5-23-2018

The Catalytic Performance of Lithium Oxygen Battery Cathodes

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DOI: 10.25148/etd.FIDC006823

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

THE CATALYTIC PERFORMANCE OF LITHIUM OXYGEN BATTERY
CATHODES

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

MATERIALS SCIENCE AND ENGINEERING

by

Neha Chawla

2018

To: Dean John Volakis
College of Engineering and Computing

This dissertation, written by Neha Chawla, and entitled The Catalytic Performance of Lithium Oxygen Battery Cathodes, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Date of Defense: May 23, 2018

The dissertation of Neha Chawla is approved.

Dean John Volakis
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Vice President for Research and Economic Development
And Dean of the University Graduate School

Florida International University, 2018

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DEDICATION

I dedicate this thesis to my Parents and my Bua.

Without their love, patience and support, the completion of this work

would not have been possible.

ACKNOWLEDGMENT

First and foremost, I would like to express my sincere gratitude towards my advisor Dr. Bilal El-Zahab for his constant support during my Ph.D. research, for his patience, motivation and immense knowledge. His guidance helped me during my research and writing of the thesis. I would like to thank my committee members, Dr. Chunlei Wang, Dr. Norman Munroe, Dr. Yu Zhong, and Dr. Irene Calizo for their guidance and suggestions.

I would like to thank my fellow labmates, Meer, Amir, Elnaz, Ata and Marcus for always being very supportive. I would also like to thank AMERI staff, Dr. Alexander Franco and CESMEC staff, Dr. Vadym Drozd and Dr. Andriy Durygin for their time and support. My sincere thanks to Dr. Wang and her students, Richa and Ben for FTIR and Dr. Pala's students for Raman spectroscopy. I am grateful to Mabel for always loving me and being there for me.

I am grateful to all my roommates and friends for always being there for me. I really do cherish all the memories that we had together during the last 6 years. Thank you Chandan, Abirami, Mouna, Sushma, Raghavendra, Aishwharya, Tiyyash, Sudheer, Vishal, Aditya, Charles, Bala, Jaini, Trushil, Laith, Faris, Sid, Valli, Niru and Sandeep for the best times. I would like to thank Vishal for his guidance during my proposal defense. Thank you, Maria for being a great support always. I would like to thank Lily Colon, Kaushalya Aunty and Ralph Colon for their immense love. I would also thank Parija, Navneet, Ankit, Apurva, Siddhesh, Shivam for their constant encouragement to complete my PhD.

I cannot be thankful enough to my parents for loving me unconditionally, supporting me, encouraging me and always believing in me. Without your love, this journey would never be possible. I would like to thank Girish Singhania for his love, patience, constant support and faith in me. My sincere thanks and love to all my family members, especially Geeta Bua, Sudarshan Fufaji, Hitesh Bhaiya and Ritu Bhabhi. In loving memory of my late grandparents and Harinder Tauji who always loved me and supported my decisions.

My sincere thanks to one and all.

ABSTRACT OF THE DISSERTATION

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CATHODES

by

Neha Chawla

Florida International University, 2018

Miami, Florida

Professor Bilal El-Zahab, Major Professor

High energy density batteries have garnered much attention in recent years due to their demand in electric vehicles. Lithium-oxygen (Li-O₂) batteries are becoming some of the most promising energy storage and conversion technologies due to their ultra-high energy density. They are still in the infancy stage of development and there are many challenges needing to be overcome before their practical commercial application. Some of these challenges include low round-trip efficiency, lower than theoretical capacity, and poor rechargeability. Some of these issues stem from the poor catalytic performance of the cathode that leads to a high overpotential of the battery.

In this doctoral work, Li-O₂ cathodes containing nanoparticles of palladium were used to alleviate this problem. Cathodes composed of palladium-coated and palladium-filled carbon nanotubes (CNTs) were prepared and investigated for their battery performance.

The full discharge of batteries showed 6-fold increase in the first discharge of the Pd-filled over the pristine CNTs and 35% increase over their Pd-coated counterparts. The Pd-filled CNTs also exhibited improved cyclability with 58 full cycles of $500 \text{ mAh}\cdot\text{g}^{-1}$ at current density of $250 \text{ mA}\cdot\text{g}^{-1}$ versus 35 and 43 cycles for pristine and Pd-coated CNTs, respectively. The effect of encapsulating the Pd catalysts inside the CNTs proved to increase the stability of the electrolyte during both discharging and charging. Voltammetry, Raman spectroscopy, XRD, UV/Vis spectroscopy, and visual inspection of the discharge products using scanning electron microscopy confirmed the increased stability of the electrolyte due catalyst shielding.

The electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) on carbon nanotubes (CNT) cathodes with palladium (Pd) catalyst, Pd-coated CNT and Pd-filled CNT, have been evaluated in an ether-based electrolyte solution to develop a lithium oxygen (Li-O_2) battery with a high specific energy. The electrochemical properties of CNT cathodes were studied using electrochemical impedance spectroscopy (EIS). The infrared spectroscopy and SEM are employed to analyze the reaction products adsorbed on the electrode surface of the Li-O_2 battery developed using Pd-coated and Pd-filled CNTs as cathode and an ether-based electrolyte.

Studies in this dissertation conclude that the use of nanocatalysts composed of palladium improved the overall performance of the Li-O_2 batteries, while shielding these catalysts from direct contact with the electrolyte prolonged the life of the battery by stabilizing the electrolyte.

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1. INTRODUCTION

Energy demand and supply have always been crucial factors for the evolution of civilization. Energy in the form of electricity is produced from wind, nuclear power, solar, burning fossil fuels, etc. Intermittent energy sources, such as the renewable sources wind and solar require storage devices for their effective usage. Electrochemical energy storage devices such as batteries therefore play an important role in the efficient use of renewable energy. A battery is a device that contains positive (+) and negative (-) terminals known as cathode and anode, respectively. Batteries reversibly transform stored chemical energy directly into electrical energy. When an external load is connected to a battery, electrons pass from the negative to the positive terminal through the external circuit, creating an electrical current. This current is used to power electrical appliances such as electrical vehicles, electronic devices, and others.

The Voltaic pile was the first battery developed by Volta circa 1800. It consisted of a series of copper and zinc discs separated by cardboards moistened with a salt aqueous solution. After more than 200 years of research and development, batteries can now be quite safely used for various applications for the transportation of electricity without heat loss.

Batteries are generally classified into primary and secondary batteries. Primary batteries are non-rechargeable or disposable batteries and include alkaline batteries, Leclanche, silver oxide, zinc/air batteries, and zinc-carbon batteries. Secondary batteries, also called rechargeable batteries, include lead-acid, nickel-cadmium, nickel-metal hydride and lithium ion batteries. According to the chemical reaction involved, rechargeable batteries

can further be classified as lead-acid, nickel-metal hydride, zinc-air, sodium-sulfur, nickel-cadmium, lithium-ion, and lithium-air batteries [1].

One of the most well-known energy storage technologies is lithium-ion battery (LIB) with applications including portable consumer devices such as laptops, mobile phones, digital electronics, and power tools. The first LIB was commercialized by Japan's Sony in 1991[2]. Since then several companies manufactured LIB commercially. LIBs have higher voltage, higher energy density, and longer cycle life as compared to traditional rechargeable batteries such as lead acid and nickel-cadmium (Ni-Cd) batteries [2]. In 2008, Tesla launched their Roadster electric car that ran on lithium ion batteries which are also used to power everything from smartphones to laptops to toys. Since then, the market for electric vehicles has grown and with it the average range of the batteries that power them has also grown. Batteries with high specific energy densities have attracted a lot of attention due to their demand in electric vehicles (EVs). Increase in demand for LIBs in the automobile industry is due to their lighter weight and smaller size afforded by their high energy and power densities [3]. The global LIB market is expected to reach USD 93.1 billion by 2025, growing at 17.0% a year, according to a new report[3]. Technological advancements to reduce the weight and cost of batteries and increase the power output are expected to augment this industry's expansion [3]. The energy storage field is expected to witness the fastest growth over the forecast period at 21% annually from 2017 to 2025 owing to new developments in wind and solar PV in industrial countries such as Germany, China and U.S. [3]. Panasonic Sanyo, AESC (Automotive

Energy Supply Corporation), Samsung, and LG Chem. Ltd. are expected to emerge as the major manufacturers of LIBs[3].

1.1. Mechanism of Li-ion batteries

A lithium ion battery consists of three main components, positive electrode (cathode), negative electrode (anode), and an electrolyte.

Figure 1.1. Schematics of Li-ion battery using LiCoO_2 as cathode and graphite as anode. Reproduced “Adapted” from [4] with permission of The Royal Society of Chemistry.

As can be seen in the Figure 1.1, during discharging, the anode gets electrochemically oxidized and releases an electron. This electron moves through the outer circuit towards the positive electrode which accepts this electron.

During charging, Li^+ moves from LiCoO_2 to carbon through the electrolyte which causes oxidation of Co^{3+} to Co^{4+} and the reverse process happens during discharge; Li^+ moves from carbon to LiCoO_2 . The electrolyte acts as a transfer medium of ions between the two electrodes while remaining electronically insulating. In general, a lithium salt dissolved in organic solvent is used as electrolyte in lithium ion batteries.

1.2. Significance of Li-O₂ battery

Due to the increase in demand for energy storage devices for applications such as load-levelling of electrical energy supply and demand [1] propulsion for electric vehicles and microelectro-mechanical devices, the research for new classes of electrode materials that provide high energy, high power, and cycle life longer than lithium-ion batteries is being motivated [5][6]. Lithium-oxygen batteries have high theoretical specific energy density and they can achieve four times higher energy density than the current lithium ion batteries [5][6].

Figure 1.2 shows the energy storage technologies and compares their respective theoretical energy densities [2] . The energy density of LIBs is between 75 and 160 Wh.kg⁻¹ due to limitations of anode and cathode active material content. Several metal–air batteries have been investigated due to their promising energy densities such as zinc–air, aluminum–air, etc. [7]. Aluminum–air batteries have been studied since aluminum is one of the earth’s most abundant metals and also due to their high specific energy; however, they are limited by a low Coulombic efficiency [8]. Zinc–air batteries have higher energy densities compared with conventional primary batteries [9]. However, the energy densities of zinc–air batteries still cannot meet the requirements of many high-energy applications. Lithium–air batteries promise to far exceed the energy densities of intercalation electrode-based energy storage technologies with predictions setting them at 5–10-folds higher than lithium-ion batteries [10]. The large theoretical energy density of the lithium–air battery can be attributed to the cathode oxidant, oxygen, which is not stored in the electrode but is obtained from the surrounding environment [2]. Considering the atomic mass of lithium metal, the gravimetric energy density of the lithium–air battery with respect to the anode is approximately 13,000 Wh.kg⁻¹ [11], which is comparable to the energy density of gasoline 13,200 Wh.kg⁻¹ [2].

Figure 1.2. Energy storage technologies and their respective theoretical energy densities

Figure 1.3 shows a Ragone plot which compares the practical power and energy densities of current and developing energy-storage technologies [2]. The diagonal lines indicate the discharge times with low discharge rates displayed at the top left corner of the Ragone plot. At high discharge rates, lower energy densities are obtained due to the increase in internal resistance that is typical of high discharge rates. The figure also shows the energy density of the Li-air battery; however, the Li-air battery still suffers from a relatively low power density as compared to the internal combustion engine that uses gasoline [2].

Figure 1.3. Ragone plot comparing the practical energy and power densities of current energy storage technologies with the lithium–air battery. Reprinted from [2] R. Padbury, X. Zhang, Lithium-oxygen batteries - Limiting factors that affect performance, J. Power Sources. 196 (2011) 4436–4444, Copyright 2011, with permission from Elsevier.

1.3. Fundamentals of Li-O₂ battery

Metal-air batteries are important and unique because the cathode material i.e. oxygen can be obtained from the atmosphere instead of storing it in the battery. The first primary lithium-air batteries were introduced by Littauer and Tsai in 1976 in which an aqueous alkaline solution was used as an electrolyte[12]. Their batteries had a typical open circuit voltage of 2.9–3.0 V and cell voltage of ~ 2 V at current density of approximately 200 mA·cm⁻². The electrochemical efficiency of the cell was low due to rapid self-discharge

of the anode at OCV. First instance of rechargeable Li-air battery was developed by Abraham and Jiang [6] using a gel polymer electrolyte (GPE) containing a non-aqueous electrolyte. The cell consisted of a lithium metal as an anode, a GPE, and a carbon air cathode. The observed OCV was ~ 3.0 V at room temperature and lithium peroxide (Li_2O_2) formation on the cathode surface after discharge was also confirmed in the same study. In 2002, Read [13] developed a high capacity carbon air cathode using Super P carbon black in carbonate-based electrolyte (propylene carbonate (PC) and diethyl carbonate (DME)) containing LiPF_6 salt. In 2006, Bruce *et al.* [10] reported improved cycling of Li-air battery by using Super P carbon black with an electrolytic manganese dioxide.

Based on the electrolyte used, four types of lithium-air batteries have been developed: non-aqueous, aqueous, hybrid non-aqueous/aqueous, and solid-state lithium-air batteries [4]. These types of Li-air batteries are schematically illustrated in Figure 1.4.

