Electron Transfer Kinetics on Non-Precious Group Metal Catalyst in Non-Aqueous Electrolytes for Li-air Batteries

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Abstract of Thesis

For a clean, sustainable, and secure energy future, rechargeable Li-air batteries attract a great deal of interest for the next generation energy storage and conversion devices because of their extremely high theoretical energy density (up to 2-3 kWh/kg). This technology promises to bring the electrical vehicles to the market with a car that can travel 500 miles range on a single charge, which is roughly 10 times higher than current state of the art Li-ion batteries. However, the practical realization of this technology is still hindered by many challenges. One of the most challenging tasks in developing Li-air batteries is the lack of fundamental understanding of oxygen reduction reaction (ORR) and oxygen evaluation reaction (OER) on the oxygen electrode, especially when catalysts are used. The role of the catalytic material and the electrolyte must also be understood for improving the stability, kinetics, and activity of the batteries. In addition, for Li-air batteries to be economically competitive, inexpensive non-precious group metal catalysts must be developed.

Chapter 1 provides an introduction to current state of the art energy storage devices and their energy density comparison with Li-air batteries. An introduction to Li-air batteries, and the limiting factors for the performance
of a reversible Li-air battery is provided. In light of the hard soft acid base (HSAB) theory, the effect of the electrolyte composition on battery performance is discussed. Inner & outer sphere electron transfer kinetics is discussed for supported catalytic systems. This chapter also covers the literature review on the non-precious metal catalysts for Li-air batteries.

Chapter 2 discusses the performance of a Fe-based metal-organic framework (MOF) catalyst for non-aqueous Li-air batteries. The synthesis and characterization of the Fe-based MOF catalyst are described. The effect of the MOF catalyst on the electron transfer kinetics for ORR studied in two different non-aqueous solvents, namely dimethyl sulfoxide (DMSO), tetraethylene glycol dimethyl ether (TEGDME) are described. The results indicate that, in high-donor number solvents such as DMSO, the solvent acts as a catalyst and promotes outer sphere electron transfers. However, in the presence of catalyst the system promotes inner sphere electron transfer occurring concurrently with outer sphere transfer via Fe active centers of the catalyst. This slightly increases the ORR activity of the system. On the other hand, in low-donor number solvents such as TEGDME, the catalyst significantly changes the ORR activity from the inner Helmholtz layer. These results are discussed according to hard soft acid base (HSAB) theory.
In addition, a three-electrode electrochemical cell was designed, fabricated and used for the in-situ Raman spectroscopy observation of reduction products. The reduction products such as Li$_2$O$_2$ and LiO$_2$ and the active center of the catalyst were identified in DMSO.

Chapter 3 provides a conclusion and offers insights toward future directions for the investigation of the non-precious catalysts for Li-air battery applications and their in-situ spectroscopic observation.
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Chapter 1  Introduction and Literature Review

1.1 Renewable Energy

Advancement of energy storage technologies is required for the effective performance of renewable energy sources. For a clean, sustainable, and secure energy future, electrical energy storage and conversion is crucial. Figure 1 shows Ragone chart, which compares the practical power and energy densities of current and developing energy storage technologies\textsuperscript{1,2}. Considering Li ion battery as one of the most well-known current state of the art energy storage technologies, it is limited by gravimetric energy density of both the anode and cathode\textsuperscript{3}. Iron-air batteries have a long cycle life, but suffer from low voltage and specific energy density compared with other metal-air batteries\textsuperscript{4}. Aluminum is one of the most abundant elements in the world, which makes aluminum–air batteries desirable because of their high specific energy. However, they are limited by low Coulombic efficiency\textsuperscript{5}. Although zinc-air batteries exhibit flat discharge voltage, long shelf life, high safety, they suffer from lower energy densities, which cannot meet the requirements of many high-energy applications\textsuperscript{6}. 
Figure 1 Ragone plot of current and developing energy storage technologies.

After the discovery of rechargeable non-aqueous Li-air battery technology by Abraham et al., lithium-air batteries have generated a great deal of attention because they offer potential advantages over other existing battery systems in terms of specific energy density.
1.2 Li-air Battery

Non-aqueous Li-air cells operate at ~3V. Therefore, they have a significantly higher specific energy density (excluding oxygen ~11000 Wh/kg)\(^8\) than other metal air batteries, which approaches that of gasoline and is almost 10 times higher than the Li-ion batteries\(^9\). The theoretical specific energy of Li-air batteries enables today’s acceptable driving range, which is 300 miles per charge compared to the current 100 miles per charge for Li-ion batteries. This could bring public interest in electric vehicles, particularly for long distance travel and advantages of reducing battery cost and weight. However, critical challenges in cell operation are yet to be overcome, and fundamental research is required on the development of efficient and reversible air electrodes. One of the most challenging tasks in developing Li-air batteries is the fundamental understanding of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on the cathode, especially when catalysts are used. In addition, noble metals and their alloys are too expensive although in some cases have shown excellent catalytic activity for ORR and OER\(^10\). For Li-air batteries to be economically competitive, inexpensive non-precious group metal (Non-PGM) catalysts must be developed.
1.3 Oxygen Reduction Reaction (ORR) Mechanism and Discharge Products

