

**SAKARYA UNIVERSITY
INSTITUTE OF NATURAL SCIENCES**

**DEVELOPMENT OF LITHIUM-OXYGEN BATTERY
NANOSTRUCTURED ELECTRODES FACILITATED
BY M13 VIRUS AND PLANT EXTRACT**

Ph.D. THESIS

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DECLARATION

I declare that all the data in this thesis was obtained by myself in academic rules, all visual and written information and results were presented in accordance with academic and ethical rules, there is no distortion in the presented data, in case of utilizing other people's works they were refereed properly to scientific norms, the data presented in this thesis has not been used in any other thesis in this university or in any other university.

Sara PAKSERESHT

26.05.2021

PREFACE

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LIST OF SYMBOLS AND ABBREVIATIONS

A	: Amper
Ar	: Argon
a.u.	: Arbitrary unit
Bio	: Biological
C	: Capacity
CV	: Cyclic voltammetry
CMC	: Carboxylic methyl cellulose
EDS	: Energy dispersive X-ray spectroscopy
EIS	: Electrochemical impedance spectroscopy
FESEM	: Field emission scanning electron microscopy
FTIR	: Fourier transform infrared spectroscopy
g	: Gram
HRTEM	: High-resolution transmission electron microscopy
Li_2CO_3	: Lithium carbonate
Li_2O_2	: Lithium peroxide
mA	: Miliampere
N_2	: Nitrogen
nm	: Nanometer
NPs	: Nanoparticles
OER	: Oxygen evolution reaction
ORR	: Oxygen reduction reaction
SEI	: Solid electrolyte interface
TEGDME	: Tetraethylene glycol dimethyl ether
TGA	: Thermo gravimetric analysis
V	: Voltage
W	: Watt

XPS	: X-ray photoelectron spectroscopy
XRD	: X-ray diffraction
2θ	: Scattering angle
Ω	: Ohm



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SUMMARY

Keywords: Lithium-oxygen battery, Green method, Air electrode materials, M13 bacteriophage, electrocatalyst

Lithium-oxygen (Li-O₂) batteries are a promising candidate for next-generation rechargeable battery systems due to their superior theoretical energy densities (11,586 W h Kg⁻¹), which is near to those of gasoline (11,860 W h Kg⁻¹). The principle of Li-O₂ cell is relied on the formation of Li₂O₂ by the interaction between Li cations and oxygen (from the air) during discharge at the cathode surface and decomposition of Li₂O₂ upon charging. Therefore, the highly stable and reversible electrochemical reactions in Li-O₂ cell is dependent on accelerating formation and decomposition of Li₂O₂. One solution to solve this issue is selecting an appropriate cathode catalyst with high porosity, good electronic conductivity, chemical stability, and high catalytic activity.

In this thesis, our purpose is to develop novel efficient cathode materials for Li-O₂ batteries using non-aqueous electrolytes by utilizing bio-inspired materials such as plant extract and M13 viruses. The M13 virus is a phage that infects bacteria but is harmless to humans and serves as a bio-template due to its unique morphology. Plant extracts are a rich source of bioactive chemicals. They have been demonstrated to be promising as reducing and capping agents for the biosynthesis of a variety of metal/metal oxide nanoparticles. Therefore, TiO₂ nanoparticles with a cauliflower morphology were synthesized by using chamomile extract. Bio-TiO₂ electrode containing 5 wt.% carbon black, showed a large overpotential and 30 stable cycles at the limited capacity of 500 mAh g⁻¹. Therefore, to increase the cycle life of the Bio-TiO₂, a core-shell-like structure was formed with α -MnO₂ as a shell, and the content of the carbon black was increased from 5 wt.% to 10 wt.%. The obtained TiO₂/ α -MnO₂ showed 60 stable cycles at the limited capacity of 600 mAh g⁻¹. However, 10 wt% carbon black caused the formation of by-products and limited the cycling behavior of the cathodes. As a result, to increase the electrical conductivity and catalytic activity of metal oxides without using carbon additives, the unique one-dimensional α -manganese oxide nanowires incorporated with ruthenium nanoparticles were constructed with the assistance of M13 bacteriophage. The virus-templated Ru/ α -MnO₂ nanowires offered a high porosity and an extensive surface area as a cathode material. This cathode demonstrated a high capacity of 14,383 mAh g⁻¹ with 48 stable cycles at a limited capacity of 1000 mAh g⁻¹.

In conclusion, these biosynthesis methods could provide an eco-friendly and cost-effective approach to develop high-performance battery electrodes. The design strategy manufactured in this thesis could be applied not only to batteries but also to other applications, which require nanoscale materials.

LİTYUM-OKSİJEN PİLLER İÇİN NANO YAPILI ELEKTROTLARIN M13 VİRÜS VE BİTKİ ÖZLERİ İLE ÜRETİMİ

ÖZET

Anahtar kelimeler: Lityum-oksijen pil, Yeşil yöntem, hava elektrot malzemeleri, M13 virüs, elektrokataliz

A Lityum-Oksijen (Li-O₂) pilleri, sahip olduğu yüksek teorik enerji yoğunlukları (11,586 Wh kg⁻¹) sebebiyle geleceğin şarj edilebilir batarya sistemleri arasında en ön plana çıkan sistemlerdir. Li-O₂ pillerin çalışma prensibi, lityum iyonları ile havadan elde edilen Oksijen atomlarının katot yüzeyinde tersinir reaksiyonlar ile Li₂O₂ oluşumuna dayanmaktadır. Bu sebeple Li-O₂ pillerinde yüksek kararlılığa sahip tersinir elektrokimyasal reaksiyonların oluşumu, Li₂O₂ oluşum ve bozunma kinetiklerinin arttırılmasına bağlıdır.

Bu tez çalışmasında bitki özleri ve M13 virüsleri kullanılarak Li-O₂ piller için yüksek verimliliğe sahip, yenilikçi katot malzemelerin üretimi amaçlanmıştır. M13 virüsleri insanlar için zararsız, bakterileri enfekte eden bakteriyofaj'lar olarak, sahip oldukları özgün morfolojileri sebebiyle biyolojik şablon olarak görev yapmaktadır.. Bitki özlerinin çeşitli metal/metal oksit nanoparçacıkların biyosentezinde indirgeyici olarak kullanıldığı çalışmalar literatürde mevcuttur. Bu sebeple, bu tez bağlamında, karnabahar morfolojisine sahip TiO₂ nanopartiküller papatya özü kullanılarak sentezlenmiştir. Biyolojik yöntemlerle üretilen, ağırlıkça %5 karbon siyahı içeren TiO₂ elektrotlar, 500 mAhg⁻¹ kapasite limitli testlerde yüksek polarizasyon göstererek ancak 30 çevrim kararlı şarj-deşarj performansı göstermiştir. Üretilen katotların çevrim kararlılığını arttırmak amacıyla, α-MnO₂'nin kabuk olduğu çekirdek-kabuk morfolojisinde ağırlıkça %10 karbon siyahı içeren katotlar üretilmiştir. Üretilen TiO₂/α-MnO₂ yapıları, 600 mAhg⁻¹ kapasite limitli testlerde 60 çevrim kararlı şarjdeşarj performansı göstermekle beraber, yüksek karbon siyahı içeriği nedeniyle çeşitli yan reaksiyon ürünlerinin oluşumuna sebep olmuştur. Karbon siyahının varlığından kaynaklanan problemlerin aşılması amacıyla, yüksek elektronik iletkenlik ve katalitik aktiviteye sahip karbonsuz katotlar, M13 virüslerin yardımıyla rutenyum katkılanmış tek boyutlu α-MnO₂ olarak üretilmiştir. Üretilen virüs şablonlu Ru/ α-MnO₂ nanoçubuklar yüksek porozite ve yüzey alanı göstermektedir. Katotlar 1000 mAhg⁻¹ kapasite limitli testlerde 48 çevrim kararlı şarjdeşarj performansı göstermekle beraber, ilk çevrimde 14,383 mAh g⁻¹ 'lık oldukça yüksek kapasite elde edilmiştir. Sonuç olarak, bu tez çalışması bağlamında kullanılan biyo-sentez yöntemleri, yüksek performanslı batarya elektrotlarının üretiminde çevre dostu ve düşük maliyetli bir yaklaşım sunmaktadır.

CHAPTER 1. INTRODUCTION

1.1. Energy Systems

Energy storage systems (EES) are effective methods and technologies to store different energy forms for use on demand. In the past century, the energy storage industry has been developed to meet energy needs and advances in technology and innovation.

To manage our power supply in order to facilitate more durable energy, saving costs, and eliminate environmental pollution, EES provides a broad technological approach. The current power productions are the usage of natural gas, oil, and coal. Figure 1.1. indicates the source of energy worldwide in 2017, which 67% demands from fossil fuels that emit huge amounts of carbon dioxide and other greenhouse gases, leading to global climate change [1]. A conventional current energy production releases greenhouse gases, thereby alternative energy storage such as compressed air, solar power, hydrogen, pumped hydropower, thermal, and batteries.

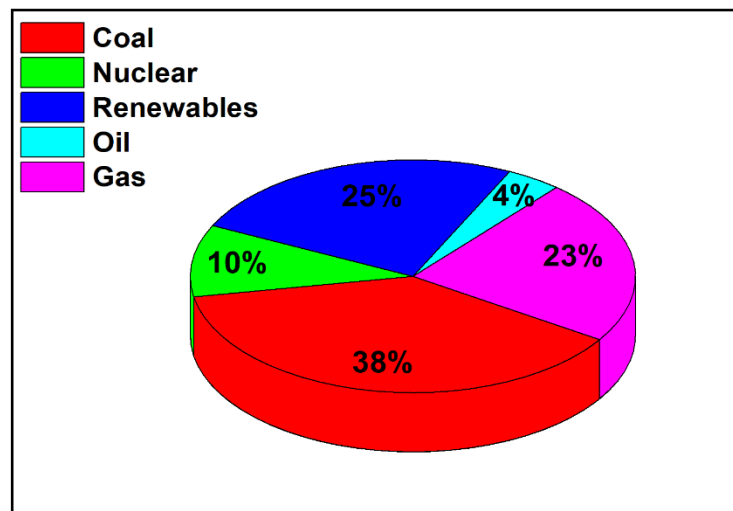


Figure 1.1. World power generation sources in 2017 (International Energy Agency).

Compressed air energy storage power plants utilize wind turbines to conduct compressed air into underground aquifers. When the air is released from storage, it expands to a combustion turbine and generates electricity. This system is a fast start-up but requires a specific location.

The pumped hydropower plant (PSH) can generate energy by lowering the water through the turbine and generating energy by pumping water to the upper reservoir. PSH may store a large capacity of electricity but is required massive cost and geographical dependence. Moreover, it is caused by soil erosion and silting of dams. Hydrogen is a chemical energy carrier like gasoline or natural gas; hydrogen is not yet widespread because of the increased cost.

An initial solution to the problem of energy storage for electrical purposes was the production of batteries as an electrochemical storage system. The battery system involves the transformation of chemical energy into electrical energy. Batteries are the most widely used in energy storage in industry and daily life. A detailed description will be given in the following section.

1.2. Batteries

All batteries are composed of three main parts in each cell: an anode, a cathode, and an electrolyte. Batteries are widely classified into primary and secondary. Primary batteries are not rechargeable (i.e., the chemical reaction is irreversible). They are disposable, and electricity is produced from chemicals that are sealed. On the contrary, secondary batteries are rechargeable and have a long life cycle. Different types of primary and secondary batteries and their application are noted in Table 1.1. Rechargeable batteries are operated through electrochemical reactions and transform chemical energy into electrical energy. In the past years, different secondary battery systems have been explored and used such as lead acid, nickel metal hydride and lithium ion and redox flow batteries. Owing to their superior specific energy, they have utilized within different applications, including mine locomotives, submarines, power instruments, and electric vehicles. By increasing the necessity for advanced

energy storage demands for portable laptops and cell phones, industrial machines, and other consumer implementation, further research has followed to discover high specific energy systems than Li-ion batteries, where metal-oxygen batteries have been the aim of this work [2,3]. Lithium ion batteries have been utilized widely in electric vehicles and electronic devices. They have high power density and specific energy (300 Wh Kg^{-1}) among commercial batteries, but their energy density is not near to the gasoline energy density ($11,680 \text{ WhKg}^{-1}$) [4]. The limited energy density of the conventional Li-ion batteries cannot provide the necessities of electric vehicles for a driving range (>400 kilometers or 250 miles). Therefore, new battery technologies are required to develop batteries with higher specific capacities and a long lifetime. Beyond Li-ion batteries, the ultra-high energy density of lithium-oxygen batteries (Li-O_2) ($\sim 3500 \text{ Wh kg}^{-1} \text{Li}_2\text{O}_2$) have been investigated as one of the best feasible options for next-generation rechargeable batteries (Fig. 1.2.) [5].

Li-O_2 batteries are remarkable because the oxygen gas (cathode material) can be acquired from the atmosphere rather than stored in the battery, thus reducing the overall weight of the batteries.

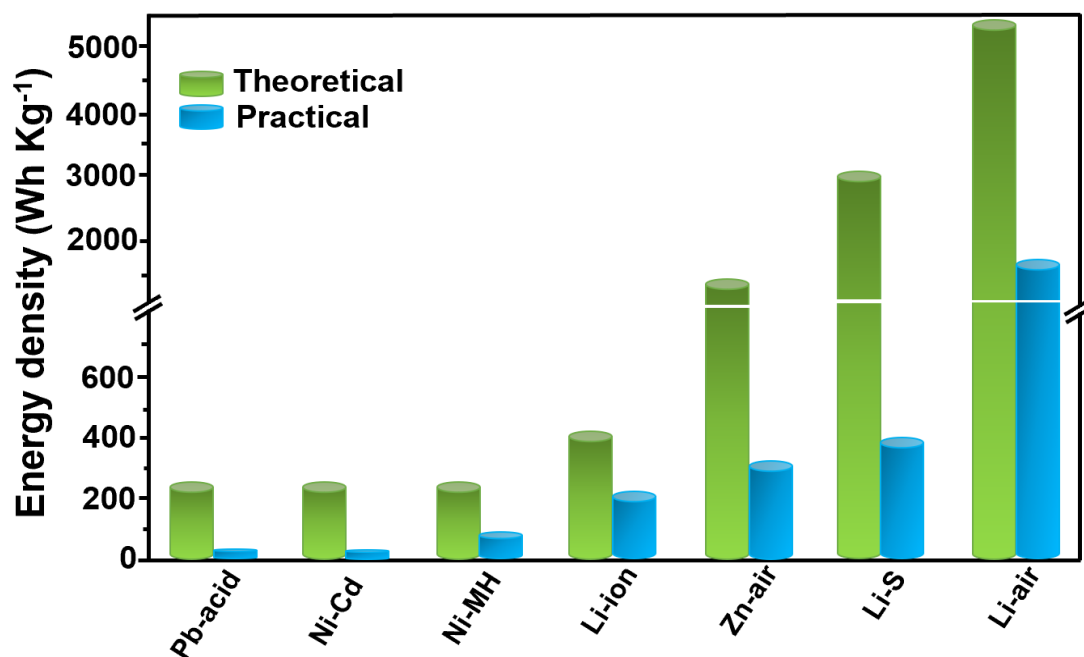


Figure 1.2. A comparison of the specific energy densities of several rechargeable batteries: lead acid (Pb-acid), nickel cadmium (Ni-Cd), nickel metal hydride (Ni-MH), zinc air (Zn-air), Li ion, lithium sulfur (Li-S), and lithium air (Li-air) batteries.

Table 1.1. Application and features of primary and secondary batteries.

Primary batteries	Features	Applications	Secondary batteries	Features	Applications
Zinc-carbon	Cathode: Carbon Anode: Zinc Electrolyte: salt-base.	Use in clocks, torches, and radios. (lifetime 3-5 years)	Lead-acid	Anode: Metallic lead Cathode: Lead dioxide Electrolyte: Sulphuric acid.	Often use in vehicles. (lifetime 2-5 years)
Alkaline batteries	Cathode: Manganese dioxide Anode: Zinc Electrolyte: alkaline.	It can be used in remote control, torch, and watch. (lifetime 5-10 years)	Lithium-ion	Anode: Carbon or graphite Cathode: Lithium metal oxide Electrolyte: anion salts.	Use in portable electronics and electric vehicles. (lifetime 7-12 years)
Silver-oxide	Cathode: Silver dioxide Anode: Zinc Electrolyte: alkaline.	Often use in watches. (lifetime 3-7 years)	Nickel-cadmium	Anode: Cadmium Cathode: Nickel oxide hydroxide and a separator Electrolyte: Potassium hydroxide	Use in power tools, medical devices, and toys. (lifetime 1-3 years)
			Nickel-metal hydride	Anode: Hydrogen ion Cathode: Nickel hydroxide and a separator Electrolyte: Potassium hydroxide	Used in medical devices, electrical tools, and automotive batteries. (lifetime 3-5 years)

1.3. Scope Of Work

The main goal of this thesis lies in the unique design of effective electrocatalysts as cathode materials for Li-O₂ battery electrodes. Herein, we have shown the biomaterials could be applied to form a nanostructure for Li-oxygen batteries cathodes with a high surface area and cost-efficiency. Metal and metal oxides,

including TiO_2 , MnO_2 , and Ru, were proposed with the utilization of plant extract and M13 bacteriophage by applying into the mechanism of the reaction and current challenges Li-oxygen battery. Bifunctional catalysts materials enhanced the operation of the battery along with their unique structures.

In chapter two, the principle and challenges of current lithium-oxygen batteries are discussed. To enhance the electrochemical activity of Li- O_2 cells, various cathode materials with various properties are developed in this study. The as-prepared cathode materials are based on metal and metal oxides, which their properties are investigated in chapter three. The experimental works in this thesis are shown in chapter four as follows:

A comparative study is performed to prepare TiO_2 via sol-gel and green methods. The TiO_2 nanoparticles were biosynthesized using *Matricaria chamomilla* flower extract. Chamomile flower extracts are used as a surfactant to reduce Ti ions and convert them into stable Bio- TiO_2 nanoparticles, which are then fabricated into an air electrode for a lithium- O_2 cell. This is the first research that we are aware of that uses Bio- TiO_2 nanoparticles as an air electrode in Li- O_2 batteries. We expect that the stabilized Bio- TiO_2 nanoparticles will enhance the cyclability of the Li- O_2 cell. The effects of various parameters (e.g., precursor concentrations, pH, temperature, and reaction time) were optimized to synthesize the nanoparticles. The pH of the solution was manipulated, and its effects on the structure, size, and optical properties of bio- TiO_2 nanoparticles were examined. This study aims to observe the electrochemical performance of TiO_2 as a cathode material; TiO_2 is expected to demonstrate remarkable cyclic stability. According to the results, the biosynthesized nanoparticles investigated in this study could be utilized not only in Li- O_2 batteries but also in Li-ion batteries, cosmetics, ceramic membranes, and solar cells. This study was published in *ceramics international*. <https://doi.org/10.1016/j.ceramint.2020.09.264>.

In the next work, MnO_2 nanocrystals are grown on the surface of biosynthesized TiO_2 nanoparticles over a range of reaction times to study their morphology and crystalline structure. At last, urchin-like core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanostructures are

obtained to improve the electrochemical performance of TiO_2 . This work was published in Advanced powder technology. <https://doi.org/10.1016/j.appt.2021.01.036> Moreover, an advanced one-dimensional virus-templated MnO_2 polymorphisms (α -, δ -, γ - MnO_2) and a hybrid nanostructure composed of α - MnO_2 nanowires and Ru nanoparticles through a bio-templated method is presented. The Ru nanoparticles are incorporated on the virus-templated α - MnO_2 nanowires surfaces, and their electrochemical performances are studied as an efficient carbon-free cathode material to eliminate side reactions.

The phase structures, elemental composition, and surface morphology of all products are also characterized and inspected in chapter 5. Furthermore, the electrochemical behavior of all cathode materials is evaluated using ECC-air cells at room temperature. The Li-O_2 cell with $\text{TiO}_2/\alpha\text{-MnO}_2$ as bifunctional catalyst reduced the polarization gap between charge and discharge potentials compared to only TiO_2 catalyst electrode. The high electrochemical performance of $\text{TiO}_2/\alpha\text{-MnO}_2$ could be attributed to their bifunctional catalytic activities toward ORR/OER, along with urchin-like $\alpha\text{-MnO}_2$ shell architecture on the surface of Bio- TiO_2 nanoparticles, which increase the number of active sites for Li_2O_2 storage.

Moreover, it is intended to minimize cathode degradation by highly stable nanostructured metal-oxides and decrease side reaction formation. To the best of our knowledge, the urchin-like core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanostructures have not been reported as a highly efficient cathode catalyst for Li-O_2 batteries. The resulting core-shell nanostructure is favorable for high-performance lithium-oxygen storage applications due to its superior catalytic activity and good stability.

In addition, to increase the conductivity of metal oxides, carbon black is added, which resulted in the formation of further side reactions. So, the key to address this challenge is to design carbon-free cathode materials. The conductivity is a vital parameter to facilitate electron transport throughout the electrodes. Therefore, Ru nanoparticles are decorated on the surface of virus-templated $\alpha\text{-MnO}_2$ nanowires. The incorporation of Ru indeed enhances the capacity and life cycle due to its

superior electronic conductivity and catalytic activity compared to the carbon material. Therefore, designing a carbon-free virus-templated Ru/ α -MnO₂ hybrid electrode eliminated the by-products and significantly increased the specific capacity and life cycle of Li-oxygen cells.

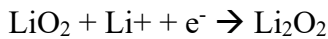
In Chapter 6 the general conclusions of this thesis and future work have been discussed.



CHAPTER 2. LITHIUM-OXYGEN BATTERIES

2.1. Lithium-Oxygen Batteries Fundamentals

In attempts to amend the energy density of batteries, metal-oxygen batteries received much attention, especially zinc air, lithium air and aluminum air batteries. The lithium-oxygen (Li-O₂) battery has been considered the most between the metal-air batteries, because lithium possesses the lightest weight the highest theoretical capacity, which contributes to the energy density of 11,586 Wh kg⁻¹. The fundamental principle of Li-air battery involves oxidation and evolution reactions on the cathode and decomposition and deposition of the Li on the anode side. Abraham et al. proposed the first Li-air battery in 1996 and have investigated it in energy systems [6]. Li-O₂ batteries are categorized into four classes by the form of the electrolytes: (1) non-aqueous, (2) aqueous, (3) all-solid-state, and (4) hybrid systems [7-9], as illustrated in Fig. 2.1. The non-aqueous system has been extremely interested owing to its excellent rechargeability and energy density. The non-aqueous Li-oxygen is constructed of lithium as the anode and air-breathing cathode soaked in an aprotic electrolyte (lithium salt in aprotic solvent). The reactions that can occur to form the main discharge product Li₂O₂ are shown in the equations (2.1, 2.2):



or



and upon charging, Li_2O_2 is decomposed as given in equations (2.3, 2.4):



or



However, a practical non-aqueous Li-air battery confronts many technical issues. These issues are included poor rate capability due to a low practical, specific energy.