A typical non-aqueous lithium-air battery is made up of a lithium electrode and an air electrode saturated with a non-aqueous electrolyte composed of a lithium salt dissolved in a non-aqueous solvent. Lithium metal anode gets oxidized during discharging and releases Li^+ ions in the electrolyte. During charging the reverse process occurs. At the cathode, O_2 enters the cathode from atmosphere, dissolves in the electrolyte and gets reduced at the electrode surface on discharge. When a suitable non-aqueous electrolyte is employed, O_2^{2-} is formed, which, along with Li^+ from the electrolyte, forms Li_2O_2 as the final discharge product. The peroxide is then decomposed on charging [15]

Some have reported formation of Li_2O during discharge which is difficult to reverse during charging [16][17].

Aqueous electrolytes involve formation of OH^- and ultimately LiOH at the cathode on discharge according to equation [15]

During charging the LiOH gets oxidized.

Direct contact between lithium and solid electrolyte can be avoided to increase Li^+ conductivity by filling a non-aqueous electrolyte in between. Figure 1.4. (c) shows a hybrid non-aqueous/aqueous system. Instead of forming solid Li_2O_2 , the discharge product is a soluble lithium hydroxide (LiOH). However, the solubility of LiOH is limited. A solid-state battery design was developed to eliminate leakage and improve safety as shown in Figure 1.4. (d). Current solid-state Li-air batteries use lithium anode, ceramic, glass, or glass-ceramic electrolyte, and a porous carbon cathode. The anode and cathode are typically separated from the electrolyte by polymer-ceramic composites that enhance charge transfer at the anode and electrochemically couple the cathode to the electrolyte. The polymer-ceramic composites reduce the overall impedance. The main drawback of the solid-state battery design is the low ionic conductivity of most glass-ceramic electrolytes.

Figure 1.4. Types of Li-O₂ batteries. Reprinted from [14] P. Tan, W. Kong, Z. Shao, M. Liu, M. Ni, *Advances in modeling and simulation of Li-air batteries*, *Prog. Energy Combust. Sci.* 62 (2017) 155–189, Copyright 2017, with permission from Elsevier.

1.4. Challenges in Li-O₂ batteries

An efficient charge transfer mechanism and low internal resistance result in good kinetics which lead to high performance cells [2]. In a typical Li-O₂ battery, the electrons are confined to the electrode material, lithium ions are present in the electrolyte while the

oxygen is present in both the gaseous and solution phases. During discharging, the oxygen molecules accept electrons from the cathode and combine with lithium ions to complete the half-cell reaction. To complete the combination, each reactant overcomes their respective boundaries which results in slow kinetic reaction thus affecting the overall performance of the battery [2].

The major issues with non-aqueous systems are high polarization for charge and discharge processes, electrolyte decomposition, and contamination by moisture. Whereas for aqueous system, the main problem is the development of a water stable electrode in which the lithium anode is covered with Li^+ -conducting solid electrolyte so that it does not react with water [18] [8]. The major problem with the lithium-air battery is safety, reliability and electrochemical performance. They are flammable, flowing and of volatile nature since organic liquid electrolytes are used.

1.4.1. Overpotential

Thermodynamically, the cell voltages for ORR and OER are 2.96 V and 3.1 V, respectively [19]. However, the actual ORR potentials typically range from 2.5–2.8 V. The OER potential is more severe, often exceeding 4.0 V. The increase in overpotential results in significant reduction of the round-trip efficiency. The lifecycle of Li-O_2 cells, if fully discharged, is limited to less than 10 cycles with extremely low Columbic efficiency [19]. During charging, carbon decomposes to form lithium carbonate (Li_2CO_3) [20]. Increase in Li_2CO_3 increases the potential of the battery. One of the major challenges for the development of Li-O_2 batteries is to lower the high overpotential during charge. A large overpotential on charge, even at very low current densities, can result in a very low round-trip efficiency (<60%), low power capability and poor cycle life [21].

1.4.2. Clogging of pores

Most of the current limitations in the development of the lithium-oxygen battery are at the cathode. Carbon has been the most widely used as the porous cathode in lithium-oxygen batteries[22]. Incomplete discharge due to blockage of the porous carbon cathode with discharge product such as lithium peroxide is a serious issue which results in low efficiency and cyclability of the battery[23,24]. The liquid electrolyte readily permeates into the pores of the air electrodes which is necessary to provide the necessary lithium ions. However, once the pore in the air electrode is completely filled with the liquid electrolyte, the diffusion of oxygen is blocked. This results in electrochemical reactions being based solely on dissolved oxygen in the electrolyte which results in high polarization, safety problems from corrosion of anode, poor rate capability and poor reversibility [24,25]. This also prevents the extension of this battery in ambient humid air. The porous electrode of the lithium-oxygen battery must support diffusion of oxygen gas so that the oxygen is transported to electrolyte/electrode interface as much as possible through the gas phase rather than by slower diffusion in the electrolyte. The major side products result due to the electrolyte decomposition. Clogging of the pores by Li_2O_2 (lithium peroxide) was less problematic in non-aqueous cell [26].

1.4.3. Dendrite formation

Lithium metal is the main anode material used in Li-O_2 batteries due to its extremely low weight, low negative potential (-3.04 V vs. standard hydrogen electrode (SHE)) and high specific energy ($11,680 \text{ Wh}\cdot\text{kg}^{-1}$). Usage of lithium metal as the electrode has issues including the uncontrollable lithium dendritic growth and the limited Coulombic

efficiency during cycling. Dendrite growth may lead to short circuiting of the battery[27,28]. In non-aqueous Li-O₂ batteries, the reactions on the interface between the lithium anode and electrolytes become more complicated due to the water/oxygen/side products crossover[1]. Hence, it is often important to protect the Li anode through suitable electrolytes or passivation films [1].

1.5. Lithium anode

Lithium is the lightest member of the alkali metal group and has the smallest atomic radius of all metals due to which it has ultrahigh capacity and quick transfer nature [1]. Li has high reactivity and reacts slowly in dry air like other alkali metals. Li oxidizes rapidly with trace amount of water. Li anode has the most negative potential of all the currently known electrode materials [1]. The instability of Li metal encountering electrolytes (aqueous and non-aqueous liquid electrolytes, polymer and inorganic electrolytes) in rechargeable batteries is due to the ultra-low potential and high reactivity [1].

1.6. Electrolytes for Li-O₂ batteries

In Li-O₂ batteries, electrolytes are used to transport Li⁺, dissolve oxygen gas and transport it to the reaction sites, and protect the lithium anode. Electrolytes are critical components to achieve a long cycling life. For non-aqueous electrolytes, stable solvents and lithium salts and their stability in the oxidation environment are currently the main challenges that need to be overcome to obtain good cycling life. For the ideal non-aqueous electrolyte for the Li-O₂ battery should have the following features [28,29]:

- (i) Should be a good Li-ion conductor and electronic insulator
- (ii) Should be stable over the operating voltage window

- (iii) Should have a high oxygen solubility, to effectively transport oxygen
- (iv) Should be chemically compatible with the cell components and electrodes
- (v) Should be thermally stable
- (vi) Should not have any charge accumulation and concentration polarization

Carbonate-based liquid electrolyte solvents such as propylene carbonate (PC) and ethylene carbonate (EC), which were used in non-aqueous Li-O₂ batteries initially, resulted in poor cycling performance. Tetraethylene glycol dimethyl ether (TEGDME) is an ether based solvent and has been widely used due to relatively high stability with respect to superoxide radicals and oxidation potentials [13,30–36]. Dimethyl sulfoxide (DMSO) is another solvent, however, the chemical reaction between DMSO and Li₂O₂ could decompose DMSO to DMSO₂ and forms LiOH thus affecting the reversibility[37] .

The selection of lithium salt also plays a significant role in the electrolyte system. An ideal lithium salt should have high solubility in the solvent to support ion transport and be inert to the solvent and other battery components, especially to the oxygen reduction intermediates[38]. The salts commonly employed in non-aqueous Li-O₂ batteries include are LiPF₆, LiClO₄, LiCF₃SO₃, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The compatibility of lithium salts with solvent is important for the stability of the electrolyte.

1.7. Cathodes for Li-O₂ batteries

Several cathodes have been used to date for Li-O₂ batteries. Carbon is the most common porous conducting material for the O₂ cathode due to its low cost, high electronic

conductivity, and its easily modifiable surface area and pore sizes [20]. Porous carbons with and without various catalysts have been used abundantly as cathode materials in LiO₂ batteries[6,13,34]. They have typically shown good initial discharge capacities but poor cycle life. Besides carbon, various other carbon structures such as carbon nanotubes (CNTs) [36][39–43], mesoporous carbon [44], graphene and its derivatives [45–49] have been investigated as cathode materials for Li-O₂ batteries. These structures are useful since they increase the surface area of the carbon structure to improve oxygen diffusion while allowing easier accommodation of Li₂O₂ formed upon discharge. CNTs are an attractive material for Li-O₂ battery cathodes due to the possibility of making free-standing cathodes composed solely of CNTs, which can eliminate the requirement for weight-adding binders[27,50–52].

Ding *et al.* used different carbon materials as air electrodes for Li-air batteries and figure 1.5 shows their initial charge-discharge voltage profiles. According to them, MWCNT delivers a capacity of 1300 mAh.g⁻¹ followed by Ketjenblack, acetylene black and Super P electrodes with a discharge capacity of 2865, 3512, and 3399 mAh.g⁻¹, respectively [54].

Figure 1.5. Comparison of initial charge/discharge curves with various carbon materials. Reproduced “Adapted” from [53] with permission of The Royal Society of Chemistry.

1.8. Catalysts for Li-O₂ batteries

Catalysts have been shown to improve both the battery capacity and the recyclability of these batteries when used in cathodes. Till date many nanoparticles such as platinum, palladium, silver, rhodium, ruthenium, cobalt, nickel and other inorganic compound nanoparticles have been linked on the surface of the multi walled carbon nanotubes for lithium-ion batteries, Li-O₂ batteries as well as for several other applications [8].

Nanoparticles are of great scientific interest as they are, in effect, a bridge between bulk materials and atomic/molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale size-dependent properties are often observed. Thus, the properties of materials change as their size approaches the nanoscale

and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer, the percentage of atoms at the surface is insignificant in relation to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material.

Noble metal nanoparticles are important because of their large surface area and various functions and applications. Intrinsic properties of these are determined by shape, composition, size and crystallinity [56]. Several catalysts have been discovered for lithium air batteries. Debart *et al.* used several catalysts for lithium-oxygen batteries with non-aqueous electrolyte. The electrocatalysts used by them included Pt, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, Fe_2O_3 , NiO, CuO, CoFe_2O_4 . Co_3O_4 exhibited highest discharge capacity and best cycling performance. Later Debart *et al.* examined manganese oxides as catalysts for lithium-oxygen batteries. Mn_3O_4 , bulk Mn_2O_3 , bulk α , β , λ , γ - MnO_2 , α - MnO_2 nanowires and β - MnO_2 nanowires were used as catalysts [9]. The air cathode with α - MnO_2 as the catalyst showed the highest capacity of about 3000 mAh.g^{-1} (carbon).

Liu *et al.* explored and indicated that nickel foam can be used as a current collector in rechargeable lithium air battery [57]. Interfacial stability between Ni foam and electrolyte improved significantly under O_2 atmosphere. Electrolyte decomposition was not observed between 2.0 and 4.0 V vs Li/Li^+ , due to which Li_2O_2 decomposes.

Various electrochemical catalysts for the air electrode have been studied to improve the energy conversion efficiency and the cycling performance of lithium air batteries

recently, such as bifunctional electro-catalyst of platinum-gold nanoparticles loaded on the XC-72 carbon [21], nitrogen-doped carbon nanotubes [48], MnO₂ nanoflakes coated multi-walled carbon nanotubes [58], etc. These batteries would use carbonate electrolytes. However, carbonate electrolytes were found to decompose in Li-O₂ batteries[6][59] and consequently researchers turned to ether-based electrolytes, which have greater stability [60][61][32][62][63].

Palladium coated α -MnO₂ was used as a catalyst by Zhang *et al.* in the Li-O₂ batteries and the initial discharge of 1220 mAh.g⁻¹ and capacity retention rate of 47.3% after 13 cycles was obtained [64] . In this case Pd particles were deposited on the surface of MnO₂ nanoneedles.

Lu *et al.* developed the cathode which utilizes atomic layer deposition (ALD) of palladium nanoparticles on a carbon surface with an alumina coating for passivation of carbon defect sites [65]. Pd nanoparticles on ALD surface act as effective electrocatalysts and promote Li₂O₂ formation thus improving electronic transport. Super P carbon was used to support the catalyst material. 1 M LiCF₃SO₃ in tetra-ethylene glycol dimethyl ether (TEGDME) electrolyte on glass fiber separator and lithium metal anode was used for the charge discharge cycles. After discharging to 1000 mAh.g⁻¹ and charging, the charging potential was reduced to 3.2 V which is comparable to the theoretical of 3.0 V. The low potential could be maintained upto 10 cycles at 500 mAh.g⁻¹. The full discharge capacity obtained was 2750 mAh.g⁻¹. Degradation of lithium anode and poisoning of Pd catalyst by contaminants or passivation could be the reasons for the battery failure.

Lim *et al.* investigated the use of Pt as a catalyst material for CNT based [66]. They embedded Pt nanoparticle on CNTs which reduced charging potentials as compared to pure CNTs. Pt/CNT cathodes showed a stable capacity of 1000 mAh.g⁻¹ for over 120 charge/discharge cycles. 80 cycles were obtained when the cathodes were cycled at 1500 mAh.g⁻¹ between 2-4.7 V.