A typical Li-air battery is composed of Li metal anode, serving as the repository of Li ions, lithium conducting electrolyte and porous oxygen electrode where the regenerative oxygen reactions occurs (Figure 2). The overall polarizability (kinetic, ohmic and mass transport) of oxygen reduction reaction (ORR) during the discharge and oxygen evolution reaction (OER) during the charge play a crucial role in improving the power density\textsuperscript{11}, cyclability\textsuperscript{12}, and energy efficiency\textsuperscript{13} of the battery.
batteries. During the discharge, in non-aqueous electrolytes, oxygen is first reduced to superoxide (O$_2^-$) and reacts with Li$^+$ to form the lithium superoxide (LiO$_2$). Lithium superoxide is unstable in the presence of Li$^+$ ions with a very short half-life and decomposes to lithium peroxide (Li$_2$O$_2$)$^{14}$. For the non-aqueous electrolytes, possible ORR reactions can be described as:

$$2\text{Li}^+ + \text{O}_2^- = \text{Li}_2\text{O}_2 \quad (E^0=2.96\text{V}) \quad \text{or} \quad (1)$$

$$4 \text{Li}^+ + \text{O}_2^- = \text{Li}_2\text{O} \quad (E^0=2.91\text{V}) \quad \text{(2)}$$

Theoretically, full four–electron reduction, which converts O$_2$ to Li$_2$O is desired because of its high specific energy. However, this full four-electron reduction is generally not achieved in Li-air cells due to kinetic factors$^{15}$. It is also undesirable considering the immiscibility of the monoxide in most organic medium$^{16}$. The reduction of O$_2$ to Li$_2$O$_2$ provides 3623 Wh/kg theoretical specific energy whereas the reduction to Li$_2$O provides 5204 Wh/kg at the same voltage. During charge, reverse reaction of ORR occurs, Li$_2$O$_2$ can decompose via either a two-electron process or a one-electron process (Li$_2$O$_2 = 2\text{Li}^+ + \text{O}_2$). Bruce et al.$^{17}$ demonstrated the decomposition of the Li$_2$O$_2$ to Li$^+$ + O$_2$ on charging with or without a catalyst using in-situ mass spectroscopy. The cell potential was raised in 100 mV steps
from 4.2 V, and gas evolution at each step was analyzed. The results showed that
\[2\text{Li}^+ + 2\text{e}^- + \text{O}_2 = \text{Li}_2\text{O}_2\] reaction is reversible in a non-aqueous lithium battery.

1.4 The Role of Catalyst in Li-Air Batteries

Although Li-air batteries have extremely high energy density, their theoretical energy density cannot be fully realized in practice because of kinetic limitations in both ORR and OER, effect of electrolyte and salt composition each with their own internal polarization loss\textsuperscript{18}.

As per review of prior literature, especially those emanating from NUCRET\textsuperscript{15,19} efficacy of catalyst materials especially in a regenerative mode is yet to be clearly understood. Fundamental questions, which remain to be answered, include:

(1) In light of the HSAB theory, what is the effect of electrolyte composition on engendering inner and outer sphere charge transfer?

(2) Can a concerted inner sphere and thus catalyzed process work in tandem with a non-concerted outer sphere charge transfer step?

(3) What is the ideal nature of active site and the role of redox centers in oxygen regenerative reactions?

(4) Is there a preferred coordination of metal oxygen bonds within the context of a particular inorganic structure preferred as a binding site?

(5) What is the role of the transition metal electronic states in the binding and activation of various species involved in ORR/OER?
Nature of the electron transfer reactions at electrode/solution interface should be well examined for developing an efficient battery. Marcus, Hush and many others have been made major contributions in electron transfer reactions with the structural aspects of double layer. In addition, Taube\textsuperscript{20} introduced the concept of inner-sphere and outer-sphere electron transfer for redox reactions of coordination complexes in solutions. Conceptually, the mediation reaction can be either inner or outer sphere electron transfer for the redox systems. If the inner-sphere reactions take place during ORR, redox species penetrates to the inner Helmholtz layer and direct contact can be made with the electrode surface. On the contrary, if the reactions take place on the outer Helmholtz layer, redox species do not interact with the electrode surface and electron transfer occurs by tunneling across at least a monolayer of solvent. Considering ORR in Li-air battery, solvent molecules can coordinate with Li+ ions, support fast Li+ ion transport through the cell and stabilize the reduction intermediates, which result in product formation. This interaction has been simulated and demonstrated to be strongly related to the cycling performance of the batteries. In addition, the interaction between electrolyte and cathode catalyst plays an important role in the mechanism of ORR since the adsorption of molecular oxygen and intermediates determines the inner- and outer-sphere electron transfer mechanism\textsuperscript{19c}. 