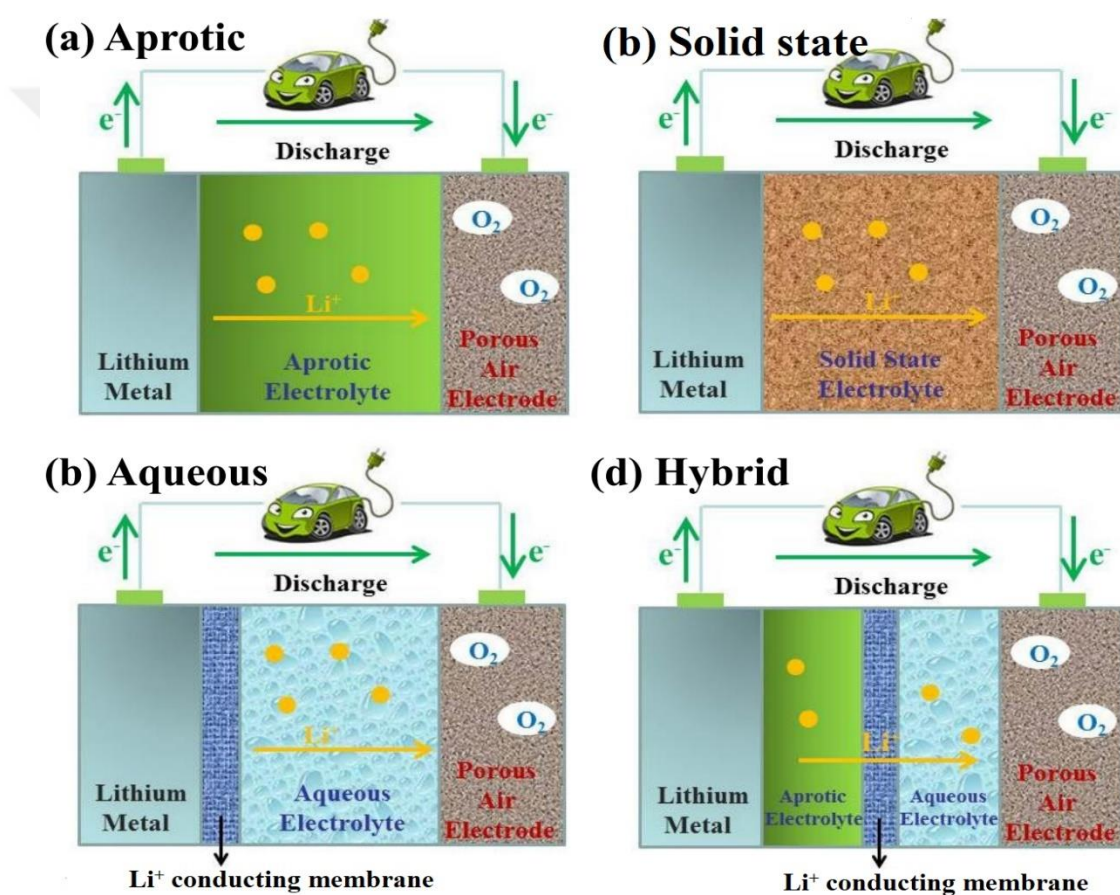


Figure 2.1. Schematic classification of Li- O_2 battery based on electrolytes [11].

A large overpotential during cycling, leading to poor energy efficiencies. Therefore, the high overpotentials account decomposition of electrolyte, electrode and as a result, the cycle life is restricted. Moreover, other air components (e.g., dioxide carbon, and humidity) can mediate with the Li- O_2 performance and form further by-products. To overcome this issue, Visco et al. [10] proposed an aqueous Li-air

battery. The basic of this battery is similar to a non-aqueous lithium-air cell. A solid-state conducted membrane is designed to maintain Li anode from the aqueous electrolyte. The main reaction in this battery occurs as equation (2.5):



The discharge product LiOH is soluble at room temperature. Although, the capacity of an aqueous lithium-air could be lower than non-aqueous when electrolyte (H_2O) participates in the reaction, and $\text{LiOH} \cdot \text{H}_2\text{O}$ is formed, therefore decaying the capacity.

To avoid using liquid electrolyte and improve lithium-air batteries' safety, a solid-state lithium-air battery has been developed, including some types of solid-state Li-ion conducting materials, such as Nasicon-type glass-ceramics (LATP, LAGP), polymers. The discharge product in a solid-state is Li_2O_2 and decomposing during charge, similar to a nano-aqueous system.

In recent years, many studies have been investigated to overcome issues and limitations in Li- O_2 batteries, such as designing effective cathode materials, stable electrolytes, and coating lithium anode to protect from corrosion. In the following discussion, the fundamental features of the theoretical and technical issues in proceeding with a successful non-aqueous Li- O_2 battery have been investigated.

2.2. Overview Of Non-Aqueous Lithium-Oxygen Battery

A typical non-aqueous Li- O_2 cell comprises an anode (Lithium), a porous cathode that is soaked in the electrolyte, and a separator. The fundamental operation of rechargeable nonaqueous lithium- O_2 batteries is the formation of Li_2O_2 upon discharge (oxygen reduction reaction, ORR) through a reaction between O_2 (from the air) and Li^+ and decomposed into Li^+ and O_2 during charge (oxygen evolution reaction, OER) at the cathode electrode. Excellent performance of rechargeable non-aqueous lithium- O_2 battery requires to encompass numerous specific capacity,

reversible, good rate capability, and excellent lifetime. There are many factors that can influence the cell's performance.

The main challenges with non-aqueous Li-O₂ cells are high polarization during charge and discharge states, contamination by humidity, and electrolyte decomposition. The other problems with the lithium-O₂ battery are safety, reliability, and electrochemical performance. They are flammable due to using organic liquid electrolytes. In addition, insulated parasite products (e.g., lithium carbonate, lithium hydroxide, and carboxylates) can be decomposed at a lower voltage in the presence of catalysts; therefore, they do not deposit and cover the cathode. Some electrolytes are inclined to effectively break down the common parasite products or generate very soluble dissociation products, thus delaying cell death. These poor performances of Li-O₂ cells are mostly suffered from the electrolytes instability due to the high reactivity of discharge products. Besides the stable electrolytes, the air cathodes still remain an obstacle to fully utilize the advantage of lithium-O₂ batteries. As discussed above, the critical issues of a non-aqueous lithium-oxygen battery can be assorted pursuant to the battery components: anode, electrolyte, and an air cathode. The relevant challenges and solutions will be discussed in detail.

2.2.1. Anode material

Lithium is engaged as a great candidate for anode materials due to its superior energy density, lightweight, and small atomic radius. Li has high reactivity and the most negative potential among known electrode materials. When lithium metal is encountered with organic electrolyte, a conductive Li-ion thin film forms at the interface, causing a corrosion-resistant lithium salt barrier named the solid electrolyte interface (SEI). Also, lithium metal undergoes dendritic growth, which may arise to short-circuiting of the cell. The instability of lithium metal confronting electrolytes (organic and inorganic) in lithium-oxygen batteries is due to the high reactivity of lithium. One of the concerns throughout the lithium-oxygen system function is the reaction of lithium metal with the electrolyte and form parasite residue such as lithium hydroxide and lithium carbonate. Besides, O₂ could dissolve in the

electrolyte and disperse to the anode to further react with the Li metal. It is essential to progress a coating film with excellent chemical and mechanical stability and ionic conductance or novel electrolytes that would provide a stable SEI film to avoid lithium metal anode corrosion later. Thereby, the commercialization of the Li-oxygen battery stresses the safety concerns before mass production.

A variety of strategies has been suggested (Figure 2.2.) to protect dendrite suppression and reactivity of Li with electrolyte, such as developing an artificial layer on Li anode, using altered electrolytes, or directly replacing Li metal, including alloy anodes (such as Li-Na, Li_xAl , and Li_xSi).

Many sorts of pre-treatments have been conducted to alter the Li surface. Fluoroethylene carbonates (FEC) have been approved as an efficient additive in Li-ion batteries, which was also recommended in lithium- O_2 batteries.

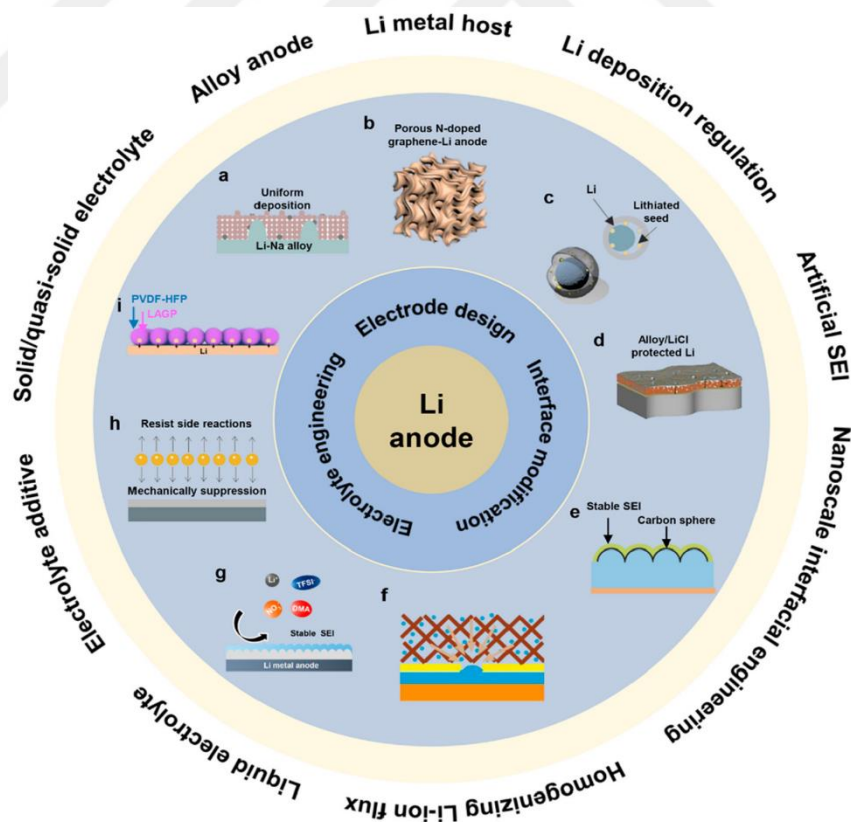


Figure 2.2. Some strategies to protect lithium anode [12].

2.2.2. Electrolyte

In Li-O₂ batteries, electrolytes are served for Li⁺ transferring, dissolving O₂ gas, transporting it toward the reaction sites, and preserving the lithium anode. Electrolytes are vital constituents to obtain a long-lasting span of life. In aprotic electrolytes, the stability of solvents and lithium salts in the oxidation environment is the major issue that must be overcome to achieve a long life cycle. Different electrocatalysts are applied to alleviate the charge voltage of lithium-O₂ batteries in recent years.

Unfortunately, the majority of non-aqueous electrolytes are combustible and evaporative, therefore gives safety concerns and not easy to be applied in an open system. Conventional aprotic electrolytes can replace by ionic liquid electrolytes because they are non-volatile and non-flammable [13].

The solid-state electrolytes likely can be another outcome for electrolyte evaporation and permeation. The operation mechanism of solid-state lithium-O₂ batteries is yet a challenge. Luo et al. investigated the surface-mediated mechanisms in an original plotted solid-state lithium-air battery. During discharge, LiO₂ is formed, and then a disproportionation reaction occurred that generates Li₂O₂ residue, which afterward gives rise to the formation of a hollow structure [14]. In particular, they found the Li₂O at the external surface of the hollow particles, that excess O₂ was directly intimate with the discharge residue.

Early Li-O₂ batteries applied carbonate-based electrolytes because they are low volatility, good oxidative stability, abundant, and utilized in Li-ion batteries; While recent research has indicated that organic carbonate electrolytes are unstable due to the formation of peroxide. Thereby, the development of new stable aprotic electrolytes has been proceeding in most researches. The next generation of aprotic electrolytes can be classified based on amides, ethers, sulfonates, ionic liquids, and dimethyl sulfoxide (DMSO). These electrolytes have been reported to elevate the formation and decomposition of lithium peroxide in the ORR and OER processes.

Carbonate-based aprotic electrolyte solvents comprising ethylene carbonate, propylene carbonate indicated instability and broke down upon the electrochemical reactions and resulted in poor cycling life. Ether-based electrolytes, including dimethoxyethane and tetraethylene glycol dimethyl ether, are widely utilized due to high stability at upper voltages (4 V versus Li/Li⁺) and low volatility. However, their decomposition gives rise to the substantial formation of Li₂CO₃, results in dramatic capacity decay after the first cycle [15].

Electrolyte salts have an essential impact on Li-O₂ batteries. They possess high ionic conductivity and stability. Lithium hexafluorophosphate (LiPF₆) was the first candidate for utilization in lithium-O₂ batteries and is so far the most widely applied. The other salts under study include LiBF₄, LiClO₄, Li Imides such as Bis(trifluoromethane) sulfonimide (TFSI). The selection of lithium salt is also critical in the electrolyte apparatus. An ultimate lithium salt ought to possess high solvability in the solvent to promote ions transportation and not interact with the solvent and the oxygen reduction species. The consistency of the electrolyte requires compatibility between the lithium salts and solvent. Nasybulin et al. investigated the stability of different salts in TEGDME. Their experiments demonstrated LiTFSI and LiTF are the most stable, delivering the highest capacity after the 1st cycle and the highest capacity retention after 20 cycles [16].

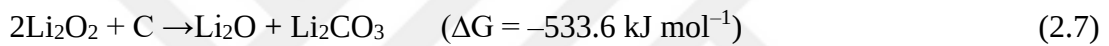
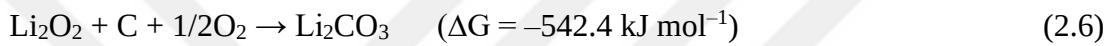
Overall, the non-aqueous electrolyte is utilized in the fundamental research of Li-O₂ systems but can not satisfy all the necessities. Ionic-liquid, solid-state, aqueous electrolytes, with their composites, are considered to achieve a safe, stable cycle and practical lithium-O₂ battery. Particularly, Ionic-liquid and solid-state electrolytes may provide high capacity and safety in lithium-O₂ batteries. However, further experimental, theoretical, and feasible studies are still required to develop the field of lithium-O₂ systems.

2.2.3. Cathode material

The catalytic efficiency of air cathodes entails being improved as they form or decompose extremely insulated Li_2O_2 throughout the electrode upon the operation. The discharge products (Li_2O_2) are not soluble in the organic electrolyte of the aprotic lithium- O_2 cell but accommodates into the cathode's pores during ORR process. Therefore, the Li- O_2 cell capacity is estimated by the content of the discharge product at the cathode. The discharge residue can be abruptly terminated by blockage of pores at the cathode, and oxygen diffusion is further inhibited at reaction sites. Usually, highly effective catalysts, optimum catalyst content, and porous structure will improve the cathode structure, by that means enhancing the specific capacity of the cell. A stable porous structure could provide channels for oxygen diffusion. A cathode with high electrolyte wettability can accelerate ionic transfer upon the (dis)charge states. Remarkably, the catalysts as the cathode materials may promote oxygen reduction and evolution kinetics. The efficient cathode material with rational structure and design can spare more void for discharge product storage and facilitate the diffusion of oxygen.

A bi-functional catalyst could alleviate the overpotentials upon the (dis)charge states by providing catalytic activities for both oxygen reduction and evolution reactions at the cathode surface, that means the discharge potential is increased, and the charge potential is decreased through promoting the ORR and OER kinetics, thus increase the round-trip efficiency. Besides the rapid release of oxygen and the high transport of electrons and ions into the air cathode, the rapid reaction rate of ORR and OER on the cathode is also significant through improving the rate capability of lithium- O_2 cells. An effective catalyst improves the reversibility formation of Li_2O_2 as a discharge product and eliminates the occurrence of side reactions from electrolyte decomposition and the erosion of the electrode materials. In general, a stable cathode constructed from porous and electrical conductivity materials can deliver a high battery performance.

Carbon materials: numerous carbonaceous substances have been utilized as cathodes for lithium-O₂ systems, including carbon nanoparticles [17], carbon nanotubes [18,19], carbon nanofibers [20], graphene [21,22], and other forms of carbons [23]. Carbon materials are noticed due to their high electrical conductivity, large surface area, many active sites for reactions, and chemical stability. These features introduce them to a suitable selection as cathode materials. However, many studies have investigated parasite reactions of carbon incurred during (dis)charge states. McCloskey et al. [24] first described that carbon interacts with Li₂O₂ upon discharging and form Li₂CO₃ as the following reactions with highly exothermic behavior:



Ottakam Thottil et al. indicated that CO₂ was released due to dissociation of carbon in the presence of Li₂O₂ while charging at a voltage upper than 3.5 V (vs. Li⁺/Li) [25]. The side product lithium carbonate forms an insulating layer on the cathode surface as the reaction proceeds and results in overpotentials. Li₂CO₃ decomposition needs a high potential, above 4 V, that is near to the cutoff potential upon charge, thus decreasing the round-trip efficiency and coulombic efficiency of the lithium-O₂ cells. These reports unveil the instability of carbonaceous cathode materials in lithium-O₂ batteries. There is still further investigation on the formation of lithium carbonates and dioxide carbon due to the electrochemical processes during discharge and charge, but there is obvious evidence of the poor stability of carbon cathodes. Therefore, alternative carbon-free cathode materials are suggested to promote the performance of the Li-O₂ cell. The carbon-free materials also serve as a catalyst during charge and discharge. Thereby, they can be alternative cathode materials for Li-O₂ cells.

Catalyst is one of the major constituents of the cathode, which has a critical impact in reducing overpotential by improving the catalytic activities toward OER and ORR

processes. It is noted that mechanisms of reaction are different for each electrocatalyst, and the catalytic activity is influenced by many parameters. In general, O_2 is adsorbed on the cathode surface and then reduced to peroxide species, followed by desorption, diffusion, and generation of Li_2O_2 . If the peroxide species fail to decompose rapidly, the active sites will be clogged and limit the capacity of the lithium- O_2 system. Therefore, the rational selection of electrocatalysts is required to promote the formation and decomposition of the discharge products.

The most common catalysts contain noble metal catalysts, metal oxides/carbides/nitrides, perovskite oxides, etc., which will be discussed in the following discussion.

Metals and metal oxides: Noble metals and their oxides are explored as the best catalysts for electrochemical reactions due to their high catalytic activity and corrosion and oxidation resistance. However, their high cost and scarce resources hinder the commercialization of Li- O_2 batteries and further fundamental research. The major precious metals studied in the cathode of lithium- O_2 cells include gold, ruthenium, palladium, iridium, and platinum [26,27].

The gold electrode possesses extreme chemical stability, and it has excellent advantages in structure and syntheses. In addition, it is also an effective cathode material to study the reaction process of the lithium-air system. Peng et al. analyzed the nanoporous gold electrode in different electrolyte systems in lithium-air cells and reported the gold electrode possesses good durability in the DMSO/ $LiClO_4$ electrolyte [28]. The capacity sustained more than 95% after 100 cycles, and during cycling, the decomposition of the Au electrode was minimized. Lu et al. investigated the catalytic activities of noble metals Pt and Au and reported that the gold catalyst could be utilized for catalysis of ORR [29]. In comparison, Pt revealed good OER performance. Therefore, they designed to emerge Pt and Au. The bifunctional Pt-Au alloy compound alleviated the overpotential of both ORR and OER in the lithium-air systems.

Su et al. constructed polyhedral gold nanocrystals as active catalysts in $\text{LiNO}_3/\text{DMSO}$ electrolyte for lithium-air cells [30]. The Au nanocrystals reduced the charge voltage and enhanced reversible capacities. Noble metals oxides were also broadly used as catalysts for lithium-air batteries. Noble metal oxides possess the highest electronic conductivity and catalytic activity compares with transition metal oxides. Liao et al. synthesized RuO_2 nanosheets by a two step procedure, heat treatment, and exfoliation [31]. The electrochemical tests demonstrated low (dis)charge overpotentials and high specific capacity. Ruthenium oxide nanosheets delivered a reversible capacity of more than 900 mAh g^{-1} and overpotentials of 0.15-0.59 V in the 50 cycles.

As discussed above, noble metals show superior catalytic activities, but they are such expensive and rare resources. Transition metal oxides are anticipated to replace noble metal catalysts owing to their abundance, cost-effective, and high catalytic activity. Several transition metal oxides are explored as catalysts in lithium- O_2 batteries, such as Co_3O_4 , Fe_3O_4 , MnO_2 , CuO , and TiO_2 [32-34]. Manganese oxides are the most extensively used materials because they are low toxic, low cost, abundant, and easy to synthesize. Different crystalline phases of manganese oxides have been applied and investigated as cathode electrocatalysts in lithium- O_2 systems. For instance, Zhang et al. produced hierarchical porous δ -manganese oxide nano boxes. δ - MnO_2 nano boxes improved the catalytic activity and reduced the overpotentials [35]. The cycling performance was stabled up to 112 cycles at a limited discharge capacity of 1000 mAh g^{-1} with a rate of 0.16 mA cm^{-2} .

Liu et al. fabricated TiO_2 nanowire arrays on carbon textiles as a free-standing cathode for Li-air batteries with $\text{LiCF}_3\text{SO}_3/\text{TEGDME}$ electrolyte [36]. Superior catalytic activity and long cycling performance could be obtained. Cui et al. studied the better catalytic activity and inferior overpotential with the $\text{Co}_3\text{O}_4/\text{Ni}$ electrode than those reported for carbon-based Co_3O_4 and pure Co_3O_4 [37]. They exhibited the utilization of carbon leads to the discharge residue accumulation on the cathode surface. Albeit, when Co_3O_4 is utilized with no carbon, oxygen species are stabilized on the surface, preventing the reaction with the electrolyte. The enhanced

performance was contributed to good adhesion between the Co_3O_4 and the nickel foam through the deposition method.

Riaz et al. synthesized bare Co_3O_4 electrodes with various morphologies of nanosheets, nanoneedles, and nanoflowers through an electrodeposition-conversion method and reported the performance relied on the design of the Co_3O_4 cathode [38]. The discharge capacity was enhanced from nanosheets (1127 mAh g^{-1}), nanoflowers (1930 mAh g^{-1}), to nanoneedle (2280 mAh g^{-1}) at a current density of 20 mA g^{-1} . The further result indicated that between the three designs, the nanoneedles Co_3O_4 electrode exhibited the longest cyclability. However, all three electrodes had a similar discharge potential of 2.75 V and charge potential of 3.85 V vs. Li/Li^+ .

Perovskite: Perovskite and perovskite-related oxides materials have been broadly applied as catalysts in superconductors, fuel cells, sensors, and metal-air batteries [39-41] due to their defective structures, excellent catalytic activity in both ORR and OER processes, and less expensive. Recently, perovskite oxides have also been considered in non-aqueous lithium- O_2 cells to promote OER and ORR kinetics. Cheng et al. prepared the perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) nanoparticles as the cathode catalyst for aprotic Li-O_2 batteries [42]. The tests indicated the excellent electrochemical activity of LSCF and could actively reduce the overpotential. LSCF catalyst delivered an ultimate discharge capacity of 13979 mAh g^{-1} and cycled stability of 20 cycles at 200 mA g^{-1} . They proposed that the introduction of LSCF nanoparticles can enhance the formation and decomposition of Li_2O_2 . Du et al. prepared Mg-doped perovskite oxides $\text{LaNi}_{1-x}\text{Mg}_x\text{O}_3$ ($x = 0, 0.08, 0.15$) bifunctional catalysts via a sol-gel method [43]. The ORR and OER performance is improved respectively as LaNiO_3 , $\text{LaNi}_{0.92}\text{Mg}_{0.08}\text{O}_3$, and $\text{LaNi}_{0.85}\text{Mg}_{0.15}\text{O}_3$. They found $\text{LaNi}_{0.92}\text{Mg}_{0.08}\text{O}_3$ and $\text{LaNi}_{0.85}\text{Mg}_{0.15}\text{O}_3$ as the electrocatalysts enhanced performances in comparison with LaNiO_3 catalyst.

