoxide Diffusivities in TBAX electrolytes

<table>
<thead>
<tr>
<th>Salt</th>
<th>E₁/₂ (V)</th>
<th>Superoxide Diffusion coefficient (cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAPF₆</td>
<td>2.48</td>
<td>3.60 x 10⁻⁷</td>
</tr>
<tr>
<td>TBACIO₄</td>
<td>2.55</td>
<td>4.68 x 10⁻⁶</td>
</tr>
<tr>
<td>TBACF₃SO₃</td>
<td>2.53</td>
<td>1.65 x 10⁻⁶</td>
</tr>
<tr>
<td>TBAN(CF₃SO₂)₂</td>
<td>2.53</td>
<td>4.31 x 10⁻⁶</td>
</tr>
</tbody>
</table>

The mass transport parameters presented in Table 3.1 show similar oxygen diffusivities in TBA⁺ salt solutions with PF₆⁻, ClO₄⁻ and CF₃SO₃⁻ anions, whereas in the N(CF₃SO₂)₂⁻-containing salt solution this value is slightly higher. In general, the data in Table 3.1 are in good agreement with those reported previously determined using macroelectrodes. The oxygen permeability represents the product of oxygen diffusion coefficient and its solubility and is a useful parameter for Li-O₂ cell modeling. Superoxide diffusion coefficients calculated using half wave potentials (equation 3.5) are also shown. The $D_{O₂}^-$ values are significantly lower than $D_{O₂}$ calculated for the different electrolyte systems. Strong ion pairing between the superoxide ion and the bulky TBA⁺ ions seems to decrease the diffusivity of O₂⁻ in these electrolytes. In an attempt to explain the observed trend in oxygen diffusion coefficient seen in Table 3.1 and 3.2, we measured the physical properties of the electrolytes of interest and are depicted in Table 3.4. The anion donor numbers previously calculated in dichloroethane solutions are also present in this table. Perchlorate-based electrolytes have the highest conductivities whereas the bis(trifluoromethanesulfonyl)imide solutions exhibit the lowest
conductivities probably due to the low mobility of this large anion. However the conductivity differences are small. The slightly higher $O_2$ diffusion coefficient seen in the TBAN(CF$_3$SO$_2$)$_2$ solution in Table 3.1 does not appear to be due to viscosity effects but rather it may be associated with the lower $O_2$ solubility.

3.3.7. ORR in Lithium Ion-containing Electrolytes

Figure 3.3b displays the scan rate dependent current-voltage curves obtained on the microelectrode in oxygen saturated 0.1 M LiPF$_6$ in DMSO. The current reached its maximum at around 2.5 V (at 50 mV s$^{-1}$) and started to decrease at lower potentials. Most interestingly, the current-voltage curve has the appearance of a cyclic voltammogram. There was no sigmoidal shaped limiting current behavior as observed for $O_2$ in TBA salt-containing solutions. Considering that ORR limiting currents are observed in TBA$^+$/DMSO electrolytes, clearly this behavior are not arising from oxygen mass transport limitation in the electrolyte. On the contrary, it probably arises either from the passivation of the electrode by the deposition of insoluble lithium oxides on the electrode surface or due to limited reactant transport, which is not purely diffusion controlled. Any insoluble products formed on the electrode would block enough $O_2$ from reaching the electrode surface to maintain a limiting current. In this context, it is useful to recall that previous studies on macroelectrodes have shown that in presence of small cations like Li$^+$ and Na$^+$, ORR becomes less reversible$^{22, 32}$ probably due to the precipitation of the corresponding peroxide and monoxide on the electrodes.
Figure 3.3: Current-voltage characteristics at the carbon microelectrode for O₂ purged 0.1 M LiPF₆/DMSO recorded: a) at scan rates ranging from 50-1000 mV s⁻¹, b) at various potential windows, c) Oxygen reduction half-cycle in 0.1M LiPF₆/DMSO to passivate the electrode for the test in d, d) ORR currents obtained in 0.1M TBAPF₆/DMSO on the electrode after the oxygen reduction half-cycle in 0.1M LiPF₆/DMSO as shown in c.

Figure 3.3a shows current-voltage behavior obtained on microelectrodes in O₂-purged LiPF₆/DMSO electrolyte, for various cathodic limits. A small anodic peak was observed when the cathodic potential was limited half-way through the first reduction peak. The peak separation between the cathodic and anodic peaks in this case was much higher than 59 mV suggesting that the anodic peak is not arising from superoxide oxidation. The multiple anodic peaks and the large peak separation are similar to those observed by Cormac et al.²² for the
ORR at a glassy carbon disc electrode and supports the view of electrochemical reduction of $O_2$ followed by chemical decomposition, as displayed in equations 3.10 and 3.11.

As an attempt to quantify the passivation of the microelectrode in Li$^+$ salt solutions after ORR, we have recorded ORR currents on this same microelectrode in TBAPF$_6$ solutions after they have been removed from the ORR in Li$^+$-containing solutions. Newman et al.\textsuperscript{75} have reported that ferrocene oxidation limiting currents can be used as a measure of the amount of passivation at the electrode from solid electrolyte interphase (SEI) formation in lithium ion battery electrolytes. However, our attempts to use ferrocene oxidation as a measure of the extent of passivation due to ORR on the carbon microelectrode revealed that the bulky ferrocene molecules can overestimate the electrode area passivation. Consequently, we used ORR in the TBAPF$_6$/DMSO solution to determine passivation in Li salt solutions. In this method involving the reduction of oxygen in a TBA salt solution to measure the extent of electrode passivation from ORR in Li salt solutions, the small oxygen molecules can still penetrate through the pores of any oxide film on the electrode, and give a fair estimate of the extent of passivation from ORR in Li salt solutions. Figure 3.3d shows the ORR current plateau obtained in a TBAPF$_6$/DMSO solution after an ORR run in 0.1M LiPF$_6$/DMSO. Surprisingly, the extent of passivation is small and insufficient to cause the bell shaped CV response observed in figure 3.3b. Therefore, the most probable explanation for the peak-shaped current-voltage response is the migration-diffusion controlled reaction that occurs at the microelectrode\textsuperscript{66} as discussed earlier.

The reduction of $O_2$ to $O_2^-$ in either TBA or Li salt solutions (equation 3.10) does not involve a charged reactant which can be repelled from the negatively charged electrode. In TBA salt solutions the superoxide is highly stabilized and a second reduction to peroxide does
not occur at low overpotentials. On the other hand, the superoxide reduction to peroxide ions (equation 3.12) is favored in Li\(^+\) solutions and it starts at a rather low overpotential. However, the negatively charged superoxide ions as soon as they are formed are repelled away from the negatively charged microelectrode surface (in accordance with equation 3.9 and related discussion earlier) which depletes superoxide concentration below that necessary for the limiting current behavior. In other words, the peak shaped voltammograms in the Li\(^+\) salt solutions appear to arise mainly from mass transport limitations of the superoxide reactant necessary for superoxide reduction to peroxide at the carbon microelectrode. This conclusion is in agreement with the observed large separation between anodic and cathodic peaks. The superoxide oxidation peaks are not visible on a microelectrode due to (1) efficient removal of the soluble products by the large concentration gradient and (2) due to migration away from the electrode surface by electratstatic repulsion during the negative scan (Figure 3.3a).

3.3.8. ORR Product Analysis

Scanning electron microscopy (SEM) images recorded on the electrode surface after holding the glassy carbon electrode at 2.42 V for 60 min are displayed in Figure 3.4. The image on the electrode after ORR in TBA\(^+\)/DMSO looks similar to the pristine glassy carbon surface whereas the electrode surface after ORR in the presence of Li\(^+\) ions has crystalline product deposits. Energy dispersive spectra (EDAX) were used to characterize this crystalline material detected by SEM images. The oxygen in the passivation product on the microelectrode surface is about 10 atomic percent of the total elements which is consistent with the presence of a lithium oxide layer formed on the electrode surface during the ORR. Raman spectra obtained for a carbon cloth electrode after potential hold at 2.32 V and 2.12 V are displayed in Figure 3.5. The lithium oxide products formed were Li\(_2\)O\(_2\) at 2.32 V (Figure 3.5a)
Figure 3.4: SEM micrographs of the glassy carbon electrode surface, (a) pristine electrode, (b) after ORR in TBA+/DMSO, (c) after ORR in Li+/DMSO, d) EDAX analysis of electrode surface after ORR in Li+/DMSO. Images on the right show the corresponding elemental compositions of the electrode

and Li₂O at 2.12 V (Figure 3.5b). The peak at 1088 cm⁻¹ in Figure 3.5a indicates that some Li₂CO₃ is also formed at 2.32 V, produced presumably by the reaction of the Li₂O with
atmospheric CO₂ during spectral recording. XRD spectra recorded on Li-O₂ cell cathodes after discharge also showed crystalline Li₂O₂. The formation of Li₂O₂ as the sole product in Li-O₂ cells is due to the potential control of the cell under constant oxygen pressure in the cell.

**Figure 3.5:** Raman spectra of the oxygen reduction products formed on the carbon electrode; potential hold at a) 2.32 V, b) 2.12 V, each versus Li/Li⁺ for 5hrs. Raman spectra for pure reference samples are given in the upper panel

3.3.9. Irreversibility of Oxygen Reduction Reaction in Lithium Salt Solutions

The electrochemically irreversible nature of the oxygen reduction reaction in the Li⁺ electrolytes in comparison to ORR in TBA⁺ electrolytes can be explained by the hard soft acid
base (HSAB) concept we previously advanced. Small cations like Li⁺ possessing high charge densities are strong Lewis acids. Superoxide being a soft Lewis base, LiO₂ is unstable and undergoes chemical decomposition/electrochemical reduction to the more stable Li₂O₂ which is deposited on the electrode surface. At lower potentials, the Li₂O₂ is reduced to Li₂O and appears as the sole product as evidenced by the Raman spectra discussed earlier. These data unequivocally confirm the four-electron reduction of O₂ in DMSO-containing Li salts. The various ORR processes in Li⁺ salt solutions are depicted in equations 3.10 – 3.13.

\[ Li^+ + O_2 + e \rightarrow LiO_2 \]  \[ 3.10 \]

\[ 2LiO_2 \rightarrow Li_2O_2 + O_2 \]  \[ \text{chemical} \]  \[ 3.11 \]

\[ LiO_2 + Li^+ + e \rightarrow Li_2O_2 \]  \[ 3.12 \]

\[ Li_2O_2 + 2Li^+ + 2e \rightarrow 2Li_2O \]  \[ 3.13 \]

3.3.10. The Role of the Li Salt Anion on ORR

Current voltage characteristics recorded for oxygen purged LiCF₃SO₃, LiClO₄ and LiN(CF₃SO₂)₂ electrolytes in DMSO are shown in Figure 3.6. Similar to the ORR voltammograms observed in LiPF₆/DMSO electrolyte, potential dependent (bell shaped) mass transport limited currents were observed in all cases. In contrast to the second reduction reaction (O₂⁻ → O₂⁻) observed at higher potentials (lower over-potentials) in all electrolytes, there was a significant difference in the magnitude of oxidation peaks observed in different salt solutions.
Figure 3.6: Current-voltage characteristics at the carbon microelectrode obtained for O₂ purged solutions of a) 0.1M LiClO₄/DMSO, b) 0.1M LiN(CF₃SO₂)₂/DMSO, c) 0.1M LiCF₃SO₂/DMSO electrolytes, d) ORR at the Planar GC macroelectrode

We have calculated the Columbic efficiencies of the OER/ORR reaction (i.e.; capacity of OER divided by ORR) in each electrolyte and they are listed as a function of potential sweep rate in Table 3.3. Columbic efficiency is a measure of the amount of insoluble product deposited on the microelectrode since there is minimal contribution from the soluble products accumulated in the double layer as compared to a planer macrodisc electrode.

On a microelectrode, soluble ORR products diffuse away and are not available for oxidation at the scan rates used here. Then, the oxidation currents observed are for the insoluble products that remain on the electrode surface from the ORR. When the total
capacities involved in the ORR processes in the different electrolytes are of the same magnitude, the difference in the columbic efficiencies can be attributed to the differences in the solubility of the reduction products; the higher the solubility of the reduction products, the lower is the columbic efficiency. As shown in Figure 3.6, the ORR peak currents and the total charge involved in these electrolytes are very similar in the first cycle.

Scan rate dependence of ORR voltammograms in the presence of lithium ions can be explained by the comparison of the rates of superoxide reduction both chemically and electrochemically. At low potential sweeps (1) chemical decomposition of lithium superoxide to lithium peroxide will occur near the electrode, and (2) more peroxides will start to form from the electrochemical reduction of superoxide at higher potentials. Both of these effects lead to instantaneous reduction of the surface activity of the electrode through passivation which in turn leads to low reduction currents. Therefore, an increase in columbic efficiency of ORR by decreasing scan rate is expected if passivation film formation was the major contributor to columbic efficiency.

Comparison of the Columbic efficiencies (OER/ORR) at scan rates of 200 mV s\(^{-1}\) or higher shows that of the four electrolytes, the ORR in the LiCF\(_3\)SO\(_3\)/DMSO has considerably lower columbic efficiency for OER at all scan rates. The observed trend in columbic efficiencies listed in Table 3.3 is consistent with product solubility with time since the ORR capacities involved are very similar for all salts. In support of this view, we found that the SEM of the microelectrode surface after the ORR showed much less products in the LiCF\(_3\)SO\(_3\)/DMSO electrolyte than in LiPF\(_6\)/DMSO. Solubility of Li\(_2\)O\(_2\) in a solvent is determined by the solvation energy of its Li\(^+\) cation compared to the lattice energy of this oxide. In the presence of an abundance of DMSO molecules as in a 0.1 M Li salt solution, it is
less likely that the Li$^+$ solvation energies of the electrolytes are significantly different. Therefore, the observed low Li$_2$O$_2$ precipitation (higher solubility) in LiCF$_3$SO$_3$/DMSO solution is accounted for by the relative strengths of ion pairing, which will be discussed momentarily. Figure 3.6d shows voltammograms obtained at a planar glassy carbon macrodisc. It is clearly observed that in LiCF$_3$SO$_3$/DMSO, the second reduction peak appears at a lower potential than that observed in the rest of the electrolytes of interest.

**Table 3.3**: Columbic efficiencies for OER/ORR (OER divided by ORR) processes in the presence of Li$^+$ ions

<table>
<thead>
<tr>
<th>Salt</th>
<th>Coulombic efficiency at a scan rate of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000 mV s$^{-1}$</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>46.7%</td>
</tr>
<tr>
<td>LiClO$_4$</td>
<td>50.1%</td>
</tr>
<tr>
<td>LiCF$_3$SO$_3$</td>
<td>16.5%</td>
</tr>
<tr>
<td>LiN(CF$_3$SO$_2$)$_2$</td>
<td>40.0%</td>
</tr>
</tbody>
</table>

Continuous cycling of the potentials in the cathodic and anodic directions as shown in Figure 3.7 (carried out in 0.1 M LiPF$_6$/DMSO, and LiCF$_3$SO$_3$/DMSO electrolytes) showed data consistent with the above conclusion. The anodic limit in these scans was restricted to 3.4 V to allow the ORR lithium oxide products to accumulate on the electrode surface without being oxidized at higher potentials. While similar ORR currents were seen in the first cycle, the ORR current reduction through the 40$^{th}$ scan in LiCF$_3$SO$_3$/DMSO electrolyte was significantly less and comparable to the reduction current observed in LiPF$_6$/DMSO through just the 10th scan. This suggests that there is less precipitation of the ORR products on the electrode in LiCF$_3$SO$_3$-containing electrolyte. The higher solubility of the ORR products at least in part may explain the better rechargeability previously observed for Li-air cells utilizing LiCF$_3$SO$_3$-based electrolytes.$^{76}$
Figure 3.7: Continuous cycling of potential in O₂ saturated a) LiCF₃SO₃/DMSO and b) LiPF₆/DMSO electrolytes at 100 mV s⁻¹.