Our previous studies show that solvent donor numbers play a crucial role on determining the ORR pathway in terms of inner and outer sphere electron transfer reactions in non-aqueous environment. For instance, high donor number solvents such as dimethyl sulfoxide (DMSO) promote outer sphere electron transfer reactions during ORR while stabilizing the superoxide anion\textsuperscript{15}. In light of HSAB theory, superoxide is relatively soft base and has a low affinity to hard acid Li cation. High donor number DMSO solvates the Li\(^+\) ions and lowers the acidity of the cation, which increases the affinity between Li-solvent complexes and O\(^2-\) anions. Although Li\(^+\) behaves as a hard acid, its acidity is lowered by the strength of the coordination bonds in Li\(^+\)-(solvent)\(_n\) complex which formed by the solvent\textsuperscript{21}. DMSO molecules affect the ability of an electron to tunnel from the electrode to the solution species for an outer sphere electron transfer and resulting that high donor number solvents act as a catalyst and stabilize the superoxide intermediate. On the other hand, relatively low-donor number solvents such as tetraethylene glycol dimethyl ether (TEGDME) and dimethyl ether (DME) do not have the ability of lowering the acidity of Li\(^+\) ions as much as high donor number solvents\textsuperscript{22}. Therefore, low donor number solvents promote inner sphere electron transfer involving concerted charge transfer that the kinetic of the ORR depend on the electrode surface. Such systems are primarily sensitive to the electronic structure of the electrode. In this case, an effective catalyst should be added to the
system to improve the kinetics of the electron transfer reactions for a high efficient battery.

In ORR, carbon based catalysts have been the subject of many investigations and in general, electron transfer rates of carbon electrode are strongly depend on carbon surface structures, i.e., the nature of active sites and the role of redox center. In this context it is useful to refine the definition of the term “site” as applied generally to mean any location where electron transfer is facilitated, it could apply to either an electronically modified region such as highly ordered pyrolytic graphene (HOPG) defects, glassy carbon (GC) or specific functional groups on carbon involved in electrocatalysis. Gerischer et al.\textsuperscript{23} have made an important point that the kinetic effects of the electrode’s electronic properties are conceptually distinct from reactive sites. According to Kneten et al.\textsuperscript{24} if the density of defects on HOPG is kept low, redox systems exhibit slow electron transfer rates, often several orders of magnitude slower than those on (GC). They also concluded that if there is lack of specific chemical sites on the basal plane, redox systems on the HOPG show slow electron transfer.

Redox systems can be classified into two sections; outer sphere redox systems and surface sensitive electrocatalytic redox systems, where electron transfer kinetics depends on the surface chemistry. Some catalysis like Metal organic frameworks can be utilized for sequential or concurrent tandem catalysis. Further,
many outer sphere redox species like Ru(NH$_3$)$_6$ $^{2+/3+}$ Ru(NH$_3$)$_6$ $^{3+/2+}$ represent the simplest case of an outer sphere electron transfer reactions without any chemical interactions with the surface. It is nearly unaffected by a monolayer of uncharged adsorbates and acts as electrocatalysis. In contrast, Fe$_{aq}$$^{3+/2+}$, V$_{aq}$$^{2+/3+}$ and Eu $^{2+/3+}$ redox reactions strongly depend on the surface oxides$^{25}$. Although Fe(CN)$_6$$^{3-/4-}$ is sensitive to the state of the carbon surface, it is often used as an outer sphere redox reaction. Clearly any “activation” or modification of a carbon surface must be considered in light of the particular redox system involved.

1.5 Carbon-Based Catalyst Materials and their role in the Li-air batteries

Carbon-based catalysts have been extensively studied in Li-air batteries due to its low cost. The fundamental questions related to the use of carbonaceous electrodes amount to the following:

(1) Does the ORR and OER activity scale in some fashion (linear or non-linear with higher surface area afforded by many high surface area carbon supports?)

(2) Is there any effect of surface functionality on either ORR or OER activity?

(3) What is the role of pore size and other shape effects?
(4) The role of the redox changes in the ORR/OER activity. Is there a relationship between the onset potential of ORR/OER and the redox behavior?

(5) Is there a support synergy, which could be engendered if these were created within the framework of a high surface area support material?