Han et al. studied the porous perovskite CaMnO_3 prepared through a sol-gel method by citric acid and applied it as an electrocatalyst for lithium-air cells [44]. The CaMnO_3 electrode exhibited an overpotential of 0.98 V , which was lower (620 mV)

than that of the only carbon electrode at a limited capacity of 500 mAh g⁻¹ with a current density of 50 mA g⁻¹. Moreover, the CaMnO₃ electrode showed stable cycles up to 80 cycles with a discharge platform higher than 2.35 V. In contrast, the only carbon electrode maintained less than 25 cycles with a current density of 100 mA g⁻¹ at a limited capacity of 500 mAh g⁻¹.

Perovskites materials are attracted for their efficiency in lithium-O₂ cells in spite of their poor catalytic activity towards OER. They indicated low voltage during ORR, which in turn reduced the overpotential and enhanced the round-trip efficiency. Although perovskite oxides have been considered for lithium-air batteries, the impacts by partial substitution in both cation sublattices have not been comparatively inspected, and the mechanisms are still unknown. Therefore, further research on perovskite catalysts ought to be progressed in detail in the future to enhance the catalytic activity towards both ORR and OER to facilitate advanced lithium-O₂ batteries.

CHAPTER 3. METAL/METAL OXIDE-BASED CATHODE MATERIALS IN LITHIUM-OXYGEN BATTERIES

The poor performance of the Li-O₂ batteries is generally related to the catalyst effect of the air cathode. Because oxygen reduction reaction takes place much slower than oxygen evolution reaction. As a result, unexpected side reactions could occur, covering the permeation pathway for electrolyte and oxygen gas diffusion and failing the battery capacity. So far, several materials have been intensively explored to overcome issues of Li-O₂ batteries, including transition metal oxides/carbides/nitrides [45], noble metals [46], graphene [47], and carbon nanotubes [48]. Carbonaceous materials are widely utilized in battery applications because of their high electronic conductivity, surface area, porosity, and lightweight [49]. However, carbon is unstable in the presence of Li₂O₂ and leads to the formation of irreversible lithium carbonate and other side products at the interface. These reaction intermediates cause large overpotential and block the oxygen and electrolyte pathway, eventually fading the cell's capacity and life cycle. Bruce et. al reported a systematic work on ORR performance of catalysts including Pt, Fe₃O₄, NiO, Co₃O₄, CuO, Fe₂O₃, La_{0.8}Sr_{0.2}MnO₃, and they have found the effect of the catalyst on the oxygen reduction was minor as the discharge voltage was similar for all catalysts whereas the charging voltage (OER) was significantly altered with the nature of the catalyst [50]. The apparent poor performance of these catalysts on OER might be due to the presence of carbon matrix, which increased the occurrence of side reactions. To prevent the occurrence of side reactions, carbon-free materials have been proposed as cathode materials in the lithium-O₂ cell, including metal oxides. Metal oxides (e.g., Fe₂O₃, Co₃O₄, MnO₂, and TiO₂) are one of the most convenient catalysts due to their low-cost, easy preparation, high catalytic activity, and chemically stable in the presence of Li₂O₂ [51,52]. For instance, Co₃O₄ nanoparticles can efficiently

decrease the charge voltage and enhance the cycling performance of a lithium-O₂ system. However, the oxides usually suffer from poor electronic conductivity results in lower specific capacity and sluggish ORR/OER kinetics. Consequently, to enhance the electrical conductivity and catalytic activity of metal oxides without using carbon additives, they can be served as supports for noble metals (e.g., Ru, Pd, Au, and Pt). Noble metals have been studied as both ORR and OER electrocatalysts for lithium-O₂ cells and have shown excellent stability and catalytic activity. The main work of this thesis is the construction of cathode materials based on MnO₂, TiO₂, and Ru. Their properties are discussed in the next sections.

3.1. Titanium Oxide

TiO₂ is a unique semiconducting transition metal oxide material that has several beneficial properties (e.g., high photocatalytic activity, non-toxicity, biocompatibility, a wide bandgap, excellent resistance to chemical erosion, and thermal and chemical stability) [53]. As such, this material has been used in a wide range of applications, such as a component in solar cells, pigments, ceramics, cosmetics, sensors, pharmaceuticals, catalysts, self-cleaning systems, and batteries [54,55]. Additionally, TiO₂ is an attractive electrocatalyst with excellent electrochemical activities due to its high stability, unique physicochemical properties, and improved safety when compared with carbon materials [56,57]. Zhao et al. studied the use of TiO₂ nanotubes as a support material for electrocatalysts (Pt and RuO₂), thereby enhancing the cycle life of a Li-O₂ battery. They reported that the stability of TiO₂ was remarkably better than that of carbon; specifically, TiO₂ reduced side reactions and electrolyte decomposition [58].

TiO₂ demonstrates three crystalline forms: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) (Fig. 3.1). Anatase and brookite phases are transformed into rutile when the calcination temperature reaches above 600 °C. Generally, the anatase phase is the most active polymorph and has a higher degree of hydroxylation than the other phases. It also has unique chemical and physical properties and a

larger gap band than rutile [59]. Moreover, anatase can store much lithium and shows high lithium diffusivity [60].

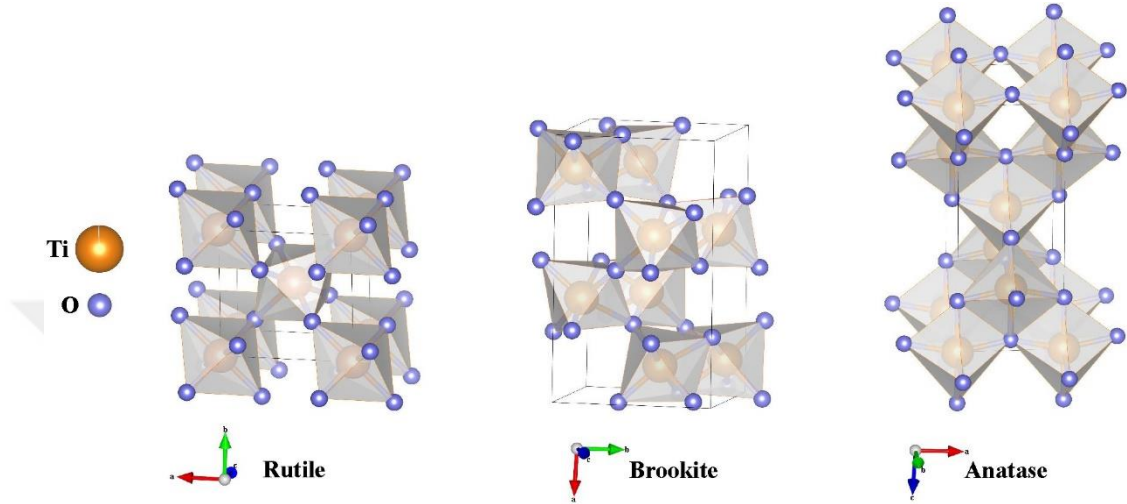


Figure 3.1. Polymorph crystalline phases of TiO_2 .

3.2. Manganese Oxide

As one kind of metal oxides, MnO_2 has drawn extensive attention in various applications such as catalysts [61], batteries [62], sensors [63], and photocatalysts [64], owing to its low toxicity, abundance, and high catalytic activity. Various crystalline structures of MnO_2 are existed including α , δ , γ , λ , β , and ϵ (Figure 3.2.) due to the linkage of the MnO_6 octahedral in different ways, that results in the variation of chain and tunnel structures. MnO_2 properties rely on crystalline structures and morphologies. For instance, Bruce et al. reported the catalytic activity of various manganese oxides, including γ -, λ -, β -, α - MnO_2 , Mn_2O_3 , and Mn_3O_4 [65]. Their results indicated that α - MnO_2 is the most efficient catalyst among them as the electrocatalyst for lithium- O_2 cells at a capacity of 3000 mAh g^{-1} . Recent experimental and theoretical calculations are devoted that α - MnO_2 with a large tunnel structure (2x2) is suitable for storing sufficient alkali cations (e.g., Li^+ , Ba^{2+} , Na^+ , K^+), therefore, showing good catalytic performance in the batteries. On the contrary, β - MnO_2 possesses a narrow tunnel size of (1x1) which cannot

accommodate a sufficient number of cations [66]. Besides the critical role of crystalline structure, the morphology of MnO_2 also significantly influences the electrochemical performance of the lithium- O_2 cells. MnO_2 has been known for its high specific capacity, low charge potential, and superior ORR activity. However, the electrochemical performance of the battery is influenced by different parameters, such as particle size, surface area, porosity, and morphology. These parameters can be adjusted during the synthesis of metal oxides. Therefore, it is vital to elucidate the growth behavior and evolution of morphology and crystalline structure for efficient integration and control of nanostructures.

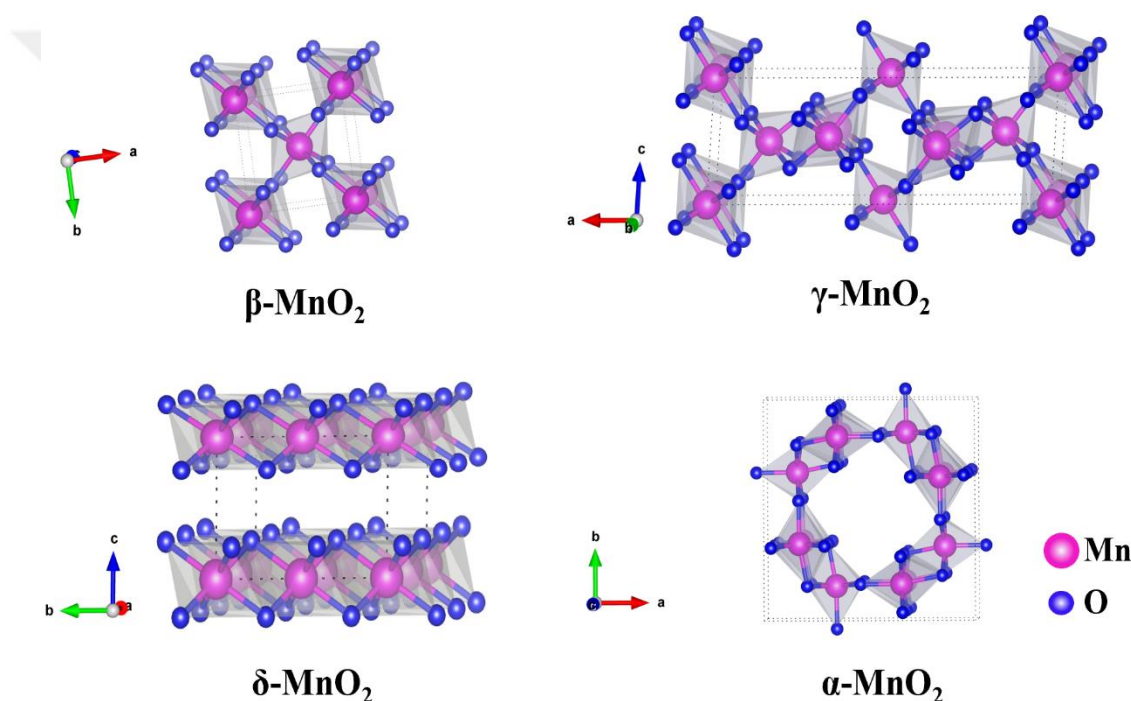


Figure 3.2. The MnO_2 polymorphs with well-defined crystalline.

3.3. Ruthenium

Ruthenium-based materials containing metallic ruthenium and ruthenium oxide have been dynamically investigated as catalysts in different chemical and electrochemical oxidation reactions. Jung et al. explored the electrocatalytic activity of Ru-based nanostructures decorated on reduced graphene oxide (rGO) to enhance the OER in lithium- O_2 batteries. They demonstrated the hybrid Ru-based rGO electrode with a

charging potential of 3.7 V at a high current density 500 mA g⁻¹ [67]. The Shao-Horn group approved the RuO₂ has good catalytic activity for oxygen evolution in acid and alkaline aqueous solutions and higher stability than that of ruthenium-carbon compounds [68]. Therefore, Ru-based materials have been considering as a superior catalyst in Lithium batteries.

3.4. Metal Oxide-Based Nanocomposites

Currently, the metal oxides and their composites have been significantly evaluated to evolve competitive ORR and OER electrocatalysts over the precious metals for high-performance lithium-O₂ batteries. Emerging two different catalysts in the form of nanocomposite/hybrid catalysts has been established to accomplish the limitation of one catalyst by synergistic effect. Among metal oxides, titanium dioxide (TiO₂) has been highly regarded in energy storage because of its abundance, non-toxic, low cost, good resistance to corrosion, and high thermal and chemical stability [69]. Nevertheless, TiO₂ has low conductivity and sluggish transport kinetics for both electrons and Li⁺ ions, hindering the optimal electrochemical performance from TiO₂ cathode. Therefore, developing TiO₂-based composites has been studied. Kim et al. [70] and Zhao et al. [71] have fabricated TiO₂/RuO₂ composites to enhance conductivity and ORR activity of air electrodes for Li-O₂ batteries. They have reported a lower charge potential (3.7 V) for RuO₂ than only carbon (4.35 V). Moreover, the TiO₂ based cathode materials reduced the side reactions resulting in stable capacity behavior.

Recently, the synergistic effects of TiO₂ and MnO₂ have been explored for electrochemical energy storage applications [72,73]. Su et al. have reported the synthesis of a double-shell hollow structured MnO₂/TiO₂ through a two-step template method as an anode material for lithium-ion batteries [74]. Chen et al. has fabricated TiO₂/MnO₂ nanocomposites via two-phase wet chemical approach for photocatalysis purposes [75].

Wang et al. covered α -MnO₂ with Co₃O₄ nanoparticles to utilize the benefit of the two-catalyst catalytic activity [76]. The hybrid catalyst indicated a specific capacity 3900 mAh g⁻¹ with cyclability over 60 cycles at a limited capacity of 1000 mAh g⁻¹.

3.5. Metal Oxide Synthesis Techniques

As discussed earlier, electrocatalysts as cathode materials display a significant role in accelerating the performance of lithium-O₂ systems. They should possess a stable porous structure to provide discharge product storage and pathways for O₂ diffusion. Moreover, the catalysts need to have high electrolyte wettability to provide ionic transfer upon the (dis)charge states. Notably, the cathode materials, including the catalyst, need to promote both ORR and OER kinetics. The appropriate cathode material with excellent design, shape, and crystal forms can provide higher voids for storing discharge products and enhancing the O₂ diffusion. The porosity, pore volume, surface area, and pore size of the cathode are reported to have significant impacts on the Li-O₂ batteries' performance (Figure 3.3.).

Bey et al. fabricated Li-O₂ cells by phenol-formaldehyde-based activated carbon by various mesopore volumes and reported the discharge capacity could be enhanced with increasing mesopore volume, and a capacity of 1852 mA h g⁻¹ with a current density of 70 mA g⁻¹ could be delivered by a pore volume of 1.8717 cm³ g⁻¹ [77]. It is suggested the cathode with a large surface area is advantageous for increasing the discharge capacity by the high active site numbers to deposit the discharge products. However, along with the surface area, other factors affect the performance, particularly pore size and the dispensation in the electrode. When the pore size is so minor, as micropores, they can block easily, leading to discharge capacity fading. Nimon et al. presented the capacity of an electrode could be controlled by the volume of mesopores with a radius up to 10 nm [78].

The morphology of cathode materials is another key parameter in enhancing the performance of the lithium-O₂ battery. A significant challenge for study morphology effects on catalytic systems is the exploitation of methods that can provide

simultaneous control over particle size, density, film thickness, and substrate adhesion, among other factors.

The top-down and bottom-up methods are the two main fundamental procedures of metal oxides synthesis. The top-bottom methods involve a bulk material slice into nano-sized particles, including sputtering, ball milling, chemical etching, and laser ablation. Whereas in the bottom-up approach, the nanomaterials are assembled from atoms or molecules such as vapor deposition, spray pyrolysis, electrochemical deposition, sol-gel process, and atomic/molecular condensation (Figure 3.4). However, these methods suffer many challenges such as non-uniformity properties of nanomaterials, high-cost raw materials instruments, and involve poisonous and dangerous chemical agents.

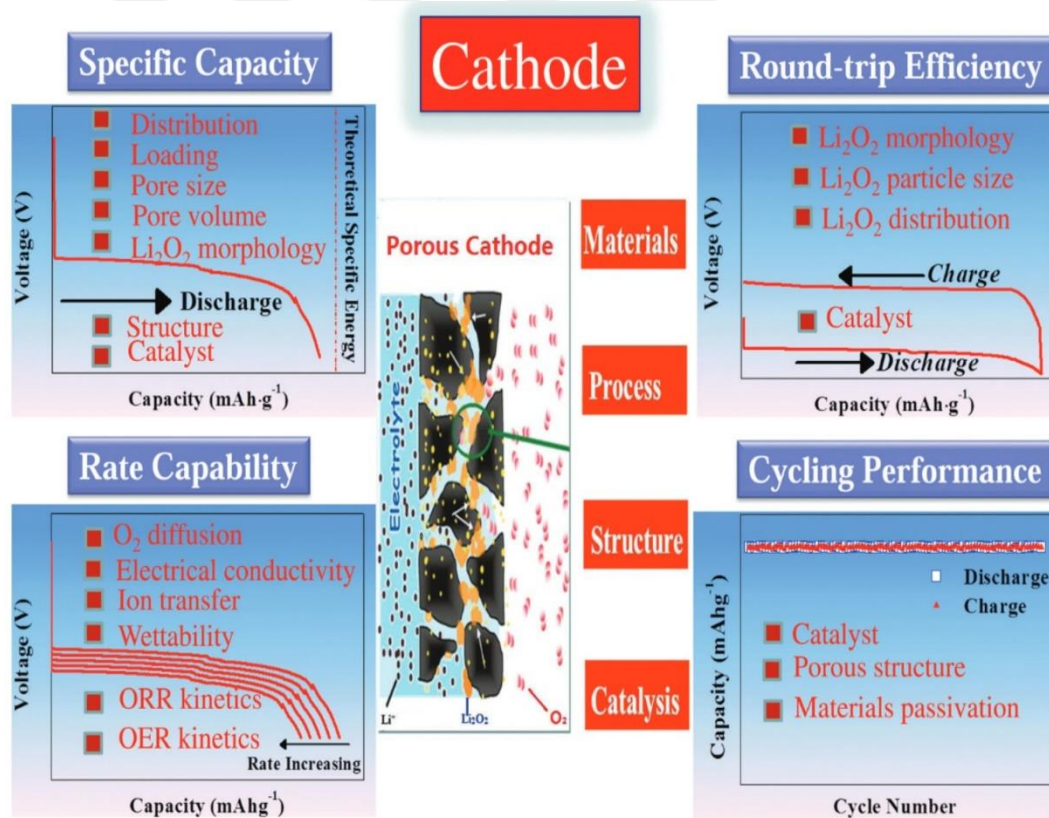


Figure 3.3. The properties of effective cathode materials for Li- O_2 battery [11].

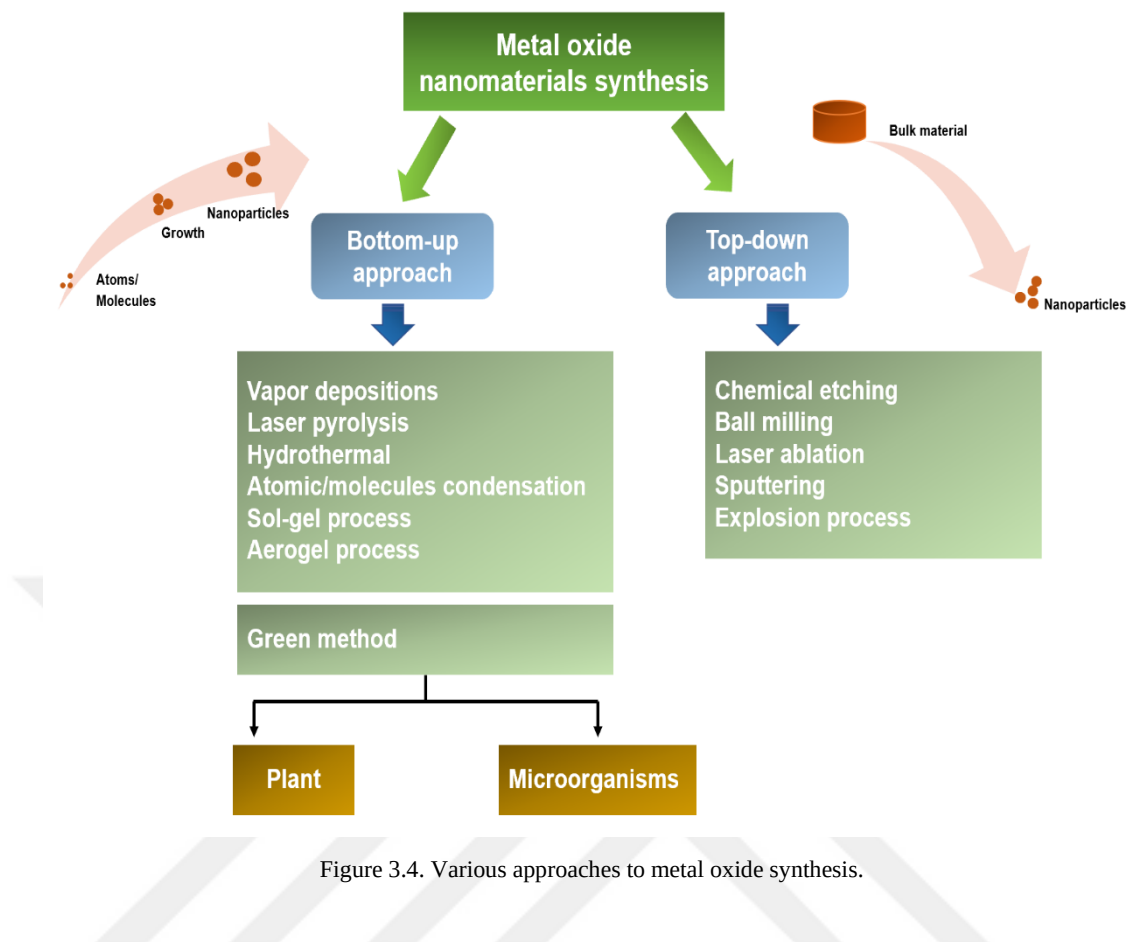


Figure 3.4. Various approaches to metal oxide synthesis.

In contrast, the green synthesis is a relatively facile, environmentally friendly, easy-to-control, less expensive, and non-toxic process. So far, different biological materials have been utilized for inorganic materials synthesis, including viruses, bacteria, diatom, plants (stem, peel, seed, flower, leaves), and proteins (Figure 3.5.). Here, some previous reports on synthesis metal oxides nanomaterials using biomaterials have been discussed.

Plant extracts do not need a cell culturing process and, thus, are suitable for large-scale production. According to previous research, biomaterial contains biomolecules that act both as stabilizing and reducing agents in the biosynthesis of nanoparticles. Many researchers have used the green method to fabricate metal and metal oxide nanoparticles such as gold [79], silver [80], copper oxide [81], palladium [82], ruthenium oxide [83], and reduced graphene oxide [84] for various applications (e.g., drug delivery, antibacterial coating, environment, energy storage). Bio-TiO₂ nanoparticles are synthesized using different plant extracts such as *Cicer arietinum* L.

[85], *Ocimum Tenuiflorum* [86], *Jatropha curcas* L. [87], *Calotropis gigantea* [88], *Alcea* and thyme [89], and *Vitex negundo* Linn [90].

Recent studies have shown that the green method is an alternative to chemical methods and produces better energy materials. For instance, Kashale et al. studied the incorporation of biosynthesized TiO_2 from soaked Bengal gram beans in lithium-ion batteries. The Bio- TiO_2 electrode had a high reversible capacity of 164 mA g^{-1} after 60 cycles, with 98% capacity retention [91].