3.3.11. FT-IR Evidence for Ion Pair Formation

FT-IR spectra recorded in LiPF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂ salts in DMSO are shown in Figure 3.8. The spectrum of neat DMSO showed an intense band consisting of two shoulders at 1050 cm⁻¹. The peak at 1045 cm⁻¹ was assigned to the symmetric stretching vibration of the S=O group whereas the shoulder at 1022 cm⁻¹ was assigned to rocking vibrations of the methyl groups. Appearance of a new peak at 1028 cm⁻¹ with increasing concentration of LiPF₆ salt
suggests ion pairing between DMSO and lithium ions (Figure 3.8a). A similar trend was observed in the presence of both LiN(CF₃SO₂)₂⁻ and LiCF₃SO₃ in DMSO. Symmetric stretching vibrations, νₚₛ of free CF₃SO₃⁻ ions appear at 1031 cm⁻¹. This new peak leaned towards lower frequencies with the increasing triflate ion concentration, indicating ion pair formation between the S=O of CF₃SO₃⁻ and Li⁺ ions. Asymmetric stretching vibrations (νₚₘ) of free triflate ion appear at 1270 cm⁻¹. When the triflate ions are coordinated with small cations such as Li⁺, this peak splits into two peaks, which appears slightly below and above the νₚₘ arising from the free ion. In higher donor number solvents such as DMSO, peaks arising from Li⁺ ion paired triflate may not be clearly visible. However, with the increasing concentration of triflate ions, νₚₛ of free triflate ions shifted towards a lower frequency (Figure 3.8b inset). It has been reported that the FT-IR peaks arising from Li⁺-triflate aggregates appear at 1062 cm⁻¹. We can conclude from these data that as the salt concentration increases the triflate ions form ion pairs and aggregates with the Li⁺ in the corresponding electrolyte solution. Surprisingly this lowering of νₚₘ was not observed (Figure 3.8c) in the νₚₘ peaks from the S=O of N(CF₃SO₂)₂⁻ ions (νₚₘ = 1352 cm⁻¹). This is explained below in Figure 3.9, in relation to the ability of contact ion pair formation between Li⁺ and the anions in these electrolytes.
Figure 3.8: FT-IR spectra of DMSO-Lithium salt solutions. (a) LiPF$_6$-DMSO, (b) Li CF$_3$SO$_3$-DMSO, (c) LiN(CF$_3$SO$_2$)$_2$-DMSO.
3.3.12. Lithium Ion-Anion Ion Pair Formation

The trend in the rechargeability of the oxygen half-cell observed above can be explained from the Lewis basicity of the salt anions, which determines the strength of ion pairs formed with the Li⁺ cation. First of all, it is important to consider the impact of the solvent molecules themselves on the basicity of the Li⁺ ion. Solvation energy for the adduct formation between Li⁺ and DMSO can be calculated using the formula in equation 3.14, developed by Drago et al.⁷⁷

\[-\Delta H = E_A E_B + C_A C_B + R_A T_B\]  \hspace{1cm} [3.14]

In equation 3.14, \(\Delta H\) is the enthalpy (in kcal/mole) of formation of a Lewis acid-base adduct, \(E_A\), \(C_A\) and \(R_A\) are parameters characteristic of the acid (Li⁺ here), and \(E_B\), \(C_B\) and \(T_B\) are parameters characteristic of the base. These parameters for Li⁺ are \(E_A = 11.72\), \(C_A = 1.45\) and \(R_A = 24.21\) and these for \((\text{CH}_3)_2\text{SO}\) are \(E_B = 2.4\), \(C_B = 1.47\), and \(T_B = 0.65\) all values in kcal/mole.⁷⁷ The enthalpy of formation calculated for a 1:1 adduct between Li⁺ and DMSO is 46.00 kcal/mole whereas that for Li⁺ and CH₃CN is 40.34, about 12% lower. A similar trend should follow for adducts of Li⁺ formed with a larger number of solvent molecules. Clearly, the higher solvation energy involved in the formation of the complex Li⁺(DMSO)ₙ translates to lower Lewis acidity for the Li⁺ in this solvate than for the Li⁺ in Li⁺(CH₃CN)ₙ. The higher solvation energy calculated for the solvate formed between DMSO and Li⁺ is consistent with that expected from its high donor number of 29.8 compared with a donor number of 14.1 for CH₃CN. These data provide theoretical support for the HSAB concept to explain the ORR mechanism and the products formed in electrolytes prepared with different solvents.

The Li⁺ cation is usually solvated by four solvent molecules to form the solvent-separated ion pairs; e.g., Li⁺(DMSO)₄PF₆⁻ in LiPF₆/DMSO electrolyte.
Table 3.4: Physical properties of the electrolytes at 20°C

<table>
<thead>
<tr>
<th>Electrolyte in DMSO</th>
<th>Viscosity (cSt)</th>
<th>Conductivity (mS cm⁻¹)</th>
<th>Donor number of the anion (^{74})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M LiPF(_6)</td>
<td>2.13</td>
<td>2.10</td>
<td>2.50</td>
</tr>
<tr>
<td>0.1 M TBAPF(_6)</td>
<td>2.15</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>0.1 M LiCF(_3)SO(_3)</td>
<td>2.09</td>
<td>2.06</td>
<td>16.90</td>
</tr>
<tr>
<td>0.1 M TBACF(_3)SO(_3)</td>
<td>2.15</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>0.1 M LiN(CF(_3)SO(_2))(_2)</td>
<td>2.32</td>
<td>2.04</td>
<td>5.40</td>
</tr>
<tr>
<td>0.1 M TBAN(CF(_3)SO(_2))(_2)</td>
<td>2.11</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>0.1 M LiClO(_4)</td>
<td>2.16</td>
<td>2.26</td>
<td>8.44</td>
</tr>
<tr>
<td>0.1 M TBACIO(_4)</td>
<td>2.19</td>
<td>2.10</td>
<td></td>
</tr>
</tbody>
</table>

Despite its four oxygen atoms, the perchlorate ion (ClO\(_4\)^-) cannot form direct ion pair with Li\(^+\) in high donor number solvents like DMSO.\(^{78}\) Trifluoromethanesulfonate (CF\(_3\)SO\(_3\)^-) (triflate) and bis(trifluoromethanesulfonyl)imide (N(CF\(_3\)SO\(_2\))\(_2\)) (trflimide) anions can replace some of the solvent molecules and form direct ion pairs with Li\(^+\) (Figure 3.9). Most stable coordination is calculated to be bi-dentate for bis(trifluoromethanesulfonyl)imide\(^{79}\) where the two oxygen atoms come from two different sulfur atoms of the anion. However monodentate coordination is the most stable for the trifluoromethanesulfonate anion in polar aprotic solvents.\(^{80}\) Prior work supports Li\(^+\) coordination with the oxygen atom rather than the nitrogen in the bis(trifluoromethanesulfonyl)imide ion.\(^{79,81}\) The negative charge on the bis(trifluoromethanesulfonyl)imide ion is delocalized onto the neighboring sulfonyl group and as a result it is less available for coordination with Li\(^+\). Thus, the Lewis basicity of the trifluoromethanesulfonate anion is higher than that of the bis (trifluoromethanesulfonyl) imide anion due to the three electron rich oxygen centers. Consequently, two triflate anions would have a more stable coordination with lithium cations. In fact the donor numbers presented in Table 3.5 lend further support for the ability of the triflate ion (with a high donor number of 16.90) to form strong internal coordination with Li\(^+\). The high donor capability of the triflate anion has two possible advantages in the Li-air cathode reaction; it 1) stabilizes the superoxide
ions by the softer Li(triflate)$_x$($^{(n-1)}$+)($^n$+solvent)$_y$ cations and mitigates its chemical decomposition/electrochemical conversion to peroxide, 2) possibly helps solvate the Li$^+$ in Li$_2$O$_2$ leading to some solubility for the peroxide in the LiCF$_3$SO$_3$/DMSO electrolyte and removing it from the electrode surface to mitigate electrode passivation. Our experimentally observed trend in Columbic efficiencies suggests possible contributions from both of these effects. Note that on the microelectrode, soluble products would diffuse away quickly from the electrode surface making it unavailable for oxidation, while insoluble products that remain on the electrode surface are more efficiently oxidized. The results presented here indicate a unique role for the triflate anion on ORR in DMSO and point out the ability of microelectrode data to help diagnose the role of the Li salt on O$_2$ electrode reversibility in the Li-air cell.

![Figure 3.9: Solvation and contact ion pair formation](image)

**Figure 3.9:** Solvation and contact ion pair formation in a) LiCF$_3$SO$_3$/DMSO and c) LiN(CF$_3$SO$_2$)$_2$/DMSO electrolytes. Ion pair between solvated Li$^+$ and superoxide ion in b) LiCF$_3$SO$_3$/DMSO, d) LiN(CF$_3$SO$_2$)$_2$/DMSO electrolytes.
3.3.13. Oxygen Reduction Kinetics in TBA and Li Salt-based Electrolytes

We have plotted $E - E^0$ vs. $[(i_{f} - i_{r})/i]$ - $[(i_{f}' - i_{r}')/i']$ (as shown in equation 3.7) for the four Li$^+$-based electrolyte systems (Figure 3.10). Currents observed in the corresponding TBA electrolyte have been used as the current values in a reversible system. The transfer coefficient, $\alpha$, and the heterogeneous rate constant, $k_s$, calculated are shown in Table 3.6. According to the data in Table 3.1 and 3.2, the size of the cation does not have a significant impact on the viscosity or oxygen transport parameters in DMSO. Therefore, in the presence of Li$^+$ ions, it is reasonable to use the limiting current in TBA$^+$/DMSO electrolyte for that in Li$^+$/DMSO electrolytes. Apart from the large differences between TBA$^+$ and Li$^+$ salts, comparison of the voltammetric responses obtained in different Li$^+$-based electrolytes revealed valuable distinguishing features. In LiCF$_3$SO$_3$/DMSO and Li(CF$_3$SO$_2$)$_2$N/DMSO solutions, transfer coefficients are close to 0.5 whereas in LiPF$_6$/DMSO a much low transfer coefficient (~0.3) was observed. The slow kinetics observed in LiPF$_6$/DMSO can be possibly attributed to the electrode surface modified with insoluble products formed at high potentials. A transfer coefficient of 0.57 in the triflate electrolyte suggests a more desirable ORR and OER kinetics in this electrolyte.
Table 3.5: Kinetic parameters of ORR in Li⁺-based electrolytes

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transfer coefficient -α</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPF₆</td>
<td>0.28</td>
</tr>
<tr>
<td>LiClO₄</td>
<td>0.42</td>
</tr>
<tr>
<td>LiCF₃SO₃</td>
<td>0.57</td>
</tr>
<tr>
<td>LiN(CF₃SO₂)₂</td>
<td>0.54</td>
</tr>
</tbody>
</table>

3.4. Conclusion

We have found that a microelectrode can be used as a diagnostic tool to select and optimize the properties of electrolytes for non-aqueous Li-air batteries, and to elucidate O₂ redox reaction mechanisms in the presence of different ion-conducting salts. Distinct differences were observed in the current-voltage response of a microelectrode in oxygen-saturated DMSO solutions containing a series of TBA⁺ and Li⁺ salts. The characteristic
limiting currents observed in TBA$^+$ salt solutions due to the exceptional stability and solubility of the ORR products were contrasted with the bell shaped CV responses in Li$^+$ salt solutions, attributed to the passivation of the microelectrode surface by insoluble ORR products combined with the electrostatic repulsion of O$_2^-$, the initial O$_2$ reduction product. The final O$_2$ reduction products were identified be Li$_2$O$_2$ and Li$_2$O formed at different potentials. Our data confirm the four-electron reduction of O$_2$ to Li$_2$O in DMSO. Overall oxygen transport was not influenced by anion of either the TBA or Li salts. The trend in OER/ORR coulombic efficiencies in Li$^+$-based electrolytes suggested that there is improved O$_2^-$ stability and ORR product solubility in LiCF$_3$SO$_3$/DMSO electrolytes, probably due to increased solvation of the Li$^+$ cation by the triflate anion which may translate into better ORR and OER kinetics for the Li-air cell utilizing this electrolyte as previously observed.
The Influence of Lithium Salt Anions on Oxygen Reduction Reactions in Ether Electrolytes for Li-air Batteries

4.1. Introduction

The promise of the high theoretical energy density has not yet been translated into practical devices due to the shortcomings of the electrode and electrolyte materials used in the battery as well as an incomplete understanding of the chemical and electrochemical processes involved in its operation. In Chapter 3 I discussed the strong effect of non-aqueous solvents on the oxygen reduction reaction (ORR) electrochemistry in Li$^+$-containing electrolytes.\(^{22, 30, 32, 67, 71, 82}\) In that work a carbon microelectrode has been successfully employed to quantify oxygen transport parameters and elucidate the influence of the Li salt on the reversibility of the ORR in tetrabutylammonium (TBA) and lithium salt-containing electrolytes in dimethyl sulfoxide (DMSO).\(^ {31, 36}\) It has become increasingly clear that the ORR in the non-aqueous Li-air battery is solvent controlled\(^ {29}\) with a secondary role of the Li salt through the solvates formed between the solvent and the salt.\(^ {83}\)

The stability of the electrolyte solvent in contact with the O$_2$ reduction products in the non-aqueous Li-air battery plays a key role on the reversibility of the oxygen reduction reactions (ORR). Organic carbonate solvents such as propylene carbonate (PC), ethylene carbonate (EC) and diethyl carbonate (DEC) readily decompose through their reactions with the superoxide (O$_2^-$) radicals formed as the ORR intermediate in these electrolyte media.\(^ {65, 84, 85}\) Ethers are recognized as relatively stable solvents without significant superoxide mediated decomposition.\(^ {86}\) Ethers are also important due to their high oxygen solubility and low to moderate dielectric constants resulting in lower reactivity towards the superoxide ions. In this chapter, we present ORR electrochemistry data gathered from electrolytes in, 1, 2-dimethoxyethane (DME) and
tetraethylene glycol dimethyl ether (TEGDME), ethers that have been studied as solvents for Li-air batteries. Their low dielectric constants (DME, 7.07 and TEGDME, 7.79)\textsuperscript{87, 88} are important as this property influences the wettability of the carbon cathode and provide better stability in the presence of ORR products. Even though DME is a low boiling point solvent, its ability to form well conductive electrolytes makes it an attractive representative medium to elucidate ORR mechanism in ether-based electrolytes. TEGDME is especially desirable as a practical solvent for Li-air batteries because of its low vapor pressure and other desirable properties as we stated in our original reason for the selection of this solvent.\textsuperscript{32, 82, 89}

In our previous publication on the utility of microelectrodes for Li-air battery diagnostics, we presented a detailed analysis of the ORR in an electrolyte based on a high Donor Number (Lewis basicity) solvent namely, DMSO (DN = 29 kcal/mole).\textsuperscript{31} TEGDME and DME on the other hand, are low Donor Number solvents (DN = 16.6 and 20 kcal/mole, respectively). It is our expectation that with the microelectrode studies presented in this chapter together with the previous work in DMSO, we would provide a fuller picture of the extent to which the electron donor properties of the solvent and Li salt anion, as well as the transport of O\textsubscript{2} in the electrolyte, influence the mechanism and reversibility of the ORR in non-aqueous Li-air batteries. FT-IR spectral data provided information on the structures of the electrolyte solutions to enable us to correlate O\textsubscript{2} electrochemistry with electrolyte properties.