In a rechargeable battery, the aim of using a catalyst is to achieve the reversible $O_2 + 2Li^+ + 2e = Li_2O_2$ reaction. Key role of the catalysts is to reduce the overpotential for ORR and OER, either via lowering of the activation barrier or some coverage term in the pre-exponential factor of the Arhenius kinetic perspective of the electrochemical reaction. Noble metals exhibit excellent oxygen reduction and evolution activity in the Li-O$_2$ systems$^{26}$. For example, Peng et al., (reference) introduced porous Au as a catalyst for O$_2$ cathode material. They reported reversible formation/decomposition of the main discharge product Li$_2$O$_2$ and excellent cyclic performance with in situ Raman spectroscopy. However, the use of precious metals in cathode catalysts makes them prohibitively expensive and limits their widespread implementation in Li-O$_2$ batteries. Other than noble metals, researches have focused on carbon-based catalysts because of their low cost. Carbon has discharge overpotential of approximately 0.3 V and charge overpotential higher than 1 V; these values indicate that carbon exhibits sufficient
catalytic activity for the ORR but low catalytic activity for the oxygen evolution reaction (OER)\textsuperscript{27}. In principle, ORR/OER overpotential can be reduced by accelerating the kinetic reaction with the development of advanced carbon catalysts\textsuperscript{28}.

The pore structure of carbon materials is an important parameter for non-aqueous Li-air batteries. During the ORR process; carbon surfaces are gradually covered by the insoluble products and block the oxygen diffusion pathways in the pores thus deactivating the catalytic sites\textsuperscript{29}. Significant efforts have been devoted for optimization of air electrode microstructure for non-aqueous Li-air batteries\textsuperscript{29b,30}. Im et al.,\textsuperscript{31} reported that the specific capacity was determined by the pore volume of carbon rather than its surface area and a larger pore volume that could accommodate more Li$_2$O$_2$ is preferable. Researchers from Toyota made similar conclusion with an additional claim that the mesopore was superior to the micropore to yield a higher capacity\textsuperscript{32}. However, these results are insufficient due to the lack of consideration of the differences in carbon origin, morphology, surface area, and particle size. Most recently, Ding et al.,\textsuperscript{33} studied the influence of carbon pore size and dependence of the discharge capacity of Li-O$_2$ batteries. Based on this study, eight different carbon electrode materials with various pore size and pore volumes were studied. It was concluded that the initial discharge capacity was hardly affected by the surface area or pore volume. Instead, it was
directly correlated with the pore size. They showed that the cell capacity increased with the increase of pore size and eventually reached its maximum at 7169 mA h g$^{-1}$ (current density 0.05 mA cm$^{-2}$) at a pore size of 80 nm.

From a design point of view, an ideal cathode catalyst in the Li–air battery should have highly active catalytic centers, which are densely populated over the support surface to achieve maximum interaction with the solid precipitate, such as Li$_2$O$_2$. Also active sites should also be easily accessible to the electrons necessary to complete the electrochemical reactions. It is well known that chemical doping with heteroatoms such as nitrogen into carbon structure creates more active sites and enhances the ORR performance. Nitrogen doping plays a critical role in modifying carbon materials due to comparable atomic size of nitrogen and carbon, as well as the presence of five valence electrons in the nitrogen atoms available to form strong covalent bonds with carbon atoms. Kichambare et al.,$^{34}$ showed that nitrogen doped activated carbon displayed twice discharge capacity of that for activated carbon without doping$^{34}$. The doped nitrogen atoms at the edge of the graphitic layers (pyridinic) are generally believed to be connected with ORR activity. Conjugation between the nitrogen lone-pair electrons and graphene π-systems may create nanostructures with desired properties and nitrogen doped graphene nanosheets have been reported$^{34}$ with enhanced catalytic activity for Li-air batteries.
Involvement of transition metals appears to be necessary for achieving high catalytic activity. There are two major viewpoints on the nature of the ORR active sites of these metal-nitrogen modified carbon based catalysts. First hypotheses is that the metal-N\textsubscript{4} bound to the carbon support is catalytically active on the ORR, and the central metal ion in the microcycle plays a crucial role. On the contrary, Yeager and Wieser et al. suggested that the transition metal does not act as an active site for oxygen reduction, but rather serves primarily to facilitate the stable incorporation of nitrogen into the graphitic structure of carbon during high-temperature pyrolysis of metal-nitrogen complexes. Lui et al., reported on the catalytic performance of a metal-nitrogen-carbon (Fe-N-C) composite for Li-air battery applications. Fe-N-C catalyst produced lower charge–discharge overpotentials compared to the α-MnO\textsubscript{2}/XC-72 and carbon black. Although the majority of Fe centers were present as determined using X-ray absorption spectroscopy, the role of the Fe metals still remains unknown due to lack of in-situ studies however some Fe-N\textsubscript{x} coordination such as pyridinic Fe-N\textsubscript{2+2}, pyrrolic FeN\textsubscript{4}, survived after heat treatments and have been correlated with the ORR activity.