Fungi have exhibited tremendous potentials for the preparation of different metal oxide nanomaterials with varieties of sizes and shapes. A fungus belongs to eukaryotic organisms containing biomolecules (e.g., enzymes, proteins, and other reducing agents) in its surface cell. Therefore, they have been utilized in the production of different metal oxide nanoparticles as stabilizing agents. Previous reports have shown the synthesis of silicon oxide, Titanium oxide, and magnetite nanoparticles by the fungus *Fusarium Oxysporum* [92]. Other metal oxide nanoparticles, including bismuth oxide [93] and barium titanate [94] were produced using *Fusarium Oxysporum*.

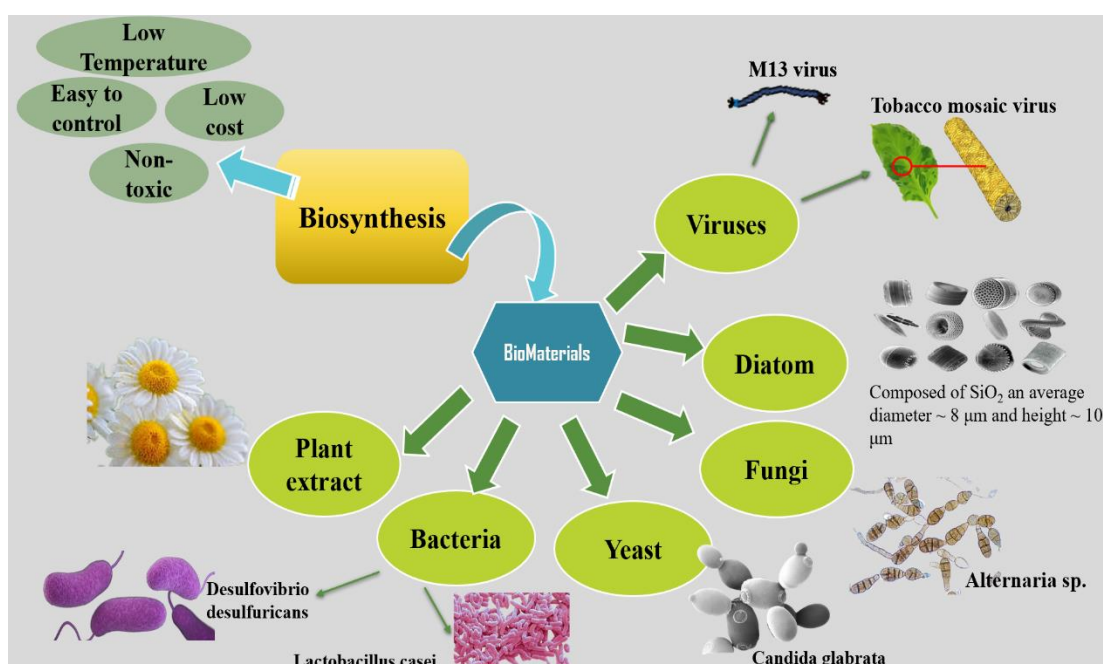


Figure 3.5. The concept of biosynthesis is to utilize biomaterials to obtain nanoscale materials in an eco-friendly and biocompatible process.

Algae belong to the kingdom Protista with ranging from unicellular to multicellular type. There are few reports on the synthesis of metal oxide by algae due to the presence of bioactive components in their cell walls. For instance, the preparation of zinc oxide has been reported using *Chlamydomonas Reinhardtii* [95], *Sargassum muticum* [96], and *Gracilaria gracilis* [97].

Recently, the bio-templating method has been proposed to synthesize the uniform structure of metal oxide nanomaterials. Biological systems are valuable examples of self-assembly to obtain inorganic materials through the biomineralization process. The bio-templating method offers non-toxic, safe, and eco-friendly substances for the preparation of desired materials. As shown in Figure 3.6, the bio-templating method has been used for inorganic materials synthesis via nature to engineered approaches. Biomineralization is a widely perceived procedure whereby biological organisms conduct the assembly of inorganic material structures. This conducted assembly in biological systems often results in entangled architectures with hierarchical organization, which enable to control of crystal patterning and build up to meso- and macroscale morphological patterns. These biological systems have been utilized for various applications involved in drug delivery, solar cells, batteries, semiconductors, and biomedical.

Chen et al. have utilized the Tobacco mosaic virus to fabricate nickel/silicon anode for Li-ion batteries [99]. A virus-templated nanocomposite electrode architecture revealed a higher capacity (3300 mAh g^{-1}) over currently available graphite anodes (372 mAh g^{-1}) with remarkable cycling stability.

Variety viable strategies have been attempted to determine different morphologies of MnO_2 (e.g., nanowires, nanoparticles, nanorods, nanobelts, nanosheets, hollow structures, and nanotubes) [100-102] by controlling experimental conditions. One-dimensional (1D) nanostructure has received intensive attention among various morphologies, which originated from their rapid electron transfer and high aspect ratio. Multiple approaches have been dedicated to fabricating 1D nanostructures such

as hydrothermal, pulsed laser deposition, vapor depositions, arc discharge, and electrodeposition [103,104].

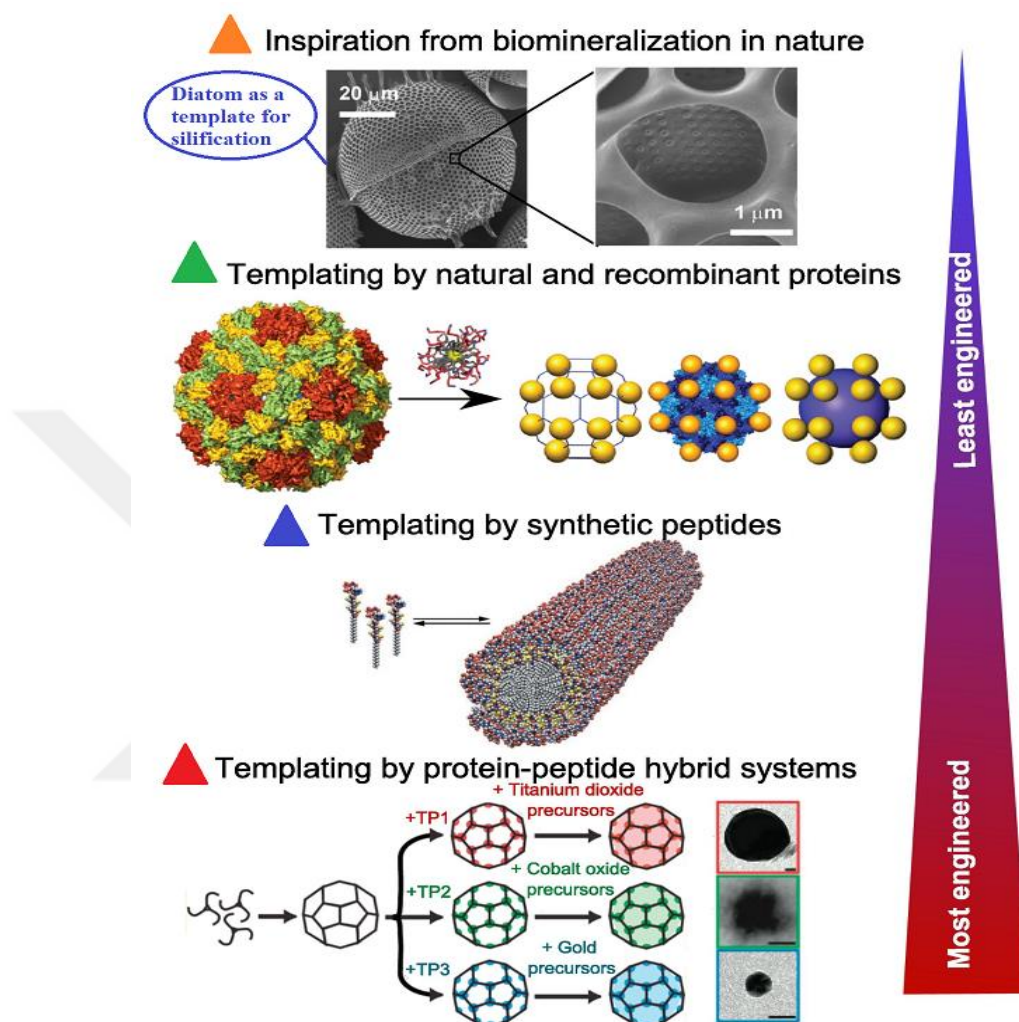


Figure 3.6. Outline of strategies for bio-templating of inorganic materials inspired by nature to engineered biological systems [98].

However, these methods require high temperature, consuming high energy, and expensive instruments. Besides, modulating the 1D morphology with uniform length and diameter is difficult in high temperatures. Therefore, templating methods, particularly, natural templates have been used for nanostructure syntheses, such as bacteria, diatom, peptide, DNA, and viruses due to their unique morphologies, nanosized scale, and eco-friendly features. Among them, M13 bacteriophages (phage) possess unique properties, such as a high aspect ratio (6.5 nm in diameter and 880 nm length), multifunctional, scale-up amplification, and self-assembly

[105,106]. M13 phage is a virus that infects bacterial cells (*Escherichia coli*) and utilizes their system cell to replicate. The surface of the M13 phage is composed of a major protein (PVIII, 2700 copies) with a negative charge due to the presence of glutamate (E) and aspartate (D) amino acids, which could interact with cationic metal ions at pH >5. There are five copies of each protein: PIII, PVI, PVII, PIX, which are located at two tips of the virus. By modification of M13 genomes, each protein's functionality can be altered, and then it can provide a specific affinity for various materials, including metals [107], metal oxides [108,109], graphene [110], and carbon nanotubes [111]. M13 has been used to fabricate nanowires, nanocomposites, and nanoparticles for different applications, such as sensors, electronic devices, food industry, batteries, drug delivery, solar, and cathode materials [112-115].

A high aspect-ratio titanium dioxide nanowires (NWs) were synthesized by Chen group [116]. The M13 viruses were used as templates and applied as efficient photoanodes. The results were compared with traditional nanoparticle-based photoanodes. Figure 3.7. illustrates a schematic view of the anatase TiO_2 (n- TiO_2) NWs network fabrication process using M13 viruses as templates.

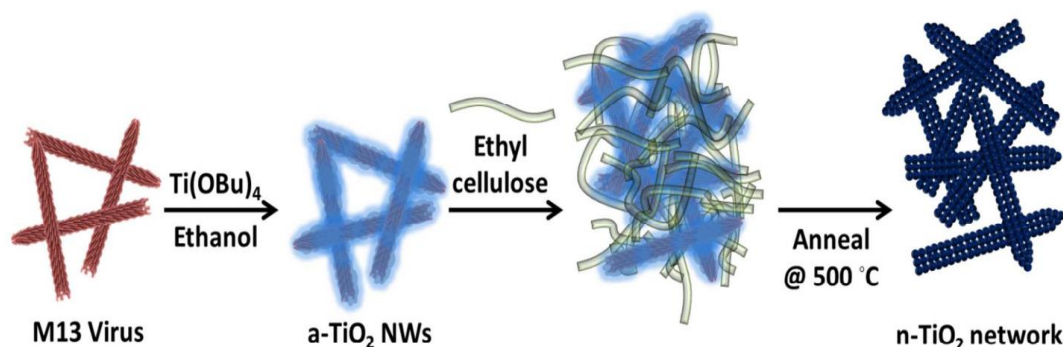


Figure 3.7. A schematic view of the anatase TiO_2 (n- TiO_2) NWs networks fabrication process uses M13 viruses as templates [116].

Diatoms are also widely found as a silicon source and template to synthesize porous Si in many applications, such as water purification, filtration, environmental remediation, optical sensing, and drug delivery due to its excellent properties, which include high porosity, surface area, biocompatibility, chemical stable, and low cost

(Fig. 3.8.). Li et al. [117] have reported the preparation of 3D MnO₂ using three diatom types with a template-assisted hydrothermal procedure. The as-prepared product employed for supercapacitors and their result demonstrated the high specific capacitance of 371.2 F g⁻¹ with a scan rate of 0.5 A g⁻¹ and a long cycle for 2000 cycles with a scan rate 5 A g⁻¹.

Using bio-inspired materials is increasingly investigating in inorganic nanotemplating. Biological systems enable architectural control over nanomaterial structure that is formidable to obtain by conventional synthetic methods. Therefore, The approach to precisely template inorganic nanomaterials will be vital to developing next-generation nanomaterials.

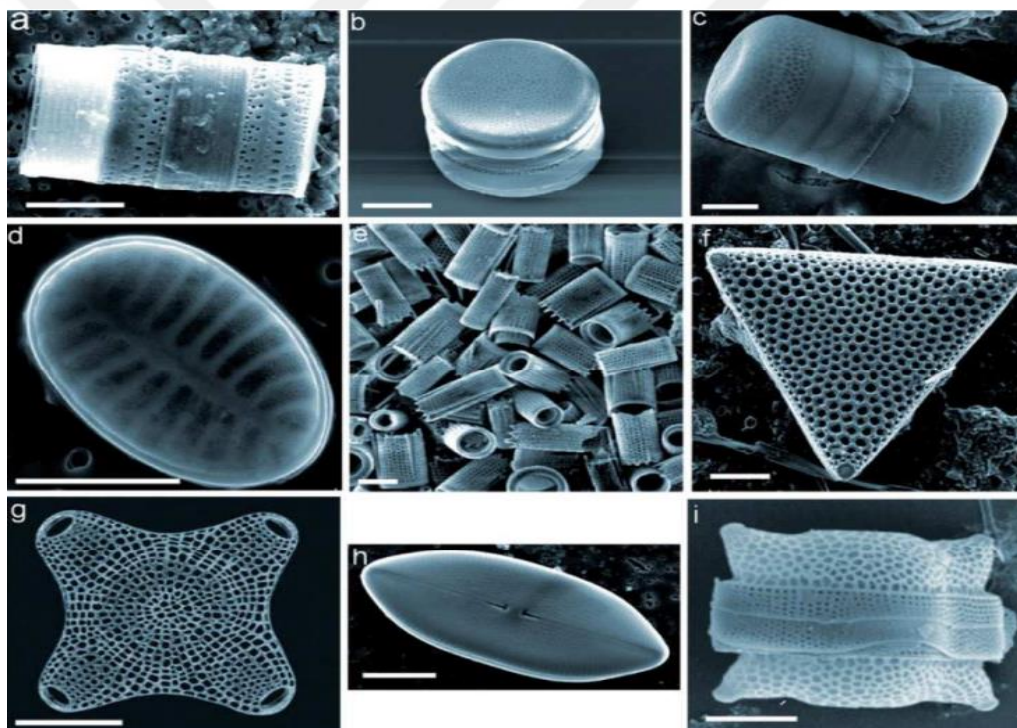


Figure 3.8. Various shapes and structures in diatom species are composed of silica [117].

CHAPTER 4. EXPERIMENTAL DESIGNS

4.1. Preparation Of Metal Oxide-Based Electrodes

The compositions of all electrodes produced within the scope of the thesis are given in Table 4.1. As metal oxides suffer from low conductivity, carbon black with different weight % was added to evaluate the electrochemical performance of electrodes. Besides, carbon-free virus-templated Ru/ α -MnO₂ was prepared to understand the impact of carbonaceous and free-carbon materials on Li-O₂ cell performance.

Table 4.1. Composition of electrodes produced within the scope of the thesis.

Electrode Composition	Carbon contents
Titanium oxide/Carbon	5%
Bio-titanium oxide/Carbon	5%
Bio-titanium oxide/Carbon	10%
Core-shell TiO ₂ / α -MnO ₂	10%
Virus-templated polymorphs MnO ₂ /Carbon	10%
Virus-templated Ru/ α -MnO ₂	-----

4.2. TiO₂ Synthesis Through A Green Method

4.2.1. Plant material

The dried flowers of chamomile were purchased from a local market in Sakarya, Turkey.

4.2.2. Chemical agents

All the chemicals were purchased from Aldrich-Sigma. Titanium tetraisoperoxide (TIIP, 97%), absolute ethanol, acetone, Ruthenium chloride (RuCl_3), Manganese (II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%), Potassium Permanganate (KMnO_4 , 99%), and double-distilled water (dd-water) were used.

4.2.3. Plant extract preparation

For the extraction of phytochemicals from Chamomile flowers, acetone and ethanol were used to prepare the plant extract. The presence of organic materials in the Chamomile extract was then confirmed using UV/vis spectroscopy. The chamomile plant (*Matricaria chamomilla*) is one of the oldest aromatic herbs in the Asteraceae family. It contains a broad range of biomolecules, including terpenoids, phenolics, caffeic acid, coumarin, and flavonoids, all of which serve as reductants and stabilizers in the formation of TiO_2 due to the presence of active functional groups in their structure. Apigenin has been identified as the main constituent of dried Chamomile flowers (840 mg/100 g) [118].

10 g of dried Chamomile flowers were weighed and dispersed overnight in 100 ml of acetone and ethanol in this study. The solution was then filtered to obtain a clear solution using Whatman filter paper. The Chamomile extract was kept at 4°C until required.

4.2.4. Biosynthesis of TiO_2 nanoparticles

For the biosynthesis of TiO_2 , two different solvents, such as ethanol and acetone, were used. One milliliter of titanium tetraisopropoxide (TTIP, Aldrich 97.0 percent) was dissolved in 160 mL acetone and stirred for 30 minutes in the first experiment. Then, 20 ml acetic chamomile extract was applied dropwise to the titanium solution until the pH reached 5. The biomolecules in the plant extract changed the color of the mixture from white to yellow. The color change signified the

encapsulation of TiO_2 by biomolecules, which helps to prevent nanoparticle aggregation. To condense the particles, the suspension was stirred for 4 hours at 50°C , then centrifuged and washed with a mixture of distilled water and ethanol. The collected yellow powder was then dried overnight in a 60°C oven. The solid powder was calcined at 400°C for 2 hours in a muffle furnace, causing the powder's color to turn to milk-white, indicating that organic content had been removed. (Fig. 4.1). A similar process was then used to investigate the impact of pH on Bio- TiO_2 NPs, with the pH being changed to 7 and 10 using 23 percent ammonia. The resulting products were given the names Bio- $\text{TiO}_2/7$ and Bio- $\text{TiO}_2/10$, respectively.

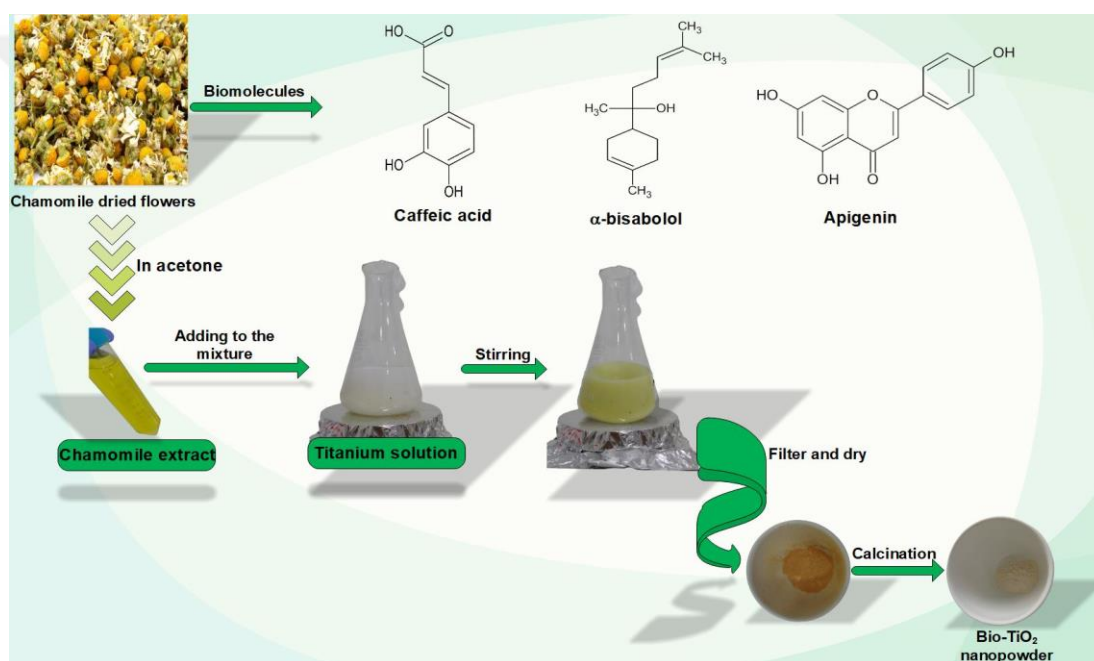


Figure 4.1. Schematic illustration of Bio- TiO_2 nanoparticles synthesis action via a green method.

In the second experiment, 140 ml dd-water was mixed with 1 ml titanium tetraisopropoxide in 40 ml absolute ethanol and stirred for one hour. After that, 20 mL chamomile extract was applied to the mixture, which was then stirred for 5 hours at 60°C . After stirring, the Bio- TiO_2 NPs solution was centrifuged for 10 minutes at 5000 rpm and rinsed with ethanol and water. To extract organic materials and increase crystallinity, the Bio- TiO_2 powder was calcined at 450°C for 2 hours.

4.3. TiO₂ Synthesis Via Sol-Gel

A beaker was filled with 38 mL absolute ethanol and 2 mL titanium tetraisopropoxide, which was stirred. The solution was then stirred for 1 hour with 160 ml distilled water containing 4 grams urea (as the hydrolyzing agent to stabilize the hydrolysis process) (hydrolysis step). HNO₃ was used to control the pH of the solution drop to 4. After that, 100 mg sodium dodecyl sulfate (SDS) surfactant was applied to stabilize the particles and prevent agglomeration. This suspension was heated for one hour at 80°C in a water bath (condensation step). Afterward, the product was separated and washed by centrifugation at 6000 rpm for 5 minutes and dried at 60 °C for 24 hours. The calcination step was performed at 400 °C for 2 hours to improve crystallinity and obtain the anatase phase of TiO₂ (C-TiO₂).

4.4. Synthesis Of Core-Shell Nanostructured TiO₂/α-MnO₂

To synthesize urchin-like core-shell TiO₂/α-MnO₂ nanostructures, 50 mg synthesized Bio-TiO₂ (Prepared by ethanol solvent) white powder was sonicated in 100 ml dd-water. Then, 120 mg MnSO₄·H₂O was added into the Bio-TiO₂ aqueous solution, followed by stirring overnight at room temperature. Afterward, 33 mg KMnO₄ was added to the solution and kept stirring at different durations (6, 12, 24 h). Next, the obtained brown product was collected and washed by centrifugation and vacuum filtration, respectively. The as-prepared sample was dried overnight at 60 °C.

4.5. Preparation Of Polymorphs Virus-Templated MnO₂ Nanowires

Propagation and purification of M13 phage: E.coli ER2738 (New England Biolabs Inc.) was used as the host bacteria for M13 phage infection. The phage propagation was conducted by incubating 50 µl overnight E. coli culture with 5 µl M13 phage from the stock (ATCC® 15669B1™) into 50 ml LB (Lennox broth) containing tetracycline (0.05 g L⁻¹) at 37 °C for 18 hrs in an incubator shaker (200 rpm). The LB medium was comprised of 5 g L⁻¹ yeast extract, 10 g L⁻¹ tryptone, and 5 g L⁻¹ sodium chloride (pH 7.8). The cells were harvested by centrifugation at 8000 rpm for 10 min

at 4 °C. The pellet at the bottom, which is composed of bacteria cells, was discarded. The supernatant containing M13 phage was purified by transferring it into a conical tube containing cooled 20% PEG-8000/2.5 M NaCl solution in a 1:4 volume ratio and inverted to mix. Afterward, the tubes were kept overnight at 4 °C. The phages were centrifuged and precipitated at 11000 rpm for 25 min at 4 °C. A white pellet was observed (Figure 4.2.a), which is the M13 phage. The pellet was resuspended in 2 mL sterile water and dissolving that pellet. Then, a 1:4 volume ratio of 20% PEG-8000/2.5M NaCl solution was added and inverted to mix. Then the tube was incubated at 4 °C for 20 minutes. The tube was spined at 11000 rpm for 15 minutes. The supernatant was aspirated and resuspend the pellet in 1 mL tris buffer saline (TBS, 50 mM tris-HCl, 150 mM NaCl, PH 7.8), and transferred into an Eppendorf tube and stored at 4 °C.

