

INVESTIGATION OF MOLYBDENUM OXIDE AS A CATALYST FOR NON-AQUEOUS LITHIUM OXYGEN BATTERIES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF SCIENCE
IN
MATERIALS SCIENCE AND NANOTECHNOLOGY

By
Kıvanç Çoban
January, 2017

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We certify that we have read this thesis and that in our opinion it is fully adequate,
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ABSTRACT

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M.S. in Materials Science and Nanotechnology

Advisor: Eda Yılmaz

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Today, one of the biggest problem which the world have to get over is the global warming and the main reason of global warming is the greenhouse gasses which are released due to usage of fossil fuels in transportation applications. Therefore, alternative energy sources are needed but it is not sufficient itself. Suitable energy storage systems are also necessary and these systems have to provide very high amount of energy density and efficiency in order to replace fossil fuels. In that case batteries are very promising technologies however, there is no manufactured battery type in the market which can provide required high energy and power density, so new and more effective technologies have to be investigated for this purpose.

One of the best candidates of such technologies is the Li-O₂ battery which is based on the Li-O₂ electrochemical couple. Li-O₂ batteries can achieve approximately ten times higher energy density than that of current state-of-the-art Li-ion batteries by storing the discharge product Li₂O₂ which occurs as a result of reaction between Li anode and active cathode material, O₂, on the porous cathode material. However, there are various challenges to overcome including high OER-ORR overpotentials, parasitic side reactions and poor cyclability in order to built commercial Li-O₂ batteries. Especially, unwanted side product formation on the cathode-electrolyte interface is the major challenge itself because these insulator side products accumulate on the cathode surface during cycling and prevent electrical and ionic transportation which cause drastic capacity fading. That is why various catalyst materials have been investigated in order to facilitate the reaction between Li-O₂ electrochemical couple.

In this study, we investigated molybdenum oxide which is decorated on multi-walled carbon nanotube catalyst support as an efficient electrocatalyst for Li-O₂ batteries. Several synthesis methods and parameters have been utilized in order to enhance its performance and adapt it for our application. Morphological, structural, chemical and electrochemical characterizations have been carried out by using X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Transmission Electron Microscopy.



Keywords: Metal Oxide Catalysts, Non-Aqueous Li-O₂ Batteries, Electrochemical Energy Storage.

ÖZET

MOLİBDENYUM OKSİTİN KATALİZÖR MALZEMESİ OLARAK SU İÇERMEYEN LİTYUM OKSİJEN BATARYALARINDA ARAŞTIRILMASI

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Günümüzde, dünyanın üstesinden gelmesi gereken en büyük problemlerden bir tanesi küresel ısınmadır ve bu problemin başlıca nedeni ulaşım araçlarında kullanılan fosil yakıtlar nedeniyle salınan sera gazlarıdır. Bu yüzden alternatif enerji kaynaklarına ihtiyaç duyulmaktadır ancak bu kaynakların varlığı tek başına yeterli bir çözüm sunmaz. Bu enerji kaynaklarından elde edilecek enerjiyi depolamak için uygun enerji depolama sistemlerine de ihtiyaç vardır ve bu sistemlerin fosil yakıtların yerini alabilmesi yeterli enerji yoğunluğunu ve etkinliğini sağlayabilmeleriyle mümkündür. Bu durumda, piller umut vaat eden teknolojilerdir ancak hali hazırda üretilmiş hiç bir pil sistemi gerekli olan yüksek enerji ve güç yoğunluğunu sağlamada yeterli değildir. Bu yüzden yeni ve daha etkili teknolojilerin araştırılması gerekmektedir.

Bu tarz enerji depolama sistemlerine aday olabilecek en iyi teknolojilerden bir tanesi Li ve O₂ elektrokimyasal çiftinin temel alındığı Li-O₂ pilleridir. Li-O₂ pilleri, deşarj sırasında Li anot ve aktif katot malzemesi olan oksijenin gözenekli katot malzemesi üzerinde gerçekleşen tepkimesi sonucu Li₂O₂ depolayarak, günümüzde kullanılan en teknolojik Li-iyon pillerinden yaklaşık olarak 10 kat daha fazla enerji yoğunluğuna ulaşabilirler. Ancak, yüksek oksijen indirgenme ve yükseltgenme tepkimesi potansiyalleri, parazitik yan reaksiyonlar ve düşük şarj-deşarj döngüsellliği gibi aşılması gereken bir çok problem bu pillerin ticari olarak üretilebilir olmasının önüne geçer. özellikle elektrolit ve katot arayüzeyinde oluşan istenmeyen yan ürünler başlı başına çok büyük bir problemdir çünkü bu yalıtkan ürünler döngü sırasında katot yüzeyinde birikerek elektriksel ve iyonik ulaşımı engelleyerek şiddetli bir kapasite azalmasına neden olurlar. Bu yüzden, Li ve O₂ elektrokimyasal çifti arasındaki tepkimeyi kolaylaştırması için bir çok

çeşitli katalizör malzeme incelenmiştir.

Bu çalışmada, molibdenyum oksit parçacıklarla dekore edilmiş çok duvarlı karbon nanotüp katot malzemesi Li-O₂ piller için etkili bir elektrokatalizör olabileceği düşünülerek araştırılmıştır. Bu malzemeyi Li-O₂ pillerine adapte edebilmek ve pillerin performansını arttırabilmek için çeşitli sentez yöntemleri ve parametreleri uygulanmıştır. Morfolojik, yapısal, kimyasal ve elektrokimyasal karakterizasyonlar X-Ray Kırınımı, X-Ray Fotoelektron Spektroskopisi, Saçılımlı Elektron Mikropkopu, Geçirmeli Elektron Mikroskopu ve Galvanostatik şarj-Deşarj Testi kullanılarak gerçekleştirilmiştir.

Anahtar sözcükler: Metal Oksit Katalizör, Su İçermeyen Li-O₂ Pilleri, Elektrokimyasal Enerji Depolanması .

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Chapter 1

INTRODUCTION

1.1 Renewable Energy Technologies

Recently, more than 85% of the worlds energy demand which grows without ceasing is supplied by fossil fuels. According to predictions of experts, demand for usable energy will increase 56% by 2040 due to growing rate of the population and increment of the industrialized part of the world. Fossil fuels, such as petroleum, natural gas and oil, are major sources for energy consumption of many countries. The amount of these sources are restricted and they are nonrenewable. If the increase in consumption continues, oil reserves can suffice for just another 20 years according to claims of some estimations [1]. In addition, global warming is one of the worlds most critical challenges today and there is increasing concern about it. It is know that large quantities of carbon dioxide (CO_2) emissions and other greenhouse gasses, which are released from combustion of fossil fuels, can be considered as main factor of this global climate change.

Various renewable energies are developed as an alternative to fossil fuels including hydro, solar, wind and geothermal energies. We can list several prospective benefits of using renewable energy. First of all, dependency on fossil fuels will reduce CO₂ emissions. Energy supplies become more diverse and it will proportionally create new job opportunities in the fields of green technologies. Wind and sun energy are the most common renewable energy sources to produce electricity. However, the sun can be harvested only during the day and wind is also circumstantial. Therefore, it is not possible to supply demanded energy when it is requested and sufficient energy storage systems is needed. Even there are number of different storage techniques exist, they all have various advantages and disadvantages such as price, capacity, power and mobility. For instance, one of the most cost-effective method to store large amount of electrical energy is pumped hydro, however it requires great capital costs and appropriate geographical conditions. Therefore, we strongly need energy storage devices which can provide high efficiencies. Battery is one of the most appropriate technologies for this demand where the stored chemical energy can be converted into the electrical energy through the electrochemical reactions and rechargeable Li battery is mostly feasible one among current technologies [2,3].

1.2 Brief History

In 1800, battery was first invented by Alessandro Volta and ever since it become mostly used power source for many industrial and household applications. Batteries may basically classified into two main groups which are primary and secondary (rechargeable) batteries. Primary batteries can be used for only one time and then discarded. On the other hand, secondary batteries can be recharged and they have been designed to use for multiple times. There are many types of commercial secondary batteries such as lead-acid, nickel metalhydrate and lithium ion(Li-ion) batteries however Li-ion batteries got more attention due to its better performance, comparatively. M. S. Whittingham firstly proposed lithium batteries in the 1970s and John B. Goodenough made many significant contribution among others [4,5].The Li-ion battery was commercialized by Sony in 1991 and

many fundamental and applied advances have been achieved in this field since then. Today, Li-ion batteries have the largest capacity among all other commercialized secondary batteries which makes them the most popular storage systems for many applications. However, they do not seem capable to supply sufficient energy densities and specific energies (energy per unit volume and unit mass, respectively) for all electric vehicles in the long term even if the theoretical capacity of the electrode material could be achieved [2]. Therefore, many researches have been dedicated huge efforts to energy storage systems recently, which can pass over the limits of a Li-ion battery. One of the best candidates of such technologies is the Li-O₂ battery which is based on the Li-O₂ electrochemical couple [6]. In contrast, Li-O₂ batteries can achieve several times higher energy density than that of current state-of-the-art Li-ion batteries by storing the discharge product Li₂O₂ which occurs as a result of reaction between Li and reactive product O₂ in air on the porous cathode material. (Fig. 1.1) [7].

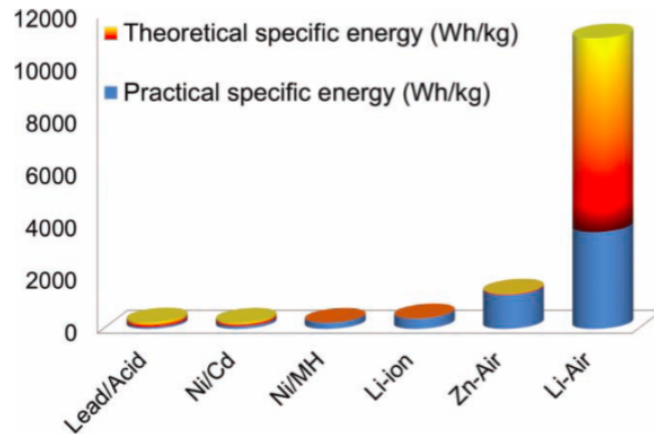


Figure 1.1: Comparison between the specific energy density of different battery technologies.[Ref.7]

In 1979, Blurton and Sammels published the first review about primary metal/O₂ batteries and right after that these batteries were drawn a big attention [8]. Primary metal-air batteries have higher theoretical specific energy densities than ion-based approaches because they are using atmospheric oxygen as a cathode so traditional cathode structure is automatically eliminated. Unluckily, electric vehicles applications for Li-O₂ cell chemistry could not seen as practical by authors

at that time. However, they recognized that they can provide high theoretical gravimetric energy density (11148 W h kg⁻¹ which is not much lower than that of gasoline (13000 W h kg⁻¹)) that could be reached with Li₂O₂ as discharge product. In 1990s, Abraham and Jiang reported the first study on a non-aqueous Li-O₂ battery system with a lithium metal anode, a gel polymer electrolyte, and a carbon substrate for the O₂ cathode and it renewed the interest in the subject [9]. In this system, Li⁺ conductive organic electrolyte polymer placed between thin carbon composite cathode and thin Li metal foil. In the cathode side, oxygen which is electroactive cathode material access provided from environment and reduced in order to generate electric power during discharge. Nevertheless, Li-O₂ batteries lost their attentions during the next decades because many technical difficulties experienced in order to achieve high energy density and long cycle life. In 2006, Bruce and his co-workers [10] replaced the polymer electrolyte with an organic electrolyte and demonstrate two essential prerequisites for the successful operation of a rechargeable Li-O₂ battery; that the Li₂O₂ formed on discharging such an O₂ electrode is decomposed to Li and O₂ on charging. After this study, the relatively simple configuration and huge specific capacity of the Li-O₂ battery quickly received much attention around the world and during last decades thousands of studies are performed to make this system more feasible.

1.3 Basic Concepts

Anode - Anode reverses during charge and discharge. Negative electrode is the anode for discharge while positive electrode is the anode for charge process. It dissolves in the electrolyte and gives electron to the load circuit.

Cathode - It is the electrode that oxidizes the anode by absorbing electrons. Cathode also reverses and it is positive electrode of voltaic cell for discharge while negative electrode of the cell during charge.

Electrolyte - It is the chemical compound that produces an electrically conducting solution when fused or dissolved in a polar solvent such as water. In fused

state, it separates into cations and anions which conduct the electric current.

Battery Cell - It is a device which is composed of three main parts including positive-negative electrodes and electrolyte. Mainly used to store the electro-chemical energy and it can be thinking as battery's basic building block.

Discharge - The conversion of the chemical energy of the battery into electric energy and the withdrawal of the electrical energy into a load.

Charge - The conversion of electric energy, provided in the form of electrical current from an external source, into chemical energy within the cell or battery to restore the chemical energy in a cell or battery.

Cycle - One sequence of a discharge followed by a recharge or just the opposite.

Battery Capacity - The total number of ampere-hours or watt-hours that can be withdrawn from a fully charged cell or battery on a service test delivered before the cell reaches a specified final electrical condition. The capacity in ampere-hours is equal to the capacity in watt-hours divided by the battery voltage.

Current Rate - The amount of current applied to battery in order to restore its capacity during discharging and charging process.

Cycle Life - The number of cycles under specified conditions which rechargeable batteries can operate before its capacity is significantly reduced. The depth of cycle type (shallow or deep) and recharging method could be greatly effective on cycle life of the battery. Inconvenient cutoff of charge cycle can greatly reduce the cycle life of a battery.

Energy Density - Ratio of the available energy from battery to its weight or volume (watt-hours per liter, or watt-hours per kilogram).

Overpotential - In electrochemistry, the difference between half-reaction potentials of thermodynamically determined reduction potential and the actual potential of electrochemically observed reaction is called as overpotential. The term is directly related to a cell's voltage efficiency. In order to drive a reaction in the electrolytic cell, more energy is needed for overpotential than thermodynamically expected. It means that less amount of energy is recovered than thermodynamically predicted in a galvanic cell. Cell design and operational conditions are effective on overpotential so it is specific to each variable. It is used more practically to define the current density at which the overpotential is measured.

1.4 Working Mechanism of Li-O₂ Battery

Many electrolytes are employed for Li-O₂ battery system in order to develop them for various areas and there are four main architecture systems according to electrolyte types which are (a) aprotic, (b) all-solid-state, (c) aqueous and (d) hybrid, as shown in Fig. 1.2 [11]. Active material for the air electrodes is oxygen for all types of Li-O₂ systems therefore there must be an open system to supply it from the air. And also, Li metal is required as an anode material which provides Li source for all the systems at the current stage.