RuO₂ is considered as a good cathode catalyst since it has electron conductivity and good catalytic activity towards oxygen evolution reaction. G. Zhao *et al.* fabricated TiO₂ nanotube arrays on Ti foam and used them as substrate for lithium air batteries [67]. RuO₂/TiO₂ cathodes exhibit good catalytic activity towards OER and exhibit a cycle performance of 130 cycles at a current of 1.77 A.g⁻¹ under 1000 mAh.g⁻¹.

A uniformly coated RuO₂ shell on the surface of core CNT was used as catalyst to prevent direct contact between CNT and Li₂O₂ thus reducing formation of Li₂CO₃ [68]. RuO₂@CNT catalyst increased the specific capacity to about 4350 mAh.g⁻¹ at a current of 385 mA.g⁻¹ and exhibited a discharge and charge overpotentials of 0.21 V and 0.51 V. Twenty cycles were obtained at a fixed capacity of 500 mAh.g⁻¹ at the current rate of 100 mA.g⁻¹.

Zahoor *et al.* synthesized α -MnO₂ nanorods and modified them with Pd nanoparticles to form Pd deposited α -MnO₂ nanostructures and used them as electrocatalyst in the air cathode for Li-O₂ battery [26]. They used Ketjenblack cathode with the Pd deposited α -MnO₂ catalyst and LiTFSi salt in TEGDME as electrolyte and lithium metal anode for battery application. They obtained a discharge and charge capacity of 8526 mAh.g⁻¹ at a

constant current density of 0.1 mA.cm^{-2} and the charge-discharge overpotential was 1.6 V.

Shao-Horn *et al.* showed improvement in round trip efficiency due to reduction in overpotential by incorporating a platinum–gold/carbon (PtAu/C) bifunctional catalyst into the carbon cathode[21]. A catalyst can enhance the charge reaction by reduction in the voltage required to dissociate the reduction products into lithium metal and oxygen[2]. Figure 1.6. shows the typical charge/discharge curves of Li-O₂ batteries with and without manganese dioxide catalysts. In this, Bruce *et al.* show how the introduction of the catalyst improves the capacity from 850 to approximately 1000 mAh.g^{-1} as well as lowers the charge potential by approximately 0.5 V.

Figure 1.6. Charge/discharge curves (A) without and (B) with electrolytic manganese dioxide catalyst. Reprinted from [69] P.G.B. Aurélie Débart, Jianli Bao, Graham Armstrong, An O₂ cathode for rechargeable lithium batteries: The effect of a catalyst, J. Power Sources. 174 (2007) 1177–1182, Copyright 2007, with permission from Elsevier

According to Padbury and Zhang, the catalyst assists the discharge reaction kinetics which results in an increase in the specific capacity of the battery[2]. Since the electron moves towards the region of the highest potential, the large voltages required to charge the Li-O₂ battery may also lead to oxidation of the electrolyte. This process results in degradation of the electrolyte solution which in turn decreases the charge/discharge performance, thus decreasing the life of the Li-O₂ battery [2]. It can thus be concluded from the examples that catalysts have aided the charge reaction by reduction in the charge potential.

1.9. Effect of shielded and unshielded catalyst

1.9.1. Effect of unshielded metal nanocatalyst on CNT

Lu *et al.* have investigated the effect of the Pd nanoparticles on carbon surface [65]. They have shown that the charge potential of the battery is reduced by 1.2 V for Al₂O₃-C cathode with Pd nanoparticles as compared to the cathode without nanoparticles. According to them, a partially oxidized Pd nanoparticle provides a good interface for electron transfer by forming bonds on the defect-free graphene surface. The electronic properties of the Li₂O₂ discharge product in presence of the Pd nanoparticles play an important role in reducing the charge overpotential. The charge overpotential depends on the electronic transport of Li₂O₂. According to Lu *et al.*, the nanocrystalline Li₂O₂ obtained in the presence of Pd-Al₂O₃-C cathode assisted in better electronic transport during charging. Pd nanoparticles provide nucleation sites for a formation of Li₂O₂ growth species [65].

1.9.2. Effect of shielded metal nanocatalyst in CNT

There exists an electronic interaction between the metal species and the CNT surfaces. The strength of this interaction varies with metals and the size of CNTs. Confinement results in the modification of the electronic structure of the metal nanoparticles thus influencing their catalytic activity as redox reactions involve electron transfer between reactants and catalysts [70]. The nano-sized channels of CNTs provide spatial restriction on metal particles, which can hamper their aggregation under reaction conditions [70]. This is important because the deactivation of catalysts can be due to aggregation of nanoparticles.

Wang *et al.* encapsulated Sn in CNT and had an overall pseudo-homogenous structure that minimized the contributions from heterogeneities such as isolated Sn particles or Sn nanoparticles on the CNT exterior walls [71]. It also allowed a more unambiguous assessment of the effects of CNT encapsulation on the volume changes in the lithium storage process [71]. The better performance was attributed to the following reasons arising from the complete and uniform encapsulation of small Sn nanoparticles in CNTs.

- CNTs were ~200 nm in diameter while Sn particles were only 6-10 nm in size, which provided ample void space in the CNTs to accommodate the volume excursion in the active Sn phase during lithium insertion and extraction reactions [71]

- Uniform distribution of Sn particles in a soft matrix capable of absorbing the stress induced by volume changes. The smaller Sn nanoparticles reduced the non-uniform distribution of stresses [71]
- Good electrical contact between CNT and Sn was ensured due to complete encapsulation. If the Sn particles were coated on the external surface of CNTs, it could lead to a permanent loss of use because of loss of electrical contact [71]

According to Astinchap *et al.*, the encapsulation structure not only modulates the catalytic properties of metal NPs but also protects metal NPs from growing larger [72].

CNTs filled with nanoparticles have been studied for a few years. In 1993, Ajayan *et al.* filled CNTs with lead [73] followed by Zhou *et al.* who filled yttrium carbide powder in carbon nanotubes [74]. Gold nanoparticles filled inside CNTs introduced changes in the electronic transport depending on the impregnation procedure [75]. Tessonnier *et al.* introduced palladium nanoparticles inside MWCNT by wetness impregnation followed by thermal treatments for selective hydrogenation of cinnamaldehyde into hydrocinnamaldehyde [76].

1.10. Importance of CNT as cathodes

CNTs were first discovered by Iijima in 1991 using arc-charge method [77]. SWCNTs and MWCNTs are two of the most important structures. The electrical and thermal conductivities of CNTs are as high as 10^4 S.m^{-1} and 6600 W/m.K , respectively [78]. CNTs have a Young's modulus and tensile strength of 1.2 TPa and $50\text{--}200 \text{ GPa}$, respectively which makes CNTs one of the strongest and stiffest materials [79]. The

unique structure and extraordinary properties of SWCNTs and MWCNTs make them promising materials for a variety of applications [80].

The applications of carbon nanotubes (CNTs) in electrical materials have attracted immense research interest due to their extraordinary thermal and mechanical stabilities, as well as high electronic conductivity. Homogeneously dispersed CNTs on the surface of active materials has the following advantages:

- (1) CNTs form a continuous conductive network on bulk of the electrode which aids in cycling performance improvement [81]
- (2) CNTs improve the adsorption and penetration of electrolyte on the surface of the electroactive materials thus facilitating the electrode reaction kinetics [81]
- (3) CNTs can act as a buffer among the electroactive materials due to their superior elasticity, their ability to restrain cracking and crumbling and maintaining the integrity of the electrode[81]
- (4) CNTs have high specific surface area, chemical stability, electrical conductivity, high accessibility of active phase and no microporosity thus eliminating diffusion and intraparticle mass transfer limitation [8]

CNTs are interesting as one-dimensional hosts for the intercalation of Li^+ , and are regarded as one of the most promising candidates for the anode materials of LIBs [82].

1.11. Palladium as catalyst

Palladium is an excellent hydrogenation and dehydrogenation catalyst available in organo-metallic forms. Palladium nanoparticles have found to be effective catalysts in many chemical reactions due to their increased surface area over the bulk metal. They

can be formed by alcohol reduction in ethanol with the addition of a hydrochloric acid catalyst. They can also be formed by a modified polyol method. The main applications of palladium nanoparticles are as catalysts/electrocatalysts, polymer membranes, in sensor design application, coatings, plastics, nanofibers and textiles and in fuel cells. Lu *et al.* reported ORR studies on polycrystalline metal catalysts of palladium, platinum, ruthenium, gold and glassy carbon surfaces in non-aqueous electrolyte. [7] They found that ORR activities on the surface of these metal catalysts are correlated to oxygen adsorption energy and the order of ORR activity is $\text{Pd} > \text{Pt} > \text{Ru} \sim \text{Au} > \text{GC}$ on bulk surfaces. Since palladium has the highest ORR activity, we chose it as a catalyst for filling inside the MWCNT.

2. EXPERIMENTAL METHODS AND THEORY

2.1. Materials

Palladium (II) chloride (PdCl_2 , 59% Pd) was purchased from ACROS organics. Bis (trifluoromethane) sulfonamide (LiTFSI , purity > 99.95%), tetraethylene glycol dimethyl ether (TEGDME, purity > 99.00%), N-methyl pyrrolidine (NMP, purity > 97.00%), multi-walled carbon nanotubes (MWCNT, D=5–20 nm, L = 5 μm , purity > 95.00% carbon basis), Titanium (IV) oxysulfate (TiOSO_4) ($\geq 29\%$ Ti (as TiO_2) basis) and lithium peroxide (Li_2O_2) were purchased from Sigma-Aldrich. Carbon cloth gas diffusion layer (CCGDL, thickness $\sim 300 \mu\text{m}$) was purchased from Fuel Cell Earth. Lithium foil chips (purity > 99.90%) and Celgard polypropylene separator (thickness $\sim 25 \mu\text{m}$) were purchased from MTI Corp. Polyvinylidene fluoride (PVDF) was purchased from Alfa Aesar.

2.2. Li-O₂ cell assembly

2.2.1. Electrode preparation

Decapping of the MWCNTs was done by nitric acid solution treatment and then 1 mM aqueous solution of PdCl_2 was used to swell 100 mg of decapped MWCNTs until a slurry was formed. Pd-coated CNTs were also prepared following the same procedure on untreated capped MWCNTs. Both slurries of Pd-coated and Pd-filled MWCNTs were dried overnight at room temperature and calcinated in air at 350°C for 2 hours. Corresponding particles were then hydrogenated in an oven under hydrogen gas to yield $\sim 5 \text{ wt}\%$ Pd nanoparticles. Cathodes were prepared by coating a slurry of MWCNT (Pristine, Pd-filled and Pd-coated)/PVDF (90/10 wt% in NMP) on 0.5" diameter carbon

cloth gas diffusion layer (CCGDL) followed by drying at 120°C for 12 hours. The cathodes were then stored in an Ar-filled glove box.

The typical loading of MWCNT was 0.5 ± 0.01 mg. All reported capacities in this manuscript are reported per total mass of active cathode (CNTs and catalyst).

2.2.2. Electrolyte preparation

The electrolyte was prepared by adding 1 mol.kg⁻¹ of LiTFSI salt into TEGDME solvent in Ar-filled glove box with control O₂ and humidity content (Mbraun, <0.1 ppm O₂ and < 0.1 ppm H₂O).

2.2.3. Battery assembly

Li-O₂ batteries were assembled using a Swagelok type cell with stainless steel rod on the anode side and a stainless-steel tube on the cathode side. Lithium metal disc was used as anode, covered by electrolyte-soaked Celgard 2400 separator, MWCNT-CCGDL and a stainless-steel mesh as a current collector. Li-O₂ batteries were rested inside Ar-filled glove box overnight before electrochemical tests. All electrolyte preparation and cell assembly were performed inside Ar-filled glove box (<1 ppm O₂ and < 0.1 ppm H₂O). The Li-O₂ batteries were removed from argon glove box and placed in the gastight desiccator filled with ultra-high purity oxygen gas (Airgas, purity > 99.994%). The batteries were rested under oxygen for 5 hours before testing. All charge/discharge and electrochemical tests were measured in a temperature controlled environment at 25°C. After charge/discharge cycling, the oxygen cathodes were recovered from the batteries in the Ar-filled glove box, rinsed with DMC and dried under vacuum.

Figure 2.1. Components of the LiO₂ Battery

Figure 2.2. Battery assembly steps

2.3. Characterization Techniques

2.3.1. Electrochemical Characterization Techniques

2.3.1.1. Cyclic Voltammetry

Cyclic Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is more than that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.

I performed the voltammetry measurements by an electrochemical workstation (Gamry reference 600) at the rate of $1 \text{ mV} \cdot \text{s}^{-1}$ in the range of 2.0–4.5 V to investigate the catalytic behavior of oxygen electrodes.

Voltammetry is a collection of electroanalytical techniques in which information about the analyte is derived from the measurement of current as a function of applied potential. It is widely used by chemists for non-analytical purposes including fundamental studies on redox processes, adsorption processes on surfaces, electron transfer mechanisms and electrode kinetics. Cyclic voltammetry is a method to investigate the electrochemical behavior of a system. It was first reported in 1938 and described theoretically by Randies. It is the most widely used technique for acquiring qualitative information about electrochemical reactions.