It was found that the presence of Co leads to a relatively higher pyridinic nitrogen, which becomes capable of catalyzing nitrogen n doping at the edge of graphene planes. In addition, Fe may play a promotional role in increasing graphitic nitrogen and catalyzing nitrogen doping at the center of graphene.
Fe and Co transition metals were studied in carbon and polyaniline (PANI) composite structures. It has been found that there is significant structural difference between Fe-C-PANI and Co-C-PANI as well as ORR catalytic activity. XPS results show that Co species in the catalyst is highly metallic and no Co-N coordination was found. In the case of PANI-Fe-C catalyst, the spectroscopy shows that there is typical Fe-N₄ structures found in macrocycle compounds. Also, RDE experiments show that Co-C-PANI provides higher catalytic activity for the ORR in nonaqueous than Fe-C-PANI catalyst which means the metal free pyridinic N dominant in Co-C-PANI catalyst is important for ORR in non-aqueous media in terms of ORR activity.

Metal organic frameworks (MOF) represent a new class of materials having a great deal of attention because of their porous structure. Their uniform pores with high surface areas and adjustable chemical environments for specific interactions with reactants lead to O₂ enrichment in the electrode. Most recently Wu et al. examined five different MOFs as cathode materials for Li-O₂ batteries. MOF structure has shown 9420 mA h g⁻¹ (at 50 mA g⁻¹ current density) primary discharge capacity, which is four times higher than the value obtained in cell without MOF catalysis. The accessible open metal sites in the uniform channels might be the reason for enhancement the population of O₂ molecules in the pores and assist the reaction efficiently towards high capacity. According to gas
chromatography (GC) results, no CO\textsubscript{2} gas evolution was observed after charge, which proved that MOF represents a promising catalysis. However, application of MOFs as the cathode materials for Li-O\textsubscript{2} cells remains largely unexplored.

Chapter 2 Investigation of Electron Transfer Kinetics on Non-Precious Group Metal Catalyst in Non-aqueous Electrolytes

2.1 Introduction

The rechargeable Li-air battery represents great deal of energy storage device due to its high theoretical energy storage capacity. Presence of the active cathode catalyst can effectively lower the activation energy required to reach full reduction of oxygen (ORR) during discharge and the oxygen evolution reaction (OER) during charge. So far, many studies have investigated the effects of the cathode catalyst on the performance of Li-air batteries. However, most of these studies used carbonate-based electrolyte such as propylene carbonate, which have been recently proven unstable during cycling\textsuperscript{26a}. Dimethyl sulfoxide (DMSO) has emerged as a promising solvent for Li-air batteries for providing high round-trip efficiency on the noble metals. However, several studies reported oxidation of DMSO to DMSO\textsubscript{2} and formation of LiOH during ORR\textsuperscript{41}. Most recently, ether based electrolytes such as tetraethylene glycol dimethyl ether (TEGDME) have shown considerably improved stability during charge and discharge process with a
cathode catalyst, however, the role of the catalyst in promoting ORR and OER are yet to be explored. In this study, we investigated the kinetics of ORR in non-aqueous media from the perspective of the reaction mechanisms and the double layer structure. Outer-sphere and inner sphere electron transfer mechanism are discussed in non-aqueous media in the presence of a Fe based metal organic framework (Fe-MOF) catalyst. The difference in performances between high and low donor number (DN) solvents has been explored. Electrochemical and in-situ spectroscopy results are evaluated for various possible ORR reaction mechanisms in non-aqueous media. We found that Lewis acidity of metal nodes play an important role for stabilizing the superoxide anion and increases the stability of low donor number solvent during charging and discharging process. Also, the data presented in this study show that ORR catalyst proceeds via both outer sphere and inner sphere reaction pathway. This information is expected to satisfactorily explain and unify the results of the various ORR catalysts studies pertaining to non-aqueous Li-air batteries.

2.2 Tools and Methods

Catalyst Synthesis:

The FeMOF catalyst was synthesized using the following procedure. Fe(Ac₂) was first mixed with 1,10 phenanthroline and dissolved in methanol at a molar ratio of 1/3 to form a Fe-Phen complex. Then, zinc nitrate hexahydrate was added
to the mixture while stirring the Fe-Phen complex solution. 1-Methyl imidazole was mixed with methanol and water in a separate beaker. The two solutions were subsequently combined and stirred at room temperature for 24 hours to obtain the structure. The resulting mixture was centrifuged at 38000 rpm for 20 min. The solid part was washed with the methanol and centrifuged again at the previous conditions for three more times. A ceramic boat containing the Fe-MOF powder was then placed in a tube furnace and heated at 1050 °C for 15 min. under argon. After initial heat treatment, the sample was heated again up to 900 °C under NH₃ gas for one hour.