Protective layer is required in the case of the aqueous and hybrid (aqueous/non-aqueous) systems in order to make them enable for desired electrochemistry because lithium reacts with water vigorously so we should prevent this undesirable reaction. It is proven by researchers that the theoretical energy density is higher and rechargeability is better for the non-aqueous Li-O₂ system is higher than that of aqueous systems because the chemical/electrochemical processes in aqueous batteries involve O₂ reacting with water in the aqueous system which fades the capacity. For both aqueous and hybrid systems, air electrode exposed to aqueous electrolyte, that's why they share same reaction mechanisms. Even though all-solid-state Li-O₂ batteries show very similar working mechanism with non-aqueous system, there are really a few detailed studies about them due to

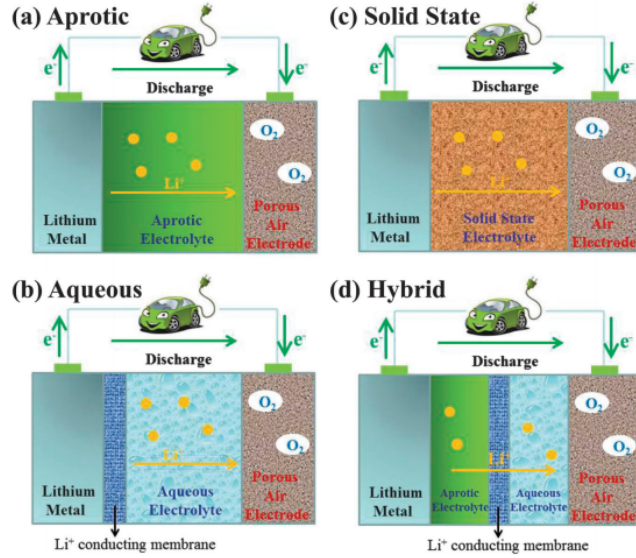


Figure 1.2: Schematic of the four different architectures of Li-air battery. [Ref.11]

insufficient lithium ion conductivity [12]. As far as, non-aqueous Li-O₂ batteries are the most studied system among others and indicate better performance comparatively, we only focus on the non-aqueous Li-O₂ systems in our study.

When non-aqueous Li-O₂ batteries are compared with all others, they own relatively the most simple structure and they are very similar to Li-ion batteries. Basically, only exception is cathode exposition by air or oxygen. Mainly cathode material, non-aqueous electrolyte, humidity, pressure of the O₂ gas and CO₂ content are main parameters which governs the performance of non-aqueous Li-O₂ batteries [13, 14]. Among other elements, researchers mostly focused on cathode materials and non-aqueous electrolyte for their studies in the early stages of the development of non-aqueous Li-O₂ batteries. Li foils are currently used as an anode, it may also cause some safety issues due to its reactive nature so it should be replaced before Li-O₂ batteries are commercialized. However, priority is to find best cathode material which can work both in ORR catalyst during charge and OER catalyst during discharge [15]. The principles of non-aqueous Li-O₂ battery operation are shown in Fig. 1.3. [16].

Generally, products which are forming on the cathode side during discharge-charge process are highly effective on the performance of Li-O₂ battery. Lithium

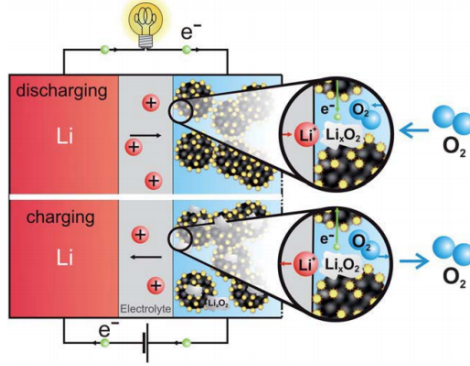
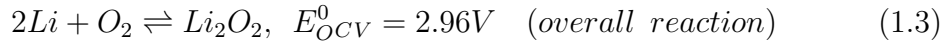
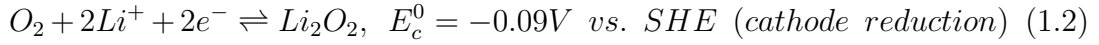
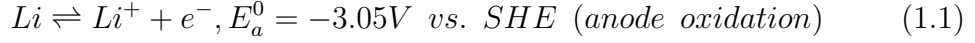
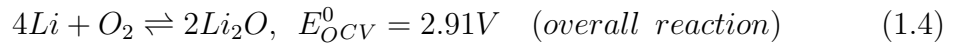


Figure 1.3: Working principle of a rechargeable Li-O₂ battery.[Ref.16]

peroxide is the major discharge product on the cathode besides small amount of lithium oxide(Li₂O). The discharge reactions in non-aqueous Li-O₂ batteries with Li₂O₂ as the product can be described as equations in (1.1)-(1.3), [12, 17].



where E_a^0 , E_c^0 and E_{OCV}^0 are the thermodynamic anode potential, cathode potential and Li-O₂ battery open circuit voltage (OCV) at standard conditions (25 °C, 1.0 atm) if Li₂O₂ is the product, respectively. For discharge product of Li₂O, the overall reaction can be expressed as reaction (1.4):



where E_{OCV}^0 is the thermodynamic open circuit voltage (OCV) of Li-O₂ battery at standard conditions (25°C, 1.0 atm) if Li₂O is the product. Reaction (1.4) is not totally reversible, it means that Li₂O as discharge product is not full rechargeable back to Li and O₂. [18]. Therefore, that reaction is not desirable and the ideal discharge product can be considered as Li₂O₂. On the other hand, several different mechanisms are suggested in the literature for the generation and decomposition

of Li_2O_2 during charge and discharge precesses and two possible discharge reaction mechanisms have been proposed for the oxygen reduction reaction on the cathode surface [11]:

Discharge reaction mechanism I:

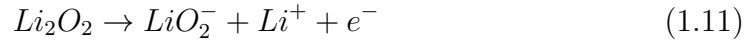


Discharge reaction mechanism II:



For the charge process, there are two major reaction mechanisms:

Charge reaction mechanism I:



Charge reaction mechanism II:



In fact, there are not common consensus about reaction mechanisms on the cathode for Li-O₂ batteries and some other mechanisms are also reported by several research groups. For example, Hummelshj et al. suggest that Li_2O_2 first nucleate on cathode material and growth continue on the surface site on Li_2O_2 during discharge [19]. For the charging mechanism, Oh et al. indicates that pyrochlores catalyse cause well-defined reversible charging behaviour at an average potential of 3.9 V and oxygen evolution occurs in three steps [20]. Several mechanisms are investigated by using theoretical conjectures or calculations and most of them

are *ex-situ*, which can not reveal the exact reaction paths in the chargedischarge process. Today, we can not confirm one of them as an actual mechanism according to lack of knowledge about Li-O₂ electrochemistry, therefore more *in -situ* characterization technologies should be well developed in the future to clarify the exact cathode mechanisms for non-aqueous Li-O₂ batteries.

1.5 Critical Challenges

Considering many research and development effort for Li-O₂ battery technologies in the last decade and comparing with state-of-art history of Li-ion and fuel cells, Li-O₂ batteries still in its infancy. Readily, we should address many scientific challenges of Li-O₂ battery in order to use them in practical applications. Ambiguous reaction mechanism , improvement of battery performance by using catalyst materials and stability of cell components in open surroundings are several critical issues on aprotic Li-O₂ batteries that recently focused on by many recent studies. In this section, these critical challenges will be discussed under three sections.

1.5.1 Li-O₂ Electrochemical Reaction Mechanisms at Air Electrode

As mentioned in the previous sections, main discharge product of Li-O₂ battery is Li₂O₂. Unfortunately, Li₂O₂ is one of the most important challenges itself due to its poor electrical conductivity. During discharge reaction, it forms on the conductive cathode material and electrically passivates the surface which cause high charge/discharge overpotentials. Therefore, how the properties of Li₂O₂ is effective on the electrochemical performance (overpotentials for ORR and OER) such as morphology and structure should be investigated. There are many studies which focused on the effect of Li₂O₂ structure to OER electrochemical behaviour

in order to clarify the mechanism. For example, Adams et al. applied different discharging current rates in tetraethylene glycol dimethyl ether (TEGDME)-based electrolyte, and checked the morphologies of discharge product, Li_2O_2 [21]. They indicated that lower current densities lead to the nucleation of large toroidal crystalline Li_2O_2 while quasi-amorphous thin films forms at higher current densities. Also, thin film like structures decompose easier during charging therefore lower overpotentials are observed because of closed contact of product with conductive electrode surface. As a result of such studies, we need to determine analysis conditions for the most suitable main discharge product in order to obtain better performance.

1.5.2 Chemical and Electrochemical Stability of Battery Components

Numerous investigations have been carried out about organic electrolytes for several years in the Li-ion batteries but they can not be directly used in Li- O_2 batteries. Organic electrolytes have similar influences on the two electrode reactions for both Li battery system, therefore they are effective on overall electrochemical performance of the Li- O_2 cells. In the following, ideal attributes for aprotic electrolyte for Li- O_2 batteries are mentioned. First of all, it should be highly stable chemically and electrochemically towards reduced species (O^{-2} , LiO_2 and Li_2O_2), oxygen and anode, This property is essential for aprotic electrolytes. O_2 should be highly soluble and diffuse easily in order to enhance mass transport rates to the cathode. Evaporation of electrolyte is not desired at the cathode so it should have high boiling point and low volatility. Lastly, it should be highly conductive to provide required rate capability. Even if various type of aprotic electrolytes developed in Li- O_2 batteries, stability towards to aggressive environment and presence of reduces species are still key challenges which should be solved. Generally, the stability of the electrolyte is related to the stability of solvents, lithium salts and additives.

In previous years, organic carbonate-based electrolytes such as, propylene carbonate (PC), dimethyl carbonate (DMC), and ethylene carbonate (EC), have been applied instead of polymer electrolyte in Li-O₂ batteries [10]. Later on it was discovered that, organic carbonate solvents are decomposed during discharge process by reacting with O₂ reduced species and lithium carbonate and other side products forms rather than main discharge product which is Li₂O₂. Generally, Li₂CO₃ accumulates on cathode surface as a passivative layer which has poor electrical conduction property and also suppresses Li₂O₂ decomposition kinetics. Moreover, it decompose at high voltage levels (> 4.0 V), thereby round-trip efficiency of the cell affected badly. LiOH which generated from the reaction between Li₂O₂ or Li and the moisture contaminant. Also, LiOH could also be formed via the reaction between DMSO-based electrolyte and a superoxide-like discharge product [22–24]. As a result, researchers are continuously searching for to replace alternative electrolytes instead of carbonates in these days.

Ether-based solvents have been widely investigated to replace organic carbonate-based solvents due to their advantages including high stability towards reduces O₂ species, high decomposition voltages values (up to 4V vs Li/Li⁺), low volatility, good wetting property, safety and lower price. Main ether based electrolytes contain tetraethylene glycol dimethyl ether (TEDGME or 4G) and 1,2-Dimethoxyethane (DME). Even if Li₂O₂ have been identified as main dominant discharge product in Li-O₂ battereis prepared with ether-based electrolytes [25], recent studies indicates that various side products are also form for ether solvent systems. Moreover, these side products cause poor rechargeabiliy, poor capacity retention and low round-trip efficiency [26, 27]. Nevertheless, ether-based electrolytes are currently the most widely used electrolyte in aprotic Li-O₂ batteries despite parasitic reactions.

Another essential part of electrolytes is lithium salts because they are also effective on reversibility and capacity of Li-O₂ batteries. Lithium salt must have high solubility in the solvent for better lithium ion (anion) transport. Anions should not react with current collector and solvent. Also, they should be stable against to harsh environment because there are many reduced species in the solvent such as reduced oxygen. In addition, compatibility of lithium salts with solvents is

very critical criteria for stability. Du et al. detected that LiPF_6 decompose in tri(ethylene glycol)-substituted trimethylsilane (1NM3) solvent to form HF while it is stable in TEGDME solvent [28]. Although effects of anion on the rechargeability and capacity can not be ignored more attention is taking for aprotic solvent for electrolyte in Li-O_2 batteries.

Metallic lithium is a very energy dense material and it can provide 13.000 Wh/kg gravimetric energy density as an anode for Li based batteries. But it can not be used in practical applications since there are many safety concerns due to dendrite formation. However, in Li-O_2 batteries Li metal anode is still the primary choice for the anode since the stability of the cathode and electrolyte are still worse than metallic Li anode. While lithium ion intercalates and deintercalates in conventional Li-ion batteries, lithium metal dissolves and decomposes during ORR/OER for non-aqueous Li-O_2 batteries. During the charge-discharge cycles in Li-ion batteries, especially if high current rates were applied, dendrite formation occurs on lithium anode surface and spread through the cathode electrode. This interaction can cause short circuit due to electrical current which passes through these dendrites. This occurrence overheated the battery cell and it can catch fire in some cases. Even if dendrite growth did not identified for Li-O_2 batteries, growth of passivated solid electrolyte interface (SEI) on the surface of lithium anode can not be avoided and it may trigger dendrite formation which occurs safety concerns.

Another problem is the corrosive environment in the battery cell which can erode the anode material. This fact will badly affect long-term cycle life of Li-O_2 batteries. Actually, anode reactions between lithium metal and electrolyte is more complicated than cathode reactions between lithium ions and O_2 , nevertheless lithium metal is the best option for now. That's why many researches mostly focused on electrolyte and cathode development.

1.5.3 Design and Construction

Insulating nature of the lithium oxides is one of the intrinsic reason of the sluggish reactions during oxygen reduction and oxygen evolution reactions. Therefore, aprotic Li-O₂ batteries have high charge overpotentials and low round-trip efficiency. Even if the most of the carbon materials show good catalytic activity during oxygen reduction reaction at low current rates, they are ineffective for oxygen evolution reaction. That's why, many investigations have been made by researchers to decrease the activation energy in the OER process in order to promote electrochemical decomposition of discharge products in Li-O₂ battery systems.

Various types of catalyst materials which are commonly tried in other metal air batteries and fuel cells have been evaluated by now to decrease OER and ORR overpotentials. To provide high energy efficiency for aprotic Li-O₂ batteries, we need to optimize catalyst design which should include their structures and phases. Detailed survey about catalyst materials and design are given in the section of catalysis and material selection.