Figure 2.3. The excitation signal for CV is a linear potential scan with triangular waveform[83]

Cyclic voltammetry is a potential sweep technique performed in an electroanalytical study, since it offers rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process. It involves sweeping the electrode potential between potential limits E1 and E2 at a known sweep rate (also called scan rate). On reaching limit E2 the sweep is reversed to E1 to obtain a cyclic scan. The CV scan is a plot of current versus potential and indicates the potential at which

redox process occur[83]. The triangular potential excitation signal sweeps the potential of an electrode between two values, sometimes called the switching potential as shown in figure.

The current measured during this process is often normalized to the electrode surface area and referred to as the current density. A cyclic voltammogram is the current vs voltage graph. The peak width and height depends on the sweep rate, electrolyte concentration and the electrode material. During an oxidation process, a positive potential ramp is applied and the electroactive species loses an electron at the electrode giving rise to an anodic peak current (I_{pa}) which usually gives an oxidation peak at a given potential (E_{pa}). Cathodic currents (I_{pc}) are observed when the potential is applied in the negative direction leading to a reduction process, typically giving a reduction peak at a given potential (E_{pc}). The CV is usually initiated at a potential where species are not electroactive.

Figure 2.4. Typical cyclic voltammogram curve[83]

The important parameters of a cyclic voltammogram are the magnitudes of anodic peak current (I_{pa}), the cathodic peak current (I_{pc}), the anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}). The basic shape of the current vs potential response for a cyclic voltammetry experiment is shown in Figure 2.4. At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidized form (point A). As the redox potential is approached, there is a net anodic current which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidized to O. Upon reversal of the scan (point C), the current continues to decrease until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current which eventually produces a peak shaped response (point D). The electrochemical reaction is said to be reversible if the redox system remains in equilibrium throughout the potential scan.

The peak potential separation for all scan rates is

$$E_{pa} - E_{pc} = (58/n) \text{ mV}$$

where n is the number of electron equivalents transferred during the redox process.

The anodic peak current I_{pa} should be equal to the cathodic peak current I_{pc} for the product stable on the time scale of experiment i.e. $I_{pa}/I_{pc} = 1$

2.3.1.2. Galvanostatic charge/discharge

Galvanostatic charge/discharge is a technique used to test the performance of batteries and determine the capacity. Charges and discharges are conducted at constant current until a set voltage is reached. While discharging a negative constant current is applied to the cell until the cut-off voltage is reached and while charging, the current is reversed and a positive current is applied to the cell. A plot of cell voltage (V) vs capacity (mA.h) is obtained with this technique. For consistency, the capacity of Li-O₂ batteries was normalized to mass of active materials (CNTs) of cathode and is denoted by mAh·g⁻¹. For this dissertation, I performed the galvanostatic charge/discharge cycling at a current density of 250 mA·g⁻¹ and cut-off voltages of 2.0-4.5 V or cut-off capacities of 250 mAh·g⁻¹, 500 mAh·g⁻¹ and 1000 mAh·g⁻¹.

2.3.1.3. Discharge product titration

I used a colorimetric method for quantitative analysis of the Li₂O₂ formed during discharge per electrode, as described by Schwenke et al.[84] and Hartmann et al.[85] Colorimetric determination of hydrogen peroxide is based on photoelectric measurement of the color intensities of hydrogen peroxide solutions treated with titanium sulfate reagent. The yellow color produced in the reaction according to Treadwell and Hall is due to the formation of pertitanic acid[86]. The reaction equation is usually written as[86]

Alkali-metal peroxides and super oxides react with water to form hydrogen peroxide as shown in the following reaction schemes:

For photometric analysis of H_2O_2 formed, the discharged cathodes were first immersed in an excess of deionized water which is based on the formation of the yellow $[\text{Ti}(\text{O}_2)]^{2+}$ complex when an aqueous solution of TiOSO_4 is added to a solution containing H_2O_2 . To quantify the Li_2O_2 amount, absorbance spectra of various aqueous Li_2O_2 solutions of known concentrations were recorded with a UV-visible spectrometer (Gamry Instrument). It was assumed that all charges during discharge are used for Li_2O_2 formation ($2\text{e}^-/\text{Li}_2\text{O}_2$) while calculating the Li_2O_2 yield, the determined mass of Li_2O_2 per cathode is related to the Li_2O_2 expected. The calculated error of the Li_2O_2 yield includes the standard error of slope and intercept of the calibration curve of the absorbance at 420 nm as well as the instrument error which was estimated to 0.005 absorbance units. H_2O_2 content of the water extracts of the cathodes were analyzed by UV-vis spectroscopy after addition of TiOSO_4 solution to confirm Li_2O_2 as the main discharge product. This method allows the quantification of small amounts of Li_2O_2 formed on the fibers during discharge. Figure 2.5 shows the Lambert–Beer type data presentation of the maximum extinction normalized to the amount of used TiOSO_4 solution (in cm^3) and the light path length (cuvette thickness). The line results from a linear fit to the data points.

UV-Vis spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. It uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved.

Li_2O_2 is quantified in the cathodes after discharge using a colorimetric method previously reported by Schwenke et al. Discharged cathodes are first immersed in water then aliquots are taken and added to 2% aqueous solution of TiOSO_4 . Instantaneously a color change occurs and the absorbance spectra of the solutions are collected using a UV-Vis spectrophotometer (Gamry UV/Vis Spectro-115E). The peak intensity at 408 nm is calibrated against solutions with known concentrations of Li_2O_2 , in the range of 0.1 to 10 mg/ml and linear calibration curve is obtained.

Figure 2.5. Lambert–Beer type data presentation of the maximum extinction normalized to the amount of used TiOSO_4 solution (in cm^3) and the light path length (cuvette thickness). The line results from a linear fit to the data points.

2.3.1.4. In-situ electrochemical impedance spectroscopy

EIS is a technique used to measure the electrical impedance of a substance as a function of frequency of an applied electrical current. Impedance is a measure of the resistance to the flow of an alternating current (AC).

2.3.1.4.1. Basics of EIS

Ohm's law defines resistance as the ratio between voltage [87], E , and current, I .

$$R=E/I$$

An ideal resistor follows Ohm's Law at all current and voltage levels, its resistance value is independent of frequency, and AC current and voltage signals through the resistor are in phase with each other. Due to the limitation of the resistance, impedance is used since it is a measure of the ability of a circuit to resist the flow of electrical current. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. We apply a sinusoidal potential excitation. The response to this potential is an AC current signal. The excitation signal, expressed as a function of time, has the form

$$E(t) = E_0 \cos(\omega t)$$

where $E(t)$ is the potential at time t , E_0 is the amplitude of the signal, and ω is the radial frequency. The relationship between radial frequency ω (expressed in radians/second) and frequency f (expressed in hertz) is:

$$\omega=2\pi f$$

The response signal, I_t , is shifted in phase (ϕ) and has a different amplitude, I_0 .

$$I(t) = I_0 \cos(\omega t - \phi)$$

An expression analogous to Ohm's Law allows us to calculate the impedance of the system as:

$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

The impedance is therefore expressed in terms of a magnitude, Z_0 , and a phase shift, ϕ .

With Eulers relationship,

$$\exp(i\phi) = \cos \phi + i \sin \phi$$

where ϕ is real number and j is imaginary unit. It is possible to express the impedance as a complex function. The potential is described as,

$$E(t) = E_0 \exp(j\omega t)$$

and the current response as,

$$I(t) = I_0 \exp(i\omega t - i\phi)$$

The impedance is then represented as a complex number,

$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0 (\cos \phi + i \sin \phi)$$

The expression for Z_o is composed of a real and an imaginary part. Nyquist plot is obtained by plotting the real part on the X axis and the imaginary part on the Y axis of a chart. On the Nyquist plot the impedance can be represented as a vector of length $|Z|$. The angle between this vector and the x-axis is ϕ .

Figure 2.6. Typical Nyquist plot [87]

The Nyquist plot is based on the circuit diagram. An example of the circuit diagram is as follows:

The impedance of elements in series is additive as shown below:

The impedance of elements in parallel is the inverse of the sum of the inverse of impedances and is represented as follows:

$$\frac{1}{Z_{Total}} = \frac{1}{Z_1} + \frac{1}{Z_2}$$

EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most models contain a resistor that models the cell's solution resistance.

Electrical Element		Impedance
Resistor		$Z_R = R$
Capacitor		$Z_C = \frac{1}{j\omega C} = -\frac{j}{\omega C}$
Inductor		$Z_L = j\omega L$
Infinite Warburg		$1/Y_0\sqrt{j\omega}$
Constant Phase element		$1/Y_0(j\omega)^\alpha$

Figure 2.7. Electrical element representation with their respective impedances

Electrolyte resistance is a significant factor in the impedance of an electrochemical cell. A 3 electrode potentiostat compensates for the solution resistance between the counter and reference electrodes.

The resistance of an ionic solution depends on the ionic concentration, type of ions, temperature and the geometry of the area in which current is carried. In a bounded area with area A and length l carrying a uniform current the resistance is defined as:

$$R = \rho \frac{l}{A}$$

ρ is the solution resistivity. The reciprocal of ρ (σ) is more commonly used. σ is called the conductivity of the solution and its relationship with solution resistance is:

$$R = \frac{1}{\sigma} \frac{l}{A} \Rightarrow \sigma = \frac{l}{RA}$$

2.3.1.4.2. Double layer capacitance

An electrical double layer exists on the interface between an electrode and its surrounding electrolyte. It is formed as ions from the solution adsorb onto the electrode surface. The charged electrode is separated from the charged ions by an insulating space, often on the order of angstroms.

$$X_C = 1/\omega C \qquad X_C = 1/2\pi fC$$

X_C is the capacitor impedance.

2.3.1.4.3. Charge Transfer Resistance

This resistance is formed by a single, kinetically-controlled electrochemical reaction.

Consider the following reversible reaction

This charge transfer reaction has a certain speed. The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

The speed depends on the kind of reaction, the temperature, the concentration of the reaction products and the potential.

2.3.1.4.4. Warburg impedance

Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants don't have to move very far. At low frequencies the reactants diffuse farther, thereby increasing the Warburg impedance. The equation for the "infinite" Warburg impedance

$$Z_w = \sigma(\omega)^{-1/2} (1 - j)$$

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5.

2.3.1.4.5. Randles model

The electrochemical interface can be described by an electron conducting electrode and an ion conducting electrolyte. Electrochemical reactions occur on the surface of the electrode.

Randles model as shown in figure 2.8 is one of the model to describe the electrochemical behavior of this interface.

Figure 2.8. Randles model describing the electrochemical interface between an electrode and electrolyte

The equivalent series resistance (ESR) represents the sum of resistances including the electrode, electrolyte, and electrical contacts. It is in series to a parallel connection of charge transfer resistance R_{ct} and double layer capacitance C_{dl} . R_{ct} represents all reversible and irreversible Faradaic reactions that occur on the electrode's surface. C_{dl} describes non-Faradaic charge storage mechanisms and is often replaced by a constant phase element for non-ideal assumptions.

2.3.1.4.6. Porous electrodes

Porous electrodes are used in energy storage and generation devices such as electrochemical capacitors (ECs), fuel cells to increase performance since they exhibit a very high surface area compared to volume or weight. Highly porous materials can be differentiated into the base electrode and the porous electrode. The base electrode is an insulated and inactive metal foil where the active material is fixed on. Figure shows a schematic setup.

Figure 2.9. Regions for a porous electrode interface

The reaction velocity within the pore of porous electrodes is limited. The access to the active interface for ions is hindered due to the small inner volume of the pores. Hence the rate of electrochemical reactions exceeded the diffusion rate of the ion in the pore. Due to these restrictions on the electrochemical reactivity, the porous electrode is divided into three regions marked A, B, and Active Interface. A represents the interface between the outer surface of the porous electrode and the electrolyte. B represents interactions between electrolyte and base electrode. Active Interface is the region that describes the interactions between active material of the porous electrode and electrolyte.

2.3.1.4.7. Transmission line model

The stepwise flux of ions within a pore are described using generally accepted vernacular of Transmission Line. Figure 2.10 shows a transmission line model in its generic form. It consists of several parallel and serially connected elements.

Figure 2.10. Scheme of a generic transmission line model

L is the length of the transmission line or the depth of the pore. The interfaces A and B are represented by impedances Z_A ($x = 0$) on the outer surface of the pore and Z_B ($x = L$) on the base electrode at the end of the pore. Along the pore, the transmission line is represented by repeating impedance elements. χ_1 is the impedance of the electrolyte within the pore. This impedance is different to the bulk electrolyte resistance that is represented as part of the ESR. χ_2 is the impedance of the porous electrode's solid phase. Both parameters describe the ohmic drop between $0 < x < L$. ζ describes the impedance at the Active Interface region.

2.3.2. Physical Characterization Techniques

2.3.2.1. Scanning electron microscopy

A scanning electron microscope (SEM) is used to study the morphology of solid state materials. It produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. It is used to study the surface of nanostructures and produce high-resolution images.

Figure 2.11. Schematic of SEM

The main SEM components include a source of electrons, a column through which the electrons travel with electromagnetic lenses, electron detector, sample chamber, and computer and display to view the images.

Electrons are produced at the top of the column, accelerated down and passed through a combination of lenses and apertures to produce a focused beam of electrons which hits the surface of the sample. The sample is mounted on a stage in the chamber area and, unless the microscope is designed to operate at low vacuums, both the column and the chamber are evacuated by a combination of pumps. The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam scanning enables the collection of information about a defined area on the sample. The electron-sample interaction results in the production of number of signals. These signals are then detected by appropriate detectors. Figure 2.11 shows the schematic of an SEM.