4.2. Experimental

4.2.1. Materials

All tetrabutylammonium (TBA) salts (TBAPF\textsubscript{6}, TBACF\textsubscript{3}SO\textsubscript{3}, TBAN(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}, TBAClO\textsubscript{4}) and lithium salts (LiPF\textsubscript{6}, LiCF\textsubscript{3}SO\textsubscript{3}, LiN(CF\textsubscript{3}SO\textsubscript{2})\textsubscript{2}, LiClO\textsubscript{4}), battery grade, were
purchased from Sigma-Aldrich and were stored in an MBraun glove-box maintained under 0.5 ppm (H₂O concentration) prior to use. An 11 µm diameter carbon disc microelectrode working electrode purchased from BASi® and a Pt mesh counter electrode were used. A Ag/AgNO₃ reference electrode was prepared as reported by Wain et al.⁶⁸ using silver wire (99%) purchased from Alfa Aesar. All the potentials in this chapter are reported with respect to the Li/Li⁺ scale obtained using a conversion factor determined by measuring the potential of Ag/Ag⁺ reference electrode versus a Li foil reference electrode in each electrolyte.

4.2.2. Cyclic Voltammetry

Cyclic voltammograms were recorded in argon saturated solutions to verify that the electrolyte itself does not undergo any reaction within the electrochemical potential window of interest. All the current densities reported in this chapter are referenced to the geometric surface areas of the electrodes. Oxygen electrochemistry was recorded at the carbon microelectrode (5.5 µm electrode radius) in O₂ saturated DME and TEGDME-based electrolytes. Current-time transients were obtained in TBA/DME salt electrolytes, by stepping the microelectrode potential from a potential where there is no reaction to a potential where the reaction is diffusion limited. Oxygen transport parameters were calculated using Cottrell plots obtained from these potential jump experiments. Oxygen reduction electrochemistry was also performed in a series of Li salt-based electrolytes (LiPF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂ and LiClO₄) in DME and in TEGDME. Most of the cyclic voltammograms at the carbon microelectrode were recorded at a scan rate of 200 mV s⁻¹. This is a relatively high scan rate. However, charging currents are minimal at a microelectrode and this allows us to record cyclic voltammograms at high scan rates at these electrodes without sacrificing any electrochemical information. In fact, a high 200 mV s⁻¹ scan
rate is preferred for studying electrochemical processes in Li\(^+\)-based electrolytes in order to avoid rapid passivation of the microelectrode surface by insoluble lithium oxide products.

### 4.2.3. RRDE Measurements

Electrochemical measurements were also obtained at a rotating ring disc electrode (RRDE) in Li salt/ TEGDME electrolytes. The rotating ring disc consisted of a glassy carbon working electrode and a gold ring secondary working electrode. The gold ring was set at a positive potential where the oxidation of the lithium oxides produced from the reduction of O\(_2\) on the carbon disc occurred.

*Ring efficiency:* Ring efficiency of the rotating ring disc electrode was determined as follows. Ferrocene was oxidized in an argon-purged Li salt/ TEGDME solution where the ring potential was set to a potential where the reduction of ferrocenium ion produced from the oxidation reaction occurred. Ring efficiency was calculated from the ratio of the ring current to the disc current. All electrochemical tests were carried out in a glove-box maintained at a humidity level < 0.5 ppm.

### 4.2.4. Lithium-Air Cell Testing

Lithium-air full cells were constructed as previously reported\(^3\)\(^0\) using Li foil anodes and KetjenBlack (EC300JD) or Vulcan XC-72R carbon porous cathodes, and microporous polypropylene membrane separators. Discharged cathodes were analyzed by means of a Rigaku X-ray diffractometer with the samples sealed in Kapton\(^{\circledR}\) polyimide film to identify the discharge products.

### 4.2.5. Scanning Electron Microscopy (SEM)
Discharged Li-O₂ cell cathodes were washed with acetonitrile solvent, dried and SEM images were recorded on a Hitachi S-4900 instrument.

4.2.6. FT-IR Characterization

A series of electrolytes composed of Li salt solution in DME or TEGDME were analyzed using a Bruker Vertex-70 FT-IR spectrometer.

4.3. Results and Discussion

Preliminary electrochemical data gathered in TBA salt/DME-based electrolytes at a rotating disc electrode (RDE) showed that the ORR does not reach a limiting current within the stable potential window of the electrolyte. This is because oxygen reduction reaction is kinetically, not mass transport, limited in DME-based electrolytes. Therefore, it is impossible to calculate the oxygen transport parameters with the aid of the RDE technique in these electrolytes. However, efficient oxygen transport observed at a microelectrode can be useful to obtain steady-state limiting current conditions. From these steady-state current-potential data at the microelectrode, one can calculate oxygen transport parameters in these electrolytes which are useful for the development of practical Li-air batteries. The first part of this chapter details our microelectrode studies in DME-based electrolytes. In the second part we extend the studies to electrolytes in the high molecular weight ether, TEGDME. The TEGDME is a low volatile solvent with a donor number of 16.6 kcal/mole, which following our original investigation has been studied as a Li-air battery electrolyte by many researchers. As we reported previously, the electron donor property of a solvent influences the mechanism and reversibility of the ORR in lithium salt-containing electrolytes through the Hard Soft Acid Base concept. The quantitative effect of the Donor Number of the solvent on ORR can only be investigated in
the absence of Li ions which otherwise would complicate the analysis by passivating the electrode surface with ORR products. However, oxygen transport properties and electrochemistry in tetrabutylammonium salt (TBA salt)-containing TEGDME electrolytes, in which passivation of the electrode surface does not occur, has not been satisfactorily performed using a planar glassy carbon macrodisc electrodes due to the high viscosity and the associated large iR drop and kinetic limitations of the ORR in the stable potential window of these electrolytes. Electrochemistry on a microelectrode is able to overcome these limitations by allowing us to study diffusion limited ORR in these electrolytes to determine oxygen transport properties, as well as ORR kinetics and mechanisms.

4.3.1. Microelectrode Electrochemistry

A microelectrode has the unique advantage of efficient transport of electro-active species to and from the electrode surface. This is demonstrated by the sigmoidal-shaped cyclic voltammograms that we have observed\textsuperscript{31} in ferrocene solution in DMSO at scan rates as high as 500 mV s\textsuperscript{-1}. The diffusion controlled limiting current at a microdisc electrode is given by equation 4.1.

\[
I_d = \frac{4nFADC}{\pi r} = 4nFDCr
\]  \hspace{1cm} [4.1]

In equation 4.1, \(I_d\) is the diffusion limited current, \(F\) is the Faraday constant, \(A\) is the geometric area of the electrode, \(n\) is the number of electrons, \(r\) is the electrode radius and \(D\) and \(C\) are diffusion coefficient and solubility of the electroactive species, respectively.

We have also shown that the oxygen transport to a 5.5 \(\mu\)m radius microelectrode in DMSO\textsuperscript{31} is approximately equal to the hydrodynamic transport of oxygen to a rotating disc electrode at a speed of 25000 rpm. Ohmic drops originating from solution resistance are
minimal on microelectrodes due to the very small current values involved. Other advantages and theoretical considerations of ORR on microelectrodes in non-aqueous electrolytes have been presented in our previous paper.\textsuperscript{31}

4.3.2. Oxygen Transport and ORR in Tetrabutylammonium Salt-based Ether Electrolytes: The Effect of the Electrolyte Salt Anion

1,2-Dimethoxyethane (DME): Dimethoxyethane has been widely used as a solvent in Li batteries, and particularly as a co-solvent with carbonate-based electrolytes. There are several studies discussing O\textsubscript{2} electrochemistry in PC: DME mixed solvent electrolytes.\textsuperscript{65, 86, 93, 94} The reasons for adding DME as a co-solvent to PC-based electrolytes are several; its low reactivity towards lithium, a low viscosity of 0.402 centipoise (cP)\textsuperscript{23} which lowers the overall viscosity of the PC: DME mixed electrolytes, and the relatively large potential stability window. The current versus potential scans for O\textsubscript{2} on the microelectrode in TBACF\textsubscript{3}SO\textsubscript{3}/DME electrolyte, shown in Figure 4.1a, depict a sigmoidal shaped voltammogram with a limiting current independent of the scan rate. The data are consistent with a one-electron reversible reaction (equation 4.2) with no passivation film formation at the electrode surface.\textsuperscript{31}

$$O_2 + e^- \rightleftharpoons O_2^-$$ \hfill \textsuperscript{[4.2]}
**Figure 4.1:** Oxygen reduction limiting currents obtained on the carbon microelectrode **a)** in 0.1 M TBACF₃SO₃/ DME at several voltage scan rates from 50-200 mV s⁻¹ (CV recorded at 200 mV s⁻¹ in an Ar saturated electrolyte is shown in black), **b)** in a series of 0.1 M TBA salt /DME electrolytes at 200 mV s⁻¹. **c)** Cottrell plots obtained for the current time transients recorded in an O₂ saturated series of TBA salt/ DME electrolytes.
Figure 4.1b depicts steady state voltamograms obtained on the carbon microelectrode in a series of TBA salt solutions in DME. These steady-state voltammograms obtained in 0.1 M solutions of TBAPF$_6$, TBACF$_3$SO$_3$, TBAN(CF$_3$SO$_2$)$_2$ and TBACIO$_4$ in DME at 200 mV s$^{-1}$ all show similar limiting currents, suggesting the same magnitude of oxygen transport rate (permeability values) in all of the electrolytes.

When the microelectrode is stepped from a potential where there is no reaction to a potential where the reaction is diffusion limited, the current (I in Ampere)-time (t in seconds.) transient at small times after polarization can be related by equation 4.3.

$$I = \frac{nFA D^2 C}{\pi^2 t^2} + n\pi FDCr$$  \[4.3\]

Current-time transients were obtained by holding the electrode potential at 2.6 V for 100 sec and then stepping the electrode potential to 1.2 V. Cottrell plots calculated from these current-time transients in each electrolyte are shown in Figure 4.1c. The oxygen diffusion coefficients and oxygen solubility values we have calculated from these data are listed in Table 4.1. The similar oxygen diffusion and solubility values obtained in all electrolytes reveal that the anion of the salt has a negligible effect on the oxygen transport in the DME electrolytes. The oxygen diffusion coefficient calculated here for LiPF$_6$/DME solution is higher than the value we previously

<table>
<thead>
<tr>
<th>TBA salt (0.1 M in DME)</th>
<th>O$_2$ Diffusion Coefficient ($10^{-4}$ cm$^2$ s$^{-1}$)</th>
<th>O$_2$ Solubility (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBAPF$_6$</td>
<td>1.79</td>
<td>4.28</td>
</tr>
<tr>
<td>TBACIO$_4$</td>
<td>1.82</td>
<td>3.91</td>
</tr>
<tr>
<td>TBACF$_3$SO$_3$</td>
<td>1.58</td>
<td>5.08</td>
</tr>
<tr>
<td>TBAN(CF$_3$SO$_2$)$_2$</td>
<td>1.75</td>
<td>4.14</td>
</tr>
</tbody>
</table>
determined from Tafel data. However, the values reported here are probably more accurate since this determination does not involve the effects of Ohmic drop and electrode roughness encountered in Tafel calculations. The present data reveal that DME has a very high oxygen transport which is keeping with its low viscosity. Furthermore, we believe that the low polarity of DME which would decrease dipolar interactions between DME and O\textsubscript{2} also would lead to a higher oxygen diffusion coefficient in this solvent. Oxygen transport parameters directly impact the discharge capacity and the rate of O\textsubscript{2} cathode reaction in the Li-O\textsubscript{2} battery. This finding not only reiterates the role of DME as a good solvent to study ORR but also promotes the view that ethers are suitable solvents in terms of mass transport for Li-O\textsubscript{2} batteries.

**Figure 4.2:** Oxygen reduction limiting currents obtained on the carbon microelectrode in a) saturated TBA PF\textsubscript{6}/TEGDME, b-c) 0.1 M TBA CF\textsubscript{3}SO\textsubscript{3}/TEGDME electrolyte, d) Cottrell plot obtained for the current time transient obtained in O\textsubscript{2} saturated 0.1 M TBA CF\textsubscript{3}SO\textsubscript{3}/TEGDME electrolyte.
Tetraethylene Glycol Dimethyl Ether (TEGDME)

The high molar weight TBAPF$_6$ is sparingly soluble in the viscous TEGDME. Initially, a TBAPF$_6$ saturated solution of TEGDME with an approximate salt concentration of less than 0.1 M was used as the electrolyte. Steady-state ORR currents were observed only at very low potentials (Figure 4.2a). As we stated in our previous publication,$^{31}$ the steady-state behavior observed in this TBA electrolyte indicates that the ORR terminates at the one-electron reduction product superoxide (with no further reduction to peroxides). These data also affirm reversible O$_2$ electrochemistry with little passivation of the electrode surface in this electrolyte.

For further analysis, ORR in 0.1 M solution of TBACF$_3$SO$_3$ in TEGDME was investigated. TBACF$_3$SO$_3$ was more soluble in TEGDME. Again, limiting current independent of the scan rates confirmed one-electron reduction of oxygen to superoxide ion in TBACF$_3$SO$_3$/TEGDME. The low charge density (weak acid) of TBA$^+$ enhances the stability of the weak base superoxide ion in the electrolyte by forming the ion pair TBA$^+$--O$_2^-$, in conformity with the Hard Soft Acid Base (HSAB) concept. This observation is reminiscent of our findings in TBA salt-based electrolytes in DMSO and the results observed in DME.$^{22,91}$ As the potential scan rate was decreased to 5 mV s$^{-1}$, a suppression of the steady-state current was observed with practically no current at 1.5 mV s$^{-1}$ (Figure 4.2c). A possible reason for the diminishing currents at very low scan rates is that the initially formed superoxide ions have some reaction with TEGDME to form passivating products on the electrode and block the electrode surface to varying levels depending on the scan rate. We can also conclude from the sigmoidal-shaped voltammogram at 5 mV s$^{-1}$ that there is no further electrochemical reduction of the superoxide ions in TBACF$_3$SO$_3$/TEGDME electrolyte at these potentials.
Oxygen diffusion rate and solubility in TBACF$_3$SO$_3$/TEGDME were calculated using the Cottrell plot (equation 4.3, Figure 4.2d) obtained from chronoamperometric current-time transients.$^{13, 31}$ Oxygen solubility was found to be 3.5 mM and the oxygen diffusion coefficient was calculated to be 3.5x10$^{-5}$ cm$^2$ s$^{-1}$. The oxygen solubility value is in agreement with that we previously reported for LiPF$_6$/TEGDME electrolyte.$^{22}$ The oxygen diffusivity determined in this work is considerably higher than what was previously reported in 0.1 M LiPF$_6$/TEGDME.$^{22}$ However, the theoretical ORR limiting current calculated from equation 4.1 using the diffusivity and solubility values determined in this study is in agreement with the observed ORR limiting current in this electrolyte. Therefore, we conclude that the oxygen diffusivity in TBACF$_3$SO$_3$/TEGDME electrolyte is higher than the previously determined value in LiPF$_6$/TEGDME.
Figure 4.3: a) current-voltage data obtained on the carbon microelectrode in 0.1 M TBAPF$_6$/DME (red), and 0.1 M LiPF$_6$/DME (blue). b) Scan rate dependent cyclic voltammograms obtained on the carbon microelectrode in 0.1 M LiPF$_6$/DME (continuously recorded second CV at 200 mV s$^{-1}$ is shown as a black dotted line), c) Comparison of anodic current-potential response on the microelectrode with different cathodic potential limits at 200 mV s$^{-1}$.