1.6 Catalyst and Material Selection for Better Cathode

High specific capacity and round trip efficiency, good cycling performance and high rate capability are the four major characteristic that rechargeable Li-O₂ battery systems should have own [29]. All these desired characteristics can be improved dramatically by electrocatalysts on the cathode electrode. Therefore, to obtain excellent performance, we need to create an efficient electrocatalyst in aprotic Li-O₂ batteries. As mentioned before, discharge products can not decompose during charging because of its poor conductive nature. Also these products plugs pores of the cathodes during discharge process and this blockage cause sudden termination of discharge and prevent the further O₂ diffusion to

the reactive sites [30]. Therefore, stable porous structure and diffusibility for oxygen transfer are essential characteristics for cathode materials in aprotic Li-O₂ batteries. Also electrode and electrolyte interaction should be very good that's why electrolyte should provide satisfactory wetting to the electrode in order to require ionic transfer during charge-discharge process.

Additionally, facilitating the kinetics of ORR and OER is the most important characteristic that should be owned by cathode material with electrocatalyst. Therefore, desired cathode material which have optimum design parameters does not only provide sufficient space for discharge products but also capable for good oxygen diffusion and quick ionic/ electronic transfer [31–33]. Currently, numerous type of cathode materials originated from fuel cells and other metal-air batteries have been investigated. In this section, the ones that related with our study were mentioned including carbon materials and transition metal oxides.

1.6.1 Carbon Materials

Carbon based materials are the most common materials which are used in capacitors, lithium ion batteries and fuel cells as an electrode or catalyst supporter due to their superior properties such as large surface area and conductivity [34,35]. Besides such properties, carbon based materials have very good catalytic activity during OER and ORR processes. Therefore, they are widely used as electrode materials in non-aqueous lithium oxygen batteries [36].

Due to the low cost, large surface area, corrosion resistance, high electrical conductivity, and good ORR/OER activity, porous carbon materials have been widely viewed as ideal candidates for metal-free cathodes for Li-O₂ batteries. Various commercial carbon materials such as Vulcan XC-72, Ketjen Black and Super P have been investigated for non-aqueous Li-O₂ batteries [37–39]. According to studies, it has been seen that, specific surface area, pore size and amount of the surface defects are key factors which effect the battery performance, especially capacity. These properties greatly differ depending on the commercial

product type, therefore it has been demonstrated that especially discharge capacities change dramatically for each product [40]. In addition, mesoporous carbon and carbon fibers are also recently studied due to their unique structures and huge number of defects [41, 42]. Even if, very good results were taken with these materials when they are used in the stable electrolytes, necessity of better materials which can provide better properties were needed to approach the theoretical specific energy density of Li-O₂ batteries.

There was a very promising material for this purpose which is carbon nanotubes (CNT). High chemical and thermal stability, high conductivity and surface area, superior strength and high elasticity resulting from carbon nanotubes unique structures made them one of the best candidate for our application. Many researchers reported their great catalytic activity during discharge, very high specific capacities and even good cyclability advantages of them. Also, ease of analysis for discharge product morphology on carbon nanotubes is very useful for Li-O₂ battery investigations [43–45]. Because of these strong reasons, CNT has been chosen as support material in our study.

1.6.2 Transition Metal Oxides(TMOs)

To date, transition metal oxides are mostly investigated materials as catalyst for both OER and ORR in Li-O₂ batteries. Manganese oxide, cobalt oxide, iron oxide and palladium oxide are very popular among TMOs and there are various reports about them [10, 46–48]. Especially, these transition metal oxides deeply studied by Bruce and co-workers as electrocatalysts in Li-O₂ batteries for years [49]. Among them, Co₃O₄ was the best candidate for initial capacity and capacity retention. Also very low charge voltages have been achieved by using this cobalt oxide. Another commonly used electrocatalysts by this research group was MoO₂ and it has been investigated with various phases and morphologies. They initiated that morphology, surface area and nature of the catalyst material was the key factor which affect the performance of the oxygen electrode [50]. In these studies, they observed that manganese oxides can improve the round-trip efficiency and

also increase the specific discharge capacity of the battery. Recently, manganese dioxide are usually used to screen highly-active catalysts as a reference. They are also employed as cathode catalysts in the studies on electrolyte performance and cathode mechanisms. Furthermore, MoO_2 is the one of the best TMO can be used as an catalyst material in the composite electrodes [11].

Another commonly used electrocatalysts was Co_3O_4 which is the best candidate for initial capacity and capacity retention. Also very low charge voltages have been achieved by using this cobalt oxide. Riaz et al. prepared different morphologies of Co_3O_4 -only electrodes including nanosheets, nanoneedles and nanoflowers by using an electrodeposition-conversion process. They found that architecture of the Co_3O_4 cathode was highly effective on performance of the battery [51]. Moreover, Zhao et al. investigated the effect on calcination on the Li- O_2 battery performance. They fabricated a carbon-free $\text{Co}_3\text{O}_4@\text{Ni}$ electrode and then calcined at various temperatures in Ar atmosphere. They showed the dependence of the performance to the calcination temperature. The film calcined at 300°C exhibited the highest discharge capacity of 2460 mAh/g at a current density of 200 mA/g while capacities of about 2000, 700 and 450 mAh/g were displayed for the films calcined at 250, 350 and 450°C , respectively [52].

Recently, ruthenium oxide also took great attention due to its excellent performance on OER when used with carbon material support. Hun-Gi et. al tested Ru-based nanomaterials supported on rGO for the oxygen reduction and oxidation in the Li- O_2 cells. They showed that this hybrid electrode provide outstanding catalytic activity, remarkably reducing charge potentials to 3.7V even at high current density of 500 mA/g and high capacity of 5000 mAh/g [53].

Shortly, TMOs have several advantages such as high OER and ORR activity, well known and controllable synthesis, low cost, high abundance, environmental friendliness and so on. Also they are prone to obtain desired nanostructures. Moreover, they can withstand high voltage values which is very problematic for Li- O_2 batteries and also tolerate the oxygen nucleophiles attacks. However, they have large molecular weights and low electrical conductivity which cause lower

energy and power density for batteries. In addition, some of them are very expensive to use in practical applications. To overcome these problems, conductive substrates, especially carbon materials, have been utilized in many studies. In this way, both catalytic activity and conductivity enhanced and better capacities and cycling stability have been provided [54, 55]. Nevertheless, new candidates of metal oxide catalyst are needed in order to use them in practical applications because none of the studies could offer applicable oxygen electrode material for this aim.

1.7 Motivation

Various cathode materials have been investigated until today as mentioned in the previous sections and promising results are obtained. Especially, transition metal oxide and carbon material composites have been studied a lot due to their bifunctional ORR/OER catalytic activities in non-aqueous media. However, there is still no applicable investment which can provide stable cathode material for Li-O₂ battery system. Today, CNT is the best alternative as catalyst support due its superior properties as mentioned in the previous sections but it cause some side reactions which occurs because of the high charge voltage values and corrosive environment in the battery cell. To prevent this, stable and highly active catalyst material is needed. Therefore, new and better candidate which can provide these properties have been searched in the literature. Mostly similar energy related applications such as supercapacitors and fuel cells are considered because it has been thought that catalyst materials which are utilized in these applications may provide similar properties for Li-O₂ batteries.

Molybdenum oxide have been chosen as catalyst material due to its great catalytic effect on some other applications [56, 57]. Results of these studies were very promising to use molybdenum oxide in Li-O₂ battery system. In this study, we investigated molybdenum oxide which is decorated on multi-walled carbon nanotube catalyst support as an oxygen electrocatalyst for Li-O₂ batteries. Several synthesis methods and parameters have been utilized in order to enhance its

performance and adapt it for our application. Morphological, structural, chemical and electrochemical characterizations have been carried out by using X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Transmission Electron Microscopy.



Chapter 2

EXPERIMENTAL

2.1 List of Materials and Chemicals

Materials List			
Materials/chemicals	Chemical Formula	Purity (%)	Supplier
2-propanol	$CH_3CH(OH)CH_3$	99.5	Emprove
Acetone	CH_3COCH_3	99.5	VWR
Ammonium molybdate tetrahydrate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	99	Sigma Aldrich
Citric Acid	$C_6H_8O_7 \cdot H_2O$	99.5	Sigma Aldrich
Celgard	-	-	Whatman
Ethanol	C_2H_6O	92-96	Kimetsan
Glass Fiber	-	-	Whatmann
Hydrochloric Acid	HCl	37	Honeywell
Hydrogen Peroxide	H_2O_2	30	VWR
Molybdenum(V)Chloride	$MoCl_5$	95	Sigma Alrich
Nafion	-	-	Ion Power
Nitric Acid	HNO_3	65	Honeywell
Sulfuric Acid	H_2SO_4	95-97	Honeywell

Table 2.1: List of Materials and Chemicals

2.2 Experimental Procedures

Overall experimental procedures can be classified into three major parts in this master study. Firstly proposed materials are synthesized, then their morphological and physical characterizations are performed by using instrumental analysis techniques. Finally, electrochemical performances involving the application of active nanostructured composite materials as electrode were tested in Li-O₂ battery cell.

2.2.1 Materials Preparation

Firstly, materials were tried to synthesized with bare MWCNTs. However MWCNT is hydrophobic itself so, homogeneous and well distributed metal oxide particles could not obtained in the aqueous media by using bare MWCNTs. Therefore, methods that can attach functional groups on MWCNT's wall were investigated and utilized methods are given in the further section.

2.2.1.1 Functionalization Process of MWCNTs

In this work three different methods are applied to obtain functional groups on multi-walled carbon nanotubes (MWCNT) in order to grow well distributed metal oxide nanoparticles on the surface due to homogeneous functional spots.

We used H₂O₂ for the first method. In this treatment, %30 H₂O₂ and MWCNT are mixed with specified amounts and stirred on the magnetic stirrer for 5 days at 65°C. In order to define desired functionalization amount, 5ml of mixture was taking with pipette at the 1st, 3rd, and 5th days of treatment and 5ml of H₂O₂ was added to keep the concentration of mixture constant. All three samples are washed and filtered with di-ionized water. At first they dried in the oven at 110°C for overnight and then put in the vacuum furnace at 150°C for 6 hours.

For second oxidization method, only nitric acid is used. MWCNT are treated with HNO_3 at 70°C for various synthesis times on the magnetic stirrer. After that it cooled down to room temperature and diluted with distilled water. Same drying process with H_2O_2 treatment is applied after this dilution process.

MWCNT were chemically treated by a mixture 3:1 (v/v) of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ for the final method. Although this treatment can modify the MWCNT surface, it has not disrupted its main structure. Oxidization using strong acids (e.g., mixture of HNO_3 and H_2SO_4) is one typical and widely used approach to generate defects on the surface of nanotubes. After oxidization, the functional carboxylic acid or hydroxyl groups on CNT have a rich chemistry. Subsequently, such kind of CNT can be treated with a further chemical reaction. For this process, sufficient amount of MWCNT weighted and mixed with HNO_3 . H_2SO_4 is gradually added on this mixture in the ice bath while mixing by hand. Total mixture stirred at 70°C for 2 hours on the magnetic stirrer. After MWCNT and acidic mixture cooled down, they are added into the 5% HCl solution and filtered by using di-ionized water until its pH value become neutral. At final step, filtered sample dried in the atmospheric conditions.

2.2.1.2 Solvothermal Synthesis

Many types of materials can be synthesized by using solvothermal method such as metals, ceramics and polymers. In this process, moderate to high temperature (100 to 1000°C) and pressure (1 to 10.000 atm) are used which makes the interactions of materials in the solvent easier during synthesis. It is called hydrothermal synthesis when water is used as solvent. Various geometries can be obtained such as thin films, nanocrystals and bulk powder by using this process. Moreover, crystal morphology can be controlled by changing the chemical concentrations, kinetic control and manipulating the supersaturation of solvent. Due to unique nature of the nanocrystals, many solvothermal synthesis method have been performed to obtain required properties and morphologies of nanoparticles over the last decades. This method is particularly suitable for the growth of

large good-quality crystals while maintaining good control over their composition. Also, it is economic, facile and versatile technique in comparison with other techniques. In this study, conventional and microwave solvothermal methods are used to produce our samples.

In conventional method, autoclaves are used as reaction vessels. They are commonly made from stainless-steel with air-proof seal which should tolerate high pressure and temperatures for long time reaction periods. Most of the solution which are used in solvothermal experiments are steel corroded. Therefore, autoclave material should be inert with respect to the solvent. In addition protective inserts (mostly teflon) are used to prevent corrosion and they have the same shape with the internal cavity of autoclave. In our experiments, MWCNTs and distilled water are homogenized in the ultrasonic bath. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and ethanol mixed on the other side. After stirring, specified amount of HNO_3 is added drop by drop into the molybdenum solution. These two solution are mixed and transferred to the teflon cup and then autoclave was kept in a conventional oven for the preset time and temperature. After reaction is completed, mixture is washed by centrifugation and dried in the oven.



Figure 2.1: The hydrothermal autoclaves used in this master thesis work.

The hydrothermal autoclaves used in this work are acid digestion bombs with 100

ml capacity , as is shown in Fig. 2.1. The outer parts are made of stainless steel to seal the polytetrafluoroethylene (PTFE) cup. The temperature can reach up to 230°C and the pressure can reach up to 3 MPa.

Microwave synthesis is the another effective method which was used in this study to obtain desired nanostructures. In the basis, conventional method and microwave synthesis are similar. However, heat energy is transferred electrochemically and quickly through the whole volumetric part while heating is applied as a thermal heat flux for autoclave. Therefore, less overall energy is used and temperature can be easily controlled with microwave synthesis. Also, higher temperatures and pressures can be accessed with microwave reactors while it is difficult with autoclaves. In our experiments, molybdenum precursor (MoCl_5) and reducing agent (citric acid) were mixed with functionalized-MWCNT (FCNT)/distilled water solution while it was stirring. It should be noted that the used weight amounts of carbon material and metal precursor for first synthesis defined as (1:1) ratio. Various combinations of contents are tried and labeling arranged due to this first amounts. Total mixture was loaded into the glass vessel of microwave furnace and transferred through the machine. Synthesis was carried out at 160°C for 30 minutes by applying 160W power. After synthesis, solution cooled down by air flow. Washing process applied by centrifugation and sample dried in the oven.