After discharge/charge process, the cathodes were extracted from the battery in the glovebox with argon atmosphere, to investigate the morphology of discharge products. The cathodes were rinsed with TEGDME solvent to remove the LiTFSI salt residue. After rinsing the samples were transferred to the vacuum chamber connected to the glovebox and dried at room temperature. After drying the samples completely, they were fixed on the SEM sample holder with the double-sided tape inside the glovebox to avoid contamination due to moisture. JEOL SEM 7000 was also used to investigate the cathodes.

2.3.2.2. Transmission electron microscopy

Transmission electron microscopy (TEM) is a technique used to study the structural information of nanomaterials. TEM uses high energy electrons accelerated to nearly

speed of light. The electron beam behaves like the wavefront with wavelength about a million times shorter than lightwaves.

Theoretically, the maximum resolution, d , has been limited by the wavelength of the photons that are being used to probe the sample, λ , and the numerical aperture (NA) of the system.

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2 \text{NA}}$$

where n is the index of refraction of the medium in which the lens is working and α is the maximum half-angle of the cone of light that can enter the lens. The wavelength of electrons is related to their kinetic energy via the de-Broglie equation. An additional correction must be made to account for relativistic effects, as in a TEM an electron's velocity approaches the speed of light, c .

$$\lambda_e \approx \frac{h}{\sqrt{2m_0 E \left(1 + \frac{E}{2m_0 c^2}\right)}}$$

where, h is Planck's constant, m_0 is the rest mass of an electron and E is the energy of the accelerated electron. Electrons are usually generated in an electron microscope by a process known as thermionic emission from a tungsten filament. The electrons are then accelerated by an electric potential and focused by electrostatic and electromagnetic lenses onto the sample. The transmitted beam contains information about electron density, phase and periodicity which is then used to form an image.

Figure 2.12. Layout of optical components of a basic TEM

TEM employs a high voltage electron beam to create an image. Figure 2.12 shows the basic TEM. An electron gun at the top of a TEM emits electrons that travel through the microscope's vacuum tube. The TEM employs an electromagnetic lens which focuses the electrons into a very fine beam. This beam then passes through the very thin specimen and the electrons either scatter or hit a fluorescent screen at the bottom of the microscope.

An image of the specimen with its assorted parts shown in different shades according to its density appears on the screen. This image can be then studied directly within the TEM or photographed.

Phillips CM-200 200 kV was used in this dissertation to inspect our carbon nanotubes.

2.3.3. Composition analysis of discharge products

2.3.3.1. X-Ray Diffraction

X-ray diffraction (XRD) is a technique which reveals detailed information about the crystal structure, chemical composition and physical properties of materials. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths like the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

Small angle scattering is useful for evaluating the average interparticle distance while wide-angle diffraction is useful for refining the atomic structure of nanoclusters. The widths of the diffraction lines are closely related to the size, size distribution, defects and strain in nanocrystals. As the size of the nanocrystals decreases, the line width is broadened due to loss of long range order relative to the bulk. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when

conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

Bruker GADDS/D8 X-ray powder diffraction (XRD) with MacSci rotating Molybdenum anode ($\lambda=0.71073$) operated at 50 kV generator and 20 mA current was used to collect the diffraction patterns. A parallel X-ray beam in size of 100 μm diameter was directed on to the samples and diffraction intensities were recorded on large 2D image plate during exposure time.

The cathode sample was placed on the sample surface with double sticky tape. Care was taken to create a flat upper surface. For data collection, the intensity of diffracted X-rays was continuously recorded as the sample and detector rotated through their respective angles. A peak in intensity occurs when the mineral contains lattice planes with d-spacings appropriate to diffract X-rays at that value of θ . Although each peak consists of

two separate reflections ($K\alpha_1$ and $K\alpha_2$), at small values of 2θ the peak locations overlap with $K\alpha_2$ appearing as a hump on the side of $K\alpha_1$. Greater separation occurs at higher values of θ . Typically these combined peaks are treated as one. The 2λ position of the diffraction peak is typically measured as the center of the peak at 80% peak height.

The results are presented as peak positions at 2θ and X-ray counts (intensity) in the form of a table or an x-y plot (shown above). The relative intensity is recorded as the ratio of the peak intensity to that of the most intense peak (relative intensity = $I/I_1 \times 100$).

The d-spacing of each peak was obtained by solution of the Bragg equation for the appropriate value of λ . Once all d-spacings were determined, automated search and match software program database compares the ds of the unknown to those of known materials. Because each mineral has a unique set of d-spacings, matching these d-spacings provides an identification of the unknown sample. A systematic procedure is used by ordering the d-spacings in terms of their intensity beginning with the most intense peak.

2.3.3.2. Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to obtain the vibrational, rotational information of chemical bonds in materials by determining the photon energy shift which is caused by the interaction between the laser light and the molecular vibrations. Typically, a sample is illuminated with a laser beam. Electromagnetic radiation from the illuminated spot is collected with a lens and sent through a monochromator. Elastic scattered radiation at the wavelength corresponding to the laser line (Rayleigh scattering)

is filtered out by either a notch filter, edge pass filter, or a band pass filter, while the rest of the collected light is dispersed onto a detector.

A Raman spectrum is a plot of the intensity of Raman scattered radiation as a function of its frequency difference from the incident radiation (units is wavenumbers, cm^{-1}). This difference is called the Raman shift. Raman shift is independent of the frequency of the incident radiation because it is a difference value. This vibrational technique provides information in terms of the structural properties and chemical bonds by probing the potential energy surface of the atoms around the equilibrium lattice geometry. Raman intensity peaks are related to change in the polarizability of the system due to deformation introduced by lattice vibrations[88]. Therefore, when the polarizability changes with lattice vibrations, these vibrational modes are Raman active[88].

The detection of Li_2O_2 by Raman spectroscopy has been well established and complements techniques like XRD. In the first report of a non-aqueous $\text{Li}-\text{O}_2$ battery by Abraham and Jiang[6], Raman spectroscopy was used to demonstrate the formation of Li_2O_2 (795 cm^{-1}) on a cobalt-catalyzed carbon electrode after discharging. The lack of a Li_2O signal (521 cm^{-1}) was used as evidence that Li_2O_2 could be formed and evolved reversibly[89].

Raman scattering spectra were recorded on a BaySpec's Nomadic Raman spectrometer system equipped with a 532 nm laser.

The two main typical graphite bands present in the Raman spectrum of MWCNTs are at 1580 cm^{-1} (G band) and at 1342 cm^{-1} (D band) as shown in figure 2.13. The figure also

shows the D and G bands of various CNTs and D and G bands obtained with the Pd-coated and filled CNTs.

Figure 2.13. Raman spectra of SWCNT, DWCNT and MWCNT [70] (Reprinted (adapted) with permission from Pan, X. & Bao, X. The effects of confinement inside carbon nanotubes on catalysis. *Acc. Chem. Res.* 44, 553–562. Copyright 2011 American Chemical Society) Bottom: Raman spectra of Pd-filled and Pd-coated CNTs showing the D and G bands.

The superoxides play an important role in oxygen reduction and evolution reactions of Li-O₂ batteries. The ability of Raman spectroscopy to finger-print the most relevant electrochemically generated products (Li₂O₂, LiOH, Li₂CO₃ and Li₂O) should encourage its use as an essential characterization method for Li-O₂ systems[89].

Gittleson et al. provided the standard spectra for commercially purchased Li₂O₂, Li₂O, Li₂CO₃ and LiOH powders for comparison[89] as shown in figure 2.14.

Figure 2.14. Raman spectra of commercial powders[90]. Reprinted (adapted) with permission from Gittleson, F. S., Ryu, W. & Taylor, A. D. Operando Observation of the Gold – Electrolyte Interface in Li – O₂ Batteries. *Appl. Mater. Interfaces* 6, 19017 (2014). Copyright 2014 American Chemical Society [90]

2.3.3.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic, polymeric, and, in some cases, inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. FTIR provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Infrared spectroscopy gives a positive identification (qualitative analysis) of the material. Also, the size of the peaks in the spectrum indicates the amount of material present. The IR region is commonly divided into, near-IR ($400 - 10\text{ cm}^{-1}$), mid-IR ($4000 - 400\text{ cm}^{-1}$), and far-IR ($14000 - 4000\text{ cm}^{-1}$). IR spectra can be measured using liquid, solid, or gaseous samples that are placed in the beam of infrared light.

I used JASCO FT-IR 4100 for analysis of my cathodes in the mid-IR region for this dissertation.

The cathodes after discharge/ charge cycles were treated with DMC to remove the LiTFSi salt residue in the Ar-filled glovebox. The cathodes were then placed in the sample holder of the FTIR instrument for analysis. The instrumental process followed in FTIR shown in Figure 2.15 is as follows:

Figure 2.15. Schematic diagram of FTIR

Infrared energy is emitted from a glowing black-body source which passes through an aperture that controls the amount of energy presented to the sample. The beam enters the interferometer where the ‘spectral encoding’ takes place. The resulting interferogram signal then exits the interferometer. The beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed. The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. The measured signal is digitized and sent to the computer

where the Fourier transformation takes place. The final infrared spectrum is then presented for interpretation.

3. PALLADIUM-FILLED CNT CATHODE FOR IMPROVED ELECTROLYTE STABILITY AND CYCLABILITY OF Li-O₂ BATTERIES

3.1. Background

High energy density batteries have garnered much attention in recent years due to their demand in electric vehicles. Lithium oxygen (Li-O₂) batteries have nearly 10 times the theoretical specific energy of common lithium-ion batteries and in that respect have been regarded as the batteries of the future [6]·[5]·[15]. A typical Li-O₂ battery consists of Li anode, porous cathode open to oxygen and Li⁺ ion conducting electrolyte separating the electrodes. Li-O₂ battery stores energy via a simple electrochemical reaction ($2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$) in which Li₂O₂ is deposited on the surface of cathode via the forward reaction (oxygen reduction reaction, ORR) during discharge and backward reaction (oxygen evolution reaction, OER) takes place during charging to decompose Li₂O₂ on the surface of cathode[5]. Since the main discharge product (Li₂O₂) and other discharge/charge byproducts in Li-O₂ batteries are electrically insulating and not soluble in electrolytes, the structure and electronic conductivity of cathode materials have been critical factors in determining the limiting capacity of Li-O₂ batteries[91]·[92]. Carbonaceous materials such as carbon nanoparticles[18]·[93], carbon nanofibers[42]·[51], carbon nanotubes[93]·[42]·[48], graphene platelets[94]·[95], and other forms of carbons[96]·[65] have been commonly used as cathode materials in Li-O₂ batteries. Among carbon-based materials, carbon nanotubes (CNTs) have been widely used in Li-O₂ cathodes due to their high specific surface area, good chemical stability, high electrical conductivity, and large accessibility of active sites[72]·[97]. Zhang *et al.* reported one of the early uses of CNT

(single-walled) as cathode materials in Li-O₂ batteries in which discharge specific capacities as high as 2540 mAh·g⁻¹ were obtained at 0.1 mA·cm⁻² discharge current density[42]. Although many research studies have been done to improve the performance metrics of Li-O₂ batteries, they are still in their early stages and many technical challenges have to be addressed before their practical applications[98][99]. The most common problems impeding the development of Li-O₂ batteries have been low rate capability, poor recyclability and low round-trip efficiency[100][15]. All these issues are originally stemmed from sluggish kinetics and irreversible characteristic of the OER and ORR reactions which causes high overpotentials in discharging/charging process. Hence, increasing the efficiency of OER/ORR reactions and minimizing the overpotentials during the discharging/charging process have been regarded as a meaningful approach to overcome the aforementioned problems in Li-O₂ batteries. Various additives have been explored to remedy this problem including the use of redox mediators [101]. Redox mediators minimize charge polarization by acting as charge carriers between the cathode and Li₂O₂ surface [102]. Alternatively, the use of different noble metals and metal oxide catalysts has also been integrated in the cathodes of Li-O₂ batteries [103][104][105][55]. The catalyst may influence the performance of Li-O₂ batteries by destabilizing the oxidizing species which decreases the charging overpotential [106][107]. They may also increase the surface active sites and facilitate charge transport from oxidized reactants to the electrode which could also lead to formation of nanocrystalline Li₂O₂ [65]. However, it has been recently shown that the catalyst on the oxygen cathode in Li-O₂ batteries is easily deactivated due to continuous accumulation of discharge and charge products upon cycling [68][108]. It has been also reported that coarsening and agglomeration of catalyst

upon charging/discharging reduces the efficiency of catalyst in Li-O₂ batteries [104][109]. Besides the catalyst deactivation/agglomeration upon cycling, Gittleson *et. al.* have also shown the impact of catalyst-electrolyte compatibility on Li-O₂ battery performance [110][111]. According to the report, platinum (Pt) and palladium (Pd) catalysts promote Li₂O₂ oxidation at low potentials but also cause electrolyte decomposition resulting in the formation of Li₂CO₃ and thus deactivating the catalysts. Advanced approaches such as dispersing catalysts in polymeric membrane over the oxygen electrode, chemically binding the catalysts on the surface of CNTs by atomic layer deposition, and encapsulation of catalysts inside carbon cathodes have been developed to overcome the deactivation and agglomeration of catalysts in Li-O₂ batteries[112][113][114][115][116].

In this study, we report the effect of filling CNT with Pd nanoparticle catalysts to assist the ORR/OER reactions in Li-O₂ batteries while minimally destabilizing the electrolyte. To assess the effectiveness of this approach, various electrochemical, spectroscopic, and microscopic techniques have been used.