The concentration of phages was determined by spectrophotometer, rely on the absorbance of the virus in ultraviolet light at 269 nm and 320 nm. The phages concentration was calculated by the formula below:

Phage particles/ml = $(6 \times 10^{16}) \times (A_{269} - A_{320}) / (\text{number of DNA bases in the phage genome})$.

Phage concentrations were approved with an overnight plaque-forming assay. Phage samples were diluted 10^7 to 10^{10} -fold with TBS buffer by serial dilution. A hundred microliters of each diluted sample were mixed with 200 μL of E. coli culture (containing 5 mM MgCl_2 to increase the yield of M13 phage), vortexed gently, and incubated at 37 °C for 15 min. Two hundred milliliter LB medium (with 15 g L^{-1} agar powder) was prepared using an autoclave and was evenly poured into glass Petri dishes. After the media solidified, each incubated sample was added to 3 ml soft agar and poured on the media. Petri dishes were incubated at 37 °C overnight. The plaques started to appear after 5-6 hours, indicating the phage infection slows down bacteria's growth. As shown in Figure 4.2b, the zones that are clear on the bacteria lawn indicate the infected cell by phage. This area is called plaque, and infected cells

grow less than uninfected ones. The plaques were also counted as plaque-forming units (PFU).

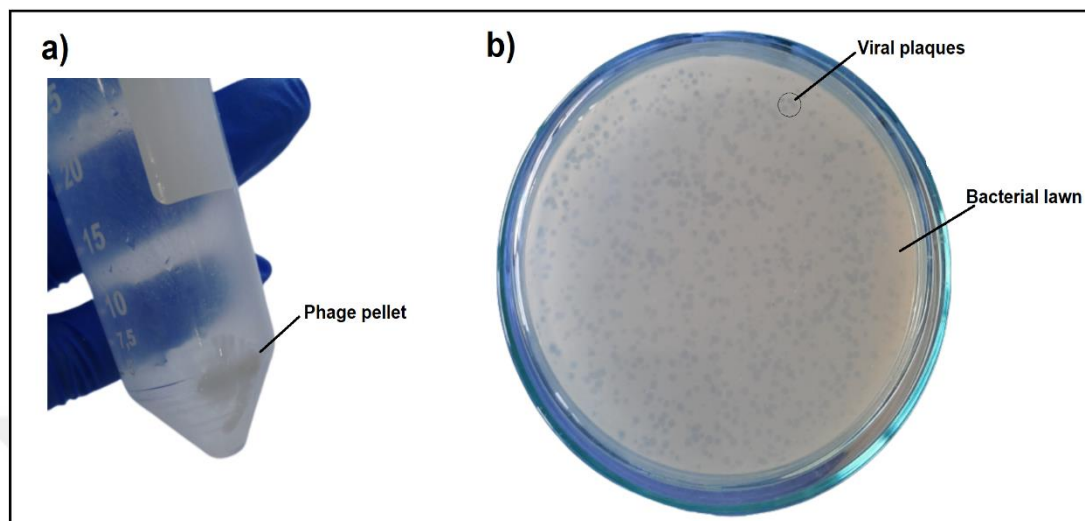


Figure 4.2. a) Phage pellet precipitated by PEG-NaCl, b) the plate shows a uniform (yellow) lawn of *E. coli* bacteria, on which M13 phages have formed visible plaques.

Preparation of polymorphs virus-templated MnO_2 nanowires: To obtain virus-templated MnO_2 nanowires, the process was controlled using a cold incubator, optimizing virus concentration and adjusting the pH of the initial solution to 10 during the reaction. The virus-templated MnO_2 was synthesized through a redox reaction similar reported by the belcher group [119]. In the typical synthesis, 5 ml manganese sulphate monohydrate solution (50 mM) was added to 30 ml of deionized (DI) water (pH adjusted to 10 by 23% ammonia) in a 50 ml conical tube. The wild-type M13 phage (1.4×10^{12} pfu ml^{-1}) was added to the solution. After the addition of the phages, the conical tube was inverted and placed on an orbital shaker and incubated at 4 °C overnight. 5 ml potassium permanganate solution (20 mM) was then added into the mixture, and the conical tube was inverted and incubated at 4 °C overnight. The obtained product was collected by centrifuged at 4000 rpm for 5 minutes and rinsed with DI water and collected by vacuum filtration, and freeze-dried. Here, the different volume ratio of $\text{MnSO}_4\text{:KMnO}_4$ was used to control the crystalline structure of MnO_2 (e.g., 2:8, 5:5, 8:2 for $\delta\text{-MnO}_2$, $\alpha\text{-MnO}_2$, and $\gamma\text{-MnO}_2$, respectively) and we have shown the effect of K^+ ions concentration in the formation of MnO_2 crystal phases.

Preparation of virus-templated Ru/ α -MnO₂ nanowires: To incorporate Ru nanoparticles on the surface of virus-templated MnO₂, the obtained bio-templated MnO₂ was dispersed into 30 ml DI water in a 50 ml conical tube by a brief ultrasonication. After that, 20 ml ruthenium (III) chloride (10 mM) solution was added to the mixture. The suspension was inverted three times and incubated at 4 °C for 2 hours. 500 μ l sodium borohydride (100 mM, NaBH₄) was dropwise added to reduce Ru ions and incubated at 4 °C overnight. The final solution was vacuum filtered and rinsed with DI water and then freeze-dried.

4.6. Electrolyte Preparation

1M lithium perchlorate (LiClO₄, Sigma Aldrich) was provided as an electrolyte. 1.069 g LiClO₄ was dissolved in 10 ml tetra (ethylene) glycol dimethyl ether (Sigma Aldrich) and stirred for 9 hours in a glovebox.

4.7. Cathode Preparation And Electrochemical Measurements

The first step toward preparing the cathodes was to produce a slurry by mixing the prepared active materials, Super P carbon black, and carboxymethyl cellulose (CMC) as binder into distilled water at an 85:5:10 or 80:10:10 mass ratio for carbonaceous electrodes and 90:10 for a carbon-free electrode. The slurry was then poured onto nickel foam (as a current collector), and a doctor blade was used to spread the slurry uniformly, as shown in Figure 4.3. The prepared cathode was dried in a vacuum oven at 90 °C to remove the solvent. The electrode was then cut into circles (18 mm diameter). The average loading of active materials on the nickel foam was approximately 0.8-1 mg. At last, the ECC-air cell (supplied from EL-Cell GmbH) were assembled in an argon-filled glove box. The cell was composed of the prepared electrode as the working electrode, lithium foils as anode and a glass fiber separator, and 1 M LiClO₄ as the electrolyte. The cells were purged with pure O₂ at a gas flow rate of 8 mL min⁻¹, and the cells rested 6 h before the initial test. Next, the ECC-Air cell was assembled in an argon-filled glove box. The charge/discharge test was carried out using Potentiostat/Galvanostat (Gamry Reference 1000) devices at a

constant current of 100 mA g^{-1} and 200 mA g^{-1} in the voltage window of 2 V to 4.5 V. The internal resistance of the cell was measured using electrochemical impedance spectroscopy (EIS), with frequency ranging from 1000 kHz to 0.1 Hz. Further, the reactions of the cathode active materials with Li^+ were investigated by cyclic voltammetry within the voltage range of 2.0 V to 4.5 V.

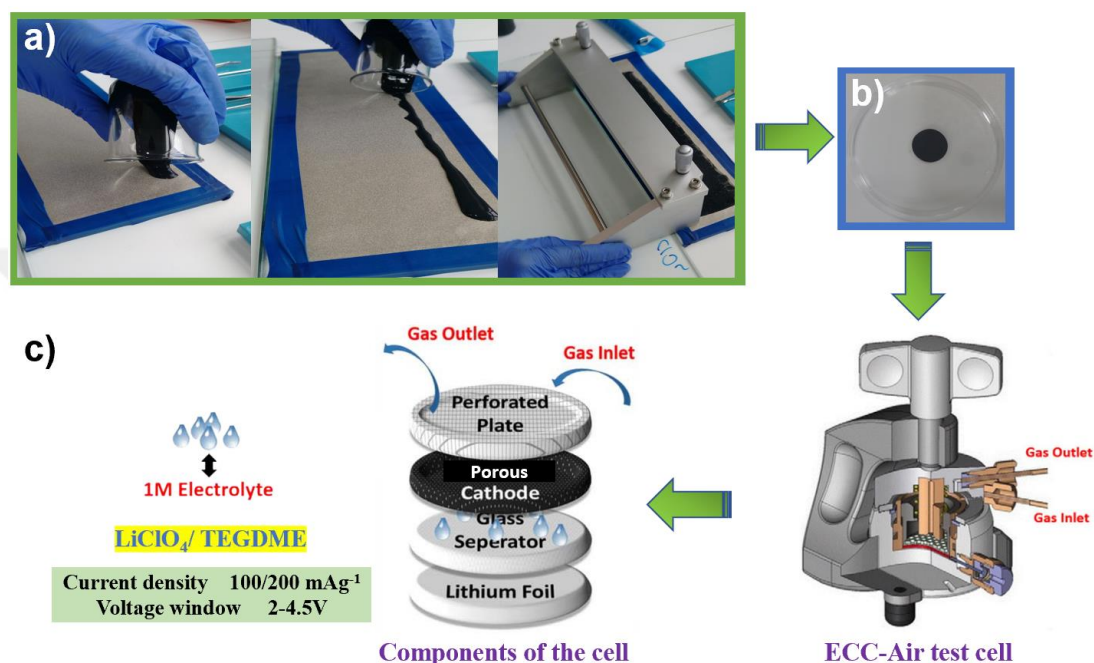


Figure 4.3. a) Cathode slurry and casting on nickel foam by a doctor blade, b) cut electrode into 18 mm, and c) ECC-air test cell and its components.

4.8. Instruments And Materials Characterization Techniques

The absorption spectra of the Chamomile flower extract aqueous solution were recorded using a UV/Vis spectrophotometer (Shimadzu UV-1900) to observe the presence of organic materials and the formation of TiO_2 NPs and to calculate bandgap. The scanning range of the samples was 200-500 nm. The concentration of M13 phages was calculated using a UV/VIS spectrophotometer at the wavelengths of 269 nm and 320 nm. To determine the charge surface of M13 phages, 1 mg mL^{-1} M13 phages were dispersed in several tubes with 23% ammonia with a pH value of 5, 7, 8, and 10, and charge surfaces measured with the particle analyzer (Malvern Zetasizer Nano ZS). XRD is an analytical technique used to identify the crystal phase

of TiO_2 , MnO_2 and, detection of discharge products and calculate the crystalline size of nanoparticles. XRD patterns were obtained on X-ray powder diffraction with a Rigaku D/MAX 2000 X-ray generator and diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) within the range of $5\text{--}90^\circ$. Raman spectroscopy is a spectroscopic technique used to detect a unique chemical fingerprint of molecules by observing Raman scattering from a sample. Raman spectroscopy was performed using the RamanRXN with a 785 nm laser excitation systems spectrometer. The spectra obtained were within the range of 200 to 1200 cm^{-1} . The morphology and grain size of the synthesized samples were determined by field emission scanning electron microscopy (FESEM, Quanta FEG 450) and FEI TALOS F2005 transmission electron microscopy (TEM) with an accelerating voltage of 15 kV and 200 kV , respectively. Then, the FESEM was coupled with an EDX detector to determine the elemental composition of the products.

The thermal behavior of the TiO_2 nanoparticles was recorded using TGA-DTA analyses (NETZSCH STA 449 F1). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out to examine the thermal stability of the nanoparticles. The analysis was performed, ranging from room temperature to 900°C at a heating rate of $10^\circ\text{C min}^{-1}$ in the air.

Fourier transform infrared spectroscopy (FTIR) was performed on an IRPrestige-21 Shimadzu spectrometer for discharged-charged electrodes. X-ray photoelectron spectroscopy (XPS) measurement (Thermo Scientific K Alpha spectrometer with a source of $\text{Al K}\alpha$ X-ray) was performed to analyze the chemical state of MnO_2 samples and the composition of Ru.

Finally, the nitrogen adsorption/desorption isotherms were measured at 77.3 K using a Micromeritics 3Flex analyzer. The surface area and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The surface area is crucial to studying the electrochemical performance of cathodes, as a high surface area means more active sites for oxygen reduction.

CHAPTER 5. RESULTS AND DISCUSSION

5.1. Physical Characterization Of C-TiO₂ And Bio-TiO₂ Nanoparticles

The formation mechanism of Bio-TiO₂ NPs using Chamomile extract is illustrated in Fig. 5.1. The first step is to investigate the reaction between the titanium tetraisopropoxide and acetone. Acetone sustained aldol condensation and water removal. The phytochemicals present in chamomile extract (e.g., apigenin) are assumed to possess functional groups in their structure. Thus, they are essential to Bio-TiO₂ formation. Functional groups of biomolecules bind to the surface of Ti⁴⁺ and form complexes due to the van der Waals, hydrogen bonds, and π - π interaction. Then, nucleation and crystal growth occur and encapsulate the TiO₂, which stabilizes, and forms compact and uniform nanoparticles. After calcination at 400 °C for 2 hours, the biomolecules are removed and form mesoporous Bio-TiO₂ particles.

Figure 5.2a represents the UV/Vis spectra of the Chamomile extract, Bio-TiO₂, and C-TiO₂ NPs. The UV/Vis absorption spectrum of Chamomile extract reveals the absorbance peaks in the region of 215 nm and 265 nm and a broad absorption of around 320 to 340 nm. The presence of these absorption peaks approved the existence of some active chemical components, including terpenoids, flavonoids (such as luteolin-7-O- β -D-glucoside and apigenin-7-O- β -D-glucoside), and coumarins [120]. TiO₂ can absorb most of the ultraviolet light with a wavelength below 400 nm because of its intrinsic bandgap of anatase-TiO₂ (3.2 eV). The Bio-TiO₂ NPs produced in the current study exhibited absorbance at a wavelength of 380 nm, which is higher than the wavelength at which C-TiO₂ nanoparticles exhibit absorbance (370 nm), perhaps due to the size effect as reported by Mohanraj et al. [121].

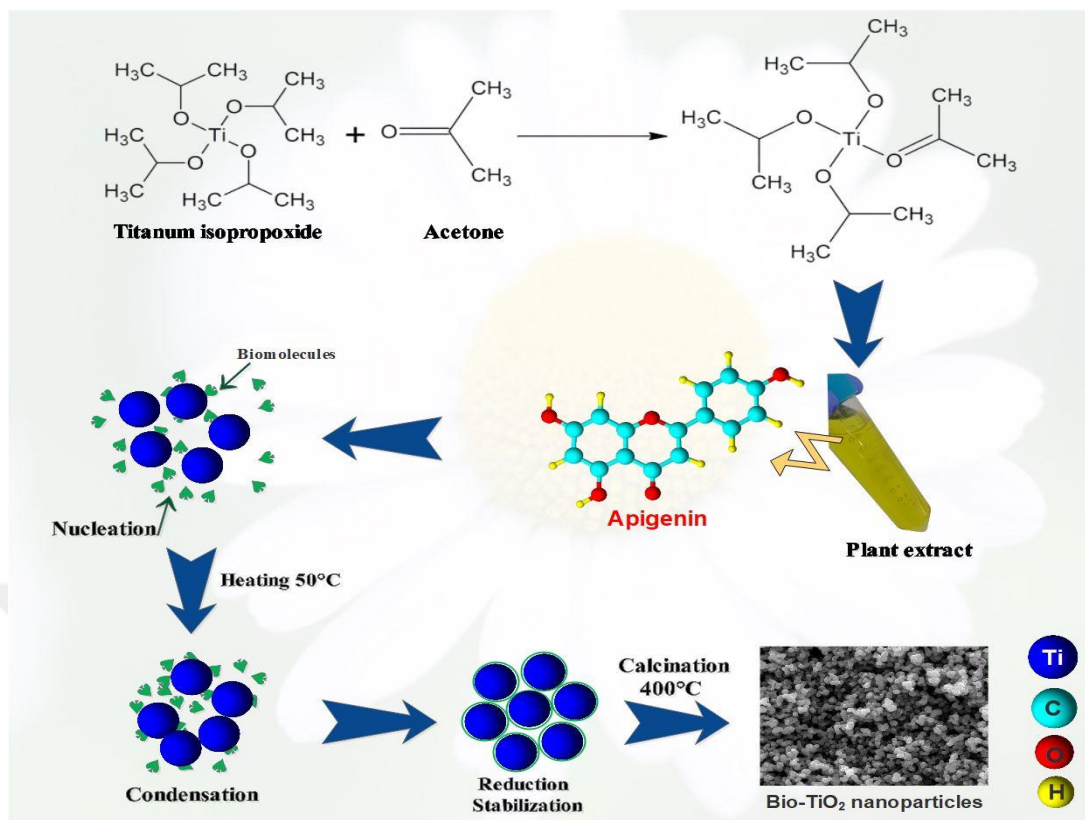


Figure 5.1. Schematic illustration for the formation mechanism of Bio-TiO₂ nanoparticles.

The DTA curve (black) of C-TiO₂ NPs (Fig. 5.2b) indicates a small exothermic peak at 400 °C, which could be associated with TiO₂ crystallization and confirm that the material has crystallized into anatase TiO₂. Also, the small peak observed at 680 °C shows the transition from anatase to the rutile phase. The TG curve (blue) illustrates that the first weight-loss stage occurred between 40 °C and 120 °C, associated with a loss of about 15% moisture. The second stage took place between 120 °C and 380 °C, in which the decomposition of organics generated by the hydrolysis of titanium isopropoxide was shown.

According to the DTA curves, TiO₂ particles crystallized at 400 °C. The XRD patterns of C-TiO₂ and Bio-TiO₂ nanoparticles are illustrated in Fig. 5.2c. Both samples show tetragonal anatase phases with diffraction angles 25.4°, 38.6°, 48.1°, 54.0°, 55.2°, 62.8°, 68.9°, 70.4°, 75.2°, and 83.3°, which correlate to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), (2 1 5), and (3 1 2) planes (JCPDS card No. 73-1764), respectively. The diffraction angle observed at 25.4° corresponds to the (1 0 1)

crystallographic plane of TiO_2 anatase. A weak peak at $2\theta = 30.8^\circ$ was observed in the XRD spectra of C- TiO_2 . This condition was attributed to the (1 2 1) plane of the brookite phase, which forms in the presence of an acidic medium during synthesis. The high crystallinity of TiO_2 NPs can be favorable for cathode material.

The Raman spectra of C- TiO_2 and Bio- TiO_2 nanoparticles exhibit three sharp peaks ranging from 200-1200 cm^{-1} (Fig. 5.2d.). Both TiO_2 samples exhibit the anatase crystal structure, which corroborates the XRD data. The modes located at 396.8 (B_{1g}), 516.1 (A_{1g}), and 640 cm^{-1} (E_g) are responsible for the Raman active modes of the anatase phase TiO_2 [122]. Meanwhile, the Raman active E_g modes of anatase are O–Ti–O bending type vibrations, and no other peaks were detected. These results indicate that the bio- TiO_2 nanopowders that were obtained possess the anatase phase only. However, a weak peak at 447 cm^{-1} was detected in Raman spectra of C- TiO_2 assigned to brookite phase of TiO_2 in consistent with the XRD result [123].

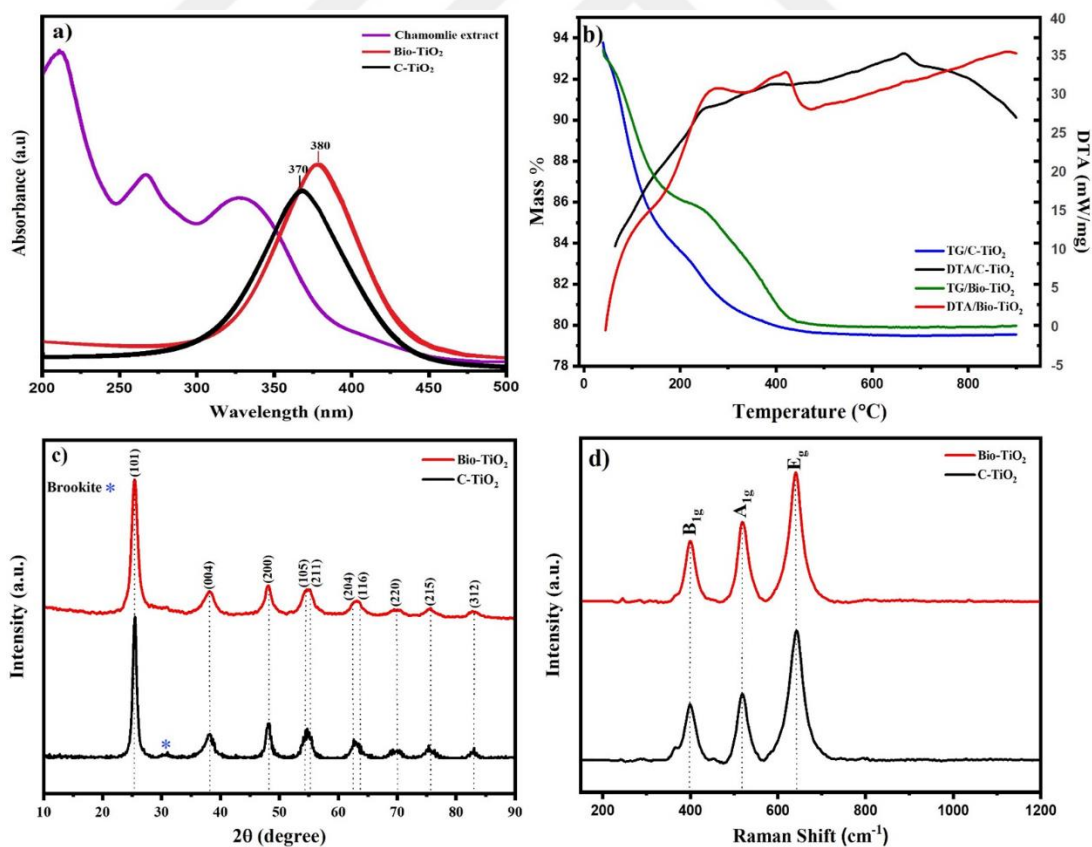


Figure 5.2. UV/Vis spectra of chamomile extract, Bio- TiO_2 , and C- TiO_2 (a), Thermal behavior of the C- TiO_2 , and Bio- TiO_2 Nanoparticles (b), the XRD pattern (c) and Raman spectrum of C- TiO_2 and Bio- TiO_2 NPs (d).

The grain size and morphology of the samples were studied using FESEM (Fig. 5.3.). The C-TiO₂ nanoparticles were spherical (150-300 nm in diameter) with slight aggregation in low and high magnification images (Figs. 5.3a. and 5.3b.). Bio-TiO₂ exhibited a cauliflower morphology composed of interconnected nanocrystals due to the high surface energy derived from small particles (10-20 nm) with a well-defined shape and low agglomeration (Figs. 5.3c. and 5.3d.). The small size and shape of the particles are caused by phytochemicals, which tend to stabilize and cap nanoparticles. Then, for both TiO₂ samples, the presence of Ti and O were recorded via EDS analysis (Figs. 5.3e-5.3f). Peaks were observed at 0.452 Kev (Ti-L λ) and 0.525 Kev (O-K α) without any impurities. The percentages of Ti (33 at.%) and O (66 at.%) determined by the EDS analysis indicate the successful synthesis of pure TiO₂ nanoparticles.