Here, the microwave oven used is a Monowave300 microwave system which is provided by Anton-Paar as shown in Fig. 2.2. The maximum power reaches up to 850 W. It has 3 different borosilicate glass vials for reaction volumes from 0.5 mL to 20 mL where reactions take place at temperatures up to 300°C and pressures up to 30 bar.

For both synthesis methods parameters are modified in order to obtain desired structure and the morphology. Various sythesis temperatures, pressures, chemical concentrations and annealing temperatures were applied to provide better performance for the non-aqueous Li-O₂ batteries. Moreover, carbon nanofibers were replaced with FCNTs in the microwave synthesis to see the effects of different carbon materials to the electrochemical and structural properties.



Figure 2.2: Monowave300 microwave system used in this study.

2.2.1.3 Cathode and Electrolyte Preparation

In order to obtain well designed cathode, three different preparation method were utilized in this study as given in the following list:

- Filtration Method: Synthesized solutions are filtered by using glass fiber filter and particles accumulated as a film. Then, this film separated from the surface by the help of tweezers. In some cases, film-like sample could not separated therefore, they used with glass fiber in the battery cell for electrochemical testings.
- Dropping Method: Cathode material is distributed in the isopropanol with ultrasonic bath or tip sonicator and then dropped on the nickel foam as a dropping method. It was not a good method in order to obtain homogeneous distribution of cathode materials on the nickel foam.
- Dipping Method: Nickel foams were dipped into the cathode solution and they stirred in the ultrasonic bath to provide homogeneous distribution of

cathode material and prevent pore clogging of foam. Also while cathode material dropped, the cathode weighted heavier so lighter cathodes were obtained by dipping technique.

All preparation methods have been applied to achieve lighter cathode material, whereat proportionally higher specific capacity.

Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and tetraethylene glycol dimethyl ether (4G) which is polar aprotic solvent is used to prepare electrolyte. Firstly, water amount of solvent is reduced by using 4A molecular sieves (Sigma Aldrich), which were regenerated in the tube furnace at 200°C for 3 hours in the argon atmosphere, for several days. Also lithium salt is dried in the vacuum oven for overnight. After that, they were transferred into the glovebox and 0.5M of solution is prepared in the argon atmosphere. Water amount was measured by Metrohm's 899 Coulometer for both solvent and final solution, separately.

2.2.2 Cell Assembly

In this study, swagelok type cell is used for all experiments. Cell involves mainly three parts which are upper cap, oxygen tank and bottom cap. While oxygen tank and upper cap is only for filling and purging process, bottom cap is the main part which electrochemical reactions take place.

First of all, battery parts and cathode material are dried in the vacuum oven overnight in order to decrease moisture amount as much as possible and quickly carried into antichamber. Components waited for 30 minutes in the vacuum and filled with argon gas. This refill-purge process repeated two more times and each following vacuums are kept for 3 minutes. After purification step finished, all parts transferred into the glovebox. There is 1 cm² circular place in the middle of bottom cap to put anode material but lithium metal did not directly cut and placed in this area. To use anode material providently, it was cut into small pieces and enlarged by rolling. Rolled film-like lithium was placed on the 1 cm² circular

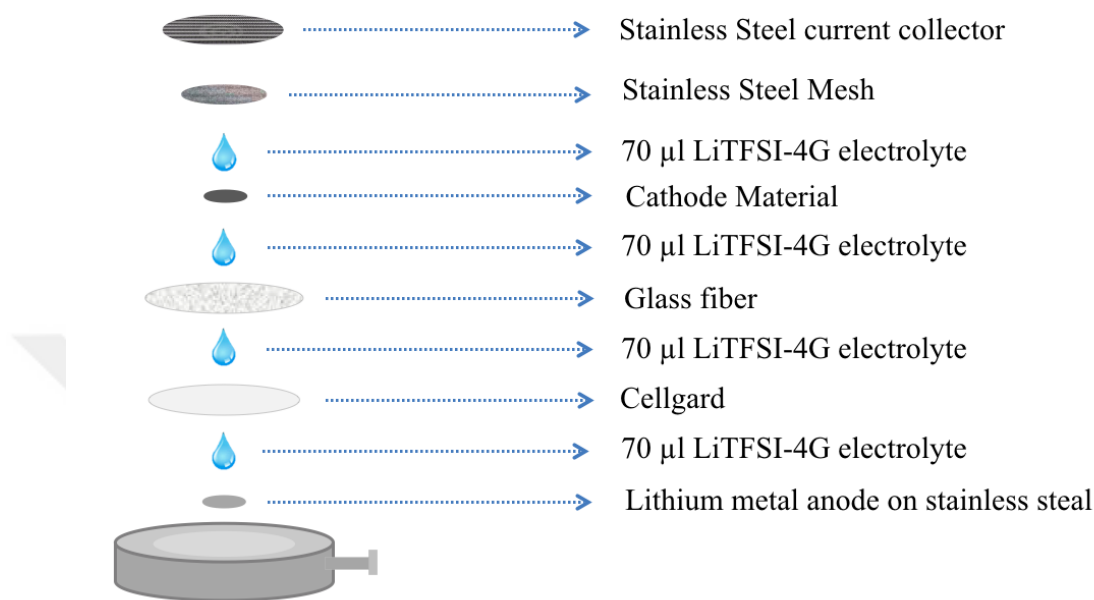


Figure 2.3: Schematic Shown of Non-Aqueous Li-O₂ Battery Preparation

stainless steel and excess parts were cut by the help of nippers. Prepared anode put downed and 70 μ l electrolyte dropped on it. Cellgard, glass fiber and cathode material are placed, respectively and adding electrolyte is repeated for each step as shown in the Figure 2.3. After stainless steel mesh and current collector are put on other parts oxygen tank and upper cap closed carefully and screwed firmly. At last step, assembled battery cell waited for 7 hours and filled with oxygen gas in order to star electrochemical battery testing.

2.2.3 Characterization Methods

Physical and structural characterizations of synthesized materials are carried out by using X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Transmission Electron Microscopy. Electrochemical testings are performed by using galvanostatic discharge-charge testing. In this section, all characterization methods are briefly introduced and sample preparations for each methods are given.

2.2.3.1 X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. XRD patterns are unique to crystalline phases and can be used as a fingerprint for phase identification in a sample. In this study, XRD measurements were carried out using a PANalyticals X2Pert Pro diffractometers diffractometer employing Cu-K radiation ($\lambda = 1.5406 \text{ \AA}$) between 5 to 85 degrees and equipped with a GaliPIX-3D detector. Samples were grinded and powder form of them placed on the sample holder for testing.

2.2.3.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range and can determine the empirical formula, chemical state and electronic state of the elements that exist within a material. XPS experiments in this thesis were carried out on a Thermo Scientific K-Alpha instrument using aluminum $K\alpha$ X-ray radiation. Powder forms of samples were just stucked on the holder with copper tape. Discharged-charged cathodes were washed and prepared in the glovebox then carried to the XPS instrument as quick as possible.

2.2.3.3 Scanning Electron Microscopy (SEM)

Electrons are focused as beam and scan the sample in order to get image with SEM which is a type of electron microscope. Sending electrons interact with sample atoms and produce various detectable signals. These signals contains lots of information about morphology, topography and composition of the sample surface. In this master study, SEM measurements were carried out using FEI's Quanta-200F instrument. For sample preparation, powder samples firstly dispersed in the acetone and dropped on the nickel plate. After they dried, they are coated

with Au-Pd with using precision etching coating system by Gatan (Model862). Coated samples were transferred into the machine and characterized.

2.2.3.4 Transmission Electron Microscopy (TEM)

TEM is a microscopy technique in which a beam of electrons is transmitted through an specimen, interacting with the specimen as it passes through. Conversely with SEM, atomic scale magnification is possible. While nanoparticles were synthesized in this study, to observe the crystal size and their structures we need to use TEM. Powder samples were dispersed in the ISP and dropped on the TEM grid to prepare specimen. In this work, TEM images were collected using a FEI's Tecnai G^2 instrument in the TEM and STEM modes with various magnifications.

2.2.3.5 Galvanostatic Charge/Discharge Testing

The capacity and cycling performance of the Li-O₂ batteries were investigated by galvanostatic charge-discharge testing at various current densities. All tests were carried out on a Land CT 2001-A. Firstly current density determined due to cathode area but after cathode weight optimized, current rates applied due to weight of cathode material. All experiments applied between 2 to 4.5 voltage range and their cycling performances also carried out up to 20 cycle. Capacity limitation was not used for any galvanostatic testing. All result are obtained from full charge-discharge of batteries.

Chapter 3

Results and Discussion

In this chapter, all results are given in the order of synthesized cathode materials. Structural, morphological and electrochemical testing results were not separated into parts. The motivation of this study is to produce effective catalyst materials for Li-O₂ batteries in order to enhance their performance and decrease their charge and discharge overpotentials. As it is mentioned in the introduction part carbon nanotube is the best candidate for base material which would be modified with metal oxide catalyst. Therefore, we performed galvanostatic testing of pristine CNT to obtain reference data for following experiments.

Firstly, molybdenum oxide nanoparticles are produced on the CNTs by using autoclave technique. Morphological comparisons and galvanostatic results of pristine CNT and CNT@MoO_x are given in the Figure 3.1. As shown in the Fig. 3.1c, MoO_x particles are accumulated on the surface but they are not homogeneously distributed. In the darker parts, metal particle concentrations is more than the rest of the structure. There are some small particle-like formation on the pristine CNT and they might be misleading. The reason of these formations might be contamination or residuals from the organic solvent which is used for TEM sample preparation.

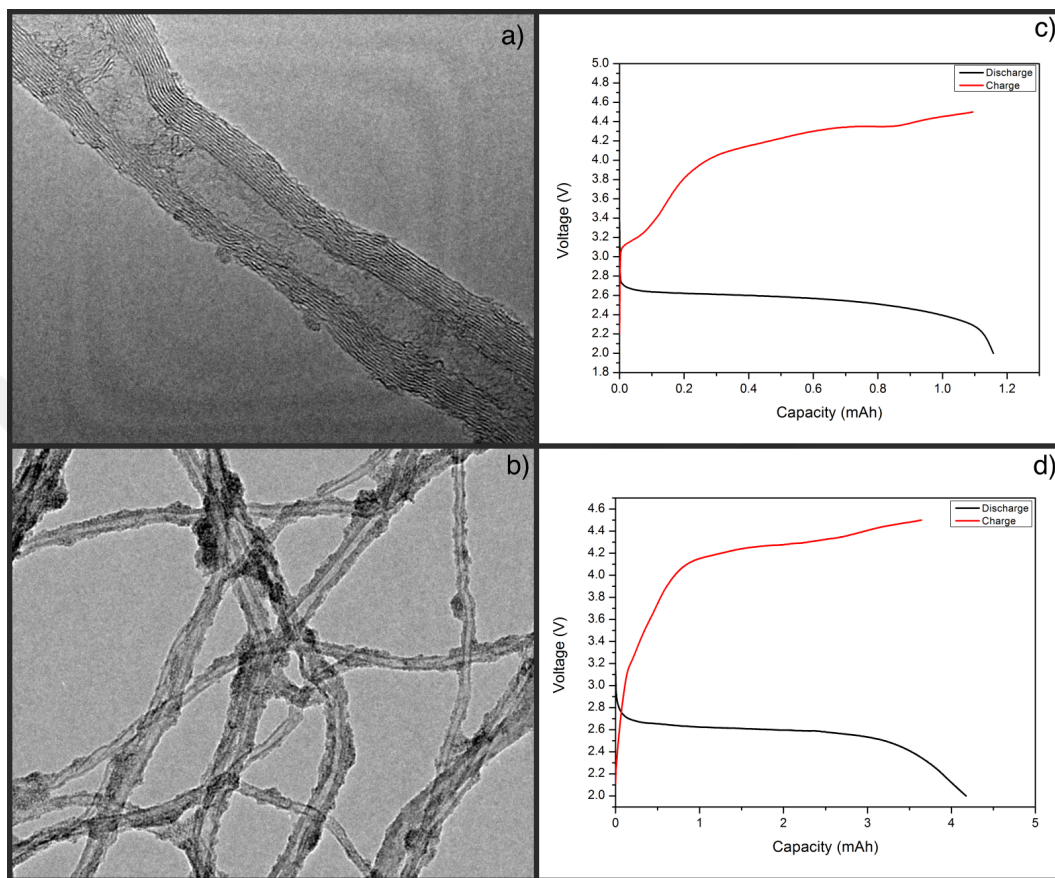


Figure 3.1: a,b) TEM images and c,d) galvanostatic discharge-charge results of pristine CNT and CNT@MoOx samples, respectively.

To see the effect of molybdenum oxide particles on the electrochemical performance, galvanostatic discharge-charge testing is applied and result are given in the Fig. 3.1 (c-d) for pristine CNT and CNT@MoOx. Unfortunately results are almost same, overpotential is slightly better than CNT and also higher capacity is obtained but this capacity is not specific capacity so the reason of these difference might be the amount of the cathode material.

According to charge-discharge testing, accumulating molybdenum oxide provide better overpotential. However, oxide particles were not well distributed. The reason of that may be hydrophobic nature of bare CNT. It prevents to obtain homogeneous mixtures during synthesis and also surface of CNTs are not capable to attach metal particles homogeneously. When they start to nucleate on some regions, other metal oxide particles thermodynamically prefer to grow on them.

Therefore, MWCNT surface was functionalized in order to create oxygen functional groups on to the surface. These functional groups may be starting point for nucleation process thus, homogeneous distribution could be obtained. This is important because interaction between cathode material and catalyst material should be as high as possible in order to provide better activity.

Functionalization of MWCNT Surface

As mentioned in the experimental chapter, three different functionalization techniques were applied in order to create oxygen functional groups on the carbon nanotube walls. Due to hydrophobic nature of the CNTs, it was difficult to obtain well distributed solution while doing synthesis and also facilitate the interactions between metal atoms and CNTs were necessary to provide better formation metal oxides on the surface. In order to investigate the oxygen functional groups after treatments, XPS measurement were carried out. C 1s and O 1s scans of all three functionalization methods were compared in the figure 3.2(a,b), respectively.