3.2. Experimental

3.2.1. Materials

Palladium (II) chloride (PdCl₂, 59% Pd) was purchased from ACROS organics. Bis (trifluoromethane) sulfonamide (LiTFSI, purity > 99.95%), tetraethylene glycol dimethyl ether (TEGDME, purity>99.00%), N-methylpyrrolidine (NMP, purity>97.00%), multi-walled carbon nanotubes (MWCNT, D=5-20 nm, L=5 μm, purity > 95.00% carbon

basis), titanium (IV) oxysulfate (TiOSO_4) ($\geq 29\%$ Ti (as TiO_2) basis) and lithium peroxide (Li_2O_2) were purchased from Sigma-Aldrich. Carbon cloth gas diffusion layer (CCGDL, thickness $\sim 300\mu\text{m}$) was purchased from Fuel Cell Earth. Lithium foil chips (purity $> 99.90\%$) and Celgard polypropylene separator (thickness $\sim 25\mu\text{m}$) were purchased from MTI Corp. Polyvinylidene fluoride (PVDF) was purchased from Alfa Aesar.

3.2.2. Electrode preparation

Pd-filled MWCNTs were prepared following the procedure detailed elsewhere[76]. Briefly, capped MWCNTs were first decapped by nitric acid solution treatment and then 1 mM aqueous solution of PdCl_2 was used to swell 100 mg of decapped MWCNTs until a slurry was formed. Pd-coated CNTs were also prepared following the same procedure on untreated capped MWCNTs. Both slurries of Pd-coated and Pd-filled MWCNTs were dried overnight at room temperature and calcinated in air at 350°C for 2 hours. Corresponding particles were then hydrogenated in an oven under hydrogen gas to yield ~ 5 wt.% Pd nanoparticles[76]. Cathodes were prepared by coating a slurry of MWCNT (Pristine, Pd-filled and Pd-coated)/PVDF (90/10 Wt.% in NMP) on 0.5" diameter carbon cloth gas diffusion layer (CCGDL) followed by drying at 120°C for 12 hours. The cathodes were then stored into an Ar-filled glovebox to be used later. The typical loading of MWCNT was 0.5 ± 0.01 mg. All reported capacities in this manuscript are reported per total mass of active cathode (CNTs and catalyst).

3.2.3. Electrolyte and battery test assembly

The electrolyte was prepared by adding 1 mol.kg⁻¹ of LiTFSI salt into TEGDME solvent. Li-O₂ batteries were assembled using a Swagelok type cell with stainless steel rod on the anode side and a stainless-steel tube on the cathode side. Lithium metal disc was used as anode, covered by electrolyte-soaked Celgard 2400 separator, MWCNT-CCGDL and a stainless-steel mesh as a current collector. Li-O₂ batteries were rested inside Ar-filled glove box overnight before electrochemical tests. All electrolyte preparation and cell assembly were performed inside Ar-filled glove box (<1 ppm O₂ and <0.1 ppm H₂O).

3.2.4. Characterization

The Li-O₂ batteries were removed from argon glove box and placed in the gastight desiccator filled with ultra-high purity oxygen gas (Airgas, purity > 99.994%). The batteries were rested under oxygen for 5 hours before testing. Solartron 1470 battery tester was used for galvanostatic discharge/charge tests within a voltage range of 2.0-4.5 V at a current density of 250 mA·g⁻¹. Voltammetry measurements were performed by an electrochemical workstation (Gamry reference 600TM) at the rate of 1 mV·s⁻¹ in the range of 2.0-4.5 V to investigate the catalytic behavior of oxygen electrodes. All charge/discharge and electrochemical tests were measured in a temperature controlled environment at 25°C. After charge/discharge cycling, the oxygen cathodes were recovered from the batteries in the Ar-filled glovebox, rinsed with acetonitrile and dried under vacuum. Cathodes were investigated by Raman spectroscopy (BaySpec's NomadicTM, excitation wavelength of 532 nm), Fourier transform infrared (FTIR) spectroscopy (JASCO FT-IR 4100), and Scanning electron microscopy (SEM) (JEOL

6330F). Bruker GADDS/D8 x-ray powder diffraction (XRD) with MacSci rotating Molybdenum anode ($\lambda=0.71073$) operated at 50 kV generator and 20 mA current was also used to collect the diffraction patterns. A parallel X-ray beam in size of 100 μm diameter was directed on to the samples and diffraction intensities were recorded on large 2D image plate during exposure time. Li_2O_2 was quantified in the cathodes after discharge using a colorimetric method previously reported by Schwenke *et al.* [84]. Briefly, discharged cathodes were first immersed in water then aliquots were taken and added to 2% aqueous solution of TiOSO_4 . Instantaneously a color change occurred and the absorbance spectra of the solutions were collected using a UV-Vis spectrophotometer (Gamry UV/Vis Spectro-115E). The peak intensity at 408 nm was calibrated against solution with known concentrations of Li_2O_2 , in the range of 0.1 to 10 mg/ml and linear calibration curve was obtained. Transmission Electron Microscopy (Phillips CM-200 200kV) was also used to inspect the carbon nanotubes.

3.3. Results and discussion

The cathodes used in this study were composed of MWCNTs (pristine, Pd-coated and Pd-filled) coated on the woven carbon cloth gas diffusion layer (CCGDL). Homogenous three-dimensional networks of carbon nanotubes over CCGDL yields high surface area with an open structure which improves the electronic contact during charging and discharging processes [24].

Figure 3.1. Transmission electron micrographs of Pd-coated CNTs (a) and Pd-filled CNTs (b). (c) Raman spectra of Pd-filled and Pd-coated CNTs

Figure 3.1(a) and (b) show TEM images of Pd-coated and Pd-filled CNTs, respectively. In Pd-filled cathodes, Pd nanocatalysts are formed in the inner tubular region of decapped CNTs [117]. Figure 3.1(c) shows the Raman spectra of the Pd-coated and Pd-filled CNTs. D and G bands of Pd-filled and Pd-coated CNTs were identical in location and intensity ratios [$I(\text{G})/I(\text{D}) \sim 1.2$] indicating that the decapped CNTs does not have high density of defects on their surface.

The first discharge and charge behaviors of Pd-coated, Pd-filled and pristine CNTs batteries using 1M LiTFSI in TEGDME electrolyte in the voltage window of 2.0-4.5 vs Li/Li^+ at the constant current density of $250 \text{ mA} \cdot \text{g}^{-1}$ are shown in Figure 3.2.

Figure 3.2. First discharge/charge capacity of pristine CNTs, Pd-coated CNTs and Pd-filled CNTs at a constant current density of $250 \text{ mAh}\cdot\text{g}^{-1}$ between 2.0 - 4.5V

The pristine CNTs show a first discharge capacity of $1980 \text{ mAh}\cdot\text{g}^{-1}$ compared to $8197 \text{ mAh}\cdot\text{g}^{-1}$ and $11,152 \text{ mAh}\cdot\text{g}^{-1}$ for the Pd-coated and Pd-filled CNTs, respectively. The ~6-fold discharge capacity improvement of Pd-coated CNTs over pristine CNTs resulted from improved ORR and increased surface sites for lithium discharge product deposition due to the presence of Pd nanocatalysts. Cyclic voltammetry (CV) measurements (Figure 3.3) confirm higher ORR and OER currents for Pd containing CNTs over pristine CNTs. This also confirms retained catalytic activity of Pd when encapsulated inside the CNTs, consistent with previously observations[115][118][114].

Figure 3.3. Cyclic voltammetry of pristine, Pd-filled, and Pd-coated CNTs in range of 2–4.5 V vs Li/Li⁺. All scans rates 1 mV.s⁻¹ under O₂ or Ar atmospheres.

In addition, the presence of Pd nanocatalysts in both Pd-filled and Pd-coated CNTs shifts the onset of ORR peak of pristine CNTs from 2.8 V to 2.9 V, showing enhanced cathodic activity [17]. The Pd-filled CNTs also demonstrated 36% increase in first discharge capacity over Pd-coated. In the figure 3.2, an oxidation peak at ~ 3.3 V is attributed to the OER and was shown to be more pronounced for the Pd-filled compared to Pd-coated. It is considered that the presence of Pd inside the CNTs strengthens the π electron density on the CNT surface yielding homogeneously distributed nucleation sites for Pd-filled CNTs compared to heterogeneously distributed nucleation sites for Pd-coated CNTs [114]. This delocalization of Li₂O₂ seeding sites contributes to intimate contact between Li₂O₂ and CNTs and helps promote the formation of high surface discharge products. At voltage

exceeding 3.7 V vs Li/Li⁺ Pd-coated CNTs show the highest rate of oxidation of electrolyte and electrolyte decomposition products [111][110][119][75][120]. The subtle OER activity in CV was previously reported by Gittleson *et al.* using TEGDME electrolyte in the presence of the noble metal catalysts[110]. Raman spectroscopic characterization on discharged cathodes revealed Li₂O₂ formation at ~790 cm⁻¹ Raman shift[89] for all discharged cathodes (figure 3.4a). However, the Pd-coated CNTs cathode showed a pronounced Raman shift peak at 1080 cm⁻¹, which corresponds to the electrolyte decomposition product Li₂CO₃ [89][121]. This peak was absent from pristine CNT cathodes. This behavior confirms the observation from CV, indicating reduced electrolyte stability due to the presence of Pd on Pd-coated CNTs and enhanced electrolyte stability for Pd-filled compared to Pd-coated CNTs. Following charging, Raman spectroscopic analyses on the cathodes revealed efficient removal of the Li₂O₂ peaks from all cathodes, and a decrease in peak intensity of Li₂CO₃ peak for the Pd containing CNTs. The decrease in Li₂CO₃ was previously reported to be enabled in catalyst-containing cathodes[122]. Li₂O₂ content in the cathode was quantified using a colorimetric approach previously reported by Schwenke et al.[84]. The amounts of Li₂O₂ in the cathode were determined to be 11.6, 21.4, and 35.4 μmoles for pristine, Pd-coated, and Pd-filled CNT cathodes, respectively. These amounts corresponded to capacity yields of approximately 88%, 23%, and 37% of the experimental capacities recorded by the pristine, Pd-coated, and Pd-filled CNT cathodes, respectively. In order to determine the molar ratio of Li₂O₂ in the discharged cathodes, the cathodes were analyzed using FTIR following the method reported by Qiao and Ye[123]. Using peak intensities ratio at 600 cm⁻¹ (Li₂O₂) and 862 cm⁻¹ (Li₂CO₃), Pd-coated and Pd-filled cathodes had 19.3% and

33.2% Li_2O_2 by mole, respectively. By only considering the Li_2O_2 and Li_2CO_3 discharge species, this observation is in agreement with the UV-Vis quantification and further confirms the stabilizing effect of the encapsulation of Pd inside the CNTs compared to coating the CNTs. The CV and Raman data also back up these claims, indicating that the electrolyte undergoes more decomposition in cells with Pd-coated CNTs cathodes. The presence of Li_2O_2 and Li_2CO_3 was additionally confirmed by XRD (figure 3.4b).

Figure 3.4. (a) Raman spectra after discharging and charging the batteries for pristine, Pd-coated, and Pd-filled CNTs. (b) X-ray diffraction patterns confirming the presence of Li_2O_2 and Li_2CO_3 in Pd-coated and Pd-filled discharged cathodes.

Figure 3.5. Raman spectroscopy was performed on fully discharged cathodes of Pd-coated and Pd-filled CNT. Small peaks of Li_2O_2 were observed $\sim 790 \text{ cm}^{-1}$ and peaks for Li_2CO_3 were observed at $\sim 1090 \text{ cm}^{-1}$.

X-ray powder diffraction is used to characterize the cathodes. The Bruker GADDS/D8 diffractometer is equipped with Apex Smart CCD Detector and direct-drive rotating anode. The MacSci rotating anode (Molybdenum) is operated at 50 kV and 20 mA. The usual collection time was 3h. X-ray patterns were collected in transmission mode. 2D diffraction patterns were integrated using Fit2D software.

We performed XRD on the fully discharged cathodes of Pd-coated and Pd-filled CNT in order to confirm the presence of Li_2O_2 . Both the cathodes confirmed the presence of lithium peroxide and small amounts of lithium carbonate. After subtracting the background and then comparing the peak intensities of the two cathodes, it is evident that Pd-coated CNT has more amount of lithium peroxide than Pd-filled CNT.

The formation of discharge products was visually confirmed using scanning electron microscopy on discharged cathodes shown in figure 3.5.

Figure 3.6. Scanning electron micrographs of cathodes after discharge for pristine CNTs (a), Pd-coated CNTs (b), and Pd-filled CNTs (c). The scale bars are 1 μm .

The discharge products (Li_2O_2) of pristine CNTs (figure 3.6a) were conformal around the cathode in rod-like structures with low porosity. The growth of layers in this morphology often yields to passivation and blockage of oxygen to the cathode and eventually limits the discharge capacity and cycle life of the battery [25]. The Pd-coated CNTs cathode (figure 3.6b) show some platelet-shaped Li_2O_2 buried by thick conformal layer, suspected to be Li_2CO_3 as shown in Raman and FTIR measurements. In contrast, the Pd-filled

CNTs show nano-thin platelets of Li_2O_2 covering the cathode (figure 3.6c). These platelets of Li_2O_2 yields high surface porosity which in turn do not block the access to the CNTs and enhance the performance.