Although the actual Li salt concentration in the electrolytes used in Li-O$_2$ batteries is much higher than the 0.1M TBA salt solutions we used in the O$_2$ transport measurements, we believe
that the transport data from the dilute TBA salt solutions can be used to project O\textsubscript{2} transport in the 1M solutions in the Li-air battery. This is because the motion of the neutral O\textsubscript{2} molecule in the electrolyte is minimally affected by the ionic environment.

4.3.3. ORR in Li Salt Solutions in 1,2-Dimethoxyethane (DME) and Tetraethylene Glycol Dimethyl Ether (TEGDME)

Li Salt Solutions in DME–based Electrolytes

Microelectrode voltammograms for ORR in Li salt/ DME solutions showed peak-shaped behavior. As we discussed before\textsuperscript{31} microelectrode response can deviate from the expected steady-state behavior observed for O\textsubscript{2} in TBAPF\textsubscript{6}/DME (Figure 4.1a), due to two main reasons: i) the electrostatic repulsion of the species being reduced at the commencement of the second reduction reaction of the initial ORR product, i.e, reduction of O\textsubscript{2}\textsuperscript{−} to O\textsubscript{2}\textsuperscript{2−} (equation 4.4)

\[
\text{O}_2^- + e^- \rightarrow \text{O}_2^{2-} \quad [4.4]
\]

and ii) from passivation of the electrode surface by the ORR product(s), e.g; Li\textsubscript{2}O\textsubscript{2}. Bell shaped oxygen reduction currents in Li salt/DME solutions (Figure 4.3a (blue) and Figure 4.3b) suggest that further electrochemical reduction of the initially formed superoxide ion (O\textsubscript{2}\textsuperscript{−}) to peroxide (O\textsubscript{2}\textsuperscript{2−}) occurs at lower potentials\textsuperscript{31} along with electrode passivation by the deposition of this product on the electrode surface. As a test of the cyclability of the ORR/OER processes, we repeated the CV in 0.1 M LiPF\textsubscript{6}/DME at 200 mV s\textsuperscript{−1}(Figure 4.3b – red (200 mV s\textsuperscript{−1}) and it showed zero reduction current in the second cycle (Figure 4.3b – black dotted line), which was surprising considering the very low columbic efficiency (zero anodic current) in the first cycle. The latter behavior on a microelectrode is usually indicative of solubility of the ORR products\textsuperscript{31}. Figure 4.3a reveals a significantly smaller peak current in LiPF\textsubscript{6}/DME than the steady state current seen in TBAPF\textsubscript{6}/DME. This contrasts with our previous observation in DMSO-based
electrolytes in which ORR in TBA and Li salt-containing solutions showed similar limiting or peak currents.

**Figure 4.4:** Cyclic voltammograms recorded at the 11 µm carbon electrode in O₂ saturated electrolytes. a) Anodic response in LiCF₃SO₃/DME at different cathodic limiting potentials. b) Cyclability of the ORR/OER in LiCF₃SO₃/DME, c) Scan rate dependent ORR/OER in LiCF₃SO₃/DME.
The ORR/OER behavior in LiCF₃SO₃/DME was markedly different from that in the LiPF₆ solution. In the LiCF₃SO₃ electrolyte similar ORR currents were seen in the 1ˢᵗ and the 12ʰ cycles as depicted in Figure 4.4b. These opposing ORR behaviors in the presence of the two electrolytes certainly need an explanation. In order to ascertain if the current reduction with cycling in LiPF₆/DME is caused by the passivation of the electrode surface, we have used a technique that we previously developed. This involves determining whether there is any suppression of ORR limiting currents on the microelectrode in a TBAPF₆/DMSO-based electrolyte after the ORR in LiPF₆/DME on the same electrode. The ORR limiting current recorded in 0.1M TBAPF₆/ DMSO after one ORR half cycle in LiPF₆/DME is shown in Figure 4.5.

![Graph showing ORR limiting current](image)

**Figure 4.5:** Oxygen reduction half-cycles were recorded at a pristine carbon microelectrode in LiPF₆/ DME. ORR limiting currents recorded for the same electrode in TBAPF₆/DMSO soon after the above reaction are shown.

The result reveals that the electrode has become completely passivated in LiPF₆/DME after the ORR without any ability for it to sustain O₂ reduction in TBAPF₆/DMSO solution. In addition,
the fact that the Columbic efficiency of the reaction in LiPF$_6$/DME did not improve by limiting
the cathodic potential to 2.0 V suggests that the electrode passivation occurs from the beginning
of ORR at higher potentials, most probably by the chemical decomposition of the initially
formed lithium superoxide to insoluble Li$_2$O$_2$ (Figure 4.3c) as depicted in equation 4.5.

$$2LiO_2 \rightarrow Li_2O_2 + O_{e2}$$  \hspace{1cm} [4.5]

The high degree of passivation in LiPF$_6$-based electrolyte suggests that the peak shape of the CV
is the result of electrode passivation in addition to migration-diffusion control of the first
reduction product.

The information which can be obtained from the voltammograms recorded in LiPF$_6$/
DME is limited due to the instant passivation of the electrode surface during the first half-cycle
of the ORR. Therefore, further analysis of the DME-based electrolyte system was carried out in
0.1 M LiCF$_3$SO$_3$/DME. Figure 4.4a shows oxygen reduction reaction electrochemistry recorded
in this electrolyte for different cathodic limits at the sweep rate of 200 mV s$^{-1}$. A small shoulder
peak appeared around 2.2 V in the reduction scan (Figure 4.4c). However, when the cathodic
scan was limited to 2.12 V, there was no significant response observed in the anodic scan. This,
along with the improved cyclability of the ORR/OER processes in this electrolyte implies that
the reduction shoulder peak which appears around 2.2 V is probably from the initial one-electron
reduction of the O$_2$ to superoxide. It should be noted that the current peak in LiCF$_3$SO$_3$/DME
appears at slightly lower potentials than in LiPF$_6$/DME.

**Oxygen Electrochemistry in LiPF$_6$ and LiCF$_3$SO$_3$ Solutions in TEGDME**

The voltammograms for oxygen reduction reactions at a carbon microelectrode in LiPF$_6$/
TEGDME are shown in Figure 4.6a. We observed bell shaped oxygen reduction curves for a
range of scan rates, which as described above can be explained on the basis of the migration-
diffusion controlled currents originating from the initial one-electron $\text{O}_2$ reduction product $\text{LiO}_2$, and its one-electron reduction to $\text{Li}_2\text{O}_2$.\textsuperscript{31,66}

Cyclic voltamograms recorded at different cathodic limiting potentials provided interesting insights. First, an anodic peak appeared when the potential was scanned cathodically down to 2.15 V, which grew when the cathodic limit was decreased. This is attributed to the formation and re-oxidation of $\text{Li}_2\text{O}_2$. When the cathodic potential was limited to 1.7 V, another anodic peak emerged which is attributed to the oxidation of the ORR product $\text{Li}_2\text{O}$.

Continuous scanning of potentials between 1.5 V and 4.5 V in LiPF$_6$/TEGDME electrolyte showed rapid decaying of the ORR peak current density (Figure 4.6a). This observation conforms with the above conclusion that $\text{Li}_2\text{O}$ is formed at low potentials. The oxidation over-potential of crystalline lithium monoxide is expected to be high due to its lack of electronic conductivity. A shift of the oxygen evolution onset potential to a more positive voltage was observed when the electrode was scanned down to 1.5 V, which suggests the oxidation of additional $\text{Li}_2\text{O}$ formed from the full reduction of $\text{Li}_2\text{O}_2$ to $\text{Li}_2\text{O}$. Figure 4.6c shows cyclability of the ORR/OER reactions in the potential range of 1.7 V to 3.7 V. In this case we have restricted the anodic potential in order to prevent the full recovery of the electrode surface after passivation with ORR products. The result is a gradual decrease in the activity of the electrode with accumulated products which passivate the microelectrode.

We have also studied ORR in LiCF$_3$SO$_3$/TEGDME electrolyte. Bell shaped voltammograms obtained in this electrolyte and the cyclic voltammograms obtained from cycling in the in the voltage range of 1.5 V to 4.5 V are shown in Figure 4.7b. Unlike the behavior in LiPF$_6$/TEGDME electrolyte (Figure 4.7a),
Figure 4.6: Cyclic voltammograms recorded at a 11 µm carbon disc in O₂ saturated LiPF₆/TEGDME. a) CVs collected at scan rates ranging from 20 mV s⁻¹ to 200 mV s⁻¹, b) Anodic response at different cathodic limiting potentials, c) Cyclability of the ORR/ OER in the potential range of 1.7 V and 3.6 V (initial scan at the full potential range from 1.7 V to 4.5 V is shown in black).
continuously collected current-potential profiles in LiCF$_3$SO$_3$/TEGDME do not show any decrease in current in all of the seven scans we examined. It should be noted that, in contrast to the electrochemical responses in DMSO and DME-based electrolytes, Columbic efficiencies of the ORR in TEGDME were similar in both LiPF$_6$ and LiCF$_3$SO$_3$ electrolytes at 200 mV s$^{-1}$ (Figure 4.8a). Continuous cycling of the potentials between 1.7 and 3.7 V in LiCF$_3$SO$_3$/TEGDME displayed cyclability performance (Figure 4.8b) similar to that observed in LiPF$_6$/TEGDME (Figure 4.6c). This observation was surprising due to the significantly different donor capabilities of the CF$_3$SO$_3^-$ (DN, 16.90) and PF$_6^-$ (DN, 2.50) ions. Apparently the solubility of the ORR products that are produced at potentials above 1.7 V is minimally influenced by the Li salt anion in TEGDME solutions. The major effect appears to come from TEGDME solvent itself probably through its solvation of Li$^+$ as discussed below from Ir spectral data.

Figure 4.7: Cyclability of the oxygen reduction/evolution reaction in the potential range of 1.5 V and 4.5 V a) in 0.1 M LiPF$_6$/TEGDME, b) 0.1 M LiCF$_3$SO$_3$/TEGDME
Lithium/O₂ Cell Performance with Li salt/TEGDME Electrolytes

We studied the effect of Li salt anions on ORR by examining the capacity of Li/O₂ cells fabricated with two electrolytes; i.e., 1M LiCF₃SO₃/TEGDME and 1M LiPF₆/TEGDME electrolytes. This study also looked at the effect of carbon cathode surface area on capacity by testing cells with cathodes prepared from both XC-72R carbon (with surface area of 233 m²/gram) and EC300JD carbon (Ketjen Black with surface area of 802 m²/gram), each with the two electrolytes. The Li/O₂ cells discharged at 0.1 mA cm⁻² showed better discharge capacities with 1M LiCF₃SO₃/TEGDME than with 1M LiPF₆/TEGDME irrespective of the carbon cathode used in the cells (Figure 4.9).

Figure 4.8: Cyclic voltammograms recorded at an 11 µm carbon microdisc at 200 mV s⁻¹ in O₂ saturated a) 0.1M LiPF₆/TEGDME (black) and 0.1M LiCF₃SO₃/TEGDME (red). b) Cyclability of the ORR/OER in 0.1M LiCF₃SO₃/TEGDME in the voltage range of 1.7 V - 3.7 V (black curve shows the initial scan in the voltage range of 1.5 V - 4.6 V)

The discharge products accumulated in the cathodes of all four Li-O₂ cells were identified to be Li₂O₂ as evidenced by its characteristic X-ray diffraction pattern with d-values of 2.720, 2.568 and 1.565 Å.
Figure 4.9: Galvanostatic discharge curves for Li/O_2 cells. a) XC72R carbon cathodes, b) Ketjenblack EC300JD carbon cathodes, both discharged at 0.1 mA cm$^{-2}$ with LiPF$_6$/TEGDME and LiCF$_3$SO$_3$/TEGDME (insets shows the voltage scales expanded). Galvanostatic discharge-charge curves obtained for a Li/O$_2$ cell (KB300JD cathode) with c) LiPF$_6$/TEGDME, d) LiCF$_3$SO$_3$/TEGDME by limiting the capacity to 400 mA h g$^{-1}$ and limiting the charging potential to 4.5 V.

Li/O$_2$ cells were cycled at a limited capacity of 400 mA h g$^{-1}$ with 1M LiPF$_6$/TEGDME and 1M LiCF$_3$SO$_3$/TEGDME electrolytes. The charge-discharge performances of the cells are shown in Figure 4.9c and 4.9d. The cell utilizing the LiCF$_3$SO$_3$/TEGDME electrolyte showed a slight advantage in cycle life although the advantage was not as significant as the capacity. We were unable to reproduce the superior results published by Scrosati et al. in a similar electrolyte using the super P carbon cathode.\textsuperscript{76}
The low cycle life of the Li-O_2 cell is caused by many factors. First of all, the ORR products, superoxide and peroxide, react slowly with the solvents to degrade the electrolyte and to increase the cell’s internal resistance from the accumulation of products from these reactions in the porous cathode. Another issue is the poor cycling efficiency of the Li anode due to reactions of the plated Li with the electrolyte during charging. Further studies to determine the contributions of each of these factors on the cycle life of the Li-air battery have to be performed and appropriate solutions found for each.
**Figure 4.10:** a) Cyclic voltammograms recorded in O$_2$ saturated LiPF$_6$/TEGDME at the Au macro disc. Rotating ring disc electrode response obtained in O$_2$ purged solutions (at 800 rpm at 40 mV s$^{-1}$) b) 0.1M LiPF$_6$/TEGDME and c) 0.1 M LiCF$_3$SO$_2$/TEGDME (Disc response is shown in black and the ring response is shown in red)
Assessing the Solubility of the ORR Products Using Rotating Ring Disc Voltammetry

The relative quantities of the insoluble products deposited on the electrode during ORR with the aid of rotating ring disc electrode (RRDE) voltammetry were determined first. Before the RRDE experiments, O\textsubscript{2} reduction reaction electrochemistry on a Au disc electrode was recorded in each electrolyte in order to locate the oxidation potentials of the lithium oxides formed when the electrode was scanned cathodically from open circuit to the cathodic limit. Potential limited cyclic voltammograms recorded in this way in all Li salt/TEGDME–based electrolytes showed the first cathodic peak around 2.29 V and the corresponding anodic peak at 3.53 V. Data in Figure 4.10a show the cyclic voltammogram obtained in LiPF\textsubscript{6}/TEGDME electrolyte. It indicates a potential difference of 1.24 V between the reduction peak at 2.29 V and the oxidation peak at 3.53 V which is significantly more than 59 mV. This suggests that the oxidation peak observed at 3.53 V is probably not due to the oxidation of superoxide ions. This peak is probably coming from the oxidation of Li\textsubscript{2}O\textsubscript{2}.

In the second part of the RRDE experiment, ORR ring disc voltammetry in each electrolyte was performed at a gold ring-glassy carbon disc electrodes in which the Au ring electrode was held at 3.53 V based on the above observation. Note that at 3.53 V both lithium superoxide and lithium peroxide should be oxidized. The RRDE voltammograms recorded at 800 rpm at 40 mV s\textsuperscript{-1} for O\textsubscript{2} reduction, in the two TEGDME electrolytes, are shown in Figure 4.10b and c. The onset of the ORR at the carbon disc in 0.1M LiPF\textsubscript{6}/TEGDME electrolyte occurred around 2.75 V. The ORR current quickly reached its peak current (5x10\textsuperscript{-2} mA) at about 1.9 V and started to decrease. The oxidation reaction at the Au ring started when the carbon disc potential was around 2.25 V.
Figure 4.11: FT-IR spectra for Li salt solutions in DME for various salt concentrations. a) LiPF$_6$/DME (peak position of the solvent C-O-C vibration is shown by a dotted line at 1090 cm$^{-1}$), b) LiCF$_3$SO$_3$/DME (peak position of the asymmetric stretching vibrations of the ion paired sulfonyl groups are shown by dotted lines at 1260 and 1300 cm$^{-1}$)
The ORR in LiCF$_3$SO$_3$/TEGDME electrolyte started at 2.75 V and the current magnitude continuously increased up to $-3.5\times10^{-2}$ mA remaining steady above 1.5 V. The oxidation reaction at the Au ring in this electrolyte started when the carbon disc was around 2.5 V. In LiCF$_3$SO$_3$/TEGDME, the ring current starts soon after the commencement of the ORR at the carbon disc. In other words superoxide formation at the carbon disc coincides with the emergence of the oxidation current at the Au ring. This indicates that a significant amount of superoxide ions are contributing to the oxidation current at the Au ring in LiCF$_3$SO$_3$/TEGDME. On the other hand, the oxidation current at the Au ring lags the ORR current at the carbon disc in LiPF$_6$/TEGDME electrolyte.