At first, peaks of the H_2O_2 treated sample which is fCNT5D was examined. According to C 1s scan, only C-C bonding for unmodified carbon materials was observed at the 284.4 eV binding energy. This sp^2 hybrid carbon bonding peak is not broadening and it shows that there is no significant functional group on the CNT surface. Only $\pi - \pi^*$ shake-up is responsible from the very small broad peak at 291.5eV and it should not be confusing with functional groups. [58] Normally, there should be no peak for oxygen after O 1s scan if functionalization were not happened but O1s peak confirmed the presence of some carboxylic functions onto the CNT surface at 533.2 eV. It proves that less amount of functional groups exist in the structure. The intensity of carbon peaks are very intense. That's why this carboxylic group is not observable on the C peak.

Second functionalization trail was the HNO_3 treatment. This treatment applied for 4 hours and sample labeled as fCNT4H. Unfortunately, at C 1s scan of treated CNTs, no functional peak is seen. On the other hand, intensity of O 1s peak slightly increased. It may suggest that some functional carboxylic groups were also attached the surface of CNTs but even if their percentage is higher than

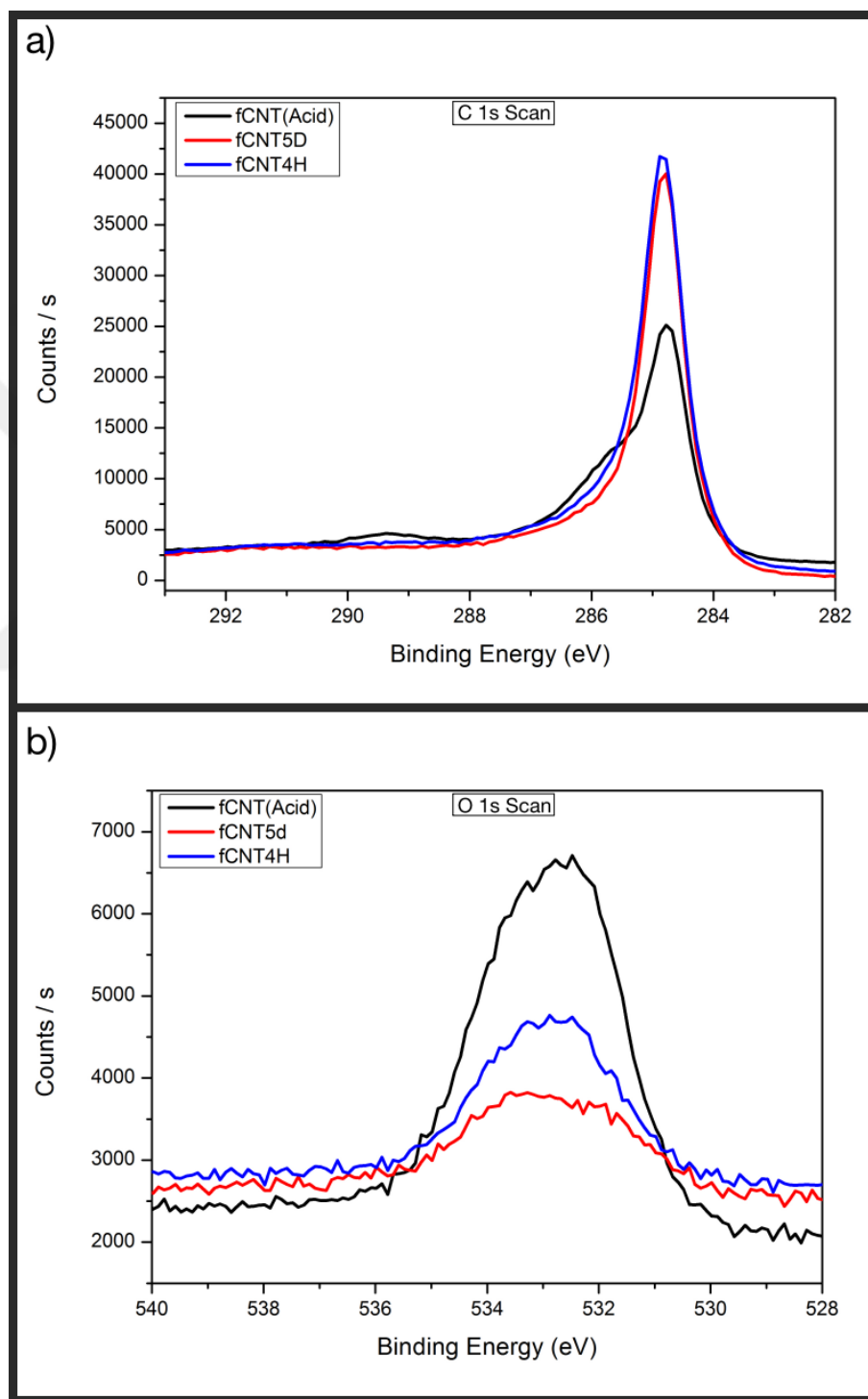


Figure 3.2: Comparison XPS of a) C 1s and b) O 1s signals from functionalized nanotubes by three different treatment.

fCNT5D sample since intensity is higher, possibly it was not required amount.

At last, the most effective method is applied for functionalization which is concentrated acid treatment involves H_2SO_4 , HNO_3 and HCl as mentioned in the experimental section. It can be clearly seen that MWCNTs showed a main peak at 284.4 eV, attributed to the graphitic structure in agreement with recent photoemission studies on MWCNTs. Moreover, a peak at 285.5 eV was attributed to defects on the nanotube structure, whereas the peaks at 286.7, 288.3 and 290 eV, correspond to carbon atoms attached to different oxygen-containing moieties which are (C-O), (-O-C=O) and carbonates, respectively. Also, XPS O1s peak confirmed the presence of some carboxylic and hydroxyl functions onto the CNT surface at 533.2 eV and 531.9 eV, respectively. [59] Consequently, required functional groups were obtained by using concentrated acid treatment. For next step, molybdenum oxide was tried to form on the these treated surfaces by using microwave synthesis method and effect of modification is investigated.

First functionalization treatment was H_2O_2 treatment and electrochemical testing of them performed before doing their XPS measurements. 5 days treated fCNTs were chosen because it has been considered that desired amount of functional groups may be obtained if treatment process was hold for longer times.

After functionalization process, microwave synthesis technique was carried out due to its advantages as mentioned in the experimental chapter. 5 days treated fCNTs used for synthesis and MoOx particles were accumulated as shown in the (Figure 3.3). fCNTs were totally covered with molybdenum oxide nanoparticles. It is almost impossible to see nanotubes clearly, therefore TEM images could only captured from the edges of the compact sample. Figure 3.3b shows that molybdenum oxides formed as very small and uniform nanoparticles on the surface of fCNT but they plugged all mesopores of cathode structure which may prevent oxygen and electrolyte transfer. Although metal particles look like forming amongst themselves, closer look proves that they are attached to the fCNT surface but their interactions may cause entanglement of carbon nanotubes. This results indicates that desired morphology could not been achieved by using H_2O_2 treated fCNT. After XPS analysis which is mentioned above the reason became

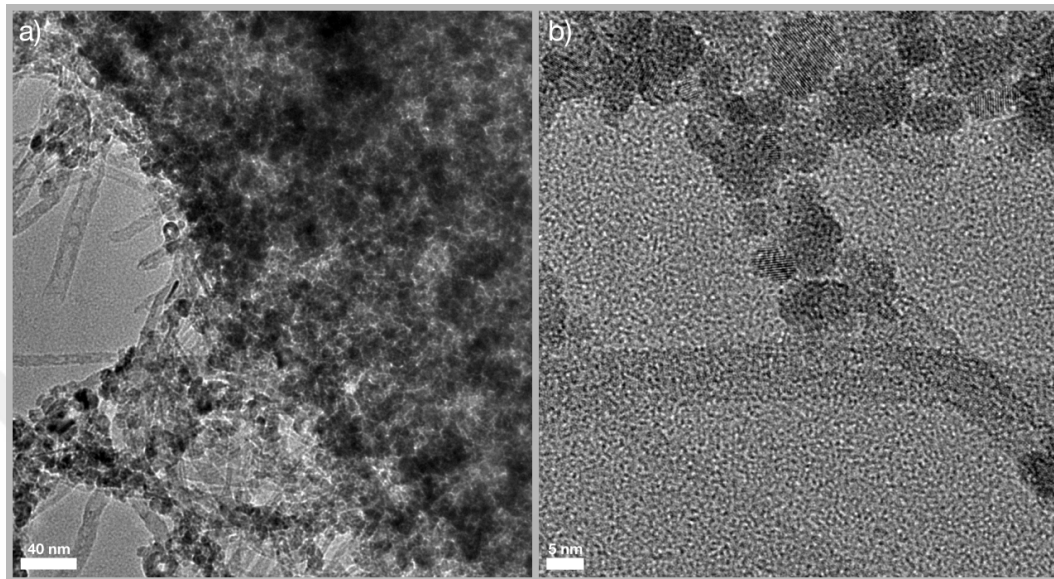


Figure 3.3: a,b) TEM images of fCNT@MoOX sample for lower and higher magnifications.

obvious. H_2O_2 does not work to attach functional groups on CNT surface, thus expected morphology could not be obtained. Therefore, concentrated acid treatment was applied even though it was very dangerous to perform.

TEM and STEM images of as synthesized fCNT@MoOx sample with concentrated acid treated fCNT are given in Figure 3.4a,b, respectively. Both figures illustrate that molybdenum oxide particles formed directly on the fCNT surface. Although particles look like well distributed, half of the carbon nanotube surface is metal oxide free, whereas smaller and totally covered metal oxide particles were desired in order to obtain film-like discharge product due to ease of decomposition than bulk structure. Also totally coated fCNT surface could be beneficial because it can prevent parasitic reactions which may happen between carbon material and electrolyte but none of them could be achieved. Figure 3.4c presents the XPS spectrum of the Mo 3d. As can be seen from that figure, the 3d profile can be fit by two pairs of Gaussian peaks. The most intense pair is centered at 235.8 and 232.7 eV which are, respectively, the binding energy of electrons in the $3d^{3/2}$ and $3d^{5/2}$ levels of molybdenum in the Mo^{+6} valence state. The other pair is centered at 234.6 and 231.6 eV corresponding to the binding energy of electrons in the same 3d levels, but in Mo^{+5} valence state. It was concluded

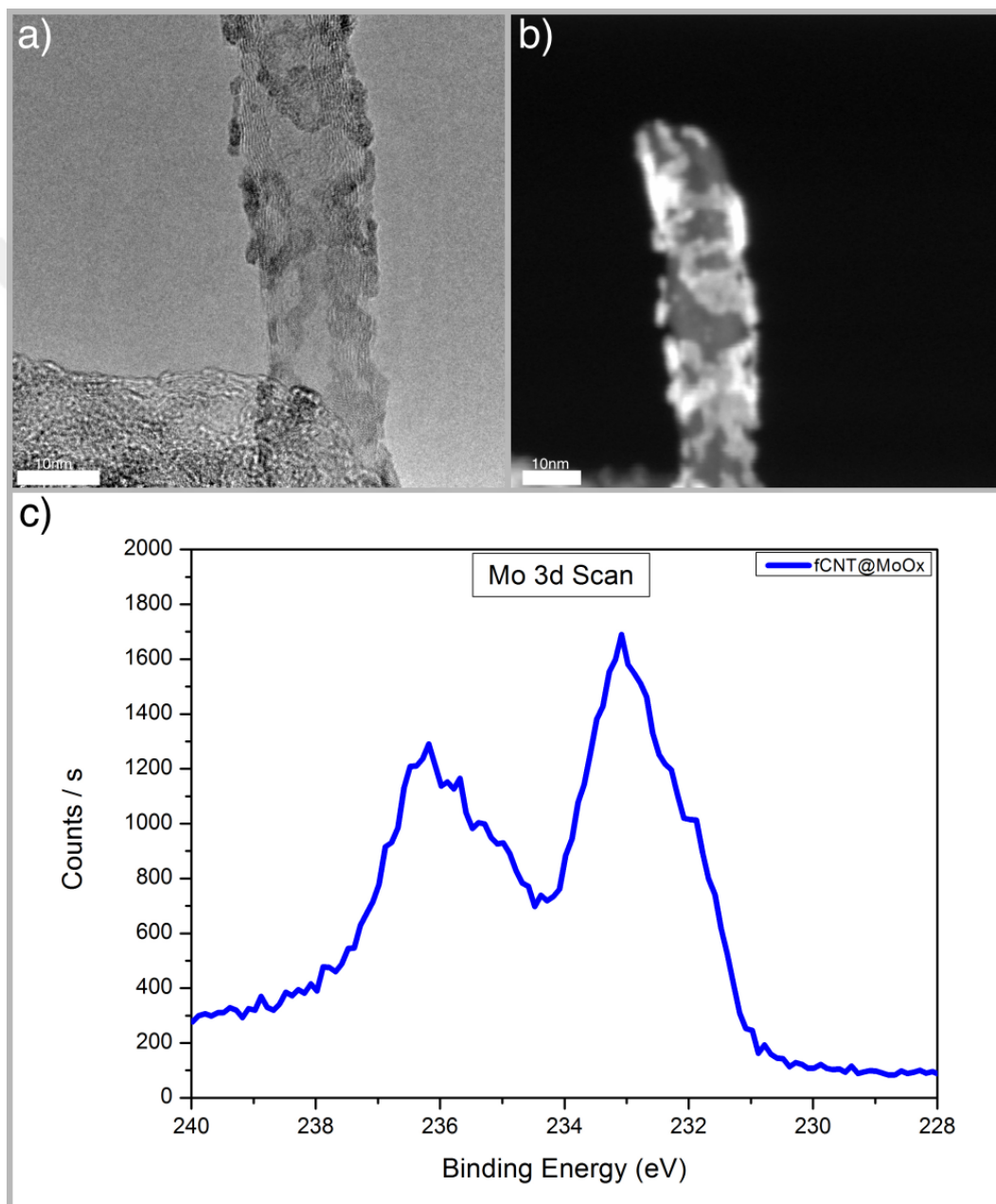


Figure 3.4: a,b) TEM images of as synthesized fCNT@MoO_x sample with concentrated acid treated fCNT c) XPS spectrum of the Mo 3d scan of fCNT@MoO_x cathodes.

that the Mo atoms were in mixed valence states, Mo^{+6} and Mo^{+5} [60,61].