In order to identify the synergy of electrolyte and Pd nanocatalysts, the oxidation stability limit of the electrolyte was determined using a chronopotentiometric stability test and linear sweep voltammetry under oxygen atmosphere. Batteries using Pd-coated, Pd-filled and pristine CNTs were assembled and charged without prior discharging at constant current density of $250 \text{ mA}\cdot\text{s}^{-1}$ up to cut-off voltage of 4.5 V. Figure 3.7 shows higher capacity for Pd-coated compared to Pd-filled and pristine. Since no discharge products existed, the capacities obtained are attributed to electrolyte and cathode undesirable reactions.

Figure 3.7. (a) Chronopotentiometric test at $250 \text{ mA}\cdot\text{g}^{-1}$ from OCV to 4.5 V for pristine, Pd-coated, and Pd-filled CNTs. (b) Linear sweep voltammetry of pre-discharged Pd-coated and Pd-filled CNTs under oxygen between OCV and 4.5 V vs Li/Li^+ at scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$

Again, this supports the claim that Pd-filled promote better stability than Pd-coated CNT cathodes. This observation was also confirmed using linear sweep voltammetry following a discharge showing increased OER peak intensity at 3.3-3.4 V and improved electrolyte stability above 3.7 V vs Li/Li⁺ for Pd-filled vs Pd-coated CNTs (figure 3.7b). These results again support previous observations that encapsulating the Pd nanocatalyst helped improve the electrolyte stability during the operation of the Li-O₂ battery.

The cycling stability of Li-O₂ batteries based on Pd-filled, Pd-coated, and pristine CNTs have been investigated and shown in Figure 3.8.

Figure 3.8. Cyclability of the Li-O₂ batteries for fixed cycle capacities of 500 $\text{mAh}\cdot\text{g}^{-1}$ at a current density of 250 $\text{mA}\cdot\text{g}^{-1}$ and with voltage cutoffs of 2.0 - 4.5 V for pristine CNTs, Pd-coated CNTs, and Pd-filled CNTs. The markers $\circ$ denote discharge capacity and $\bullet$ denote charge capacity.

Galvanostatic discharge/charge cycling of Li-O₂ batteries at a current density of 250 $\text{mA}\cdot\text{g}^{-1}$ at a limited capacity of 500 $\text{mAh}\cdot\text{g}^{-1}$ in a voltage window of 2.0-4.5 V vs Li/Li⁺

were conducted. Li-O₂ cells using Pd-filled CNTs show the highest discharge cycling performance of 58 cycles compared to 43 cycles for Pd-coated, and 35 for pristine CNTs. The cycling stability improvement in the case of Pd-coated and Pd-filled CNTs is a result of previously confirmed OER/ORR improvement due to the Pd nanocatalysts. The cycling stability improvement of Pd-filled CNTs over the Pd-coated CNTs was ultimately credited to the decrease in undesirable discharge/charge products formation, e.g. Li₂CO₃, afforded by the encapsulation approach.

3.4. Conclusion

The inclusion of Pd catalyst in CNTs for use as cathode materials in Li-O₂ batteries has been demonstrated. Using two modes of CNT loading, inside (Pd-filled CNTs) and outside (Pd-coated CNTs), showed that both approaches yielded significant improvement in full discharge capacities of the batteries while the Pd-filled cycled for 35% more cycles of 500 mAh·g⁻¹ at current density of 250 mA·g⁻¹. The encapsulation of nanocatalyst inside the CNTs improved the stability of the electrolyte by decreasing the formation of Li₂CO₃ compared to nanocatalyst-coated CNTs. These observations were confirmed by voltammetry, Raman and UV/Vis spectroscopy, FTIR, chronopotentiometry, electron microscopy, and charge/discharge cycling.

4. MECHANISM OF IONIC IMPEDANCE GROWTH IN LITHIUM-OXYGEN BATTERY ELECTRODES AND ITS CONTRIBUTION TO BATTERY FAILURE

4.1. Background

Secondary batteries are electrochemical storage systems that successfully convert chemical energy into electrical energy by the reversible electrochemical oxidation/reduction reactions. Various types of secondary battery systems have been studied, developed, and used in the past, including lead-acid, nickel-metal hydride, and lithium-ion batteries¹. Owing to their high specific energy, lithium-ion batteries have found applications in various fields. Due to the increasing demand for advanced energy storage solutions for the automotive industry, smart grids, and other stationary applications, the research for ultra-high theoretical specific energy has led to the study of beyond lithium-ion batteries, metal-air batteries have been at the forefront of this research^{2,3}. Metal-air batteries are unique because the cathode material i.e. oxygen gas can be obtained from the atmosphere instead of storing it in the battery. Lithium-air batteries have high theoretical specific energy density of 11,140 Wh/kg, many folds higher than current lithium-ion batteries^{4,5}.

Abraham and Jiang first reported on a non-aqueous lithium-oxygen battery in 1996, which consisted of a lithium anode, a polymer electrolyte, and a porous carbon-air cathode⁵. Since then, several studies have been conducted on the rechargeability of Li-O₂ batteries. During discharging of a Li-O₂ battery, Li⁺ migrate across the electrolyte to

cathode where the incoming electrons from the external circuit combine with the oxygen from the atmosphere to form peroxide ions, O_2^{2-} which in turn reacts with the Li^+ in an oxygen reduction reaction to form the discharge product Li_2O_2 . During charging, the reverse reaction occurs, and an oxygen evolution reaction (OER) occurs, regenerating the Li^+ and O_2 .

Carbonaceous materials such as carbon nanoparticles^{7,8}, carbon nanofibers^{9,10}, carbon nanotubes^{8,9,11–14}, graphene platelets^{15,16}, and other forms of carbons^{17,18} have been commonly used as cathode materials in Li- O_2 batteries¹². Carbon nanotubes (CNTs) have been widely used in Li- O_2 cathodes due to their high specific surface area, good chemical stability, high electrical conductivity, and large accessibility of active sites^{12,19,20}.

The use of different metal and metal oxide catalysts has also been reported in the cathodes of Li- O_2 batteries to improve the catalytic properties of the OER and ORR reactions^{21–23,6}. Some of the elements used were platinum²⁷, palladium²⁸, ruthenium^{22,23,29–32}, gold^{27,33}, and various metal oxides^{34–36}. The presence of a catalyst has been shown to influence the performance of Li- O_2 batteries by destabilizing the oxidizing species, which in turn decreases the charging over-potential^{24–26}, increases cyclability^{24,24–27}, and improves the overall battery performance. Gittleson *et. al.*^{37,38} have shown that platinum and palladium catalysts promote Li_2O_2 oxidation at lower potentials. However, they also reported that electrolyte decomposition also occurs, resulting in the formation of lithium carbonates and thus deactivating the catalysts. Khalil *et al.* passivated the porous carbon cathode by a protective Al_2O_3 layer applied using atomic layer deposition¹⁸ prior to coating a Pd catalysts. Their approach led to the formation of a

nanocrystalline Li_2O_2 during discharge that helped improve the electronic transport properties thus reducing the charge over-potential to about 0.2 V¹⁸. According to Li *et al.*, Ru nanocrystals when used as catalysts decomposed Li_2CO_3 at 3.5 V, thus reduced the accumulation of Li_2CO_3 in in the cathode during cycling.

Advanced approaches such as dispersing catalysts in polymeric membranes over the oxygen electrode, chemically binding the catalysts to the surface of CNTs by atomic layer deposition, and encapsulation of catalysts inside carbon cathodes have been developed to overcome the deactivation and agglomeration of catalysts in Li-O₂ batteries^{12,32,39–42}. In our previous work, the filling of CNT annulus with palladium nanocatalysts has resulted in an increase of the stability of the electrolyte during the charge and discharge process¹². In addition, the full discharge of battery to 2 V resulted in a 6-fold increase in the first discharge capacity compared to the pristine CNT cathodes, and 35% over their palladium coated cathodes.

In this study, we investigate the electrochemical impedance performance of palladium coated and palladium-filled CNTs cathodes during charge/discharge cycling to unveil the failure mechanism of the batteries. We also investigate the chemical nature and morphology of deposits on the electrodes using FTIR and SEM to corroborate the results from the electrochemical impedance spectroscopy study.

4.2. Experimental

Materials - Bis (trifluoromethane) sulfonamide (LiTFSI, purity > 99.95%), tetraethylene glycol dimethyl ether (TEGDME, purity > 99.00%), N-Methylpyrrolidine (purity

>97.00%), multi-walled carbon nanotubes (D=5–20 nm, L = 5 μ m, purity > 95.00% carbon basis). Palladium (II) chloride (59% Pd) was purchased from ACROS organics. Polyvinylidene fluoride (PVDF) was purchased from Alfa Aesar. Carbon cloth gas diffusion layer (thickness $\sim$ 300 μ m) was purchased from Fuel Cell Earth. Lithium foil chips (purity>99.90%) and Celgard polypropylene separator (thickness $\sim$ 25 μ m) were purchased from MTI Corp.

Electrode preparation - Pd-filled MWCNTs were prepared following the procedure detailed elsewhere^{48,12}. Briefly, nitric acid treatment was done to decap MWCNTs first followed by 1 mM aqueous solution of PdCl₂ to swell 100 mg of decapped MWCNTs until a slurry was formed. Pd-coated CNTs were prepared following the same procedure on untreated capped MWCNTs. Both slurries were then dried overnight at room temperature and calcinated in air at 350°C for 2 hours. Calcination was followed by hydrogenation in an oven under hydrogen gas to yield $\sim$ 5 wt% Pd nanoparticles. Cathodes were prepared as mentioned the preceding paper¹². Slurry of MWCNT (Pd-filled and Pd-coated)/PVDF (90/10 Wt% in NMP) was used to coat the cathodes on 0.5” diameter carbon cloth and it was followed by drying at 120°C for 12 hours. The cathodes were then stored in an Ar-filled glove box to be used later. The typical loading of MWCNT was 0.5 ± 0.01 mg. All capacities reported in this manuscript are per total mass of active cathode (CNTs and catalyst).

Electrolyte and battery test assembly - 1 M LiTFSI in TEGDME solution was prepared. We used Swagelok type cell with stainless steel rod on the anode side and a stainless steel tube on the cathode side. Lithium metal disc anode was covered by electrolyte soaked

Celgard 2400 separator, followed by MWCNT-CCGDL and a stainless-steel mesh as a current collector. The batteries were then rested inside Ar-filled glove box (<1 ppm O₂ and < 0.1 ppm H₂O) overnight before electrochemical tests.

Electrochemical Characterizations - The batteries were rested under oxygen for 5 hours before testing. Gamry battery tester was used for galvanostatic discharge/charge. Discharge/charge tests were performed within a voltage range of 2.0–4.5 V at a current density of 250 mA.g⁻¹. The electrochemical characteristics of the cell were investigated by Electrochemical Impedance Spectroscopy (EIS) performed with a Gamry battery tester. Impedance data were collected in the frequency range of 10⁵ – 0.01 Hz. All charge/discharge and electrochemical tests were measured in a temperature controlled environment at 25°C. After charge/discharge cycling, the oxygen cathodes were recovered from the batteries in the Ar-filled glove box, rinsed with DMC and dried under vacuum.

Infrared Characterizations - Cathodes were investigated by Fourier transform infrared (FTIR) spectroscopy (JASCO FT-IR 4100) for product characterization in mid-IR frequency region (500-4000cm⁻¹). A resolution of 4cm⁻¹ was used for each spectrum. For pretreatment for FTIR, the samples were rinsed 3 times with dimethyl carbonate (DMC) to remove the electrolyte salt and LiO₂ from the cathode surface and dried in vacuum to volatize DMC.

4.3. Results and discussion

Li-O₂ batteries with cathodes comprising Pd-coated and Pd-filled CNTs showed full discharge capacities of 8197 mAh.g⁻¹ and 11,152 mAh.g⁻¹, respectively¹². The batteries were discharged to 2 V under oxygen. Galvanostatic cycling employed to characterize the electrochemical properties on the cathodes during the ORR and OER processes. Cycle performance of the Li-O₂ batteries with Pd-coated and Pd-filled CNTs as cathode were investigated at fixed capacities of 250 mAh.g⁻¹, 500 mAh.g⁻¹, and 1000 mAh.g⁻¹ at the current density of 250 mA.g⁻¹ between 2-4.5 V (Figure 4.1). At 250 mAh.g⁻¹, 41 and 81 cycles were obtained using Pd-coated and Pd-filled CNTs respectively. At 500 mAh.g⁻¹, 44 and 58 cycles were obtained using Pd-coated and Pd-filled CNTs respectively. 16 and 25 cycles were obtained at 1000 mAh.g⁻¹. Figure 4.2 shows the terminal discharge voltages of the batteries.

Figure 4.1. Voltage profile of Li-O₂ batteries with Pd-filled (a) (c) (e) and Pd-coated CNTs (b) (d) (f) at fixed capacities of 250 mAh.g⁻¹ , 500 mAh.g⁻¹ and 1000 mAh.g⁻¹ respectively at a current density of 250 mA.g⁻¹ between 2-4.5 V.