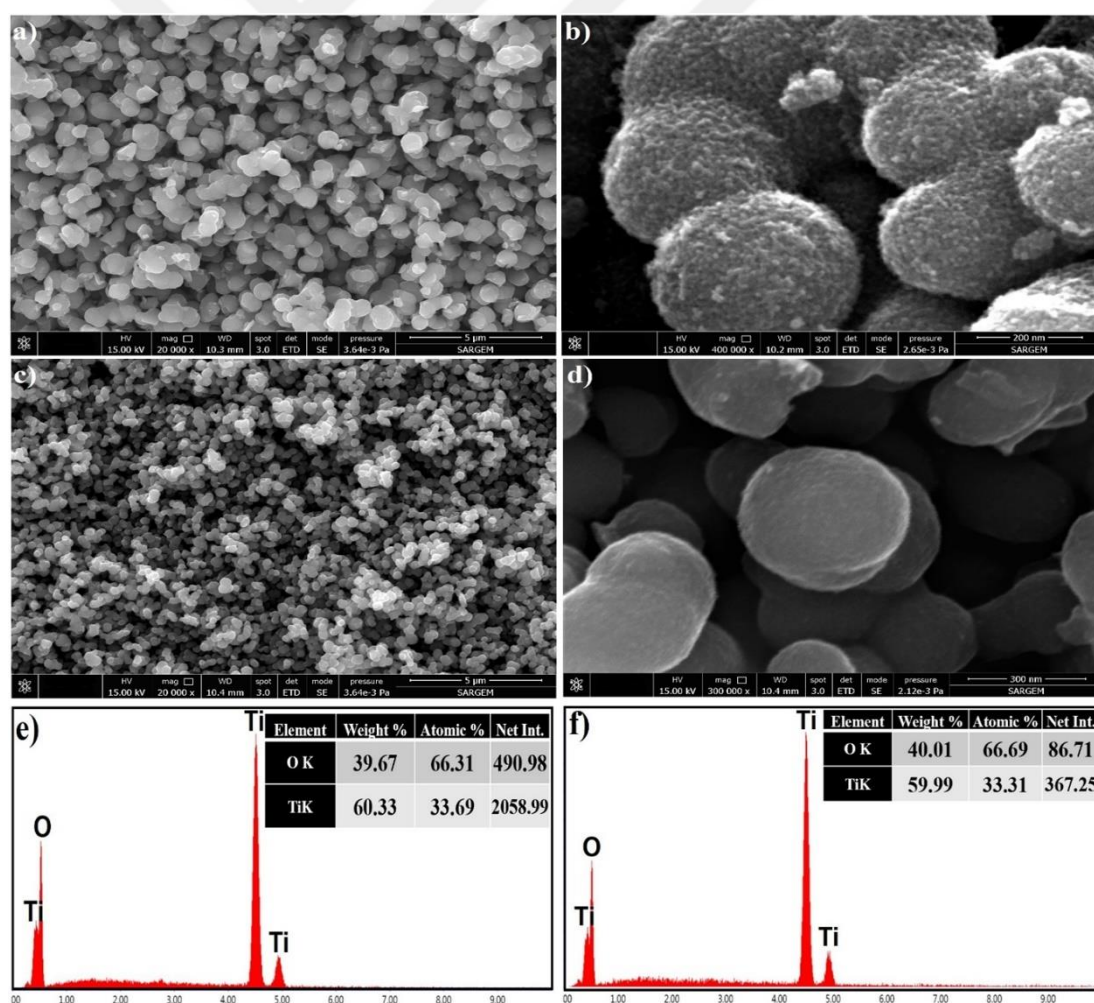


Figure 5.3. Low and high magnification FESEM images of C-TiO₂ (a,b), Bio-TiO₂ (c,d), and EDS analysis of C-TiO₂ (e) and Bio-TiO₂ NPs (f).

5.2. Effect Of PH Value On Bio-TiO₂ Nanoparticle Properties

In this section, we discuss the effect of pH on the structure of Bio-TiO₂ nanoparticles. An XRD was performed to study the structure and size of Bio-TiO₂ particles for different pH values (5, 7, and 10). The XRD spectrums of all the samples indicated the presence of anatase TiO₂, which is consistent with JCPDS card No. 73-1764 (Fig. 5.4a.). The crystalline size of the nanoparticles was calculated using Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (5.1)$$

Where D is the crystalline size of the nanoparticle, K is a constant crystalline shape factor (which equals 0.9), λ is the Cu-K α radiation wavelength (0.154 nm), β represents the full width at half maximum (FWHM) of the peak, and θ is the half diffraction Bragg's angle.

The crystallite sizes of the Bio-TiO₂ samples were estimated by applying to high-intensity peak (plane (1 0 1)), and results are noted in Table 5.1. The results reveal that increasing the pH of the initial solution reduces the FWHM of the diffraction peak. It also becomes narrower, suggesting that the crystallite size has increased. The crystallite size increased from 9 nm to 25 nm as the pH value was increased. This observation indicates that when the pH value was increased, the nanoparticles' nuclei were enlarged, thereby increasing their crystallinity. Similar findings were reported by Preetha et al. [124].

The UV-visible absorption spectrum was recorded within the range of 200 nm and 500 nm for Bio-TiO₂ samples (samples of Bio-TiO₂/5, Bio-TiO₂/7, and Bio-TiO₂/10 for pH values of 5, 7, and 10, respectively) (Fig. 5.4b). The UV-visible spectra of biosynthesized TiO₂ nanoparticles were used to determine the bandgap (E_g) using the Tauc method, which is a recommended technique to calculate the direct bandgap of semiconductors, as following formula [125]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5.2)$$

Where α is the absorption coefficient, A is a constant, $h\nu$ is the energy of the incident photons, and E_g is the energy bandgap. A linear fit was drawn from the maximum slope of the curve to the x-axis. The bandgap is the value of the intercept of the line with the x-axis. As shown in Fig. 5.4c, the bandgaps of C-TiO₂, Bio-TiO₂/5, Bio-TiO₂/7, and Bio-TiO₂/10 were 3.20, 3.10, 3.08, and 3.03 eV, respectively. This result confirms that the bandgaps of the products were reduced as the pH of the solution was increased. This finding is ascribed to the quantum size effect that arises from an enlarged crystallite size. The increase in particle size causes a significant change in the optical bandgap. Similarly, S. Muniandy et al. reported that increasing the pH solution decreases the bandgap values because of the localized gap states induced by Ti³⁺ self-doping [126].

The effect of pH on the surface area and pore size distribution of TiO₂ samples was investigated by performing N₂ adsorption/desorption measurements (Table 5.1). Regarding the isotherm of Bio-TiO₂ NPs synthesized at different pH values, all curves exhibited the Type IV isotherm with H3 hysteresis loop, thereby indicating a mesoporous structure according to IUPAC classification (Fig. 5.4d.). According to isotherms, increasing the pH value from 5 to 10, resulting in a decrease in surface area from 78 m²g⁻¹ to 30.4 m²g⁻¹, but the average pore size increases from 12.4 nm to 28.9 nm. These results indicated the pH variations have an essential effect on the surface areas and pore diameters. The high surface area at lower pH could be due to the small size of the nanoparticles and the presence of high numbers of active sites. A large specific area is expected to increase the number of active sites and the contact areas where interactions with Li⁺ and O₂ can take place. Thus, a large specific area is associated with enhanced electrochemical performance.

The pore size distributions of C-TiO₂ and bio-TiO₂ NPs samples were calculated from pore volume distribution by Barrett-Joyner-Halenda method, as given in Figure 5.4e. The pore size distributions were notably altered upon the pH variations. The pore size distribution curve of Bio-TiO₂/5 displays two peaks at centered 3.7 nm and

35.1 nm, which implying the micropores and mesoporous structure. When the pH value increased to 7, three different peaks centered at 6.8 nm, 46.3 nm, and 65.2 nm were observed. In comparison, the pore size distribution in a pH value of 10 shows three peaks at 7 nm, 48.3 nm, and 80.2 nm showing microporous, mesoporous, and macroporous structures. Therefore, it seems that the samples in a higher basic medium, displaying a multi-distribution. Pore size increased when the particle size increased. In other words, changing the particle size can lead to porosity enhancements. It is concluded that altering the pH to a higher value decreases the mesoporous structure, resulting in a decrease in surface area.

Table 5.1. Comparison of the crystallite size, surface area, average pore size, and calculated bandgap values of C-TiO₂ and all pH varying Bio-TiO₂ nanoparticles samples.

Samples	2 θ (degree)	FWHM	Crystallite size (nm)	Band gap (eV)	Surface Area (m ² g ⁻¹)	Average Pore size (nm)
A-TiO ₂ /10	25.32	0.339	25	3.03	30.4	28.9
A-TiO ₂ /7	25.36	0.517	16	3.08	43.7	27.3
A-TiO ₂ /5	25.43	0.871	9	3.1	78	12.4
C- TiO ₂	25.4	0.677	12	3.2	47.7	24

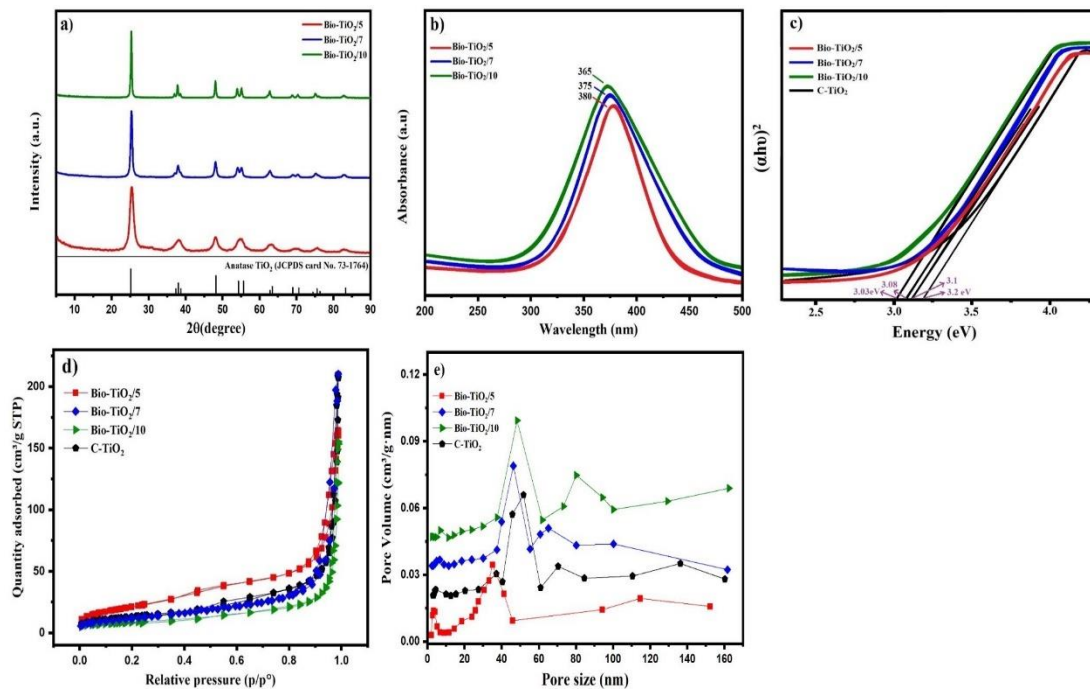


Figure 5.4. The XRD pattern of Bio-TiO₂ nanoparticles in different pH values (a), the UV-Vis spectra of Bio-TiO₂ nanoparticle samples (b), and direct bandgap energy of Bio-TiO₂ in different pH and C-TiO₂ nanoparticles (c). N₂ adsorption/desorption isotherm (d), and pore size distribution (e) of C-TiO₂ and Bio-TiO₂ samples.

5.3. Electrochemical Behavior Of C-TiO₂ And Bio-TiO₂ Air Electrodes

The electrochemical performance of air electrodes was evaluated for Li-O₂ battery using C-TiO₂, Bio-TiO₂/5, Bio-TiO₂/7, and Bio-TiO₂/10 electrodes. Full charge-discharge tests were carried out, and Bio-TiO₂/5 showed the highest specific capacity of 2000 mAh g⁻¹ (Fig. 5.5a). Bio-TiO₂/5 also exhibited a more significant oxygen reduction reaction potential (2.65 V) than Bio-TiO₂/7 (2.5 V) and Bio-TiO₂/10 (2.45 V). The results reveal that when the particle size is decreased, the surface area increases. Therefore, electrodes containing fine particles likely provided much more Li⁺ diffusion due to their high surface areas and increased O₂ adsorption, which helps to increase the formation of Li₂O₂ and boost specific capacity. Capone et al. reported that fine particles enhance cycle life and capacity because the effect of particle pulverization is reduced [127]. In the present work, after 10 full discharge-charge cycles, the specific capacities of Bio-TiO₂/5, Bio-TiO₂/7, and Bio-TiO₂/10 electrodes reached 300, 50, and 50 mAh g⁻¹, respectively (Fig. 5.5b). The capacity loss was due to the deposition of insulated Li₂O₂ and blocking of the oxygen-breathing pathway.

As the above results demonstrate, Bio-TiO₂/5 exhibited the best electrochemical performance of the investigated Bio-TiO₂ particles. Therefore, further electrochemical tests were conducted using only Bio-TiO₂/5. The results of these tests were compared to the results obtained for C-TiO₂ electrodes. Figs. 5.5c and 5.5d display the full charge-discharge profiles of Bio-TiO₂ and C-TiO₂ as catalysts in Li-O₂ cells for 10 cycles.

The initial galvanostatic discharge and charge tests for both types of electrodes were recorded at a constant current rate of 100 mA g⁻¹, with cycling between 2.0 and 4.5 V. The C-TiO₂ and Bio-TiO₂ electrodes exhibited initial discharge capacities of 1375 and 2000 mAh g⁻¹ and coulombic efficiencies of 50.9% and 92.5%, respectively. After the first cycle, the capacities of C-TiO₂ and Bio-TiO₂ decreased to 700 and

1700 mAh g⁻¹, respectively. The better capacity retention of Bio-TiO₂ could be due to the promotion of ORR and OER. As a result, the biomolecules prohibited the agglomeration and enhanced viability of active sites. Therefore, adequate void space is provided to generate a large amount of Li₂O₂ and give rise to higher discharge specific capacity of Bio-TiO₂ electrode and good reversibility.

As illustrated in Fig. 5.3c., the Bio-TiO₂ structure provides an inter-channel structure, which improves electrochemical efficiency in the air-breathing cathode. The discharge and charge plateau remained flat at 2.65 V and 4.2 V for Bio-TiO₂. Here, our reported ORR potential was higher than was reported by J. Park Group (2.2 V) [127]. This could be because, in our experiment, the biomolecules functionalized the surface of TiO₂, thus enhancing the interaction between oxygen and the TiO₂ surface. However, TiO₂ electrodes showed large overpotentials, perhaps owing to the low electrical conductivity of TiO₂. Hence, we suggest the use of a composite structure of Bio-TiO₂ and a conductive material. This combination is expected to improve the conductivity of TiO₂ and maximize the catalytic activity of Li-O₂ batteries.

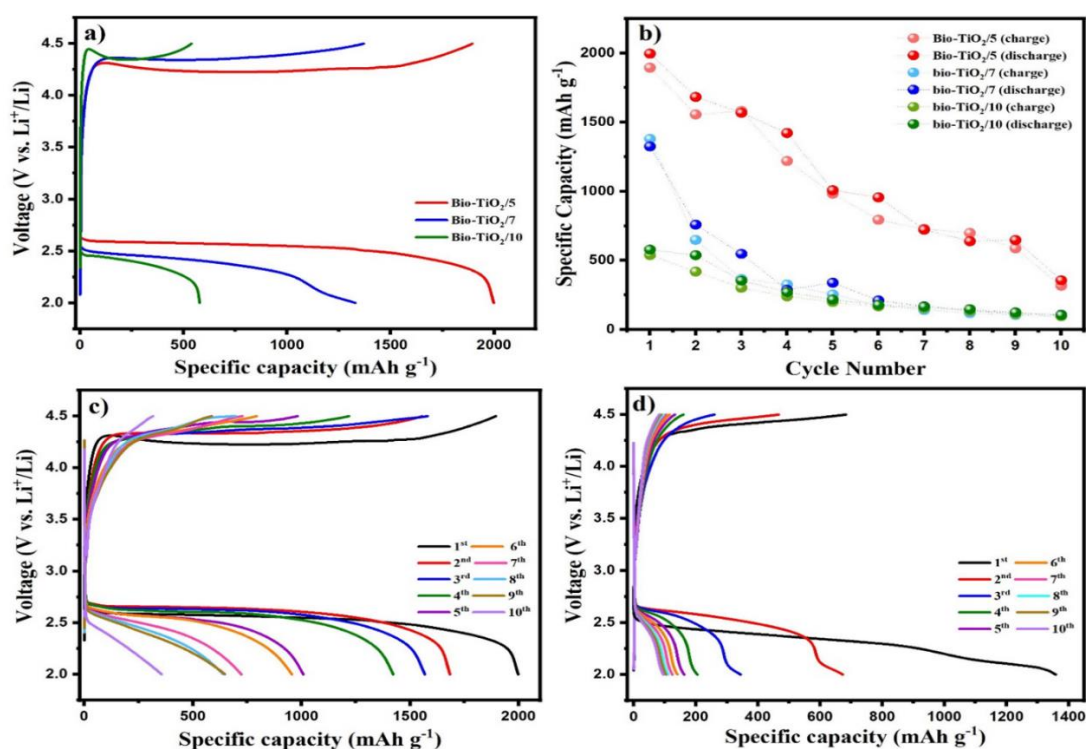


Figure 5.5. a) Full charge-discharge profile of Bio-TiO₂ at different pH values, and b) comparison the specific capacity performance of Bio-TiO₂ samples for 10 cycles. Full discharge/charge profile of c) Bio-TiO₂ and d) C-TiO₂ cathodes for 10 cycles.

The catalytic reactions of C-TiO₂ and Bio-TiO₂ electrodes were investigated by applying cyclic voltammetry (CV) measurements within the voltage window of 2.0-4.5 V at a scan rate of 0.3 mV s⁻¹. The CV curve of Bio-TiO₂ (Fig. 5.6a) demonstrates a sharp peak at around 2.3 and 2.6 V. This can be attributed to the formation of discharge products (Li₂O₂ or Li₂O) during the cathodic sweep. During the anodic sweep, three oxidative peaks (observed at 3.2 V, 3.6 V, and 4.2 V) exemplify the gradual decomposition of the bulk Li₂O₂.

As discussed above, the decomposition of discharge reactions starts at a voltage of 3.2 V, which is lower than previously reported [147]. Moreover, The C-TiO₂ electrode exhibits a lower anodic peak current intensity than the cathodic peak, indicating non-reversible reactions (Fig. 5.6b.). However, the Bio-TiO₂ electrode yields a higher ORR current than C-TiO₂, thus demonstrating efficient catalytic performance. This effect likely arises because Bio-TiO₂ can effectively interact with O₂ to chemisorb on the active sites of Bio-TiO₂, thereby enhancing O₂ activation and dissociation.

We have also compared the discharge-charge cycling capabilities of C-TiO₂ and Bio-TiO₂ electrodes with a fixed capacity regime of 500 mAh g⁻¹ (Figs. 5.6c and 5.6d). The Bio-TiO₂ electrode exhibited stable performance for 30 cycles, whereas C-TiO₂ remained stable for 20 cycles. The improved cyclability of Bio-TiO₂ is probably because this electrode is associated with less agglomeration and activated the surface by biomolecules, which leads to increased Li⁺ migration and oxygen absorption. The stability of TiO₂ has been reported by Agyeman et al. [128] and Kang et al. [129] because they prevent side reactions and are chemically stable.

Figures 5.6e. and 5.6f. represent the electrochemical impedance spectra (EIS) of Bio-TiO₂ and C-TiO₂ before and after the first discharge and charge test. The corresponding equivalent circuit model is illustrated in the inset of Figure 5.6f. The

equivalent circuit comprises ohmic resistance (R_e) that links the electrolyte, separator, and current collector in the cell. R_s attributes to solid electrolyte interphase (SEI) film resistances. R_{ct} ascribes to the charge transfer between the interface of electrolyte and an air cathode and constant phase elements instead of double-layer capacitance (CPE_2), followed by the Warburg impedance (W_{dif}) corresponds to Li^+ diffusion. After discharge, the R_{ct} value of the Bio-TiO₂ electrode increases from 274 Ω to 932 Ω as discharge products (Li_2O_2) form on the cathode surface. After the charge, R_{int} drops to ≈ 286 Ω , which closes to the pristine cell resistance, which explains the reversibility of the charge-discharge process. The C-TiO₂ EIS plot reveals that the reversibility is poor and that the R_{ct} after discharge is lower than the R_{ct} for Bio-TiO₂. This finding reinforces the notion that a higher discharge product deposition results in higher capacity. These results also explain that the higher surface area of Bio-TiO₂ provides more space for discharge products to be deposited.

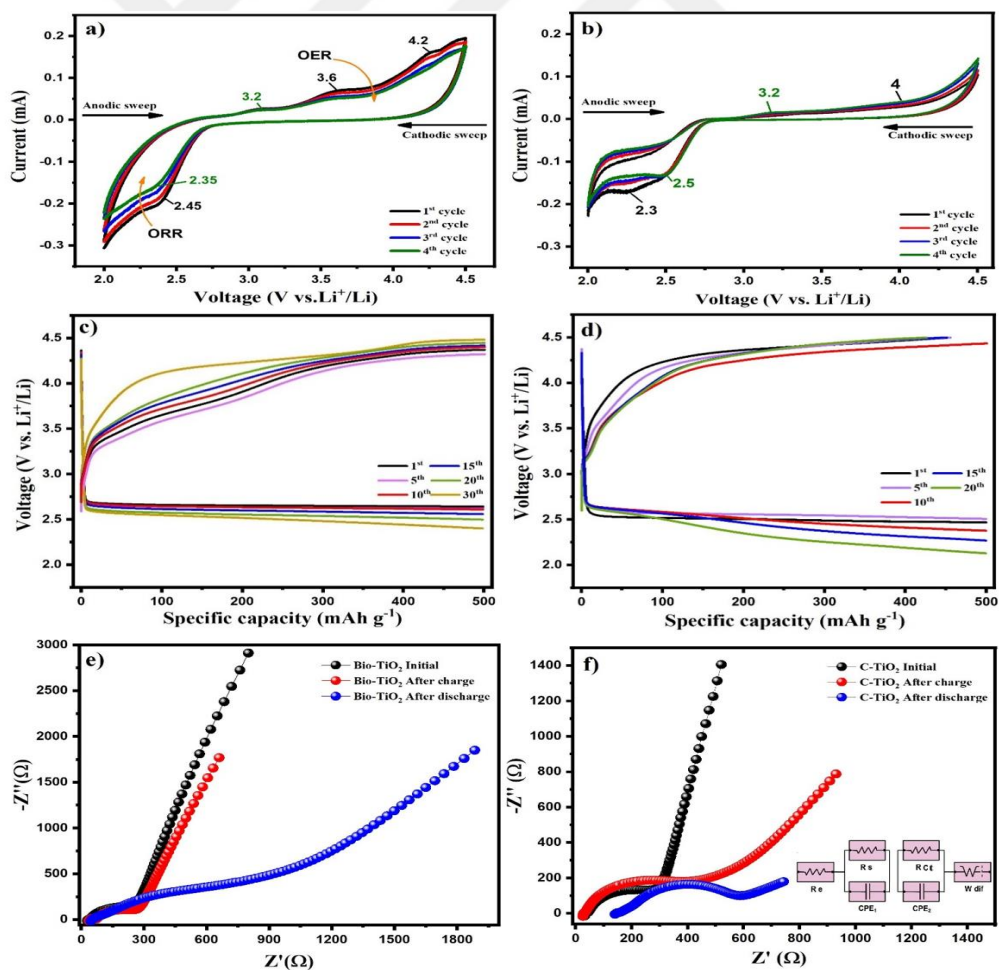


Figure 5.6. Cyclic voltammetry curves represent the electrochemical reactions of (a) Bio-TiO₂ and (b) C-TiO₂ electrodes. Cyclability behavior of (c) Bio-TiO₂ and (d) C-TiO₂ electrodes limited at a capacity of 500 mAh g⁻¹. Nyquist plots of Li-air cells with Bio-TiO₂ (e) and C-TiO₂ cathodes (f) before and after first full discharge and charge.