This information provides an insight on the stability of the superoxide ions in the two different electrolytes. The superoxide ions in the LiCF$_3$SO$_3$-based electrolyte appear to have longer lifetimes and are readily transferred to the Au ring where they are oxidized. On the other hand, the superoxide ions in the LiPF$_6$-based electrolyte appear to be less stable and are quickly decomposed to peroxide ions at the disc before being transferred to the ring where they are oxidized. The peroxide ions not only requires a larger oxidation over-potential, but also has a lower diffusion coefficient than the superoxide ions, both of which are contributing to the observed trend in ring current in PF$_6^-$-based electrolyte.

*Oxygen Electrochemistry in Other Li salt/TEGDME Electrolytes*

Oxygen electrochemistry was also recorded in two other Li-containing electrolytes namely, LiClO$_4$ and LiN(SO$_2$CF$_3$)$_2$ (LiTFSI).$^{96}$ Similar bell shaped electrochemistry was observed in both these electrolytes suggesting the same overall ORR processes as we discussed above. Rotating ring disc response obtained suggested that electrochemistry in both LiClO$_4$ and LiN(CF$_3$SO$_2$)$_2$/TEGDME are similar to that observed in the LiPF$_6$/TEGDME system. It appears
that even though sulfonyl oxygen atoms are present in the \(\text{N(CF}_3\text{SO}_2\text{)}_2^-\) (TFSI) anion, the electron density is delocalized throughout this anion providing it with low donor properties than that in the \(\text{CF}_3\text{SO}_3^-\) anion. As a result \(\text{LiN(CF}_3\text{SO}_2\text{)}_2\) behaves more like \(\text{LiPF}_6\).

4.3.4 The Impact of the Structure-Property Characteristics of \(\text{CF}_3\text{SO}_3^-\) on ORR in Ether Electrolytes

The preceding data suggest that the higher capacity of the Li/O\(_2\) cell containing \(\text{LiCF}_3\text{SO}_3/\text{TEGDME}\) electrolyte is related to the structure of the electrolyte. This is reasonable considering that the initial ORR product superoxide (O\(_2^-\)) does not undergo chemical decomposition to insoluble Li\(_2\)O\(_2\) right away in this electrolyte. The superoxide, stabilized by this electrolyte, is apparently more soluble (as evidenced by the RRDE results) and is swiftly removed from the microelectrode surface by diffusion. The removal of the soluble superoxide from the carbon electrode surface to the \(\text{LiCF}_3\text{SO}_3/\text{TEGDME}\) electrolyte bulk in the porous electrode maintains the electrode surface less passivated and, as a result the electrode has higher activity to yield higher capacity in Li/O\(_2\) cells. In order to characterize the structure of the electrolytes, the FT-IR spectra of Li salt solutions in DME and TEGDME were recorded and the data discussed below support this conclusion.

**FT-IR Spectral Characterization of Electrolyte Structures**

FT-IR spectra of 1 M \(\text{LiPF}_6\) and 1 M \(\text{LiCF}_3\text{SO}_3\) in DME and TEGDME recorded from 550 cm\(^{-1}\) to 2000 cm\(^{-1}\) are shown in Figure 4.11 and Figure 4.12 respectively. The vibrational absorption peak for the PF\(_6^-\) ion is observed at around 840 cm\(^{-1}\). The symmetric stretching peak of the ether oxygen (H\(_3\)C-O-CH-) linkage appears at about 1120 cm\(^{-1}\). As more \(\text{LiPF}_6\) is added to the \(\text{LiPF}_6/\text{DME}\) a shoulder peak appears at a lower frequency of 1090 cm\(^{-1}\). With increasing concentration of \(\text{LiPF}_6\) in DME, the peak at 1120 cm\(^{-1}\) completely disappears and when the \(\text{LiPF}_6\)
concentration is 1M (Figure 4.10a) the shoulder at 1090 cm\(^{-1}\) becomes the only absorption peak due to C-O-C stretching. A similar trend in the C-O-C absorption peak position is observed in LiPF\(_6\)/TEGDME also.

The co-ordination (solvation) of Li\(^+\) by the C-O-C linkage satisfactorily explains these spectral changes. When a significant amount of the LiPF\(_6\) is added to DME or TEGDME, the C-O bonds become highly co-ordinated to Li\(^+\) shifting the C-O-C absorption peak from 1120 cm\(^{-1}\) to the lower 1090 cm\(^{-1}\) at high LiPF\(_6\) concentrations. On the other hand, in LiCF\(_3\)SO\(_3\)/DME solution, the C-O-C absorption peak at 1120 cm\(^{-1}\) is still observed even at high Li\(^+\) concentrations. Both the 1120cm\(^{-1}\) and 1090cm\(^{-1}\) peaks are clearly visible in the spectra obtained for solutions of 1M LiCF\(_3\)SO\(_3\)/DME. This shoulder peak at 1090 cm\(^{-1}\) is not observed in the 1M LiCF\(_3\)SO\(_3\)/TEGDME solution.

This suggests that almost all of the DME molecules in the concentrated LiPF\(_6\) solution (1M and up to saturated) are solvated by the Li\(^+\) to form the solvent separated ion pair Li\(^+\)(DME)\(_n\)PF\(_6\)^-. A new peak which appears at 1130 cm\(^{-1}\) in these solutions is probably from the –CH\(_3\) groups which are originally masked by the C-O peak. In the LiCF\(_3\)SO\(_3\)/DME electrolyte, it appeared that only a portion of the DME molecules solvate the Li\(^+\). This is probably because, in the presence of CF\(_3\)SO\(_3\)^- anion some of the ether oxygens of DME in the Li\(^+\) co-ordination sphere are replaced by the sulfonyl oxygen of the triflate ions (CF\(_3\)SO\(_3\)^-). This is evident from the new strong peaks appearing between 1260 and 1300 cm\(^{-1}\) in this solution. The asymmetric stretching frequency of the free triflate ion appears at 1270 cm\(^{-1}\). This peak degenerates to two peaks centering at 1270 cm\(^{-1}\) (i.e., at 1260 and 1300 cm\(^{-1}\)) when the sulfonyl oxygen is co-ordinated to Li\(^+\). The substitution of some of the DME solvent in Li\(^+\) solvate by the CF\(_3\)SO\(_3\)^- anion is understood when it is considered that the donor number of triflate (DN=16.9) is closer to that of
**Figure 4.12:** FT-IR spectra for Li salt solutions in TEGDME for various salt concentrations: a) LiPF$_6$/TEGDME (peak position of the solvent C-O-C vibration is shown by a dotted line at 1090 cm$^{-1}$), b) LiCF$_3$SO$_3$/TEGDME (peak position of the asymmetric stretching vibrations of the ion paired sulfonyl groups are shown by dotted lines at 1260 and 1300 cm$^{-1}$).

DME (DN=20). In other words in the LiCF$_3$SO$_3$/DME electrolyte contact ion pairs of the type, (DME)$_n$Li$^+$(CF$_3$SO$_3$) are formed. A similar absorption spectral behavior is also observed in the
spectra for the LiCF₃SO₃/TEGDME solutions in the range of 1200-1400 cm⁻¹, indicating sulfonyl oxygen coordination to Li⁺ ions.

It is reasonable to state from the FT-IR spectra detailed above that the electron donor capability and the conformational structure of the solvent molecule play a role on the ORR electrochemistry in Li/O₂ batteries. The PF₆⁻ has a very low electron donor capability (DN=2.5) compared to CF₃SO₃⁻ (DN=16.9). Therefore, PF₆⁻ most probably does not form contact ion pairs with Li⁺ in its DME solution (Scheme 4.1). The Li⁺ ions in this solution are coordinated to the solvent molecules to form the solvent separated ion pairs Li⁺(DME)ₙPF₆⁻ between the Li⁺ and the PF₆⁻ anion. The DME molecules in the Li⁺ solvation sphere of Li⁺(DME)ₙPF₆⁻ appear to rapidly exchange with the free DME present in the solution as evidenced by the presence of only one strong C-O-C Ir absorption peak at 1090 cm⁻¹ for the IM solution although the Li⁺ to DME concentration ratio is close to 1:8. It is also conceivable that once the superoxide ions are formed by the ORR, they will replace one of the ether oxygen in the solvation sphere around Li⁺ in Li⁺(DME)ₙPF₆⁻ to form the superoxide-containing ion pair (Li⁺[(DME)ₙ₋₁(O₂⁻)]PF₆⁻ which can be seen as a contact ion pair between Li⁺ and O₂⁻. In short, the fluxional behavior of the DME in the coordination complex Li⁺(DME)ₙPF₆ makes the solvated Li⁺ ions more accessible to superoxide ions in the DME/LiPF₆ solution and the contact ion-paired superoxide can readily abstract another Li⁺ to be converted to Li₂O₂.
Scheme 4.1: Li$^+$ solvation and ion pair formation in LiPF$_6$/DME
Scheme 4.2: \( \text{Li}^+ \) solvation and ion pair formation in \( \text{LiCF}_3\text{SO}_3/\text{DME} \)}
A different scenario seems to exist in the LiCF₃SO₃/DME electrolyte. The similar DN of DME and CF₃SO₃⁻ enables the latter to displace some of the DME molecules in the solvate and form contact ion pairs of the type \((\text{DME})_n\text{Li}^+\text{(CF₃SO₃⁻)})\). The anion can alter the conformation of the complex and position itself to form a bidentate coordination complex (solvate) with Li⁺ since the electron density at the sulfonyl oxygen atoms is much higher than that at the ethereal oxygens. A bidentate coordination would provide strong CF₃SO₃⁻ interactions with Li⁺. The resulting solvated Li⁺ cations are probably softer acids than in the corresponding LiPF₆ solution with the propensity to stabilize the \(\text{O}_2^-\) formed from ORR in the complex \([(\text{DME})_{m-1}(\text{O}_2^-)]\text{Li}^+\text{(CF₃SO₃⁻)})\), and to dissolve and remove the superoxide from the reaction site to maintain the carbon electrode more active for further reduction of \(\text{O}_2\) (Scheme 4.2). This is probably the reason behind the significant improvement of the ORR electrochemistry in the presence of CF₃SO₃⁻ in DME-based electrolytes.

The ORR observed in TEGDME can also be rationalized on similar structure-property characteristics of the solvates of Li⁺ formed in these electrolytes.

**Scheme 4.3:** Linear Structure of TEGDME
Scheme 4.3 shows the tetraethylene glycol dimethyl ether (TEGDME) molecule (DN=16.6) in its linear form. The FT-IR spectra of the 1 M LiPF$_6$ solution in TEGDME indicate that only a fraction of the TEGDME is co-ordinated to the Li$^+$. This is consistent with TEGDME solvating the Li$^+$ cation by forming a caged structure around Li$^+$ (scheme 4.4). In this case the solvated TEGDME molecule in the Li$^+$(TEGDME)PF$_6^-$ complex is not easily exchanged with free TEGDME. This solvent separated ion pair solvate structure is apparently stable. The superoxide ion formed by the ORR, because of its basicity, is probably able to replace one of the ethereal oxygens in Li$^+$(TEGDME) to form a superoxide-containing ion pair of the structure, Li$^+$(TEGDME)(O$_2^-$)PF$_6^-$. The superoxide ion becomes somewhat shielded inside the caged Li$^+$(TEGDME) complex. In this structure, O$_2^-$ probably cannot easily access other solvated Li$^+$ ions and the result is longer lifetime and solubility for the superoxide.
Scheme 4.4: Li⁺ solvation and ion pair formation in LiPF₆/TEGDME
Scheme 4.5: Li⁺ solvation and ion pair formation in LiCF₃SO₃/TEGDME
Scheme 4.5 shows the probable ORR sequence in the presence of CF$_3$SO$_3^-$ anions. The very similar DN of TEGDME and CF$_3$SO$_3^-$ implies that the triflate could enter into the co-ordination sphere with TEGDME by substituting for some of the Li$^+$--O- bonds in the Li$^+$ (TEGDME) solvate with Li$^+$--O=S bonds to form a contact ion pair of the type (TEGDME)Li$^+$ (CF$_3$SO$_3^-$). Even though the caged solvate structure is somewhat altered in this case, the stability imposed by the strong interaction between the sulfonyl oxygens with the Li$^+$ ions will restore or even enhance the stability of the Li$^+$[(TEGDME)(O$_2^-$)](CF$_3$SO$_3^-$) complex formed with superoxide. The higher capacity obtained in Li/O$_2$ cells utilizing LiCF$_3$SO$_3$/TEGDME electrolyte is consistent with the stability of the superoxide ions shown in scheme 4.5, its increased solubility and diffusion away from the carbon electrode surface to the electrolyte bulk in the pores of the electrode where it decomposes to Li$_2$O$_2$.

Solvation enthalpy vs. lattice enthalpy: In general a crystalline solid like Li$_2$O$_2$ dissolves in a solvent when its solvation energy with the solvent exceeds its lattice energy. The following calculations indicate that Li$_2$O$_2$ will not be soluble in TEGDME or DME but LiO$_2$ could. The enthalpy of solvation calculated for Li$^+$ in diethyl ether to form Li$^+$ (diethyl ether)$_5$ using Drago’s equation we described previously is about 209 kcal/mole. On the other hand, the lattice energy calculated for Li$_2$O$_2$ is 619.4 kcal/mole. It is unlikely that the lithium peroxide dissolves in any of these ether based electrolytes. The lattice energy of LiO$_2$ has been calculated to be 210 kcal/mole. This value is comparable to the above mentioned estimated solvation energy of Li$^+$ in ether-based electrolytes. The enthalpy data provide a rational explanation for the solubility of lithium superoxide complexes discussed above in the ether-based electrolytes. The stable complexes are able to dissolve in the ether electrolytes, move away from the electrode surface to the electrolyte in the electrode pores and decompose there eventually to form Li$_2$O$_2$. In this way
the porous electrode performs better in the LiCF$_3$SO$_3$-based electrolytes in which the sup oxide complexes are more stable and soluble to yield higher capacities in the Li/O$_2$ cells.

4.4. Conclusion

We have shown that the conducting salt anion does not affect oxygen transport in TBA salt-based electrolytes in 1,2-dimethoxyethane. As a result we have been able to determine O$_2$ solubility and diffusion coefficients in these electrolytes. We have also found higher oxygen transport parameters in electrolytes prepared from both the low viscosity DME and high viscosity TEGDME compared to that in DMSO. We attribute this to the electrolyte structures.