Figure 4.2. End discharge/charge voltages of Pd-filled (a) (c) (e) and Pd-coated CNTs (b) (d) (f) after full cycles to 250 mAh.g^{-1} , 500 mAh.g^{-1} and 1000 mAh.g^{-1} respectively

EIS measurements were performed after discharge/charge cycles to investigate the cathode/electrolyte behavior during discharging and charging processes. Figures 3 and 4 show the EIS of the Pd-coated and Pd-filled CNTs after the first and last cycle of discharging and discharging. The Nyquist plot after discharge shows a high frequency intercept R_b which corresponds to the resistance of the cell which includes contributions from the electrodes, electrolyte, and contact resistance^{13,45,49–53} as shown in figure 3. R_b is the high frequency intercept and is obtained from the real EIS spectra. It is followed by the semicircle that is associated with charge transfer resistance at the cathode/O₂/electrolyte interface^{45,49,50} represented by R_{int} (interfacial resistance). R_{int} is obtained from the diameter obtained of the semicircle obtained from the EIS. This is generally attributed to the Li₂O₂ formation on the surface of the cathode after discharge which hinders charge transfer and O₂ diffusion through the pores of the cathode⁴⁵. Following R_{int} there is linear rise and is known as Warburg-like linear region which is present in other metal-O₂ battery EIS spectra too at non-Faradaic conditions. The transmission line model (TLM) used to determine the impedance behavior of the porous electrodes in Li-ion and metal–O₂ batteries assumes that the Warburg-like linear region corresponds to the resistance of lithium-ion migration at cathode and is represented as R_{ion} . We used TLM model and estimated the R_{ion} by the projection of the Warburg-like line on the impedance abscissa ($R_{ion}/3$) as shown in figure 3(b).^{13,52}

From figure 4.3, the Nyquist plot exhibits a smaller diameter of semicircle for Pd-filled CNT and a bigger diameter semicircle for the Pd-coated CNTs after first discharge to 250 mAh.g⁻¹. The semicircle diameter corresponds to the charge transfer resistance⁴⁵. Higher

charge transfer resistance leads to slower charge transfer kinetics⁴⁵. From figure 4.4, it is evident that the Pd-coated cathode has slower charge transfer kinetics as compared to Pd-filled CNTs due to higher resistance. As the number of cycles increase, we can see a shift of the high frequency intercept R_b towards the right. From figures 4.3 (a) (b) and 4 (a) (b), the shift is clearly visible for both the cathodes. After the last discharging cycle upto 250 mAh.g⁻¹ which is 41 cycles for Pd-coated CNT and 81 cycles of Pd-filled CNT respectively, R_b has shifted from 80 to 2910 for Pd coated CNT. Whereas the shift of R_b for Pd-filled CNT is from 80 to 300. This shift in R_b is attributed to electrolyte decomposition and formation of lithium carbonate (Li_2CO_3) over time⁴⁵. As seen in figure 4, R_{int} decreased minimally for the first 30 cycles of Pd-filled CNTs and then increases. For Pd-coated CNTs, R_{int} decreases for the first 10 cycles after the first discharge and then keeps increasing. R_{ion} was the major resistance in both cathodes and it keeps increasing with the number of cycles as seen from the figure. Anode/electrolyte interface initially governs the interfacial resistance of Li-O₂ batteries⁵⁴. The decrease in the value of R_{int} at initially is mainly attributed to the dissolution of the passivation film on anode/electrolyte films interface¹³. However, the increase in R_{int} during later cycles could be due to the accumulation of irreversible charge/discharge by-products on the anode/electrolyte¹³ and cathode/electrolyte interfaces^{13,54}. Yi et al.^{55,56} showed that the formation of lithium carbonates by-products on the cathode/electrolyte interface could increase the interfacial resistance in Li-O₂ batteries during cycling. According to Shui et al.⁵⁷, deactivation of cathode leads to Li-O₂ battery death. Increase in R_{ion} during cycling is an indication that the cathode pores have been clogged and thus the Li⁺ ion transport is hindered¹³.

Figure 4.3. Nyquist plots of (a) Pd-filled and (b) Pd-coated CNTs after different discharging cycles of 250 mAh.g⁻¹ capacity. Nyquist plots of (c) Pd-filled and (d) Pd-coated CNTs after different discharging cycles of 1000 mAh.g⁻¹ capacity. The batteries were cycled at 250 mA.g⁻¹ current density between 2-4.5 V.

Figure 4.4. Change of resistances after the discharging (a) (c) (e) Pd-filled CNT (b) (d) (f) Pd-coated CNT cycles of 250 mAh.g⁻¹, 500 mAh.g⁻¹, and 1000 mAh.g⁻¹ capacities respectively.

For the cycles with the fixed capacity of 1000 mAh.g⁻¹, similar Nyquist plots were observed (Figure 4.4 (c) (d)). In this case too, the Pd-filled CNT cycled for 25 cycles as compared to 16 cycles with Pd-coated CNTs. After the last discharging cycle upto 1000 mAh.g⁻¹, R_b shifted from 80 to 1350 for Pd-coated CNT. Whereas the shift for Pd-filled CNT is from 80 to 400. This indicates more electrolyte decomposition in case of Pd-coated CNTs. R_{ion} is the highest resistance for both cases. Hence in this case too, the battery failure is majorly due to pore clogging.

As shown by the EIS, the formation of Li_2O_2 hinders the charge transfer between the interfaces and decomposition of electrolyte¹³. Both the reasons lead to the failure of the Li-O₂ batteries. To investigate the composition of the deposits that clog the pores of the cathodes, we performed FTIR on Pd-coated and Pd-filled CNT cathodes after cycling for 15 and 45 cycles at fixed capacities of 1000 mAh.g⁻¹ and 250 mAh.g⁻¹. The peak at around 590 cm⁻¹ is attributed to Li_2O_2 and Li_2CO_3 produces a peak at 862 cm⁻¹⁵⁸. From figure 5, it can be observed that the peaks of Li_2CO_3 are higher in case of Pd-coated than Pd-filled CNTs, resulting in better cycling of the batteries. The cycling stability improvement of Pd-filled CNTs over the Pd-coated CNTs was credited to the decrease in undesirable discharge/charge products formation, e.g. Li_2CO_3 , afforded by the encapsulation approach¹².

Figure 4.6 shows comparison of Pd-coated and Pd-filled CNTs at capacities 500, 1000, 1500, 5000 and 8000 mAh.g⁻¹. As observed from the figure, at 500 mAh.g⁻¹, Li_2O_2 peak is present in both cathodes. A distinct Li_2CO_3 peak is observed for Pd-coated CNT but is negligible in case of Pd-filled CNT. At all the capacities, Li_2O_2 peaks are present for both

Pd-coated and Pd-filled CNT cathodes. However, the Li_2CO_3 peak for Pd-filled CNT cathodes gradually increases as the capacity increases. Low Li_2CO_3 formation in the Pd-filled CNT as compared to Pd-coated CNT results in increased battery performance⁵⁸.

SEM confirmed the formation of Li_2CO_3 dendrites on the surface of the cathode after cycling as shown in Figure 4.7. The Pd-coated CNTs cathode (Figure 4.7b) show some platelet-shaped Li_2O_2 buried by thick conformal layer, suspected to be Li_2CO_3 as shown in FTIR measurements. In contrast, the Pd-filled CNTs show nano-thin platelets of Li_2O_2 covering the cathode (Figure 4.7a). These platelets of Li_2O_2 yield high surface porosity which in turn do not block the access to the CNTs and enhance the performance¹².

Figure 4.5. FTIR spectra of Pd-filled and Pd-coated CNTs after cycling for (a) 45 cycles to 250 mAh.g^{-1} and (b) 15 cycles to 1000 mAh.g^{-1}

Figure 4.6. FTIR spectra after discharging to (a) 500 mAh.g⁻¹ (b) 1000 mAh.g⁻¹ (c) 1500 mAh.g⁻¹ (d) 5000 mAh.g⁻¹ (e) 8000 mAh.g⁻¹. All the batteries were discharged at 250 mA.g⁻¹ between 2-4.5 V

Figure 4.7. SEM images after cycling of (a) Pd-filled and (b) Pd-coated CNT cathodes

5. Conclusion

EIS study was conducted in this paper on Li-O₂ battery utilizing Pd-coated and Pd-filled CNTs and we provide insight into kinetics operating the battery operation. From EIS results, it is shown that R_{ion} is the highest resistance which indicates the failure of the batteries due to pore clogging of the cathodes. Increasing R_b resistance indicates more electrolyte decomposition in case of Pd-coated than Pd-filled CNT cathodes. FTIR and SEM further confirm that Pd-filled CNTs have better capacity retention due to less Li₂CO₃ formation on the surface of the cathode as compared to Pd-coated CNTs.

5. CONCLUDING REMARKS AND FUTURE WORK

5.1. Concluding remarks

In this dissertation, Li-O₂ batteries with high capacity, improved stability, and increased cyclability were developed. By inclusion of the palladium nanocatalysts in the cathodes, the catalytic performance of the charge and discharge reactions in the batteries were improved. However, issues with decreased stability of the electrolyte arose with the presence of these nanocatalysts. Therefore, part of the innovation in the research was to shield the nanocatalyst from direct contact with the electrolyte by using the carbonaceous CNT materials as barriers. To validate this hypothesis, two modes of palladium nanocatalyst loading in the cathode were employed, inside the CNT (Pd-filled in the annulus of the tubes) and outside the CNT (Pd-coated on the surface of the tubes). It was determined through electrochemical investigations that both approaches yielded significant improvement in full discharges of the batteries apparent in their increase full capacity. While catalyst-free CNTs showed a first discharge capacity of 1980 mAh·g⁻¹, the first discharge capacities for the Pd-coated and Pd-filled CNTs were 8197 mAh·g⁻¹ and 11,152 mAh·g⁻¹, respectively. In addition, batteries containing Pd-filled cathodes cycled 35% more cycles of 500 mAh·g⁻¹ at a current density of 250 mA·g⁻¹ than batteries containing Pd-coated cathodes. Electrochemical and spectroscopic studies were conducted including cyclic voltammetry, Raman spectroscopy, UV/Vis spectrophotometry, FTIR, chronopotentiometry, electron microscopy, and charge/discharge cycling. Shielding the electrolyte assisted in protecting and stabilizing the degradation of the electrolyte by decreasing the formation of the passivating Li₂CO₃.

As a result, the stabilizing the electrolytes noticeably increased the cyclability of Li-O₂ batteries.

Further research was done to gain insights into the kinetics of the reactions involved in battery operation. A systematic electrochemical impedance spectroscopic study was designed to pinpoint the source of the improvement within the Li-O₂ batteries for shielded and unshielded catalysts. EIS results were analyzed to deconvolute and separate the contribution of each of the various resistances within each component on the overall performance of the battery. Cathodes containing Pd-coated CNT showed higher bulk resistances, R_b , and cathodic ionic resistance, R_{ion} , than Pd-filled CNT cathodes. R_{ion} was consistently the highest resistance in the batteries, especially closer to the failure of the batteries. This observation indicates that the failure of the batteries was due to pore clogging of the cathodes. Continuous growth of R_b were deemed to be the result of electrolyte decomposition. FTIR determined that the main component of the pore-clogging species were in fact lithium carbonates, mainly Li₂CO₃. The presence of Li₂CO₃ was more prominent in Pd-coated cathodes than in Pd-filled ones, also confirming EIS observations that shielded catalyst helped increase the stability of the electrolyte. Visually, SEM imaging painted a clear image of this improvement and showed distinct features and structures that ranged in sizes and morphologies, that were distinctly different for these two cathodes.

In sum, the use of palladium nanocatalyst improved the capacity, cyclability, and stability of the battery. Shielding the nanocatalyst from direct contact with the electrolyte was found of prolong the life of the battery by reduce electrolyte decomposition and thus

reducing the formation of the passivating species Li_2CO_3 which in turn leads to pore clogging the cathodes and to exponential growth in the cathode's ionic resistance.

5.2. Future work

Future works include the optimization of the choice of the catalyst materials, composition, and loading values. In addition, our group has pioneered the development of new solid and gel polymer electrolytes that have been shown to further stabilize the electrolyte. The use of ceramic fillers such as SiO_2 , Al_2O_3 , and TiO_2 are also proposed as approaches that can be taken to further improve the cyclability of the Li- O_2 batteries especially for their ability to influence ion-complex formations and help protect vulnerable components in the electrolyte from oxygen free radicals' attacks.

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Skills:

Electrochemical characterizations, Energy storage, Microscopy (Scanning electron microscopy, Transmission electron microscopy), Raman spectroscopy, UV Vis Spectroscopy, X-ray diffraction, Electrochemical Impedance Spectroscopy, Electrochemistry, Battery testing, Lithium ion batteries, Lithium air batteries, Fumehood, Glovebox

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List of Publications

- Neha Chawla; Amir Chamaani; Meer Safa; Bilal El-Zahab, Ph.D."Palladium-Filled Carbon Nanotubes Cathode for Improved Electrolyte Stability and Cyclability Performance of Li-O₂ Batteries", Journal of Electrochemical Society, Volume 164, December 31, 2016, Pages A6303-A6307
- Meer Safa; Amir Chamaani; Neha Chawla; Bilal El-Zahab, Ph.D. ; "Polymeric Ionic Liquid Gel Electrolyte for Room Temperature Lithium Battery Applications", Electrochimica Acta Volume 213, 20 September 2016, Pages 587–593
- Amir Chamaani; Neha Chawla; Meer Safa; Bilal El-Zahab, Ph.D.;" One-Dimensional Glass Micro-Fillers in Gel Polymer Electrolytes for Li-O₂ Battery Applications", Electrochimica Acta 235, 2017, Pages 56-63
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