After the first full discharge and full charge of Bio-TiO₂ electrodes, XRD and FESEM analyses were performed to determine the phase structure and morphology of the discharge products. The FESEM images produced after the first discharge show the toroid shape of Li₂O₂ products (Figs. 5.7a. and 5.7b.). The images also reveal that most discharge products are decomposed after the charge (Fig. 5.7c.). The morphology of the electrode after 30 cycles is exhibited in Fig. 5.7d, where it can be observed that the electrode is covered with discharge products that block the oxygen pathway and cause capacity fading. The EDS spectrum of the electrode after discharge reveals that oxygen increases to 88.64 at.% due to Li₂O₂ formation. However, the oxygen ratio dramatically decreases due to the decomposition of Li₂O₂ after charging (Figs. 5.7e. and 5.7f.).

The XRD pattern after discharge confirms the formation of Li₂O and Li₂O₂ products in agreement with the JCPD-12-0254 and JCPD-09-0355, respectively (Fig. 5.7g). After charging, these peaks disappear as the discharge products decompose, further confirming the good reversibility. Also, no side reactions were observed in the XRD pattern, showing that an effective TiO₂ catalyst can prevent the formation of unwanted products. However, the XRD spectra of C-TiO₂ after charge still shows peaks in discharge products due to the poor OER behavior of the electrode. It is concluded that the particle size and aggregation of particles significantly influence the electrochemical reactions that occur in battery cells.

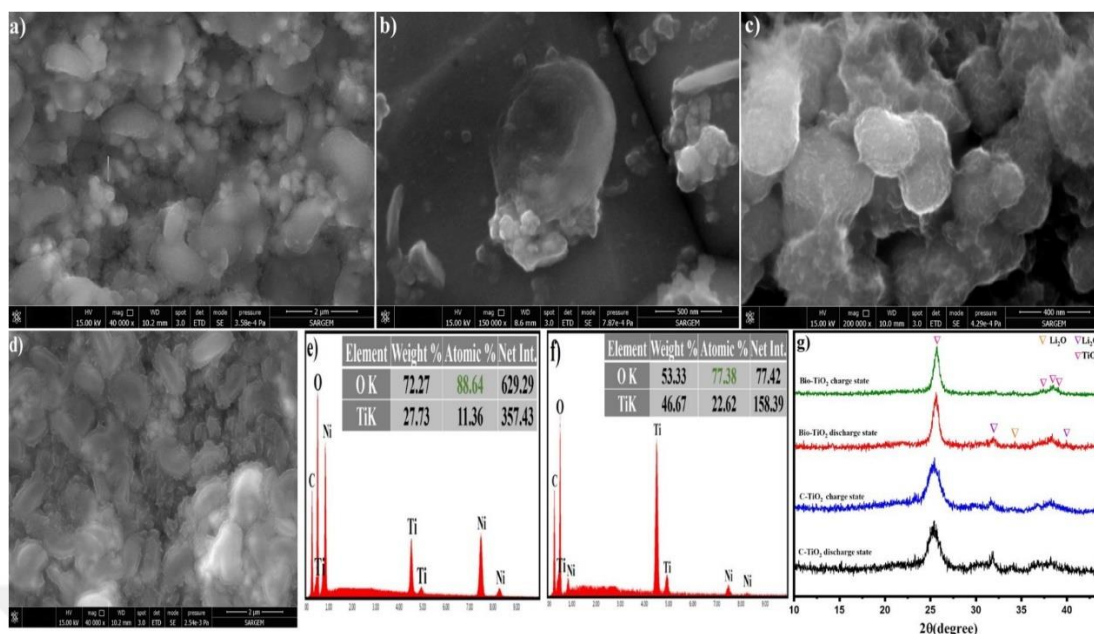


Figure 5.7. Low and high magnification FESEM images of Bio-TiO₂ electrodes after first full discharge (a,b), after the full first charge (c), after 30 cycles (d), and EDS spectrums of Bio-TiO₂ e) after discharge, f) after charge. XRD patterns of g) Bio-TiO₂ and C-TiO₂ after charge and discharge of the electrodes.

5.4. The Formation Mechanism Of Bio-TiO₂ And Urchin-Like Core-Shell TiO₂/α-MnO₂ Nanostructures

It has been reported that MnO₂ nanoparticles could enhance the specific capacity and alleviate charge potential [130]. The TiO₂-based electrodes are widely used in lithium batteries due to their good durability but suffer from low conductivity [131]. Therefore, to maximize TiO₂ utilization, it is more beneficial to grow MnO₂ on TiO₂ to enhance intimate contact. To do this, urchin-like core-shell TiO₂/α-MnO₂ nanostructures were synthesized, as described in Figure 5.8.

First, TiO₂ NPs were biosynthesized through a green route using chamomile extract as both stabilizing and reducing agents. In the synthesis, the first step was the hydrolysis reaction between titanium tetraisopropoxide and ethanol/water to form titanium hydroxide (Ti(OH)₄). The second step was reduction and stabilization of titanium hydroxide to Bio-TiO₂ by adding chamomile extract, which containing phytochemicals such as terpenoids, phenolics, caffeic acid, coumarin, and flavonoids. The main component of chamomile is apigenin (840 mg/100 g), which contains hydroxyl groups in its structure. These functional groups play a key role in

encapsulating nanoparticles due to the van der Waals and hydrogen bonds between the functional group of biomolecules and $\text{Ti}(\text{OH})_4$. In the third step, the obtained Bio- TiO_2 powder was calcined at 450°C to remove organic compounds and improve the crystallinity and porosity of Bio- TiO_2 . Besides, zeta potential analysis indicated a stable and negative charge surface of Bio- TiO_2 NPs dispersed in distilled water (Figure 5.9a). Therefore, Mn^{2+} ions could bind onto the surface of Bio- TiO_2 NPs through electrostatic interaction. Then, the nucleation and growth of MnO_2 were developed by reacting with KMnO_4 at room temperature through a redox reaction as follows:

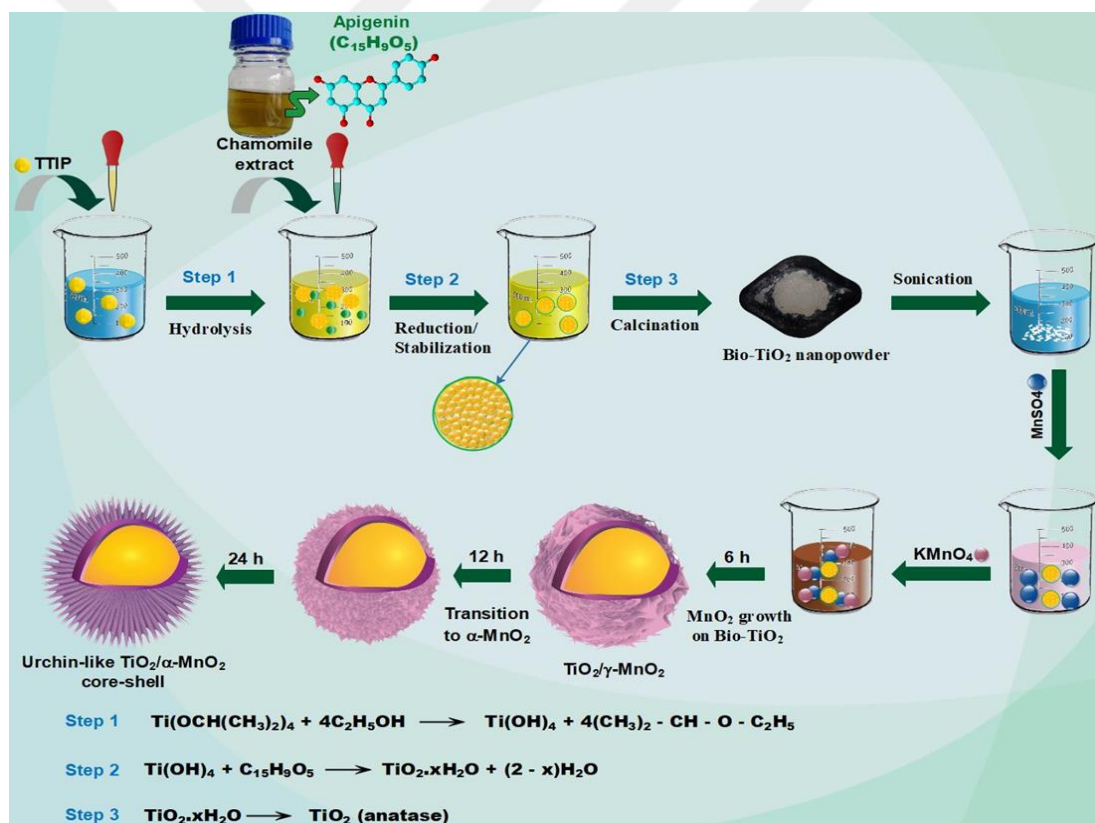
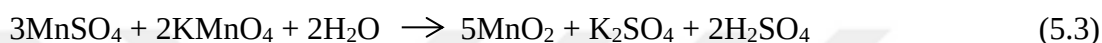


Figure 5.8. Schematic possible of the formation mechanism of Bio- TiO_2 nanoparticles and urchin-like core-shell nanostructured $\text{TiO}_2/\alpha\text{-MnO}_2$.

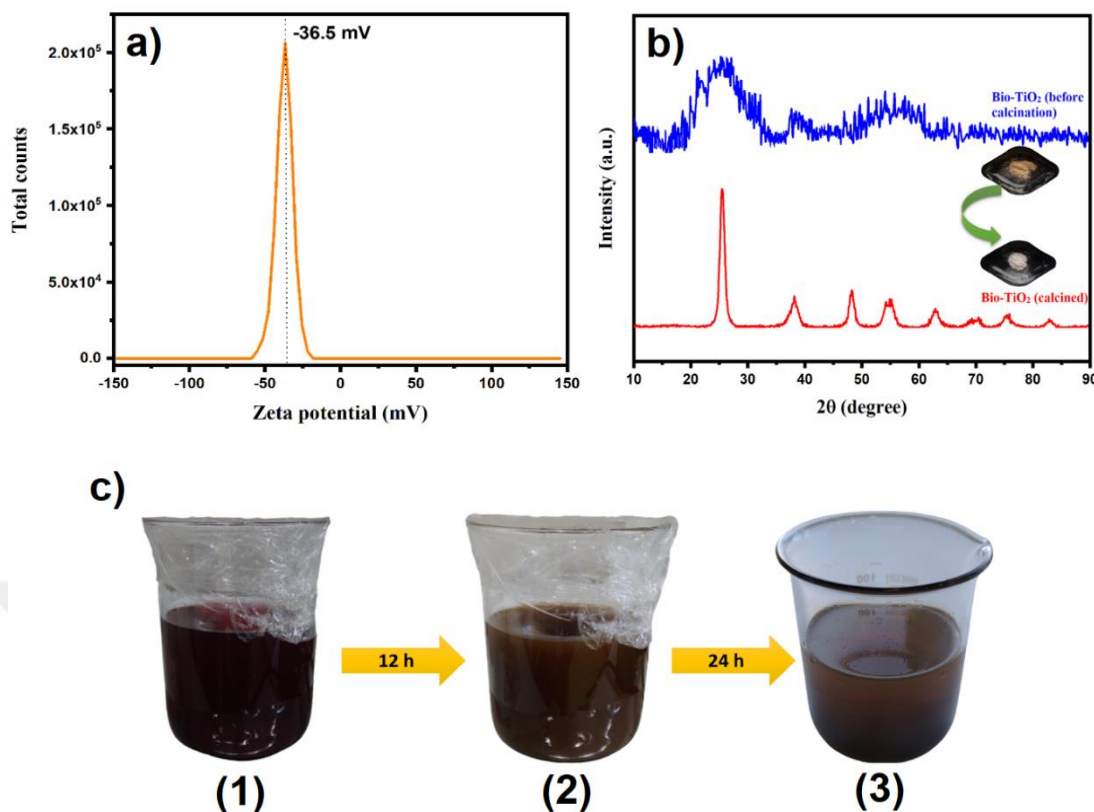


Figure 5.9. a) Zeta potential of Bio-TiO₂ nanoparticles. b) The XRD pattern of Bio-TiO₂ before and after calcination. Dispersed TiO₂/MnO₂ after 6 h (1), then after 12 h the KMnO₄ completely consumed (2), and the brown products are deposited after 24 h (3).

The surface of Bio-TiO₂ NPs plays as nucleation sites to form a large number of MnO₂ nuclei, followed by sequentially crystalline growth. To understand the formation and growth of urchin-like MnO₂ shell, time-dependent morphology evolutions and crystallinity structure at room temperature were investigated by FESEM and XRD analysis. From Figure 5.10a, Bio-TiO₂ nanospheres revealed cauliflower morphology with the size ranging between 90-400 nm, and higher magnification of FESEM image displayed the Bio-TiO₂ nanoparticles are composed of aggregated small particles (Fig. 5.10b.). This morphology is formed due to the aggregation of high surface energy fine particles. Furthermore, the morphology evolution of core-shell TiO₂/α-MnO₂ nanostructures can be observed at different reaction times in Figures 5.10c-e. Figure 5.10c indicates the surface of Bio-TiO₂ nanospheres composed of nanosheets-like MnO₂ showing MnO_x crystals compact into two-dimensional sheets after 6 h. When the reaction time is extended to 12 h, the interleaved nanosheets of MnO₂ could be seen in Fig. 5.10d. From Figure 5.10e can

be observed the nanosheets curl to nanorods after 24 h, and the surface of Bio-TiO₂ is comprised of prominent nanoneedles. The nanorods become stable and vertically oriented, resulting in the self-assembly of the urchin structure. This evolution of morphology can be explained as an Ostwald ripening process, in which the finer nanorods grow to bigger ones due to different energy surfaces between them [132]. Similar studies have been investigated the morphology evolution of urchin-like MnO₂ by controlling time duration [133,134].

The EDS spectra for the Bio-TiO₂ nanoparticles (Figure 5.10f.) detected the energy of the X-rays emitted from the sample at about 0.2, 4.3, and 5 keV, which is associated with the presence of oxygen and titanium elements. This result confirmed the presence of elemental compounds of the Bio-TiO₂ nanoparticles without any impurity peaks and indicated the high purity of the synthesized nanoparticles. From EDS spectra of TiO₂/α-MnO₂ nanostructures (Figure 5.10g.) Ti, O, and Mn elements are observed. FESEM observations clearly support the evolution of structure from flower-like to urchin structures. Thus, it is expected the emerging TiO₂, MnO₂ coupled with urchin-like nanostructures of MnO₂ can be advantageous in Li-O₂ battery performances. The urchin-like TiO₂/MnO₂ nanostructure can be a promising catalytic structure owing to its high surface area, which develops smooth pathways to improve ORR/OER kinetics by accelerating the electrons and oxygen transportation during the process.

The crystallographic structures of TiO₂/α-MnO₂ at different reaction times and Bio-TiO₂ samples were investigated by XRD to examine the crystalline growth during the synthesis process. First, the XRD pattern of Bio-TiO₂ before calcination (Fig. 5.9b.) detected a broad peak around 25.4°, which is assigned to the characteristic diffraction peak of the TiO₂ amorphous form, implying assistance of phytochemical components in the reduction of titanium ions (Ti⁴⁺). The calcined Bio-TiO₂ NPs displayed sharp diffraction peaks centred at 2θ of 25.4°, 37.9°, 48.1°, 54°, 55.2°, 62.8°, 68.9°, 70.4°, 75.2°, 83.3° corresponds to the lattice planes (h k l) of (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), (2 1 5), (3 1 2), respectively and representing the transition of amorphous TiO₂ to anatase polymorph (JCPDS file

number 73-1764). The crystallite size of the Bio-TiO₂ nanoparticles estimated by the Scherrer equation given as below:

$$D_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos \theta} \quad (5.4)$$

Where D_{hkl} is the crystallite size, K is a constant crystalline shape factor value equal to 0.9, λ is the Cu-K α radiation wavelength equal to 0.154 nm, β_{hkl} determining the full width at half maximum (FWHM) of the peak, and θ is the half diffraction Bragg's angle. The crystallite size was calculated as 11.4 nm from the high intensity peak at $2\theta = 25.4^\circ$ through the above equation.

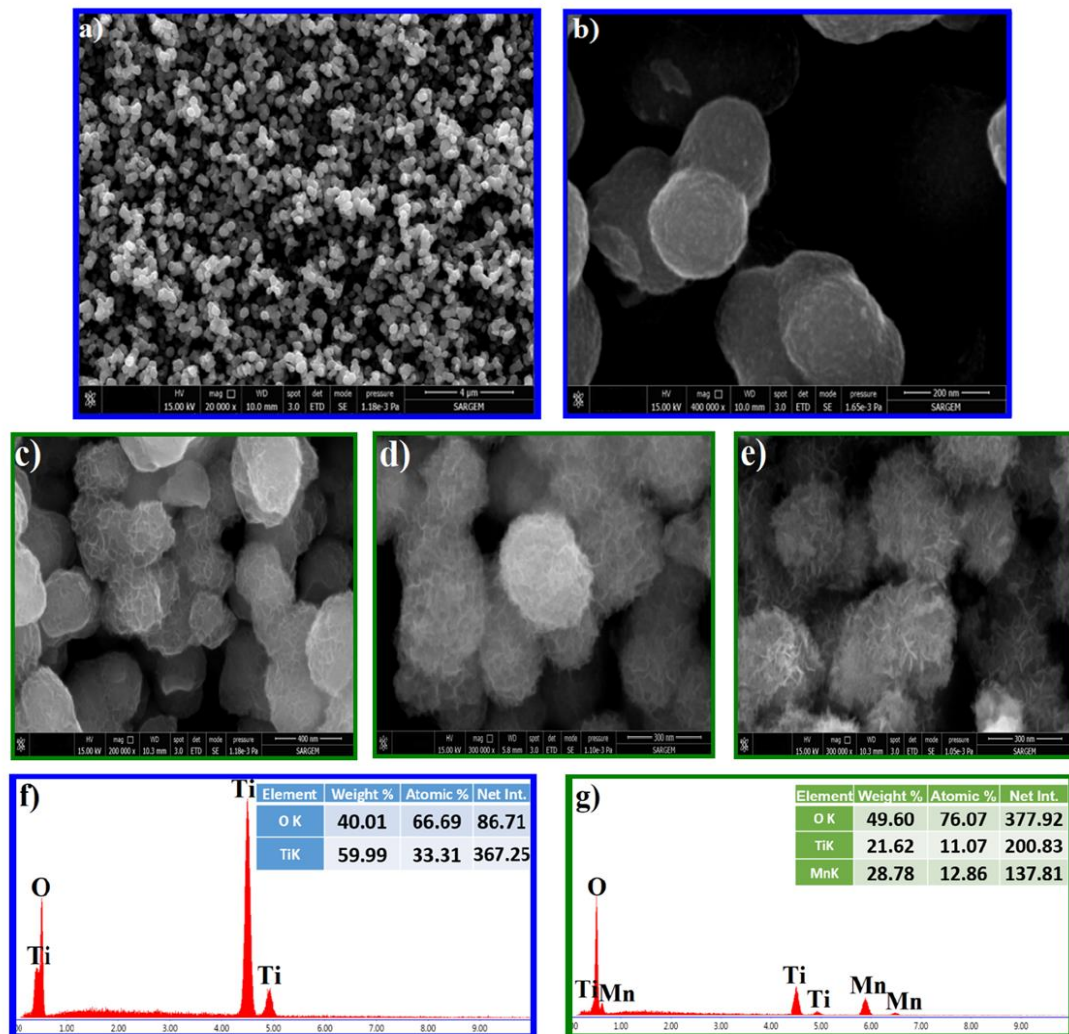


Figure 5.10. FESEM images of low and high magnification of Bio-TiO₂ nanoparticles (a and b), the morphology evolution of urchin-like core-shell nanostructured TiO₂/α-MnO₂ after 6 h (c), 12 h (d) and 24 h (e). EDS spectra of Bio-TiO₂ (f) and TiO₂/α-MnO₂ (g).

The XRD patterns of $\text{TiO}_2/\alpha\text{-MnO}_2$ at different reaction times still illustrated the characteristic anatase TiO_2 phase (Fig. 5.11a.). Meanwhile, the prepared powder after 6 h shows the weak peaks at 2θ of 22.4° , 34.3° , 37.1° , 42° , and 65.9° correspond to the (1 2 0), (031), (131), (3 0 0), and (4 2 1) planes of $\gamma\text{-MnO}_2$ phase (JCPDS No. 14-0644). When the reaction time is prolonged to 12 h, a new peak appears at $2\theta = 18^\circ$, which stands for the transition of $\gamma\text{-MnO}_2$ to $\alpha\text{-MnO}_2$. After 24 h, the weak peaks allocated to $\alpha\text{-MnO}_2$ (JCPDS No. 44-0141) were detected at $2\theta = 12.6^\circ$, 18.1° , 28.7° , 37° , and 60.3° assigned to (1 1 0), (2 0 0), (3 1 0), (2 1 1), and (5 2 1) planes.

MnO_2 can assemble into different crystalline structures, such as (1x2) and (1x1) for $\gamma\text{-MnO}_2$ and (2x2) tunnels for $\alpha\text{-MnO}_2$. Various parameters can affect the transformation of $\gamma\text{-MnO}_2$ to $\alpha\text{-MnO}_2$, such as temperature, precursor concentration, and reaction time. In our experiment, $\gamma\text{-MnO}_2$ was formed after 6 hours and gradually transform to $\alpha\text{-MnO}_2$ by exceeding the reaction time. This transformation can be elucidated due to the metastable structure of $\gamma\text{-MnO}_2$. During the experiment, the purple color of the KMnO_4 solution disappeared completely after 12 h reaction, showing the whole system becomes a thermodynamically stable environment, as shown in Fig. 5.9c. When the reaction time is prolonged, the 1 x 2 tunnel structure of $\gamma\text{-MnO}_2$ collapses, and the K^+ can be enclosed into a more stable 2 x 2 tunnel structure of $\alpha\text{-MnO}_2$.

This transition phase could be associated with the simultaneous morphological transformation from nanosheets-like to nanorods during prolonged time reaction, implying that $\gamma\text{-MnO}_2$ are gradually detached from nanosheets under reaction time. When $\alpha\text{-MnO}_2$ nuclei are formed, the $\gamma\text{-MnO}_2$ nanograins in the nanosheets will diffuse to stable $\alpha\text{-MnO}_2$ to grow into nanorods. Notably, the reaction time plays a crucial role in developing an urchin-like MnO_2 shell, transforming the crystalline structure and improving the degree of crystallinity. These results are consistent with the previous studies [135,136].