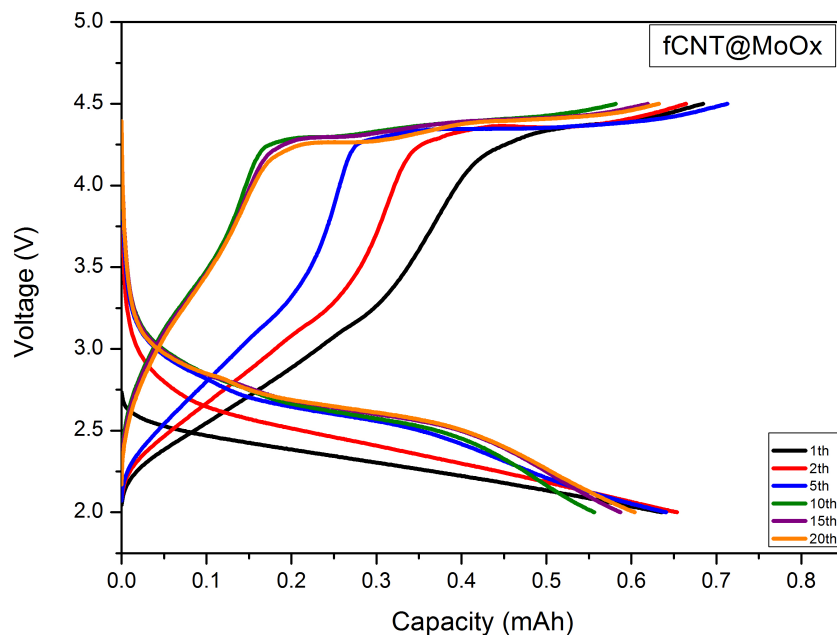


Figure 3.5: Galvanostatic charge-discharge test result of fCNT@MoOx cathode material.

For the next step, galvanostatic discharge/charge tests were conducted to further study the electrochemical activity of fCNT@MoOx electrode as shown in (Figure 3.5). The batteries were cycled within the potential window of 2-4.5 V (vs Li^+/Li) at currents equivalent to the current densities of $0.1 \text{ mA}/\text{cm}^2$ which is based on the cathode surface. Over half of the first charge process was conducted under the potential of 3.5 V, indicating good OER activity of MoOx particles. With increasing of cycle numbers, charge overpotential significantly increased, however both charge and discharge capacity slightly decreased which is demonstrates good capacity retention of fCNT@MoOx cathode. As mentioned before metal oxide distribution on the fCNT surface is inhomogeneous and catalyst materials are only effective at the region that they accumulate. Therefore, high voltage values were needed to decompose main discharge product on the carbon regions so electrolyte decomposition inevitable. Due to electrolyte decomposition some insulator side products such as Li_2CO_3 forms on the cathode surface which blocks catalyst

materials. These side products can not be destroyed and prevent the activity of molybdenum oxide step by step for following cycles. After this result, we tried to change carbon material and metal oxide precursor amount in order to obtain better distribution of catalyst materials on the fCNT surface.

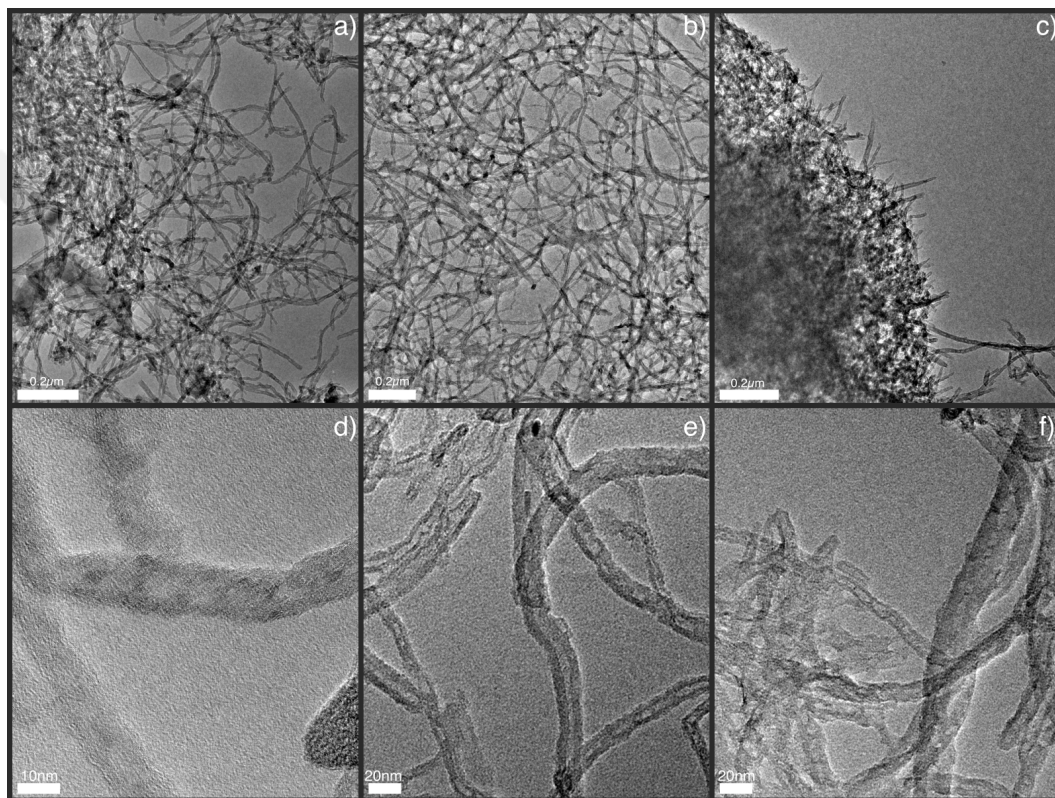


Figure 3.6: TEM images of as synthesized a) fCNT@MoOx(4:1), b) fCNT@MoOx(2:1) and c) fCNT@MoOx(1:2) cathode materials. d,e,f) shows higher magnifications of same samples, respectively.

To obtain better morphology and distribution, two possibility were considered. One of them was increasing the carbon material amount which may provide more functionalized surface, thus smaller and well distributed metal oxide particles could tend to form rather than bigger particles due to more functional groups for adding-on. Another idea was to increase molybdenum precursor amount and metal oxide free regions could be covered with them in this way. It may cut off the interaction between fCNT surface and discharge products. Therefore discharge products could be decomposed at lower voltage values. For this purpose, three different weight proportions were examined including four times

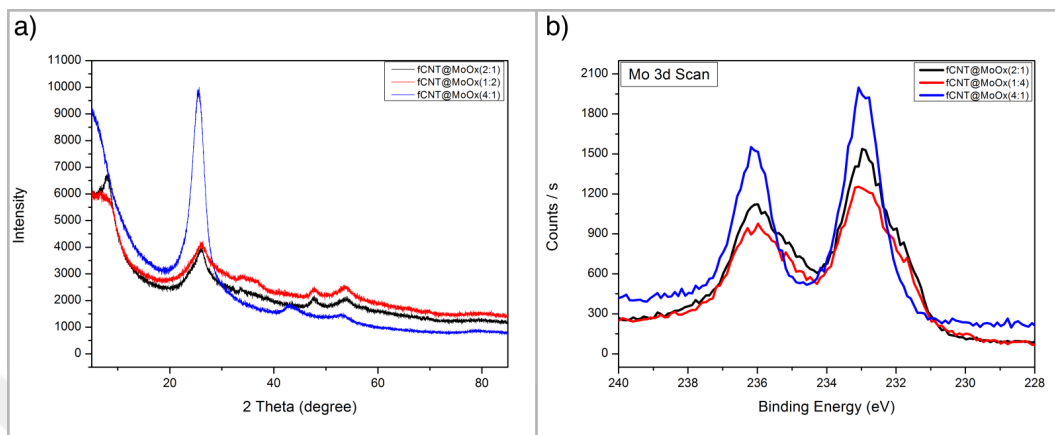


Figure 3.7: a) X-Ray diffractometer patterns and b) Mo 3d scan result of fCNT@MoOX(2:1), fCNT@MoOX(4:1) and fCNT@MoOX(1:2) cathode samples.

more fCNT, two time more fCNT and two times more molybdenum precursor amount as shown in the TEM images in (Figure 3.6a,b,c), respectively. ((Figure 3.6d,e,f) illustrates higher magnification TEM images of same samples.) Morphology of fCNT@MoOx(4:1) and fCNT@MoOx(2:1) samples look like very similar for lower magnification, however fCNTs are almost in their pristine form for fCNT@MoOx(4:1) cathode sample while very small molybdenum oxide particles can be clearly seen on the fCNT surface for fCNT@MoOx(2:1) sample in higher magnification TEM images. Even particle sizes are as small as required, they are not compact enough so this morphologies are also not desired for our application. Conversely, very dense and agglomerated particles were observed for fCNT@MoOx(1:2) cathode material. They made fCNTs cohering on each others and covered on them with big molybdenum oxide particles. Unfortunately, this morphology was not also desired one but we made their structural and chemical analysis by using XRD and XPS techniques to assure that we really obtain molybdenum oxides. Also, their galvanostatic charge-discharge tests were performed.

Figure 3.7a shows the x-ray diffraction patterns of fCNT@MoOx(2:1), (4:1) and (1:2) samples. The significant diffraction pattern of is appeared at 2 theta of 26.1°. This peaks is corresponded to (002) reflection planes or also known as interlayered spacing between adjacent graphite layers, respectively. Also, the (100)

and (004) peaks which are appeared on 2 theta 43 and 53°, respectively, represents the curved graphene sheets that make up the structure of MWCNTs [62]. There is only one clear broad peak of MoO₃ nanoparticles at 49° and it is exist only for samples which includes higher amount of molybdenum precursor [63]. As shown in the Figure 3.7a, this peak does not observable for fCNT@MoOx(4:1) sample. The results are expected because very small nanoparticles of molybdenum oxides were obtained after synthesis. That's why molybdenum oxide peaks are broaden and disappear under very intense and broad fCNT peaks. On the other hand, the Mo 3d spectra of samples (Figure 3.7b) proves that molybdenum exist in the structure. Also, peak positions are matching with the previous XPS data which indicates that these are mix molybdenum oxides. Peak intensities of fCNT@MoOx(4:1) sample is higher than other samples. Actually, this results was not expected because less amount of molybdenum precursor was used for this sample but each test performed in different times. Even same parameters were used, power of x-ray source may change during time and it may affect the intensity of the peaks.

Electrochemical galvanostatic tests were also performed for these three samples which are fCNT@MoOx(2:1), fCNT@MoOx(4:1) and fCNT@MoOx(1:2) at the same time with their morphological and structural characterizations and the results are given in the Figure 3.8 (a,b,c), respectively. The batteries were cycled within the potential window of 2-4.5 V (vs Li⁺/Li) at currents equivalent to the current densities of 0.1 mA/cm² which is based on the cathode surface. During cycling, batteries of (2:1) and (4:1) were showed almost same cyclability performance. Interestingly their charge and discharge capacities increased along several cycles and such behaviour is not common for Li-O₂ batteries. The difference from the most battery testing results in the literature, full-capacity cycle was applied for all tests in this study. It may cause to observe unexpected capacity behaviours and such increase have been also reported in some previous studies. Meini et. al. demonstrated that electrolyte decomposition occurred due to high potentials, differentiate the electrolyte decomposition and this suggestion is coherent with our results [64–66].

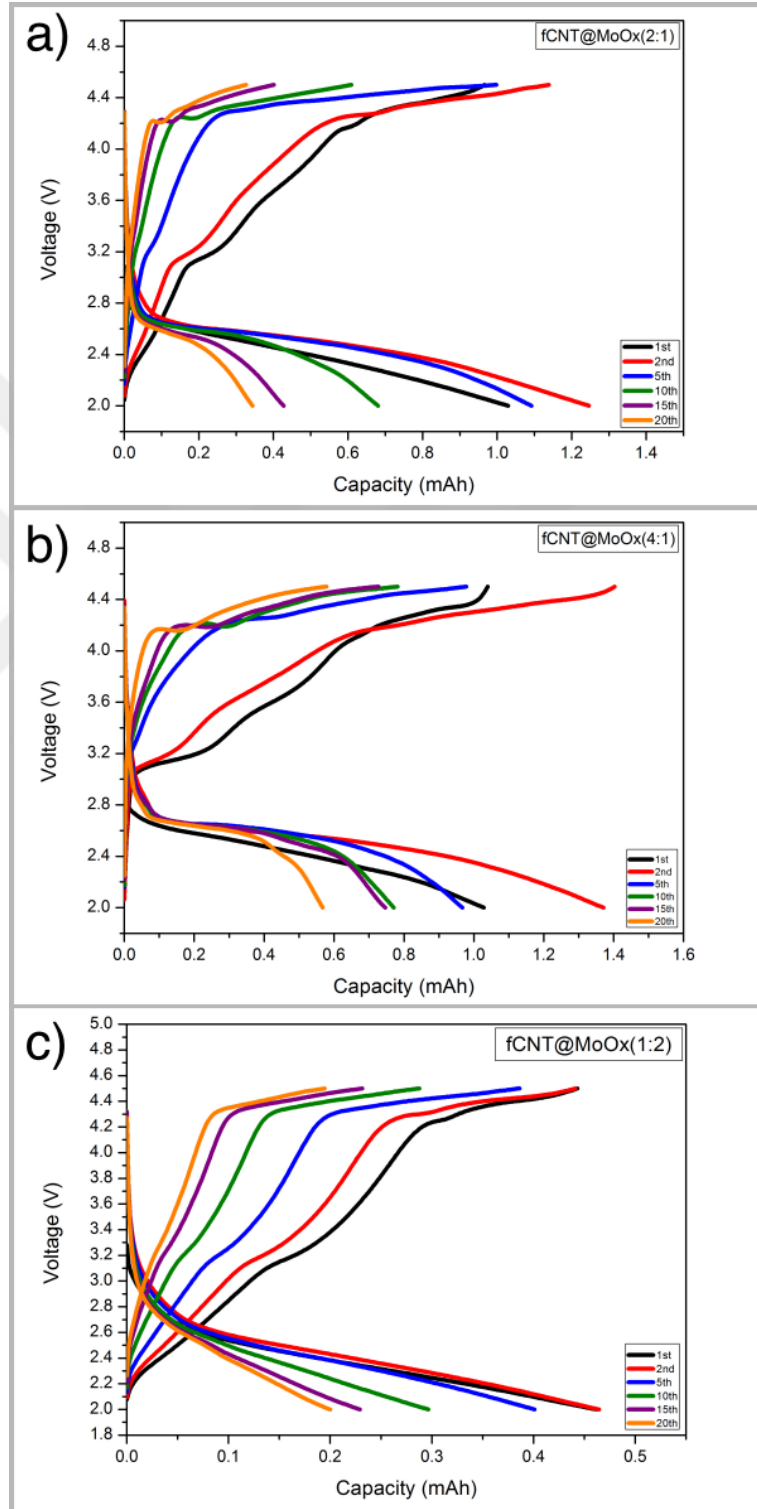


Figure 3.8: Galvanostatic charge-discharge test results of the batteries which prepared with fCNT@MoO_x(2:1), fCNT@MoO_x(4:1) and fCNT@MoO_x(1:2) cathodes.