We have found that the discharge capacities of Li/O$_2$ cells utilizing LiCF$_3$SO$_3$/TEGDME solutions are higher than in those containing LiPF$_6$/TEGDME. Our microelectrode and RRDE data combined with IR spectra suggest that the higher capacity in LiCF$_3$SO$_3$-based Li/O$_2$ cells is due to the increased stability and solubility of the ion pair species formed in the electrolyte between the initial ORR product superoxide (O$_2^-$) and the solvated Li$^+$ with a structure such as [(TEGDME)(O$_2^-$)]Li$^+$CF$_3$SO$_3$ in which the Li$^+$ resides in a TEGDME cage. The PF$_6^-$ anion does not form a similar contact ion pair with Li$^+$ in DME or TEGDME because of the very low DN of PF$_6^-$ compared to that of the TEGDME solvent and the CF$_3$SO$_3^-$ anion. This study further affirms the electrolyte-controlled ORR processes in non-aqueous Li/O$_2$ batteries.
Chapter 5

Solid Phase Bi-functional FePC Catalysts for Non-aqueous Li-air Batteries

5.1. Introduction

The limited rechargeability of the Li anode and the constraints associated with the development of suitable battery architecture are deterrents to the development of a practical rechargeable Li-O₂ battery. The major discharge product reported in a non-aqueous Li-O₂ battery is Li₂O₂ via a two-electron O₂ reduction which yields a theoretical specific energy of 3505 Wh/kg. This is sixty seven percent lower than the theoretical specific energy of 5200 Wh/kg calculated on the basis of the four-electron reduction of O₂ to form Li₂O as the discharge product. In this context a cathode catalyst that could catalyze the reduction of O₂ to form lithium monoxide (Li₂O) as the discharge product is appealing.¹²⁹, ¹³¹ Simultaneously, if the same catalyst can promote oxygen evolution reactions at lower over-potentials, then the high capacity of the Li-O₂ battery can be accessed in many charge/discharge cycles to realize the goal of an ultra-high energy density rechargeable Li-O₂ battery.

Oxygen electrocatalysts based on transition metal-N₄ centers such as porphyrins and phthalocyanines have demonstrated varying degrees of activity to catalyze ORR in fuel cells.¹²⁹, ¹³¹, ¹³² However, only a few studies have reported ORR/OER catalysis of the O₂ electrode by these metal-N₄ centers in non-aqueous electrolyte-based Li-O₂ batteries.¹⁰³-¹⁰⁵ A recent study published by Trahan et al. show that CoPC-based catalyst can influence the oxygen electrochemistry in Li-O₂ batteries.²⁹ The oxygen reduction reaction rate at the catalyst is determined by the solvent’s ability to modulate the Lewis acidity of Li⁺ ions in solution. In high Donor Number (DN) solvents the ORR proceeds at the outer Helmholtz plane since the Li(solvent)ₙ⁺–O₂⁻ intermediate is stabilized in the electrolyte solution. On the other hand, in low
DN solvents such as acetonitrile and TEGDME the ORR proceeds at the electrode’s inner Helmholtz plane on the catalyst center, since the electron acceptor property of the catalyst is higher than that of Li(solvent)\textsuperscript{n+}.

An ideal catalyst would be one that selectively catalyzes the ORR and OER reactions without interfering with the performance of the electrolyte or the lithium anode. We demonstrate that the solid phase FePC catalyst that we have developed approaches this performance. DFT calculations (for solvent free conditions) have shown that both cobalt(II) phthalocyanine (CoPC) and iron(II) phthalocyanine (FePC) have positive binding energies for O\textsubscript{2} adsorption.\textsuperscript{106} These studies have also suggested that only FePC is capable of adsorbing O\textsubscript{2} in the side-on configuration, which we believe is desired for the four-electron reduction of O\textsubscript{2} to form Li\textsubscript{2}O. Sun et al.\textsuperscript{107} employed FePC dissolved in TEGDME and DMSO-based electrolytes as a redox shuttle for electrons and superoxide ions (O\textsubscript{2}\textsuperscript{-}, the one electron reduction product of O\textsubscript{2}), between a carbon cathode and the insulating Li\textsubscript{2}O\textsubscript{2} formed on it during discharge. They concluded that the molecular oxygen adsorbed on the metal center (i.e, FePC–O\textsubscript{2}) would undergo reduction to form FePC-LiOOLi which would then diffuse to a nucleated Li\textsubscript{2}O\textsubscript{2} site and precipitate. Similarly, they claim that the Fe\textsuperscript{III}PC can oxidize the Li\textsubscript{2}O\textsubscript{2} to form FePC–O\textsubscript{2}\textsuperscript{-} which would then diffuse to the carbon surface where the superoxide would undergo further oxidation to O\textsubscript{2}. However, as we show later in this chapter the dissolved FePC reacts with the Li metal anode, possibly affecting its rechargeability in the Li-air battery. Consequently, a FePC catalyst that does not dissolve in non-aqueous electrolytes while retaining its ORR and OER catalytic activity would be of great interest for developing practical Li-air batteries. We have developed such solid phase catalysts by heat-treating mixtures of high surface carbon and FePC at selected high temperatures. The properties of these catalysts prepared by heating at precisely controlled
temperature are reported together with their ORR and OER activities in non-aqueous electrolytes and Li-air battery cells. The pyrolysis temperature of the high surface area carbon with the FePC catalyst embedded in it affects the structure and catalytic activity of the resulting solid phase catalyst. We present here a comprehensive discussion of the structure-catalytic property relationships of these solid phase FePC catalysts and the manner in which the electrolytes influence their electrochemical properties. The best catalyst has demonstrated a doubling of the cycle life of the Li-air battery.

5.2. Experimental

5.2.1. Materials

All lithium salts (LiPF$_6$, LiCF$_3$SO$_3$) battery grade, Iron(II) phthalocyanine and dry organic solvents (acetonitrile-MeCN, dimethyl sulfoxide-DMSO, tetraethylene glycol dimethyl ether-TEGDME) were purchased from Sigma-Aldrich and were stored in an MBraun glove-box maintained under 0.5 ppm prior to use. High surface area carbon Vulcan-XC72R (233 m$^2$/gram) and Ketjenblack EC300JD (802 m$^2$/gram), were obtained from Cabot corporation. The Ag/AgNO$_3$ reference electrode was prepared as reported by Wain et al.$^{68}$ using a silver wire (99%) purchased from Alfa Aesar. All the potentials in this chapter are reported with respect to the Li/Li$^+$ scale unless otherwise stated.

5.2.2. Iron(II) Phthalocyanine–based Catalyst Synthesis

Catalysts were prepared using a method previously reported by Dodelet et al.$^{91, 108}$ Iron(II) Phthalocyanine dissolved in concentrated sulfuric acid was stirred with the carbon black (Ketjenblack EC300JD or Vulcan-XC72R). The amount of high surface area carbon added was such that the weight of iron metal in the carbon matrix is 4% by weight. The resulting slurry was poured into a large volume of de-ionized water cooled to below 5°C. The suspension was filtered
and washed as required to remove any residual H\(^+\) in the catalyst. The carbon-catalyst residue was dried overnight at 60°C under vacuum and the dried powder was heat-treated at the selected temperatures (presented in the Results and Discussion section) for two hours under argon.

5.2.3. Cyclic Voltammetry

Thin film electrodes were prepared from FePC/Vulcan catalyst–based inks as follows. PVDF binder was dissolved in N-methyl-2-pyrrolidone to which the carbon/catalyst powder was added so that the binder:carbon/catalyst ratio was 90:10 by mass. A required aliquot of the ink dispersion was deposited on the clean dry glassy carbon disc electrode to obtain a 0.1 mg cm\(^{-2}\) catalyst layer. The glassy carbon disc was dried in vacuum at 80°C overnight.

Voltammograms were initially recorded in argon-saturated 0.1 M LiCF\(_3\)SO\(_3\)/MeCN, 0.1 M LiPF\(_6\)/MeCN, 0.1 M LiCF\(_3\)SO\(_3\)/DMSO, and 0.1 M LiPF\(_6\)/DMSO electrolytes to investigate the redox activity of the catalyst metal center and to verify the absence of electrochemical reactions that arise from the electrolyte within the electrochemical potential window of interest. All the electrochemical data shown in this chapter were obtained at a glassy carbon disc electrode (0.5 cm diameter) and the current densities reported here are referenced to its geometric surface area (0.196 cm\(^2\)). Oxygen electrochemistry was recorded in O\(_2\) saturated 0.1M LiCF\(_3\)SO\(_3\) or LiPF\(_6\) electrolytes prepared in acetonitrile (MeCN) and dimethylsulfoxide (DMSO) solvents.

5.2.4. Lithium-Air Cell Testing:

Li-oxygen cells were constructed using Li foil anodes and uncatalyzed cathodes using KetjenBlack EC300JD, and catalyzed carbon cathodes containing FePC/Ketjenblack-based catalyst, and microporous polypropylene membrane separators. Details of our Li-O\(_2\) cell
construction are reported elsewhere (Section 4.2.4). The Li-O₂ cells employed TEGDME as the electrolyte solvent and electrolytes prepared with 1M LiPF₆ as well as LiCF₃SO₃ were used. Some cycled cells were disassembled and the cathodes were analyzed by means of several spectroscopic techniques that are discussed later in this chapter. All electrochemical experiments and Li-O₂ cell tests were carried out in a glove-box maintained at a humidity level < 0.5 ppm.

5.2.5. Thermo-Gravimetric Analysis (TGA)

Thermal stability of commercial iron(II) phthalocyanine was measured under argon in an SDT Q600 thermal analyzer.

5.2.6. Fourier-Transform Infrared Spectroscopy (FT-IR)

Commercial iron(II) phthalocyanine samples pyrolyzed at different temperatures under argon were analyzed using a Bruker Vertex-70 FT-IR spectrometer.

5.2.7. X-Ray Diffraction

Discharged Li-O₂ cells were disassembled inside the glove-box, the carbon cathodes were separated, washed with acetonitrile to remove the Li salt, and XRD spectra were recorded with a Rigaku Ultima IV diffractometer using a Cu Kα radiation source. The cathode sample was covered with a Kapton® polyimide film to prevent contact with atmospheric moisture during the data acquisition.

5.2.8. In-Situ Raman

In-situ Raman experiments were carried out using an in-situ Raman cell obtained from MTI Corporation. In situ Li-O₂ cells were prepared using a carbon cloth cathode (facing the quartz window of the Raman cell) and a lithium anode. Raman spectra were obtained in a
DMSO-based electrolyte containing dissolved FePC of the composition 1 mM FePC/0.1M LiCF₃SO₃/DMSO, while scanning the cathode potential at 200 mV steps and holding the electrode at each potential for more than 300 minutes. Note that whereas unheated FePC is soluble in DMSO, the heat-treated FePC/carbon materials are insoluble in DMSO.

5.2.9. Scanning Electron Microscopy (SEM)

Lithium metal surfaces were exposed to 1mM FePC/1 M LiCF₃SO₃ in DMSO and 1 mM FePC/1 M LiCF₃SO₃ in TEGDME overnight. Then, they were washed with 1,2-dimethoxyethane solvent, dried under vacuum and SEM images of the specimens were recorded on a Hitachi S-4900 instrument. SEM images were also recorded for cycled cathodes from Li-air cells.

5.2.10. Transmission Electron Microscopy (TEM)

The iron(II) phthalocyanine catalysts deposited on carbon were characterized using a JEOL 2010F transmission electron microscope.
5.3. Results and Discussion

5.3.1. Electrochemistry of Iron(II) Phthalocyanine Dissolved in Dimethyl Sulfoxide

Cyclic voltammograms recorded in Ar saturated 1 mM FePC solutions in 0.1 M LiCF$_3$SO$_3$/DMSO and 0.1 M LiPF$_6$/DMSO electrolytes are shown in Figure 5.1. Three pairs of redox reactions are observed. The Fe(II)/Fe(I) reversible reaction with a reduction peak at 2.62 V is consistent with the changes observed in the in-situ Raman spectrum at this potential (Figure 5.2). While all the peaks in the Raman spectrum obtained at open circuit potential are due to the DMSO solvent, new Raman peaks appear at 260, 584, 745, 1000 cm$^{-1}$, and between 1100-1500 cm$^{-1}$ when the electrode potential is scanned below the 2.62 V peak. It is important to review the electronic configuration of Fe (Scheme 5.1) as a function of its oxidation state to understand the Raman spectra since the oxidation state changes during the potential scan.

Scheme 5.1: Iron $d$ electron configurations of FePC dissolved in DMSO as a function of the oxidation state of iron.
In solvents such as DMSO which can form coordination bonds with electron acceptor centers, iron(II) phthalocyanine is six co-ordinated\textsuperscript{109} in a structure, \((\text{DMSO})_2\text{Fe(II)PC}(-2)\), containing two DMSO molecules as shown in Scheme 5.2. At the open circuit potential the metal center is in the Fe(II) state. When the electrode is polarized to lower potentials, the Fe(II) is reduced to Fe(I) which has the \((xz,yz,xy)^6(z^2)^1\) electronic configuration. Axially coordinated DMSO molecules destabilize electronic states of iron where electrons occupy axial orbitals (Fe(I) state, Scheme 5.1). As the DN of the coordinating molecule is increased, the Fe(II) state is stabilized over the Fe(I) state and the redox potential of Fe(II)/Fe(I) is shifted downwards. The effect of the shift of the Fe(II)/Fe(I) redox potential on oxygen electrochemistry is discussed in detail in the following sections of this chapter. As shown in Scheme 5.2, following the reduction of the metal center \((\text{DMSO})_2\text{Fe(I)PC}(-2)\) releases one of the two DMSO molecules attached to Fe(II)PC to form an asymmetric five co-ordinated complex. The planarity of the coordinated FePC molecule is lost during this transition and the changes that appear in the Raman spectra below 2.6 V are consistent with these symmetry changes.
Figure 5.1: cyclic voltammograms obtained for argon purged 1 mM solution of FePC in a) 0.1 M LiPF<sub>6</sub>/DMSO and b) 0.1 M LiCF<sub>3</sub>SO<sub>3</sub>/DMSO.
Scheme 5.2: Fe(II)/Fe(I) in DMSO

\[
(DMSO)_2\text{Fe(II)PC(−2)} + e^- \leftrightarrow [(DMSO)_2\text{Fe(I)PC(−2)}]^- \quad [5.1]
\]

\[
[(DMSO)_2\text{Fe(I)PC(−2)}]^- \leftrightarrow [(DMSO)\text{Fe(I)PC(−2)}]^− + \text{DMSO} \quad [5.2]
\]

Scheme 5.3: Fe(I)PC reduction in DMSO

\[
[(DMSO)\text{Fe(I)PC(−2)}]^− + e^- \leftrightarrow [(DMSO)\text{Fe(I)PC(−3)}]^2− \quad [5.3]
\]

Figure 5.1 also indicates that the \text{Fe(I)PC(−2)} is further reduced possibly to \text{Fe(I)PC(−3)} at about 2.2 V (Scheme 5.3). Note that in this process only the PC macrocycle moiety is reduced. This reaction is reflected by the new Raman peaks that appear at 1425 and 1490 cm\(^{-1}\) in Figure 5.2 when the electrode is polarized down to 2.20 V. These Raman peaks can be attributed to the pyrrole C-C and C-N stretching vibrations arising from the reduction of the macrocycle ring as depicted in Scheme 5.3.