Electrochemical Measurements:

For the half-cell experiments; Catalyst powders (90wt%) and polyvinylidene fluoride binder (PVDF, 10wt%) were mixed in a solution of N-methyl-2-pyrolidone (NMP) and coated on 0.196 cm² glassy carbon. All the prepared electrodes were placed in an oven at 80 °C for at least 12 hours under vacuum. All cyclic voltammetry experiments were conducted utilizing a PG-STAT30 bipotentiostat equipped with a scangen module from Ecochemie Inc.

In-Situ Raman Spectroscopy:

Three-electrode electrochemical cell was designed and used for the in-situ Raman experiments. Figure 3 shows experimental setup of in situ Raman Spectroscopy. The thin layer catalyst deposited onto the glassy carbon electrode
was placed behind a 0.4 mm thick sapphire window with a gold ring counter electrode and Li foil electrode. Raman spectra were recorded using a Haribo Raman system with an excitation wavelength 532nm and an inverted microscope with a 10X objective lens. The spectrum acquisition time was typically 1s.

![In situ Raman experimental setup](image)

2.3 Results and Discussion

We performed cyclic voltammograms in oxygen saturated DMSO and TEGDME electrolytes using glassy carbon (GC) and Fe-MOF electrodes. Figure 4 (a) shows the cyclic voltammetry responses of DMSO and TEGDME electrolyte on the GC electrode. It is seen from the figure that the ORR onset potential of TEGDME is 100mV lower than DMSO. However, figure 4 (b) shows slight improvement on the onset potential in TEGDME electrolyte on the Fe-MOF electrode, indicating that electronic structure configuration as well as active sites of the catalyst increases the
activity and brings the ORR onset potential from 2.7mV to 2.8mV in TEGDME. Also, in figure 4 (a), TEGDME presents two reduction peaks in which the first peak potential at 2.5V is the typical indication of formation of Li$_2$O$_2$. However, DMSO shows only one reduction peak, thereby indicating a different reduction pathway as compared to TEGDME on the GC electrode. On the other hand, Figure 4(b) shows one peak potential on the negative scan for both electrolytes indicating that the nature of the reduction might be similar on the Fe-MOF electrode. DMSO is one of the widely studied electrolytes and it is well known that on GC the first step involves one electron reduction from the molecular oxygen to superoxide during ORR. The similarity of ORR on the Fe-MOF electrode in figure 4(b) indicates that the catalyst changes the mechanism of ORR in TEGDME and increases the onset potential to support one electron reduction. This may result from the fact that the ORR pathway depends on the surface Fe-MOF catalyst and supports one electron reduction while increasing the superoxide stability.
To analyze the electron transfer mechanism from the Helmholtz double layer perspective, three different electrode structures, namely plain glassy carbon (GC), Fe-MOF and Basolite were studied in TEGDME. The difference between Basolite and the Fe-MOF is that Basolite does not contain Fe$^{3+/2}$ redox centers in its structure. Figure 5(a) shows that there is no significant change observed on the ORR/OER onset potentials of Fe-MOF and GC in DMSO indicating that redox centers mostly do not interact with the electrode surface and electron transfer occurs by the outer Helmholtz layer in DMSO. The only difference was on the ORR half peak potential on the Fe-MOF catalyst. This could be due to the fact that
some of active centers most probably Fe$^{3+/2}$ centers promotes inner sphere tandem with outer sphere. On the contrary, there is a great difference on the onset potentials and peak potentials of three different electrode surfaces in TEGDME, indicating that the electron reactions are surface dependent, where redox species penetrates to the inner Helmholtz layer (Figure 5 (b)). Fe-MOF can be utilized for sequential or concurred tandem catalysis. Therefore, in some cases, inner and outer sphere reactions can work together depend on the characteristics of the redox centers of the metal organic frameworks. For example, outer sphere electron transfer on carbon surfaces has been previously identified$^{42}$. On the other hand, for Fe$^{3+/2}$ redox centers inner sphere route has been reported$^{25b}$. The 100mV cathode half peak potential ($1/2 \, E_{pc}$) difference between GC and FeMOF in DMSO, shown in Figure 5 (a) can be explained by the different electron transfer routes during the ORR. For plain GC, only outer sphere transfer is exhibited. However, in the presence of Fe-MOF catalyst, because of the presence of Fe$^{3+/2}$ redox centers embedded to porous carbon, in addition to outer sphere, inner sphere electron transfer also contributes to the reduction process. This could explain the shift of half peak potential 100mV in the positive direction.
The cyclability performances of the carbon and Fe-MOF electrode were investigated as a function of the voltage limits (Figure 6). It is well known that superoxide is a versatile oxidation species and immediately attacks to the electrolyte even to the cathode material, leading to decomposition of the electrolyte and results in rapid fading of the battery. If the superoxide is stabilized in the system, it reduces the overpotential and increases the cyclability performance of the battery. The challenge for the stabilization is that superoxide is a soft Lewis base and it has a low affinity for the hard acid Li⁺. The formation of Li-(solvent)n
complexes lowers the acidity of Li⁺, roughly in proportion to the donor number of solvent. Our previous studies show that donor number of solvents plays a crucial role for elucidating the ORR pathway by stabilizing the superoxide anion for full electron reduction⁴³. TEGDME is a low donor number solvent, therefore, superoxide is not expected to stabilize and quickly decompose O₂⁻ to O²⁻. Our data confirms there is a fast disproportionation on a glassy carbon electrode in TEGDME electrolyte (Figure 6a). Obviously, outer sphere electron transfer on the carbon electrode is not effective in stabilizing superoxide in low donor number TEGDME. On the contrary, high cyclability performance was observed in the presence of Fe-MOF catalyst (Figure 6b). In this case, Fe⁴⁺/²⁺ metal ligands appears to contribute to the reduction process by inner sphere electron transfer. It is well known that open metal sites of metal organic framework catalysts can act as Lewis acid centers by accepting electron pairs from reactant molecules⁴⁴. When molecular oxygen reduces to superoxide, Lewis acid centers of Fe-MOF, bind with the O₂-Li(solvent)ₙ complexes and stabilizes the superoxide in the inner Helmholtz layer with a one electron reduction pathway, which increases the cyclability performance of redox mediators in TEGDME.
To confirm the formation of superoxide as a first product with an one-electron reduction, cyclic voltammetry’s were performed with Fe-MOF catalyst at three different scan rates, 10, 50, and 100 mV/s in TEGDME (Figure 7). Despite the great difference between the scan rates, the oxidation and reduction peak potentials do not change significantly, suggesting fast kinetics of the oxygen electrode when cycled under steady-state conditions. We confirm the fast kinetics by analyzing the CV response using the Nicholson-Shain equation, which defines the relationship between sweep rate and peak current magnitudes.