When first cycles of cathodes are compared, it is clearly seen that charge overpotential is significantly decreased with increment of molybdenum precursor amount. While one third of the charge processes of fCNT@MoOx(2:1) and (4:1) cathodes was conducted under the potential of 3.5 V, half of the charge process is under the potential of 3.5V for fCNT@MoOX(1:2) cathode. However, capacity fading is the main problem for all cathodes and possible reason is also same with the previous cathodes which is undesired morphology of cathode materials. When carbon amount increased, catalytic effect of molybdenum decreased and battery showed very similar behaviour with only fCNT. High amount of molybdenum precursor cause highly agglomerated structure so although it shows good catalytic behaviour, significant capacity decrement was observed after 20 cycle.

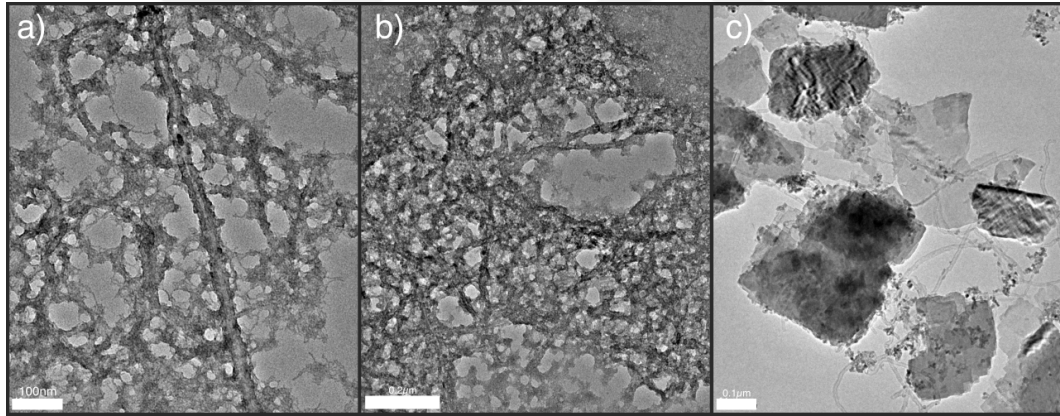


Figure 3.9: TEM images of as synthesized fCNT@MoOx samples for a) 15 minutes synthesis time b) 1 hour synthesis time c) 200°C synthesis temperature (Original parameter is 30 minutes at 160°C)

To obtain desired morphologies, carbon to molybdenum precursor amount were changed. However, first ratio which is (1:1) was defined as the best materials amount condition for fCNT@MoOx synthesis. Therefore, we thought that some other parameters may be effective on morphology and structure of the cathode material. For next step, synthesis time and temperature were changed, separately, in order to provide homogeneous distribution of finer molybdenum oxide particles or total covering of it. TEM images of as synthesized materials are given in the Figure 3.9. Original synthesis time was 30 minutes for microwave synthesis. Half of it, 15 minutes, and twice of it, 1 hour, were investigated. If we increased the

time, better covering can be provided. In the same sense, smaller and homogeneously distributed particles may formed for less synthesis time. Results were surprising. In both cases, network-like molybdenum oxide formation observed and they coated all the fCNT surfaces, however they were not only formed on fCNTs. They cross linked between themselves and some separated molybdenum oxide sheets observed in the TEM images (Fig. 3.9a and b). In addition, molybdenum oxide sheets covered most of the fCNTs for 1 hour synthesis time, which would plugged all pores and prevent electrolyte and activated oxygen diffusion. Synthesis temperature was another parameter changed to obtain better morphology. Original temperature was 160°C and it increased up to 200°C because we thought that if we increased the temperature, we could facilitate the molybdenum oxide formation on the fCNT and completed the metal oxide free regions. Unfortunately, result was not expected as shown in Figure 3.9c. Molybdenum oxides formed as micrometer scale bulk particles and they were not even linked with fCNTs. Even there are some nanometer scale particles around the fCNTs, their amount is very less. In order to define the difference between chemical structures, x-ray crystallography measurement was performed for these three samples.

The XRD pattern of the as-synthesized fCNT@MoOx powders are shown in Figure 3.10. Any molybdenum peak was observed for different synthesis times due to amorphous structure of molybdenum oxides. Only characteristic peaks of fCNT were observed as given before. However, when synthesis temperature was increased from 160 to 200°C, many new peaks emerged. These peaks were searched from the literature and it has been understood that there are not only one type of molybdenum oxide in the structure. The sample product crystallizes in the hexagonal and orthorhombic phases of MoO₃. Also some of the peaks matched with well-defined monoclinic structure of MoO₂ [63,67]. Actually we got curious about how crystallinity affect electrochemical performance so even we could not obtain desired morphology, we decided to examine fCNT@MoOx sample which is synthesised at 200°C for galvanostatic charge-discharge testing.

The battery were cycled for 20 times within the potential window of 24.5 V (vs Li+/Li) at currents equivalent to the current densities of 0.1 mA/cm² which is based on the cathode surface and result is demonstrated in the Figure 3.11.

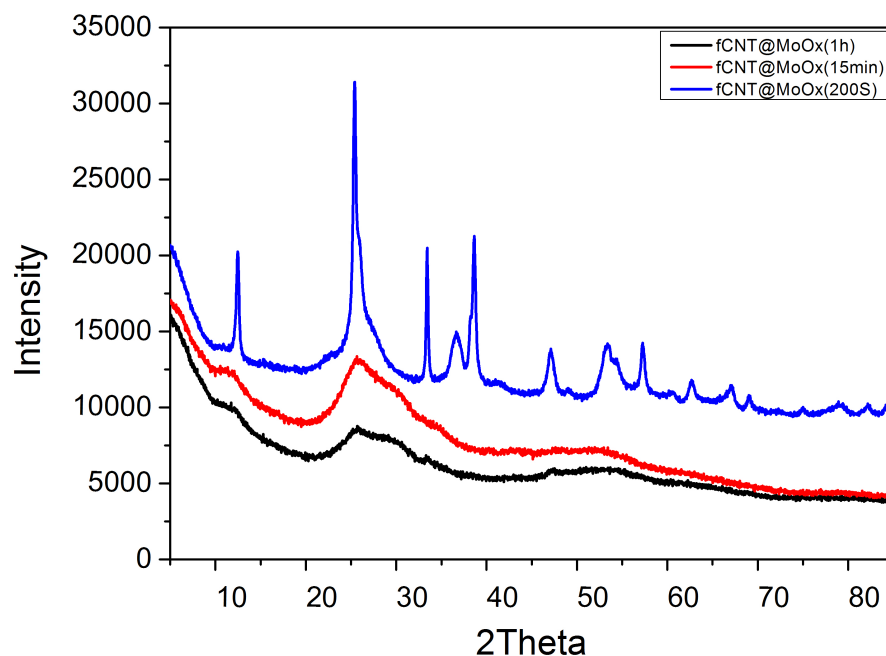


Figure 3.10: X-Ray Diffraction patterns of as synthesized fCNT@MoOx samples for a) 15 minutes synthesis time b) 1 hour synthesis time c) 200°C synthesis temperature

During first cycle, similar catalytic effect, especially on the OER performance, was observed but capacity dramatically decreased at the end of the 20 cycles. This huge capacity fading even did not seen for only fCNT cathode material.(Result of only fCNT cathode will given at the further results.) Therefore, we suggested that these micro-scale molybdenum oxide particles relocate during formation and decomposition of discharge products and prevention of electrolyte and oxygen transportation through the carbon material accreted which highly reduce the capacity. On the other hand, we got a new idea about one more parameter that we can investigate in order to obtain better electrochemical performance. What if we anneal our best sample which forms with proximate desired morphology. Crystalline molybdenum oxides may cause better performance so we defined three different annealing temperatures which are 200, 400 and 600°C.

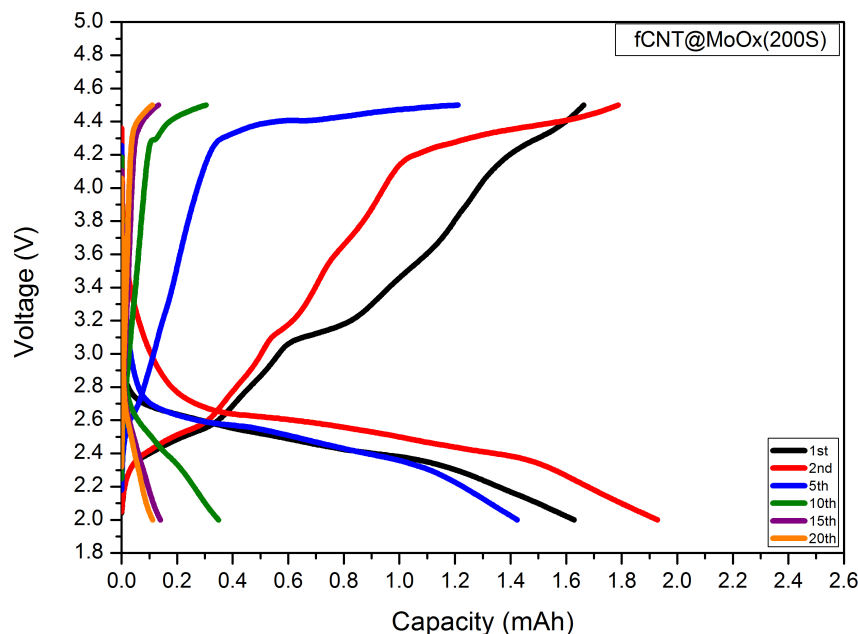


Figure 3.11: Galvanostatic discharge-charge test of fCNT@MoOx sample which synthesized at 200°C

For annealing process, best candidate was defined which was fCNT@MoOx synthesized at 160° for 30 minutes due to its better morphology and electrochemical performance. Annealing is applied under argon atmosphere and ramping rate is chosen as 10°C/min for every sample. After annealing, XPS and XRD measurement were performed in order to identify the chemical compounds and structures of molybdenum oxides. Results are given in the Figure 3.12. When Mo 3d scan of annealed samples were compared with unannealed sample, one new peak came up around 229.5 eV. After detailed survey about this new peak, we found that this peak associated with MoO₂ and its intensity increased when annealing temperature increased. Also O 1s and C 1s peak of annealed samples at 400 and 600°C slightly shifted which may be the proof of chemical transformation of MoO₃ to MoO₂ with increasing temperature [60, 68]. Also XRD patterns of samples supported the XPS results. While small peak of hexagonal phase of MoO₃ at 33 degree was observable at 400°C annealing temperature, tetragonal and monoclinic phases of MoO₂ becomes dominant [67]. These results demonstrates that

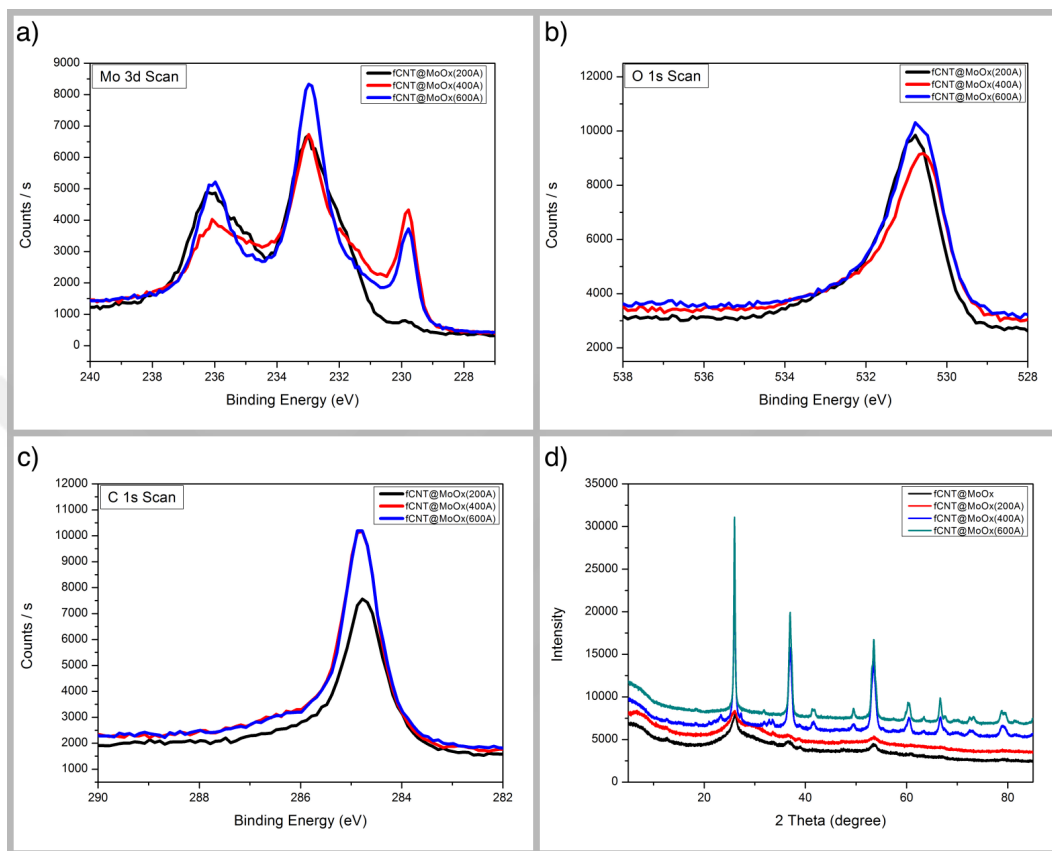


Figure 3.12: a,b,c) XPS characteristics of Mo,O,C and d) X-ray diffraction (XRD) pattern of fCNT@MoOx sample for various annealing temperatures, respectively.

new compound of molybdenum oxide forms after annealing and it may influence catalytic effect in a good way. Because of 400°C annealed sample has two forms of molybdenum oxide, we decided to use it to test for electrochemical experiments. We thought that both molybdenum oxide have different catalytic effect so they could provide better activity during charge and discharge process.