The oxidation of Fe(II) to Fe(III) that appears at 3.8 V in the reverse scan in LiCF\(_3\)SO\(_3\)/DMSO is a two-step reaction where the electron transfer is followed by substitution of a co-ordinated DMSO molecule by an anion as depicted in Scheme 5.4. The strength of the coordination bond between the counter anion (X\(^−\)) in solution and the Fe(III) center determines the redox potential of the Fe(II)/Fe(III) couple. That is, the oxidation of the Fe(II) to Fe(III) occurs at a lower potential if the anion forms a stronger bond with the Fe(III)PC formed as a result of the oxidation.\(^{110}\)
Scheme 5.4: Fe(II)/Fe(III) in DMSO

\[
(DMSO)_2Fe(II)PC(-2) \leftrightarrow [(DMSO)_2Fe(III)PC(-2)]^+ + e^- \quad [5.4]
\]

\[
[(DMSO)_2Fe(III)PC(-2)]^+ + X^- \leftrightarrow (DMSO)Fe(III)PC(-2)X + DMSO \quad [5.5]
\]

Figure 5.2: In-situ Raman spectra obtained at the carbon electrode at different potentials (Argon purged 1 mM FePC, 0.1M LiCF$_3$SO$_3$/DMSO)
We have also studied the redox behavior of FePC/Vulcan-based catalysts in argon saturated electrolytes and the data obtained are discussed along with the ORR electrochemistry later in this chapter.

5.3.2. Reaction of the Li Metal with Iron(II) Phthalocyanine

In order to investigate any possible reaction between metallic lithium and FePC dissolved in solution, we stored as-received and polished lithium metal foil pieces in contact with solutions of: 1) 1 mM FePC, 1 M LiCF$_3$SO$_3$/TEGDME, and 2) 1 mM FePC, 1 M LiCF$_3$SO$_3$/DMSO. Figure 5.3 shows SEM micrographs of the Li metal surfaces exposed to these electrolytes overnight. They reveal that the FePC is more reactive towards the polished lithium metal surface. The unpolished Li surface, always covered with a protective layer of native lithium oxide and/or carbonates, shows less reaction in the stored solution. In both TEGDME and DMSO-based electrolytes the reaction between the Li and FePC is mitigated to a great extent by this protective layer. However, the increased reactivity of the polished Li surface suggests that the dissolved FePC will react with the Li anode in a Li-air cell after it has been recharged to deposit fresh Li.

The reactivity of the FePC with the lithium metal surface we observed here underscores the importance of using an insoluble solid phase catalyst over a solution phase catalyst in the cathode of Li-O$_2$ batteries. The solid phase catalysts we have prepared by heat-treating FePC/carbon mixtures are insoluble in the electrolytes and yet have demonstrated ORR and OER catalytic properties which we present in the following sections.
Figure 5.3: SEM micrographs of the Li metal surface after being contact with 1 mM FePC in DMSO and TEGDME. a) Lithium metal surface as received, b) Lithium metal surface polished, c) Surface (a) after contact in 1mM FePC/1M LiCF$_3$SO$_3$ in DMSO and d) Surface (b) after contact in 1 mM FePC/1 M LiCF$_3$SO$_3$ in DMSO. e) Surface (a) after contact in 1 mM FePC/1 M LiCF$_3$SO$_3$ in TEGDME, f) Surface (b) after contact in 1 mM FePC/1 M LiCF$_3$SO$_3$ in TEGDME.

5.3.3. Thermal Stability and Structure of Iron(II) Phthalocyanine

The Thermo-Gravimetric-Analysis (TGA) data presented in Figure 5.4 demonstrates the thermal stability of pure iron(II) phthalocyanine (FePC) as a function of increasing temperature to 1000°C. Gradual weight loss begins at about 170°C with significant loss starting at about
575°C. The IR spectra of the samples heated to various higher temperatures discussed below provide information on the structural changes in FePC that accompany the thermal treatment.

![Figure 5.4: TGA data for pure FePC under argon in the temperature range of 20-1000°C at a heating rate of 10 deg/second.](image)

FT-IR spectra recorded to analyze neat FePC and FePC samples heated at 300°C, 600°C and 800°C under argon gas are presented in Figure 5.5. The IR peaks at 730 cm\(^{-1}\) arises from out-of-plane C-H vibrations characteristic of the polymorphic forms of the FePC.\(^{111}\) Both FePC and FePC-300°C show marked similarity in this region. As-received FePC is in the α polymorphic form which is confirmed by the FT-IR peak observed at 728 cm\(^{-1}\), and there is no change in the polymorphism at 300°C (Figure 5.5). FePC in the α polymorphic form transforms to the β form upon further heating. As the temperature is increased, randomly aligned FePC molecules will be sublimed leading to mass loss. This explains much of the weight loss up to about 500°C. At 500°C the FePC molecules in the α form will be completely converted to β, as indicated by the IR peak at 740 cm\(^{-1}\). As the temperature is further increased, the phthalocyanine
molecule will start to decompose. This is when the TGA exhibits a sharp drop in the sample mass beginning at around 575°C. However, the FT-IR spectra for the FePC-600°C material has peaks at 1080 cm\(^{-1}\), 1120 cm\(^{-1}\) and 1331 cm\(^{-1}\) which can be attributed to C-N stretching, C-H bending (in-plane) and pyrrole stretching (C=C or C=N), respectively. This observation confirms the notion that the M-N\(_4\) macrocycle is still intact after heat treatment at 600°C.\(^{112}\) Meanwhile the FT-IR peak at 730 cm\(^{-1}\) shifts to 740 cm\(^{-1}\) at 600°C. This latter peak is indicative of the \(\beta\) polymorphic form. Therefore, we can conclude that at 600°C the FePC is substantially converted to the \(\beta\) polymorph with its partial decomposition (breakdown of the benzene rings)\(^{113-115}\) also possibly occurring. However, Fe-N\(_4\) moiety appears to be retained in the resulting FePC-600°C catalyst. The FePC sample pyrolyzed at 800°C showed complete absence of the IR peaks that arise from the C-N macrocycle suggesting the destruction of the M-N\(_4\) center.

Figure 5.5: FT-IR spectra of pure iron(II) phthalocyanine pyrolyzed at a series of temperatures ranging from 300-800°C.
5.3.4. Synthesis and Characterization of Carbon Supported Catalysts

Carbon supported FePC catalysts were prepared using two types of carbon precursors—low surface area Vulcan (VC)(XC72R) and high surface area Ketjenblack (KB) (EC300JD). The FePC/Vulcan (VC)(XC72R) -based catalysts were synthesized to carry out electrochemical thin film studies, and the FePC/Ketjenblack (KB)(ED300JD) -based catalysts were prepared to evaluate Li-O\textsubscript{2} cell performance. Hereon, the Vulcan and Ketjenblack supported catalysts heat treated at 300 °C will be referred to as FePC/VC(300) and FePC/KB(300), respectively. The catalysts heat treated at other temperatures will be named in the same manner with the corresponding temperature identifiers.

The FePC/Carbon -based catalysts prepared by heat treatment were characterized by powder X-ray diffraction (XRD). The XRD spectra shown in Figure 5.6 indicate the formation of metallic Fe(2θ = 44°) in the sample pyrolyzed at 800°C. This is in agreement with the FT-IR spectra obtained for pure FePC heat treated at 800°C which suggested complete destruction of the phthaloocyanine macrocycle.
Transmission electron microscopic images obtained for the catalysts heat treated at 300, 600 and 800°C are shown in Figure 5.7. The calculated distance of 0.48 nm between the lattice planes for the crystalline regions in FePC/KB(600) is consistent with the FePC in the β polymorphic form\textsuperscript{115}. Meanwhile the FePC/KB(300) catalyst showed a distance of 0.34 nm between the lattice planes which is similar to the Fe-Fe distance observed for FePC in the α polymorphic form. These results are consistent with the IR spectra presented earlier. It appears that the FePC adsorbed on the carbon support is more stable under heat treatment than pure FePC, and as a result, the catalyst adsorbed on carbon does not undergo significant decomposition at 600°C but remains substantially as the β polymorph. The TEM image of the FePC/KB(800) also showed a crystalline region which corresponds to an inter lattice distance of 0.40 nm.
Figure 5.7: TEM micrographs of catalysts, a,b) FePC/KB(300), c,d) FePC/KB(600), e,f) FePC/KB(800) showing their crystalline nature.
5.3.5. Catalyst Solubility in Organic Electrolytes

The solubility of the carbon supported FePC catalysts in TEGDME were tested by stirring 1 mg of the catalyst in 1 ml of TEGDME overnight. The FT-IR spectra and the visual color of supernatant solutions obtained for each catalyst was compared to the neat TEGDME solvent and a solution of 1mM FePC/TEGDME (Figure 5.8). All three catalysts are insoluble in TEGDME which indicates strong adsorption of the catalyst to the solid carbon matrix.

![Comparison of supernatant color and FT-IR spectra](image)

**Figure 5.8:** a) Comparison of the supernatant color of the various catalysts dissolved in TEGDME. (I): Neat TEGDME, (II): 1mM FePC dissolved in TEGDME. Supernatant of (III):FePC/VC(300) dissolved in TEGDME, (IV): FePC/VC(600) dissolved in TEGDME and (V):FePC/VC(800) dissolved in TEGDME. b) FT-IR spectra obtained for the supernatant solutions of various catalysts dissolved in TEGDME.
5.3.6. Oxygen Reduction in High Donor Number (DN) Dimethyl Sulfoxide-based Electrolytes

Figure 5.9 shows the cyclic voltammograms obtained for O₂ in LiPF₆/DMSO at a glassy carbon electrode containing thin films of two FePC/VC-based catalysts. The onset potentials on the catalyzed electrodes suggest that the FePC/VC catalysts are not influencing the ORR in DMSO. While the Fe(II)/Fe(I) redox potential appears at 2.62 V (Figure 5.1), the onset of the O₂ reduction reaction is seen at about 2.9 V. The pre-peak observed at 3.0 V in the O₂ saturated electrolyte can be attributed to adsorption of O₂ on the metal center of the catalyst. Clearly the iron is in the Fe(II) state at the superoxide forming potential in DMSO. Since the Fe(II)/Fe(I) occurs at a lower potential, the superoxide stabilization by the catalyst is not possible here. The superoxide ion is more stable as a Li⁺(DMSO)ₙ—O₂⁻ ion pair in solution. This is similar to the previously discussed O₂ reduction on the CoPC catalyst in DMSO-based electrolytes involving an outer Helmholtz plane electron transfer mechanism.²⁹ Thus ORR on both FePC and CoPC catalysts in DMSO are electrolyte-controlled outer Helmholtz plane reactions.
Figure 5.9: Cyclic voltammograms obtained at a glassy carbon disc in O_2 saturated 0.1M LiPF_6/DMSO

5.3.7. Oxygen Reduction in Low Donor Number Acetonitrile-based Electrolytes

As we have mentioned before, two requirements must be fulfilled for the efficient catalytic ORR (i.e, inner Helmholtz plane reaction) in non-aqueous electrolytes: i) the stabilization of the superoxide ion on the metal center, which is determined by the electronic configuration of the metal atom (Scheme 5.1), and ii) lower stability of the superoxide ions in the electrolyte solution than on the metal center which is a function of the solvent DN. Available electrochemical evidence suggests that an electrolyte in a low DN solvent with DN < ~20 would facilitate ORR on the metal center (inner Helmholtz plane electron transfer). Therefore, we carried out electrochemical investigations in an electrolyte-based on the low DN solvent acetonitrile (MeCN, DN= 14.1) to determine the ORR catalyst activity of FePC.
Firstly, cyclic voltammograms were recorded in argon saturated solutions of FePC prepared in 0.1M LiPF$_6$/MeCN and 0.1M LiCF$_3$SO$_3$/MeCN. Since FePC is only sparingly soluble in MeCN, saturated solutions containing <0.5 mM FePC concentration was used. Figure 5.10 displays the cyclic voltammogram obtained at a pristine glassy carbon electrode in O$_2$ saturated 0.1M LiPF$_6$/DMSO as a dotted line.

![Cyclic Voltammograms](image)

**Figure 5.10:** cyclic voltammograms obtained for argon purged <0.5 mM (saturated) solutions of FePC in 0.1M LiPF$_6$/MeCN and 0.1M LiCF$_3$SO$_3$/MeCN. CV obtained for the O$_2$ saturated 0.1M LiPF$_6$/MeCN electrolyte is shown as a black dotted line.

It appears that the Fe(II)/Fe(I) redox reaction occurs about 300 mV above the O$_2$ reduction onset at 2.9 V on the pristine glassy carbon electrode. The resulting Fe(I) center at the ORR onset potential has the ability to stabilize the superoxide ion via an inner Helmholtz plane electron transfer to form O$_2$ reduction products.
Comparison of the CVs obtained for redox activity of FePC dissolved in LiPF$_6$/MeCN and LiCF$_3$SO$_3$/MeCN (Figure 5.10) suggests that the effect of the donor ability of the lithium salt anion$^{74}$ on the redox potentials of iron is insignificant in MeCN–based electrolytes. The reason is that MeCN is a strong $\sigma$ donor which coordinates to the Fe metal center through the nitrogen atom. It has been reported that the bond distance between the Fe atom and the nitrogen of MeCN is shorter than these distances observed for other nitrogen based solvents such as pyridine and amine.$^{116}$ We further studied the redox activity of FePC–based catalyst thin films deposited on a glassy carbon electrode.
Figure 5.11: Cyclic voltammograms obtained for FePC/VC(300) in: a) an Ar saturated solution of 0.1M LiCF₃SO₃/MeCN. (Solid line-first cycle, dotted line-second cycle), b) O₂ saturated solutons in 0.1M LiCF₃SO₃/MeCN(red) and LiPF₆/MeCN (black). c) Cyclic voltammograms obtained for FePC/VC(600) in an Ar saturated solution of 0.1M LiCF₃SO₃/MeCN (Solid line-first cycle, dotted line-second cycle).
Figure 5.11a shows the cyclic voltammograms recorded in an argon saturated solution of 0.1 M LiCF$_3$SO$_3$/MeCN. Two pairs of redox peaks were observed in the 2.7 V - 4.0 V potential region. The reduction peak observed at around 3.2 V is consistent with that expected for the Fe(II) $\rightarrow$ Fe(I) transition. The peak corresponding to the reverse reaction appears at 3.4 V in the oxidation wave. The pair of redox peaks that appear around 3.8 V is most probably due to the Fe(II)/Fe(III) oxidation. These peak positions are consistent with the redox activity of FePC dissolved in MeCN (Figure 5.10).

Comparison of the cyclic voltammograms obtained in O$_2$ saturated solutions of 0.1M LiPF$_6$/MeCN and 0.1M LiCF$_3$SO$_3$/MeCN suggest that there are three electron transfer processes at the FePC/VC(300) electrode during the reduction cycle (Figure 5.11b). Figure 5.11c shows the redox behavior of the FePC/VC(600) in argon saturated 0.1M LiCF$_3$SO$_3$/MeCN. In spite of the change in polymorphism that we observed for the catalyst heat treated at 600°C the redox activity of the FePC/VC(600) is preserved.

Figure 5.12 shows cyclic voltammograms recorded in O$_2$ saturated solutions of 0.1M LiPF$_6$ in MeCN for FePC/VC(300) at different potential scan rates. Besides the O$_2$ adsorption pre-peak there are three other distinct peaks that appear at 2.9 V, 2.7 V and 2.5 V. Nicholson-Shain plots derived from the peak currents in Figure 5.12a are shown in Figure 5.12b. The number of electrons involved in each reaction was calculated using the Nicholson-Shain equation (5.6) where $i_{pc}$ is the peak current density, $n$ is the number of electrons, $\alpha$ is the transfer coefficient, $D_o$ is the O$_2$ diffusion coefficient, $C_o$ is the oxygen concentration and $\nu$ is the scan rate.