Figure 6 (a) Cyclability testing in 0.1M LiPF$_6$/TEGDME electrolyte on the GC electrode (b) Cyclability testing in 0.1M LiPF$_6$/TEGDME electrolyte on the Fe-MOF electrode.
In equation 4, Ip is the peak current, A is the area of the electrode, \( C^* \) is the concentration of oxygen, and \( v \) is the scan rate. The CV data provide an insight into the number of electrons transferred to the analyte by comparing the peak potentials to the scan rate. According to the equation 3, the plot of the reduction peak current Ip versus the square root of the scan rate \( (V^{1/2}) \) is a straight line. A linear regression coefficient, \( R^2 = 0.999 \) was obtained from the experimental data which is close to unity suggesting that the reduction process is under diffusion control. Plots of \( V^{1/2} \) versus cathodic peak current \( (I_{pc}) \) are shown in figure 7 (b), which contains both the experimental data and the simulated plots for \( n=1 \) for ORR. This may indicate that, within the 1.6 - 4.4 V potential range, the first electron reduction process occurs with one-electron. The best theoretical fit was obtained using a transfer coefficient \( a=0.5 \), which is a typical value for reversible reactions. This result suggests that one-electron reduction from molecular oxygen to superoxide is substantially reversible for Fe-MOF catalyst in a TEGDME electrolyte, supporting our experiments.
In-situ Raman experiments were conducted in a homemade spectroelectrochemical cell for the further investigation of the role of Fe active centers superoxide stabilization. We performed in situ experiments in DMSO (high donor number solvent), which promotes outer sphere electron transfer during ORR on a carbon electrode. The CV responses of GC and Fe-MOF electrodes were expected to be same because electron transfer is surface independent. However there is a slight improvement shown on the Epc in figure 5a, as we discussed earlier. This might be due to Fe active centers, which enhances ORR activity and stabilizes the