In the Figure 3.13a, first discharge-charge cycles of only fCNT and fCNT@MoOx(400A) were compared in order to see catalytic effect of combination of metal oxide particles and annealing process on OER and ORR overpotentials. It can clearly seen that annealed fCNT@MoOx cathode decreased OER overpotential during charging process and pull the voltage value of the decomposition reaction of lithium peroxide down to almost theoretical value(2.96V).

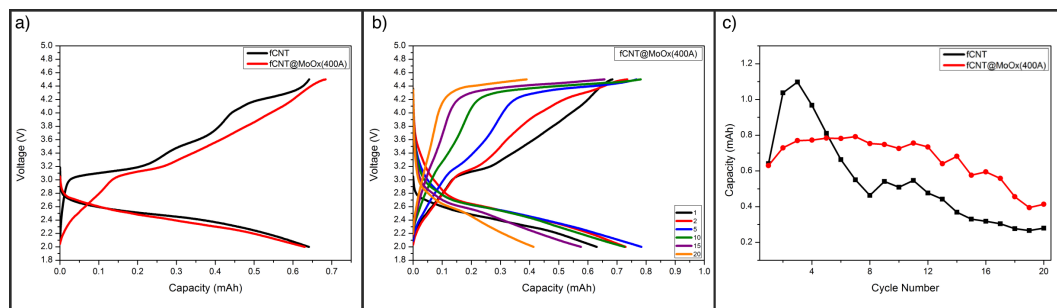


Figure 3.13: Galvanostatic charge-discharge test results of the batteries which prepared with a) fCNT@MoOX(2:1), b) fCNT@MoOX(4:1) and c) fCNT@MoOX(1:2) cathodes.

fCNT is already a very good catalyst for ORR process by itself so there is no visible effect of molybdenum oxides for this process. Moreover, cyclic performance of fCNT@MoOx(400A) was investigated and compared with only fCNT as shown in Figure 3.13(b,c). While capacity retention of annealed cathode was 65% (from 0.6303 to 0.4135 mAh), fCNT could only achieve 43% capacity retention (from 0.6409 to 0.2797 mAh) which means fCNT@MoOx(400A) cathode have 66% greater capacity retention than only fCNT. On the other hand, catalytic activity of molybdenum oxide nanoparticles during OER process decreased cycle by cycle which suggested us molybdenum oxide may not be stable during cycling and its durability also investigated in the ongoing results but first to see the real effect of annealing on charge overpotential, galvanostatic test results of fCNT@MoOx and fCNT@MoOx(400A) were compared and result is illustrated in Figure 3.14. Same current rate is applied with the previous testings for these measurements.

As it shown before, molybdenum oxide particles already are very good catalyst for OER process. However, MoO₂ occurred besides MoO₃ after annealing and this new mixture of both compounds thought to show better performance during electrochemical reactions. Results are also supported this idea as shown in Figure 3.14. Although it seems like unannealed cathode showed better activity at the beginning of the charging, total voltage plateau at lower voltage values for annealed cathode. While half of charge curves of fCNT@MoOx cathode goes under the 3.4V, more than half of charge curves of fCNT@MoOx(400A) goes under the

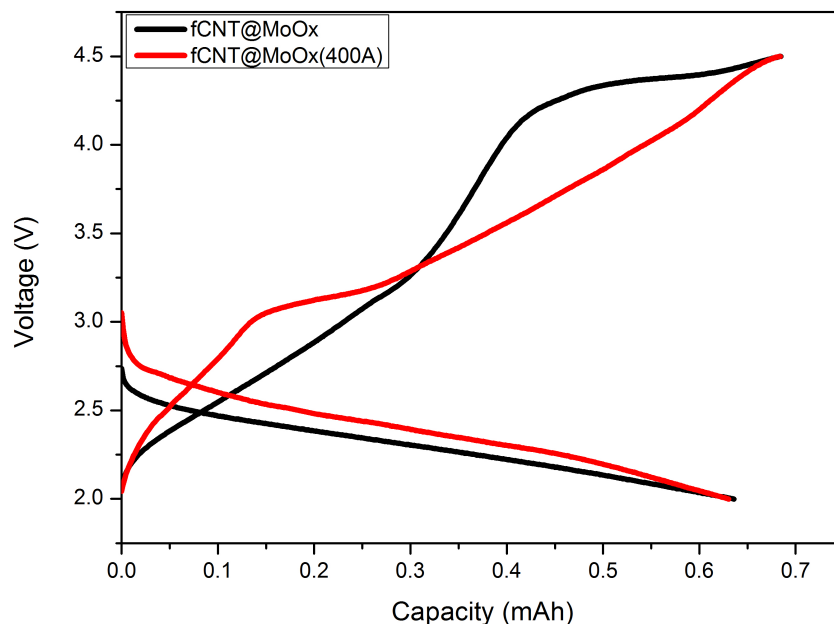


Figure 3.14: Comparison the galvanostatic discharge-charge tests of fCNT@MoOx and fCNT@MoOx(400A) cathode materials.

3.4V and also after 3.24V, charge overpotential is significantly less for annealed sample. In addition, ORR performance of annealed sample is slightly better than unannealed sample. These results indicates that phase transition of MoO₃ provide better catalytic activity for electrochemical reactions during both charge and discharge reactions.

Even promising results were obtained for the first cycles, capacity fading and charge overpotential increment made us suspicious about stability of molybdenum oxide nanoparticles. Therefore, we decided to investigate cycled cathode material after 20 cycle. Cathode material was taken out from the battery cell and washed with asetonitrile in order to remove electrolyte from the surface. Then, TEM samples are prepared and images are taken from as-synthesized fCNT@MoOx and 20 cycled fCNT@MoOx cathode materials. TEM images are given in the Figure 3.15(a,b) respectively. Results were shocking because after 20 cycles, almost no metal oxide particles observed on the fCNT surface. They looked like

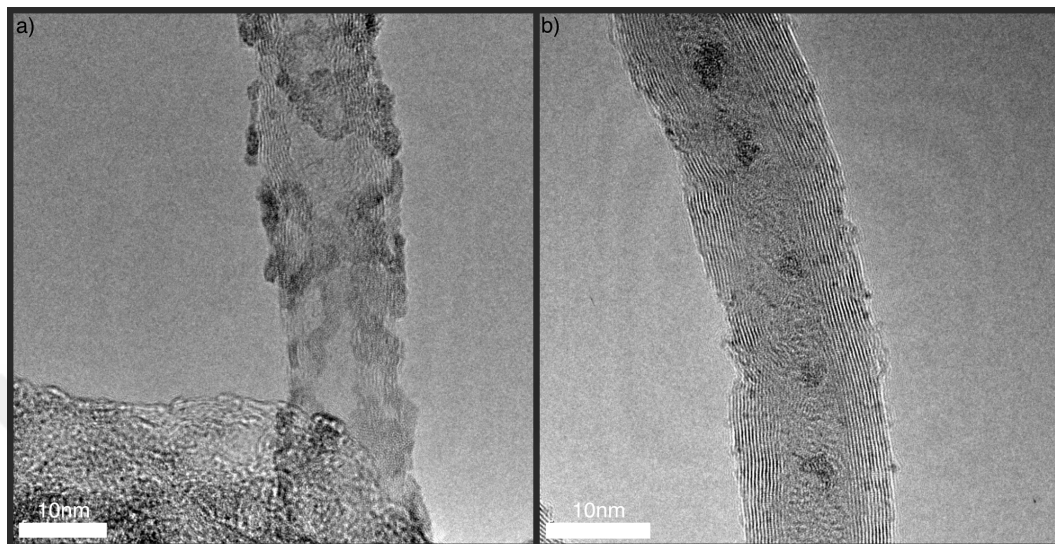


Figure 3.15: TEM images of a) as synthesized fCNT@MoOx sample and b) after 20 charge-discharge cycle.

dissolved in the electrolyte and only very small molybdenum oxides remained on the surface. It may clearly explain the charge overpotential increment during cycling. Molybdenum oxide particles were not stable in that environment so its effect gradually decreased cycle by cycle. In order to prove its dissolution in the electrolyte, XPS analysis was performed for 20 cycled cathode and separator. Their Mo, C, O and Li scans compared with the pristine cathode material. and results are given in the Figure 3.16.

For this measurement, fCNT@MoOx(400A) was chosen for investigation because the best performance obtained with this cathode material. Samples were carefully washed and cleaned from electrolyte in order to prevent specious peaks that could come from electrolyte. C 1s scan demonstrates that various side products formed on the not only cathode surface but also separator after 20 cycles. We did detailed survey about new peaks however such electrochemical systems are very complicated and identifying the exact binding energies for each products requires individual study itself. Even so, I searched for the similar studies and found that these peaks corresponds to electrolyte decomposition. And there are more than one side products which may be lithium carbonate, lithium hydroxide and lithium fluoride [69–71]. These results explain the capacity fading during cycling. In

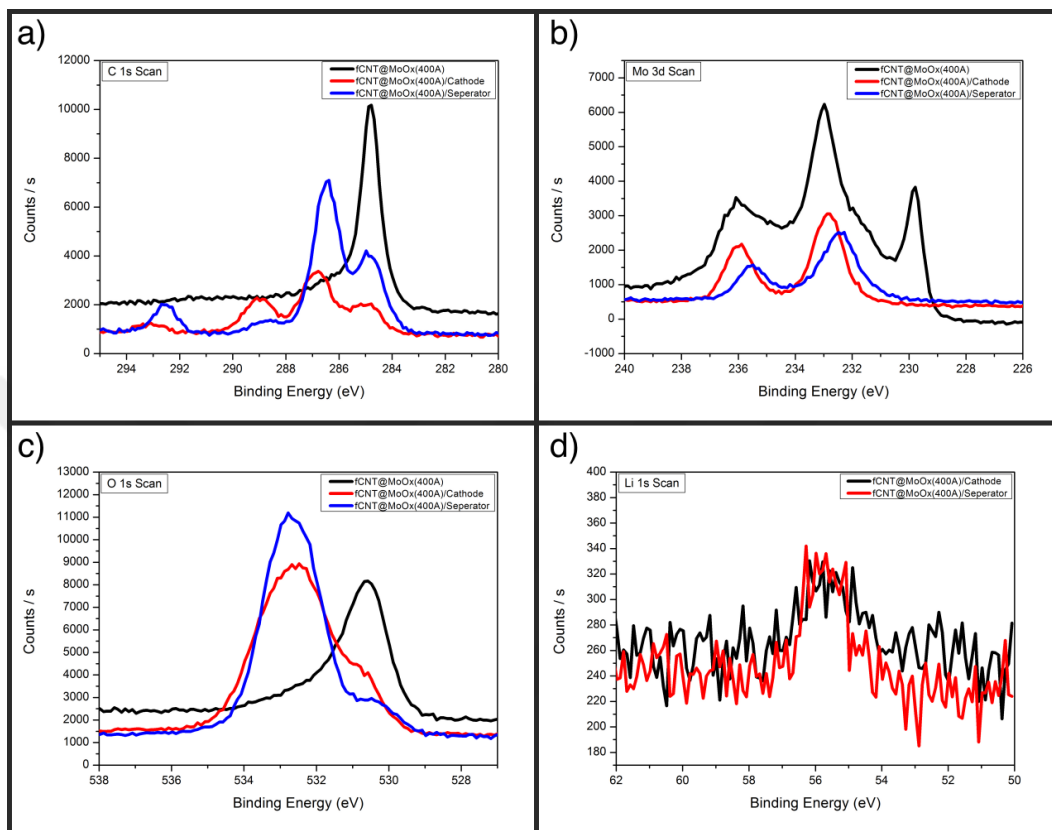


Figure 3.16: a,b,c,d) XPS characteristics of Mo,O,C and Li for fCNT@MoOx, 20 cycled fCNT@MoOx cathode and separator samples, respectively.

addition, intensity of main carbon peak at 284.6 eV decreased for cycled cathode which shows that side products covered cathode surface and prevent the signals coming from the fCNT surface.

Moreover, Mo 3d scan for cycled cathode and separator indicated that molybdenum oxides are not stable because in normal conditions we should not get any signal that is coming from molybdenum species but there was molybdenum oxides on the separator as much as on the cathode material. Interestingly, peak which corresponds to MoO₂ particles disappeared. It has been suggested that molybdenum oxide reacted with active oxygen in the electrolyte and transform to MoO₃. During this reaction molybdenum particles could not keep their forms and dissolved in the electrolyte which proves the reduction of catalytic efficiency during cycling. Also O 1s scan results supported phase changing and side product presence in the structure. Different compounds cause different interactions

between elements and it may cause shifting of binding energies.



Chapter 4

Conclusions

In this study, catalytic effect of molybdenum oxide have been investigated for using in Li-O₂ batteries. Multi-walled carbon nanotubes are used as an catalyst support due to its high surface area and electrical conductivity, high thermal and chemical stability. Hydrophobic nature of bare carbon nanotubes was the main problem during synthesis of molybdenum oxide particles on its surface. Therefore, functionalization process have been utilized to provide oxygen functional groups on MWCNT surface and presence of these functional groups are proven by using XPS. After functionalization, various precursor amounts, synthesis techniques and synthesis parameters including synthesis time and temperature have been utilized in order to obtain required structure and the morphology which is well distributed and homogeneous molybdenum oxide particles on the carbon material surface.

The best morphology were obtained for fCNT@MoO_x(1:1) sample which is synthesized at 160°C for 30 minutes. XPS results indicated that there were more than one molybdenum oxide species in the structure which provides better catalytic effect during OER process. Moreover, effect of annealing on the catalytic behaviour have been studied and it is seen that MoO₂ formed besides MoO₃ particles after 400°C annealing temperature and electrochemical test results suggest that presence of MoO₂ particles in the structure enhance the catalytic efficiency

of molybdenum oxide particles. Also, fCNT@MoOx(400A) cathode provided %66 greater capacity retention than only fCNT.

Unfortunately, XPS data of cycled cathodes proved that molybdenum oxide particles are not stable during cycling. Even they showed very promising results for the first cycles, they are dissolving in the electrolyte and phase transformation occurs for the further cycles which cause capacity fading and reduced catalytic effect. Consequently, we indicated that molybdenum oxide has very good catalytic activity, especially for oxygen evolution reaction, and improved the capacity retention performance of the Li-O₃ batteries. However, it is not stable in LiTFSI@4G electrolyte so further investigation may be carried out for another electrolyte media which can provide more stable environment for molybdenum oxide particles in the future.

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