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

[5.6]
Figure 5.12: a) Cyclic voltammograms obtained for FePC/VC(300) in oxygen saturated solutions of 0.1M LiPF₆/MeCN at scan rates ranging from 10-100 mV s⁻¹, b) Nicholson-Shain plots for the ORR peak currents obtained at FePC/VC(300). (The dotted line indicates the theoretical Nicholsan-Shain plot for n=1)

The theoretically calculated Nicholson-Shain plot for one-electron reduction of oxygen in MeCN is shown as a dotted line in Figure 5.12b. The plot calculated for the first reduction peak (a) is in
good agreement with the theoretical plot which represents one-electron reduction of O₂. Meanwhile, the slope of the plots obtained for the second (b) and third (c) reduction peaks are almost twice as that the first reduction. Therefore, we can conclude that peak (a) represents a one-electron reduction of O₂ while peaks (b) and (c) represent two-electron reduction reactions.

Figure 5.13a summarizes the electrochemical responses obtained at a series of catalyzed electrodes (FePC/VC(300), FePC/VC(600), FePC/VC(800)) in an oxygen saturated solution. The cyclic voltammograms obtained at both FePC/VC(300) and FePC/VC(600) catalyzed electrodes show a peak at 2.9 V due to stabilized O₂⁻, which is consistent with the redox behavior of these catalysts depicted in Figure 5.11a and 5.11c.

Meanwhile the FePC/VC(800) catalyzed electrode follows the typical ORR characteristics at a glassy carbon electrode as depicted in Figure 5.10. To further confirm the decreased catalytic activity on the catalyst heated at 800 °C, cyclic voltammograms were recorded for the same catalyst under argon saturated conditions (Figure 5.13b). It appears that there is no redox activity observed for FePC/VC(800) within the 2.5 V – 4.3 V potential region. The destruction of the nitrogen macrocycle with the formation of metallic iron observed at 800 °C, is consistent with this loss of redox activity. However, upon cycling the FePC/VC(800) electrode within the 2.0 V – 4.3 V potential region seems to regain some of its activity, possibly from the oxidation of metallic iron.

5.3.8. Li-O₂ Cells Utilizing FePC-based Catalysts

Li-O₂ cells utilizing FePC-based catalysts were tested for charging efficiency as shown in Figure 5.14. Both FePC/KB(300) and (600) catalyzed cells showed charging efficiency close to 90% in the first cycle for a charge cutoff voltage of 4.4V.
Figure 5.13: (a) Cyclic voltammograms obtained at catalyzed electrodes in O$_2$ saturated solutions of 0.1M LiPF$_6$/MeCN, (b) Cyclic voltammograms obtained for FePC/VC(800) in argon saturated solutions of 0.1M LiPF$_6$/MeCN.

Figure 5.14c compares the charging efficiency of an uncatalyzed cell with a catalyzed cell to a cutoff voltage of 4.65 V which yielded charging efficiencies of 79% and 96% respectively. The higher charging efficiency of the fully discharged catalyzed Li-O$_2$ cell affirms the ability of the two heat treated carbon-FePC as OER catalysts.
Figure 5.14: Full discharge and charge cyclability obtained for a) FePC/KB(300) and b) FePC/KB(600) catalysts 1M LiCF₃SO₃/TEGDME in the voltage range of 2.00 V to 4.4 V. c) Comparison of the charging efficiencies of the catalyzed cell and the uncatalyzed cell.
Lithium- oxygen cells were cycled with a capacity limit of 400 mA h g\(^{-1}\) (Figure 5.15). All three catalyzed cells with FePC/KB(300), FePC/KB(600) and FePC/KB(800) survived through their 40\(^{th}\) cycle with 100% capacity utilization. This is a two fold increase in cycle life compared to the un-catalyzed Li-O\(_2\) cell.

**Figure 5.15:** Cycling performance obtained for a) FePC/KB(300) b) FePC/KB(600) c) FePC/KB(800) catalyzed and d) uncatalyzed(Ketjenblack) cells in 1M LiCF\(_3\)SO\(_3\)/TEGDME. The cell are capacity limited at 400 mA h/g. The charge limit is 4.65 V.

### 5.3.9. Li-O\(_2\) Cell Discharge Products

Figure 5.16 is a comparison of XRD spectra obtained for uncatalyzed (Figure 5.16a) and FePC/KB(600) catalyzed (Figure 5.16b) Li-O\(_2\) cell cathodes after full discharge with a capacity
untilization of 3100 mA h g⁻¹. Weak XRD peaks corresponding to Li₂O₂ are observed. Upon standing in the atmosphere for 12 hours strong LiOH peaks were observed in the catalyzed cathode. The peaks shown by asterisks are associated with lithium hydroxide. The peaks shown by inverted triangles show the Li₂O₂ peak positions. The emergence of the strong LiOH peak upon exposure to humidity indicates that a product besides Li₂O₂, possibly lithium superoxide is accumulated on the discharged cathode which is not detected by XRD. To confirm this product, a Raman spectrum was recorded on the same cathode before exposing the electrode to the atmosphere (Figure 5.17). The Raman spectrum collected for the cathode clearly indicates the presence of LiO₂. This further confirms that the LiO₂ produced as the initial discharge product is stabilized by the Fe-N₄ metal center. Some of it is converted to Li₂O₂ and the rest is oxidized to O₂ in the charge half cycle.

Figure 5.16: XRD profile for the post discharged cathodes (PDC). a) Post-Discharge-Cathode using KB300JD, b) Post-Discharge-Cathode using FePC/KB(600).
5.3.10. Mechanism of the FePC Catalysis

The sequence of reactions that most probably takes place on the FePC/VC(300) catalyst during ORR and OER (Figure 5.18) depends on the potentials imposed on the electrode; i.e., under cyclic voltammetric conditions versus the electrode in a Li-O_2 battery cell. The reactions most probably occurring under cycling voltammetric conditions are shown in Scheme 5.5. Molecular oxygen that is adsorbed on the iron center is reduced to lithium superoxide which is stabilized on the catalytic sites, as shown in the first reaction 5.7. The second reaction involves the formation of Li_2O_2 via chemical interaction and decomposition of the superoxide residing in
two nearby catalytic sites. The Li$_2$O$_2$ still adsorbed on the catalytic sites undergo two-electron reduction to form lithium monoxide, Li$_2$O. The interatomic distance of Fe in the α-FePC is shorter than that observed in β-FePC. Apparently, this facilitates reaction 5.8 listed in Scheme 5.5, which then leads to the two electron reduction of the lithium peroxide to lithium monoxide. The longer Fe-Fe distance in the β-polymorphically form probably does not allow favorable disposition of the Li$_2$O$_2$ on the catalyst site to facilitate the reduction of Li$_2$O$_2$ to Li$_2$O. The data indicate that the FePC/VC(300) catalyst efficiently reduces O$_2$ to Li$_2$O while the FePC/VC(600) catalyst efficiently reduces O$_2$ to Li$_2$O$_2$. Equations 5.11-5.13 show the possible mechanism for the oxidation of the lithium oxides to O$_2$ on the Fe-N$_4$ center.

Analysis of the ORR mechanism at the FePC/VC(300) catalyst showed two different two-electron reduction processes. The second two electron reduction probably arises from the direct reduction of the oxygen molecule to the lithium peroxide at the catalytic center (reaction 5.10).

**Scheme 5.5**: Proposed mechanism of the catalytic oxygen reduction and oxygen evolution reactions at FePC/VC(300) under CV conditions.

Reduction pathway (i)

\[
N_4Fe + O_2 + e^- + Li^+ \rightarrow N_4Fe - O_2Li \tag{5.7}
\]

\[
2N_4Fe - O_2Li \rightarrow N_4Fe - O_2Li_2 + O_2 \tag{5.8}
\]

\[
N_4Fe - O_2Li_2 + 2Li^+ + 2e^- \rightarrow 2Li_2O + N_4Fe \tag{5.9}
\]

Reduction pathway (ii)

\[
N_4Fe + O_2 + 2e^- + 2Li^+ \rightarrow N_4Fe - O_2Li_2 \tag{5.10}
\]
Oxidation

\[
N_4Fe - Li_2O + Li_2O \rightarrow N_4Fe - Li_2O_2 + 2Li^+ + 2e^- \quad [5.11]
\]

\[
N_4Fe - Li_2O_2 \rightarrow N_4Fe + O_2 + 2Li^+ + 2e^- \quad [5.12]
\]

\[
N_4Fe - LiO_2 \rightarrow N_4Fe + O_2 + Li^+ + e^- \quad [5.13]
\]

In a Li-O_2 cell due to the continued infusion of O_2 onto the electrode the electrode potential is maintained at relatively steady value where the one electron O_2 reduction reaction prevails. The most probable catalytic reactions on the FePC/VC(300) catalyzed Li-O_2 cell are shown in Scheme 5.6.

**Scheme 5.6:** Proposed mechanism of the catalytic oxygen reduction and Oxidation reactions in a FePC/VC(300) catalyzed Li-O_2 cell

\[
N_4Fe + O_2 + e^- + Li^+ \rightarrow N_4Fe - O_2Li \quad [5.14]
\]

\[
N_4Fe - LiO_2 \rightarrow N_4Fe + O_2 + Li^+ + e^- \quad [5.15]
\]

The catalyst stabilized N_4Fe – O_2Li is oxidized at lower charging potentials. The same reactions occur on the FePC/VC(600) catalyst as well. Thus, the electrochemical data along with the significantly low charging overpotentials observed in FePC/VC(300) and FePC/VC(600) catalyzed Li-O_2 cells confirms the importance of the metal macrocycle for stabilization of the superoxide species. The FePC/VC(800) also improves the cycle life of Li-O_2 cells probably due to the oxidation of the metallic iron in the initial charging to produce active catalysts.

The improved performance of the catalyzed cells regardless of the catalysts’ activity towards oxygen reduction observed in low DN solvents can be explained as follows. The
discharge voltage plateaus of these cells operated in a continuous flow of oxygen represent the one-electron reduction reaction of oxygen to form lithium superoxide, LiO$_2$. The LiO$_2$ is converted to Li$_2$O$_2$ via the well-established chemical decomposition reaction. The stability and lifetime of the superoxide is determined by the nature of the catalytic site, which also catalyzes the oxidation of Li$_2$O$_2$ to O$_2$ at a lower voltage in the charge half cycle. The catalysis of both the discharge and charge reactions account for the doubling of the cycle life of the Li-O$_2$ cell. However, the Li$_2$O$_2$ formed in each cell by chemical decomposition would passivate the electrode during prolonged cycling and decrease the catalytic activity of the reaction sites. Therefore, in prolonged operation of the Li-O$_2$ cell the activity of the catalyst decreases and affects the cycle life of the cell.
Figure 5.18: Pathway (i) - Proposed mechanism of the catalysis of oxygen reduction and oxygen evolution reactions at the FePC/VC(300) catalyst
5.4. Conclusion

Iron(II) phthalocyanine/carbon–based catalysts prepared by heat treating FePC embedded in carbon black at 300°C, 600°C or 800°C have produced significant enhancement of the cycle lives of Li-O₂ cells. In low DN solvents such as MeCN, the Fe(II)/Fe(I) redox potential appears significantly above the ORR onset potential. As a result the electronic configuration of iron in the Fe(I) state is appropriately situated to stabilize the superoxide ion formed by one-electron reduction of O₂. The ORR takes place at the inner Helmholtz plane of
the catalyzed electrode in such conditions. The Fe-Fe interatomic distance in $\alpha$-FePC favors interaction of the superoxide species residing on Fe centers adjacent to each other with the result the superoxide is converted to peroxide by chemical decomposition. The peroxide is in turn reduced to lithium monoxide at the FePC/VC(300) while such reaction is not observed at the FePC/VC(600) electrode where the Fe-Fe distance is longer in the of FePC $\beta$ polymorph. Destruction of the Fe-N$_4$ observed in the catalyst heated up to 800°C is consistent with its inability to stabilize lithium superoxide on the catalyst center. Our data suggest that while the Fe-N$_4$ center is crucial for the catalytic oxygen reduction reaction, the metal center also is capable of catalyzing the oxygen evolution reaction. Finally, FePC/Carbon–based catalysts can be successfully employed in Li-O$_2$ batteries to catalyze both oxygen reduction reactions and oxygen evolutions leading to longer cycle life for the battery.
Chapter 6

Conclusions and Future Directions

6.1. Alkaline Anion Exchange Membrane Fuel Cells

Overcoming the challenges associated with alkaline anion membrane fuel cell technology is essential for its advancement as a potential portable power source and to replace the costly PEMFC technology as a whole. While the electrochemistry of fuel cell reactions in alkaline environments are advantageous particularly due to the electrocatalytic activity of cheap non-PGM catalysts on the oxygen cathode, there are many limitations that are yet to be resolved. As we have experimentally shown in Chapter 2, the carbonate exchange has a significant influence on oxygen reduction, hydrogen oxidation and methanol oxidation reactions pertaining to fuel cells. The results show that the ORR kinetics is not significantly affected. On the other hand, both HOR and MOR tend to proceed through the carbonate pathway at carbonate-containing anion exchange membrane interfaces. This leads to a significant decrease in the electrode activity. Strong ion pairing of doubly charged carbonate ions with the immobile quaternary ammonium ($\text{R}_4\text{N}^+$) species is shown to affect the diffusion pathways and exert hindrance to the overall transport of reactants through the polymer. To overcome these challenges it is important to develop suitable anion exchange membranes which have polymer structures less prone to change with carbonate exchange. Developing the fuel cell architecture and operating conditions to regenerate the AEM to the hydroxide form efficiently will also be beneficial. Finally, synthesis of electrocatalysts which can selectively promote the electrode reactions through the hydroxide pathway in the presence of carbonate ions will significantly improve the utility of AEMFCs as a future generation power source.
6.2. Lithium-Oxygen Batteries

Developing Li-O_2 batteries as a viable alternative for energy storage includes overcoming the many challenges stated in Chapter 1. In this sense, formulation of battery electrolytes to suitably modulate the Li^+ Lewis acidity and control the stability of reactive O_2 reduction reaction intermediates is essential. Capacity and cycle life of Li-O_2 batteries are determined by the solubility of lithium oxide products in the electrolytes, stability of the electrolyte itself and the kinetics and mechanism of oxygen reduction and oxygen evolution reactions on the electrodes. We have shown in Chapters 3 and 4 that the electron donor ability of the lithium salt anion is beneficial in improving the life-time of the lithium superoxide formed which in turn determines the extent of electrode passivation by insoluble lithium peroxide. Chelating linear solvents such as TEGDME play an important role on ORR by forming solvates with a curled conformation around Li^+ in the Li--O_2^- ion pair, thereby efficiently shielding it from further decomposition. Whereas the electron donor properties of the electrolyte benefit the reversibility of the ORR in uncatalyzed systems, it modulates the mechanism of ORR and OER on catalyzed electrodes. We have shown in Chapter 5 that the oxidation state of the catalyst which determines the Lewis acidity of the catalyst center in FePC–based catalysts facilitates superoxide stabilization of the metal center in Low Donor Number electrolytes. This in turn drives the ORR through an inner Helmholtz plane electron transfer process. In high donor number electrolytes, the oxidation state of the iron (which is coupled to the Donor Number of the solvent) and the ability of the electrolyte to decrease the Li^+ Lewis acidity promotes the ORR at the outer Helmholtz plane (outer plane electron transfer). Detailed understanding of these catalytic reaction conditions in electrolytes of high and low electron donor properties, have been extremely helpful in formulating the optimum electrolytes and cathodes for the Li-O_2 battery. However, it is clear
from our data that the Li anode itself plays a major role in determining the battery’s cycle life. Continuous oxidation (stripping) of lithium metal during discharge followed by lithium plating and on recharge will eventually damage the uniformity of the anode interface and lead to the formation of insulating bi-products that limit the cycle life of the battery. Therefore, improving the performance of the Li anode through appropriate electrode architecture and formulation of electrolytes with additives to facilitate efficient Li electroplating, is essential to develop a practical rechargeable Li-O_2 battery for the future.
References


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