Figure 7 (a) Voltammograms of a Fe-MOF working electrode in oxygenated 0.1M LiPF$_6$/DMSO collected at three different scan rates. (b) Nicholson Shain theoretical peak currents overlaid with experimental peak currents obtained from (a).
superoxide in the inner Helmholtz layer. Therefore Epc improvement on the Fe-MOF electrode in DMSO electrolyte appears to be specific to the Fe centers. The activity of Fe centers can be clearly seen in DMSO during real time. Brozek et al., earlier demonstrated that Fe-MOF, enables reactions of the inserted metal ions to undergo inner sphere charge transfer via activated nitrogen bonds (via electron transfer from the Fe center). Figure 8 shows real time reduction spectrum of 0.1M LiPF₆/DMSO electrolyte on Fe-MOF carbon electrode. From the figure, first spectrum at 3.0V is the open circuit potential (OCP), which as expected gives no dynamic peaks from the catalyst as well as from the reduction products. Once the cyclic voltammetry starts sweeping from the OCP in the negative direction, a small peak appears on the 1450cm⁻¹, which belongs to N-N vibrations. As the intensity of N-N peaks increases, a superoxide peak appears at 1095cm⁻¹ as a first product. This could be interpreted as nitrogen redox centers that are connected to the Fe⁺³/+² redox centers in the MOF structure catalyzes the superoxide stability during oxygen reduction in the inner Helmholtz layer. From the figure, N-N peaks and superoxide peaks are dynamically synchronized between 2.8V and 2.7V potential range.
MOF catalysts can be treated as composed of NH\(^{4+}\) and HCOO\(^{-}\) ions processing strong covalent bonds, and M\(^{2+}\) cations. These ions are isolated from one another by weaker ionic bonds and, therefore, vibrational modes of the studied compounds can be subdivided into internal vibrations of the NH\(^{4+}\), formate ions, and the lattice vibrations. According to Maczka et al., internal modes of the NH\(^{4+}\) and HCOO\(^{-}\)

Figure 8 In situ Raman spectrum during ORR on the Fe-MOF electrode in oxygen saturated 0.1M LiPF\(_6\)/DMSO. ♦ indicates N-N vibrations, ★ indicates O\(_2\)^{-} vibrations.
with Fe transition metal in the MOF structure gives 1360 cm$^{-1}$ strong peak and 1380 cm$^{-1}$ weak peak respectively. In our in situ Raman experiments, these peaks are enhanced due to the vibrational modes of active centers on the half negative peak potential, which could indicate excitement of Fe active centers (figure 9). In addition, Li$_2$O$_2$ and LiO$_2$ peaks appear at 800 cm$^{-1}$ and 1095 cm$^{-1}$, where these active centers contribute superoxide stabilization with the inner sphere electron transfer in DMSO.

Figure 9 In situ Raman spectrum at OCP and half peak potential during ORR on the Fe-MOF electrode in oxygen saturated 0.1M LiPF6/DMSO.
2.4 Conclusions

In this chapter, we have investigated the electron transfer kinetics of Fe-MOF catalyst in two non-aqueous electrolytes, which differ in their donor numbers. Lewis acidity of metal nodes in MOF structure promotes inner sphere electron transfer in the both electrolytes. Fe metal node helps for better stability of superoxide anion during ORR, which increases the activity. In situ Raman spectrums also showed that the stability of superoxide depends on Fe active centers.

Chapter 3 Summary and Future Efforts

3.1 Conclusions

In this study, electron transfer kinetic during ORR in two different donor number electrolytes was investigated on the plain carbon and Fe-based metal organic framework catalyst. The results show the following conclusions:

1-) On the plain carbon electrode, TEGDME presents two reduction peaks while DMSO has only one. This indicates that electron reduction continues with different ORR pathways in these two electrolytes. However, on the Fe-MOF electrode, only one reduction peak appears at the same voltage in both TEGDME and DMSO.
Also the onset potential in TEGDME shifts positively, which means that the catalyst increases the ORR activity.

2-) The differences on the onset potentials and peak potentials in low donor number TEGDME indicates that reduction process depends on the electrode surface and takes place in the inner Helmholtz layer. For the high donor number DMSO, although the onset potentials and peak potentials did not change depending on the electrode surface, only slight improvement is observed on the cathode peak potential for Fe-MOF electrode. This may suggest that inner sphere and outer sphere electron transfer works concurrently in DMSO on the Fe-MOF electrode.

3-) Fe$^{3+/2}$ active centers acts as a Lewis acids during ORR that has an affinity to moderately soft base superoxide. This increases the stability of superoxide in both TEGDME and DMSO electrolyte in the inner Helmholtz layer.

4-) Nichalson-Shain simulation confirms the stabilization of superoxide with a one-electron reduction from molecular oxygen to superoxide. In addition, in situ Raman spectroscopy results verify the stabilization of superoxide dependence on the Fe active centers in the Fe-MOF catalyst.
3.2 Future Work

Future directions of the research would be:

- In-situ Raman experiments with the FeMOF catalyst using low donor number electrolytes such as TEGDME.
- Further investigation on the role of the synthesis and development of catalyst in ORR and OER in terms of reduction products and active centers in different solvents considering the double layer perspective.
- Synthesis metal organic framework catalysts with various transition metals such as Co, Mo in-situ Raman characterization.
References


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