5.5. Morphological And Compositional Study Of Bio-TiO₂ And Core-Shell TiO₂/α-MnO₂ Nanostructures

Fig. 5.11b shows UV-Vis spectra of the Chamomile extract and Bio-TiO₂ NPs. The UV-Vis absorption spectrum demonstrated the absorbance peaks in pure Chamomile extract at 280 nm and 328 nm. The presence of these absorption peaks can be attributed to some phytochemicals, including flavonoids, terpenoids, and coumarins. These biomolecules interact with Ti⁴⁺ to form Bio-TiO₂ nanoparticles. It is noted that the addition of plant extract to the Ti(OH)₄ solution caused the emergence of a new absorption band at 370 nm showing the formation of Bio-TiO₂ nanoparticles. Moreover, the outcomes of the current study match well with the literature, representing the existence of titanium oxide band below 400 nm [90].

Raman spectroscopy was conducted for TiO₂/α-MnO₂ sample to confirm the interaction between Bio-TiO₂ and α-MnO₂ to obtain a core-shell structure. As depicted in Fig. 5.11c, Raman spectra demonstrates three peaks at 398.2, 518.6, and 641 cm⁻¹ for Bio-TiO₂, which corresponds to the B_{1g}, A_{1g}, and E_g modes of anatase TiO₂ phase [137], in line with the results of XRD analysis. The Raman spectra of core-shell nanostructured TiO₂/α-MnO₂ exhibited a strong peak located at 683 cm⁻¹, which can be allocated to the stretching mode of MnO₆ octahedra and Bio-TiO₂ peaks shifting towards the lower wavelength, showing the interaction between the TiO₂ and MnO₂ and further formation of core-shell TiO₂/α-MnO₂. The weak peaks observed at 265.5 and 359.4 cm⁻¹ originated from the formation of Mn₂O₃ or Mn₃O₄ correspond to the bending mode of O-Mn-O.

To further verify the morphology and formation of Bio-TiO₂ nanoparticles and core-shell nanostructured TiO₂/α-MnO₂, transmission electron microscopy (TEM) analysis was carried out. The high magnification of TEM image in Fig. 5.12a depicted the cauliflower morphology of Bio-TiO₂ consists of fine nanoparticles (10-30 nm) apart from each other.

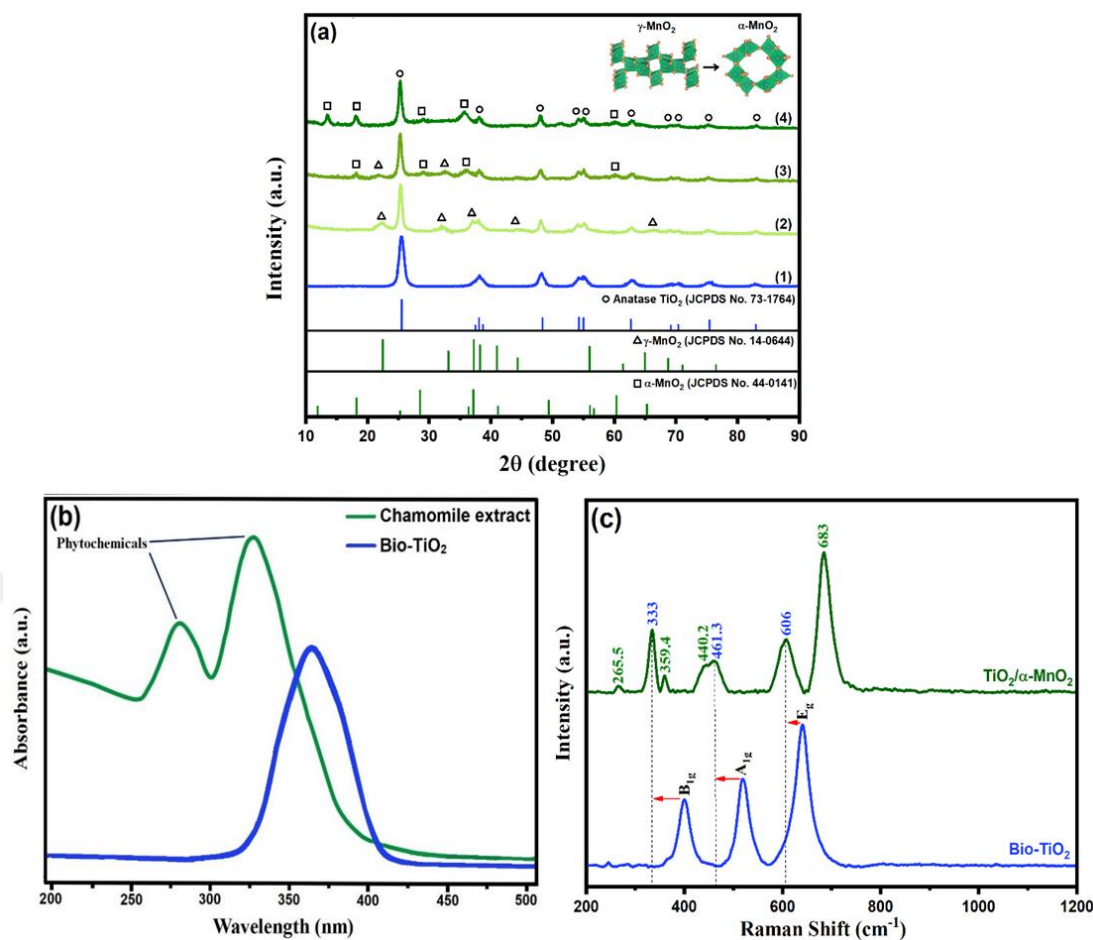


Figure 5.11. a) The XRD patterns of Bio-TiO₂ (1) and TiO₂/α-MnO₂ under different reaction time 6 h (2), 12 h (3), and 24 h (4). b) Ultraviolet-visible spectra at a range of 200–500 nm for Chamomile extract showing the two peaks corresponding to biomolecules and Bio-TiO₂ NPs, and c) Raman Spectra of Bio-TiO₂ and core-shell TiO₂/α-MnO₂.

It is evident from the TEM image that the biomolecules present in the Chamomile extract, which acted as capping molecules, prevented the aggregation of TiO₂ nanoparticles. Figure 5.12b demonstrates the HRTEM investigations into Bio-TiO₂. The lattice planes of nanoparticles were clearly examined in different orientations displaying high crystallinity of the sample. The lattice fringes spacing was estimated to be 0.352 nm, corresponding to the (101) plane of the anatase TiO₂. From the high-magnification TEM image in Fig. 5.12c, the urchin-like MnO₂ can be seen on the surface of Bio-TiO₂ nanospheres, and its corresponding HRTEM image taken near the edge is indicated in Fig. 5.12d.

The HRTEM image displays two distinct phases with a lattice fringe spacing as 0.24 and 0.35 nm, indexed to the (211) plane of the α-MnO₂ and the (101) plane of the

anatase TiO_2 , respectively. However, few visible lattice fringes for MnO_2 could be seen due to its low crystallinity. The corresponding selected area electronic diffraction (SAED, Fig. 5.12e.) pattern further approved the existence of TiO_2 and MnO_2 structures. The SAED pattern shows a series of concentric circles implying polycrystalline structure. The spotted diffraction rings are well-matched with (211) and (521) planes of $\alpha\text{-MnO}_2$, along with the (211), (215), and (3 1 2) planes of anatase TiO_2 , which is consistent with the XRD pattern. To further confirm the formation of core-shell nanostructures, EDS mapping analysis (Fig. 5.13.) was employed, and all the elements are homogeneously distributed within the overall nanosphere. The distributions of Mn and O verify a wrapped picture around Ti, approving further evidence of $\text{TiO}_2/\alpha\text{-MnO}_2$ core-shell structure.

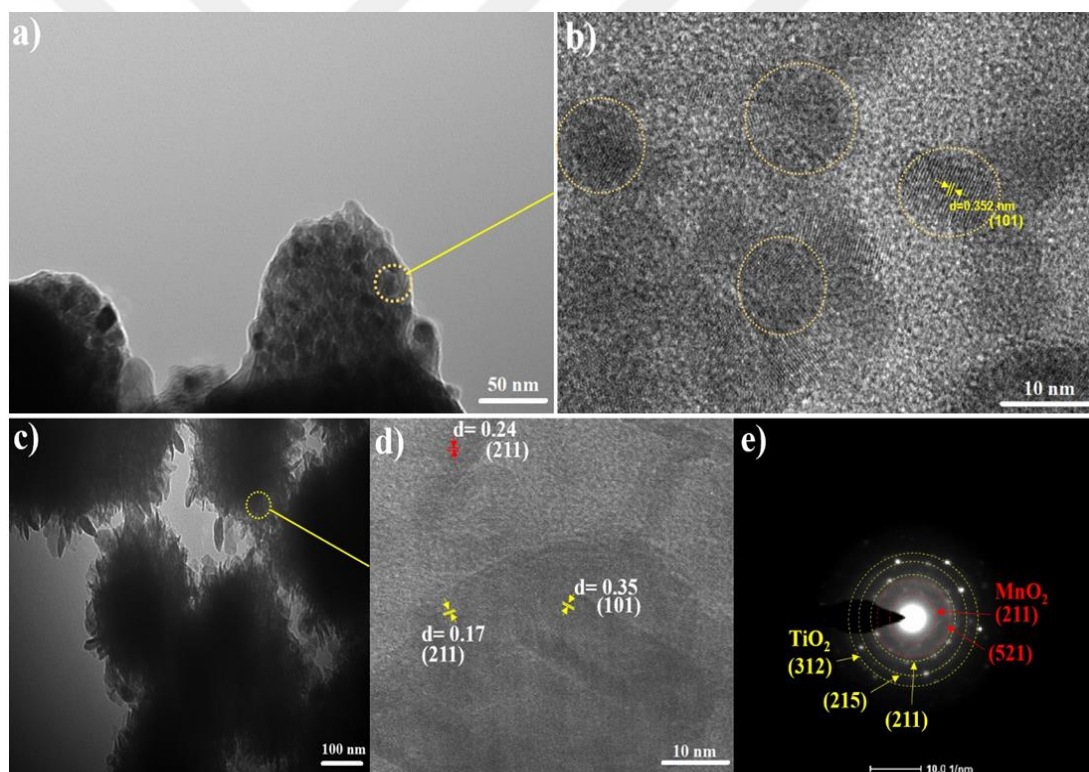


Figure 5.12. a) TEM image of Bio- TiO_2 nanoparticles. b) HR-TEM of Bio- TiO_2 (b). TEM in high magnification (c) and HR-TEM images (d) of urchin-like core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanostructures. e) selected area electron diffraction of $\text{TiO}_2/\alpha\text{-MnO}_2$.

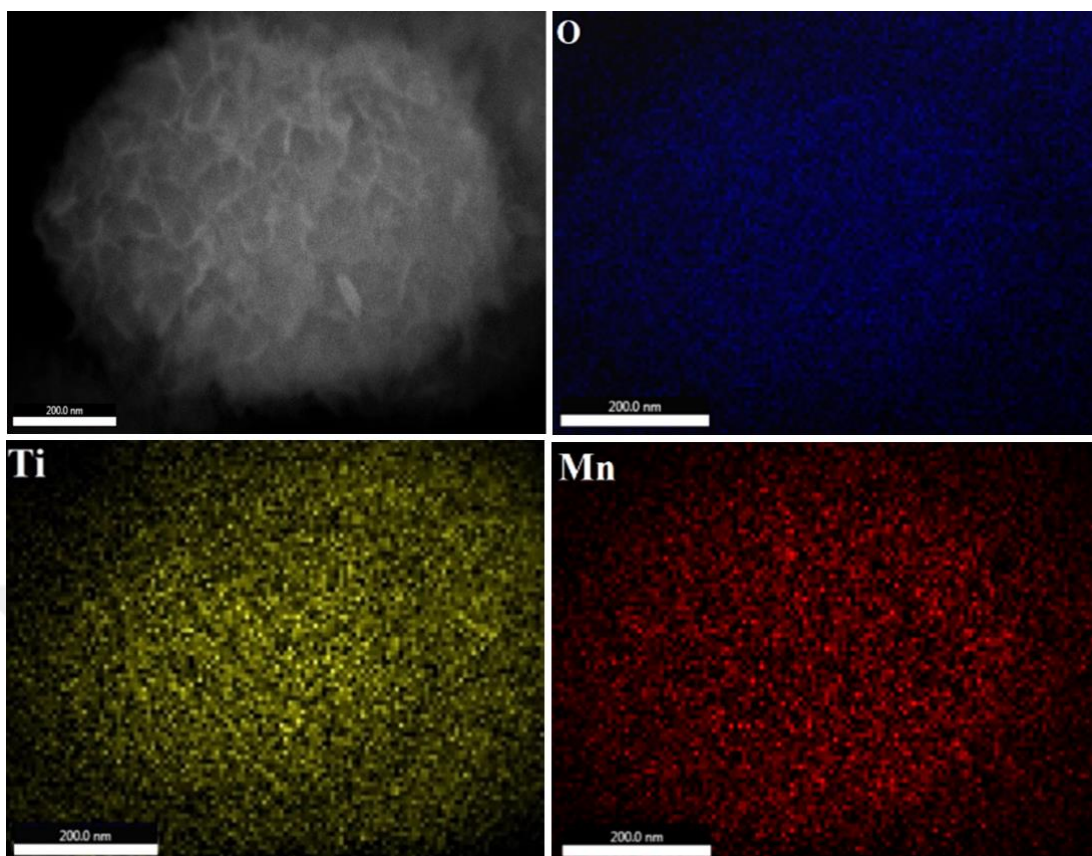


Figure 5.13. Elemental mapping of core-shell nanostructured $\text{TiO}_2/\alpha\text{-MnO}_2$ revealing the elemental distribution of Mn, Ti, and O.

N_2 adsorption-desorption isotherm of Bio-TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ were recorded to study the surface area, as shown in Fig. 5.14a. Both samples displayed a typical type IV isotherm and H3-type hysteresis loop, indicating mesopores structure with a relatively narrow pore size distribution. The BET (Brunauer-Emmett-Teller) surface area of Bio-TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ were calculated from the adsorption isotherm curve as $97 \text{ m}^2 \text{ g}^{-1}$ and $123 \text{ m}^2 \text{ g}^{-1}$, respectively. From surface area values, a consequence can be derived that growing MnO_2 on the surface of Bio-TiO_2 NPs could significantly enhance the specific surface area due to urchin-like nanostructures of MnO_2 . This rough structure can provide a large catalytic area and enough storage sites for discharge products and lead to the better electrochemical performance of the battery. Fig. 5.14b illustrates the pore-size distributions of Bio-TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ materials determined by Barrett-Joyner-Halenda (BJH) method and average pore-sizes of 7 nm and 10.6 nm were obtained by Bio-TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$, respectively. $\text{TiO}_2/\alpha\text{-MnO}_2$ showed a higher pore volume of 0.3 cm^3

g^{-1} than Bio-TiO₂ ($0.12 \text{ cm}^3 \text{ g}^{-1}$). Some research groups have studied that the pore size and volume can influence the specific capacity [138]. Ding et al. indicated that with the increase of pore size, the discharge capacity could be increased due to improving oxygen diffusion [139]. Consequently, it is expected that the higher surface area and pore volume can enhance the capacity of the Li-O₂ cell.

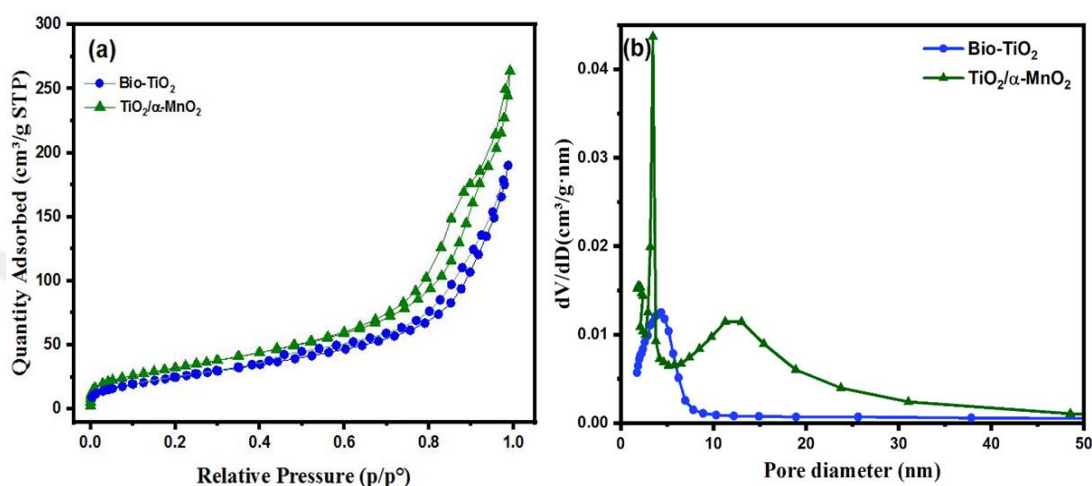


Figure 5.14. N₂ adsorption-desorption isotherms (a) and Barrett-Joyner-Halenda (BJH) pore size distribution plot (b) of biosynthesized TiO₂ nanoparticles and TiO₂/α-MnO₂ nanostructure.

5.6. Electrochemical Characterization Of Bio-TiO₂ And TiO₂/α-MnO₂ Electrodes

Electrocatalytic activity of bare Bio-TiO₂ and TiO₂/α-MnO₂ electrodes was studied by cyclic voltammograms (CV) in Li-O₂ cells at the potential window of 2.0-4.5 V vs. Li/Li⁺ and a scan rate of 0.3 mV s^{-1} , as shown in Fig. 5.15(a,b). The ORR and OER curves of the Bio-TiO₂ and TiO₂/α-MnO₂ were observed to be stabilized after 5 cycles. However, cyclic voltammetry of Bio-TiO₂ was not overlapped upon cycling, indicating irreversible reactions. Likewise, the ORR current was higher than OER current showing better oxygen reduction in Bio-TiO₂ electrode. Comparably, CV curve of TiO₂/α-MnO₂ revealed increasing voltammograms, both anodic and cathodic scans, with a higher current density of the reduction and oxidation peaks. That means the ORR and OER catalysis of TiO₂/α-MnO₂ were improved due to the reversibility of Li₂O₂ formation/decomposition reactions and can lead to enhance discharge capacity, high round trip efficiency, and low polarization. Moreover, He et

al. reported that MnO₂ had poor OER because of low oxidation peak current [140]. But in this study by the combination of Bio-TiO₂ and MnO₂, the OER of MnO₂ has improved, suggesting the bifunctional electrocatalytic activities would enhance the electrochemical performance of the Li-O₂ cell.

In CV curve of Bio-TiO₂ electrode, a peak observed between 2.2 and 2.5 V at the first cathodic scan shifting to 2.3 and 2.6 V at subsequent cycles corresponded to the formation of Li₂O₂ as below:



The small peak observed between 3.9 and 4.2 V is attributed to the decomposition of Li₂O₂ to Li⁺ and O₂. The cathodic curve of TiO₂/α-MnO₂ exhibited a peak between 2.4 and 2.8 V that ascribed to ORR, whereas the anodic scan demonstrated two broad peaks between 3.1-3.5 V and 3.6-3.8 V, which attributed to OER. It is reported that Li₂O₂ decomposition reaction could occur at two steps [141]. The onset charge potential at 3.25 V might be due to interfacial Li₂O₂ oxidation, and the decomposition of the bulk Li₂O₂ occurs at a higher charge potential (3.75 V). It is noted the discharge and charge potentials of TiO₂/α-MnO₂ electrode is inferior to Bio-TiO₂ electrode due to decreasing polarization between the formation and decomposition reaction of Li₂O₂. Therefore, it is stressed that ORR and OER are catalytically sensitive and can be enhanced by suitable bifunctional catalysts, including TiO₂ and MnO₂.

Galvanostatic full charge-discharge tests were performed to investigate the capacity performance of the electrodes. The full charge-discharge of Bio-TiO₂ was carried out in the range of 2-4.5 V and for TiO₂/α-MnO₂ in a voltage range of 2.2-4.2 V to avoid undesired reactions and electrolyte decomposition at above 4.2 V. Fig. 5.15c demonstrates that TiO₂/α-MnO₂ cathode delivers a specific capacity of 6100 mAh g⁻¹ with 80% round-trip efficiency (the ratio of the discharge voltage of 2.8 V to the

charge voltage of 3.5 V) and exhibited nearly 100% coulombic efficiency, which implies good charging efficiency. In contrast, the Bio-TiO₂ electrode indicates a discharge capacity of 2500 mAh g⁻¹ with a round-trip efficiency of 60.4% (2.6 V-4.3 V) and coulombic efficiency of 73.5%, showing poor decomposition of Li₂O₂.

Round-trip efficiency is known as the ratio of electricity put into a system that is later recaptured. The lower round-trip efficiency implies less energy lost in the storage phase. High charging overpotentials, short cycle life, and low power all contribute to low round-trip efficiency.

In battery research, coulombic efficiency has been frequently employed as a measurable metric of battery reversibility. While coulombic efficiency contributes to the prediction of a lithium-O₂ battery's lifetime and can be calculated as follow:

$$\text{coulombic efficiency} = \frac{\text{Capacity (discharge)}}{\text{Capacity (charge)}} \times 100 \quad (5.6)$$

Coulombic efficiency shows the ratio between the number of Li⁺ ions or electrons coming back to the cathode and the number of Li⁺ or electrons withdrawing from the cathode in a full cycle. Assuming no parasite reactions occur on the cathodes, reversible electrochemical reactions complete the flow of Li⁺ or electrons. However, side reactions between electrolytes and electrodes can take place and prevent reversible reactions.

Additionally, energy efficiency can indicate overpotentials, which should be reduced for practical progressions. To determine the energy efficiency of the cathode energy storage capability, the total amount of energy contribute to extracting all Li atoms and the entire amount of energy released by intercalation of all Li atoms should be evaluated. The energy efficiency of electrodes was estimated by the following formula:

$$\text{Energy efficiency} = \frac{\text{Energy density (discharge)}}{\text{Energy density (charge)}} \times 100 \quad (5.7)$$

The energy efficiencies of Bio-TiO₂ and TiO₂/α-MnO₂ electrodes were 60% and 80%, respectively. The low energy efficiency can potentially suggest a problem with the electrochemical system due to large polarization. This could aid in the development of improved electrode materials at both the structure and nanosized.

Moreover, Figures 5.15d and 5.15e indicate the full discharge and charge of Bio-TiO₂ and TiO₂/α-MnO₂ electrodes for four cycles, respectively. The TiO₂/α-MnO₂ electrode shows a slight drop in capacity after the first cycle with a capacity retention of 98.3%, while Bio-TiO₂ indicates capacity retention of 80%.

The result suggested that the growth of α-MnO₂ on Bio-TiO₂ renders a good contribution to the catalyst capacity and lowering overpotential. The favorable urchin nanostructure of α-MnO₂ shell promoted the transportation of electrons to the active sites of Bio-TiO₂ and provided a rapid reaction between O₂ and Li⁺ ions to generate Li₂O₂. During charging, TiO₂/α-MnO₂ electrode displayed two charge voltage, which was undergoing to decompose Li₂O₂ at two steps as consistent with the CV results. Moreover, it is remarkably observed that the TiO₂/α-MnO₂ cathode reduced the charge-discharge gap overpotential due to the rough morphology of α-MnO₂, which served as good channels for Bio-TiO₂ nanoparticles to decrease the inner resistance of the cell and promote migration of electrons and ions and enhance discharge-charge reactions. Therefore, it is clarified that core-shell TiO₂/α-MnO₂ nanostructures assisted as an active catalyst to reduce the overpotential. Similarly, Lim and co-workers enhanced the electrical conductivity and specific capacity of the TiO₂ air electrode by doping niobium (Nb) ions, and the TiO₂ nanoparticles were represented as a promising material for an air electrode [142].

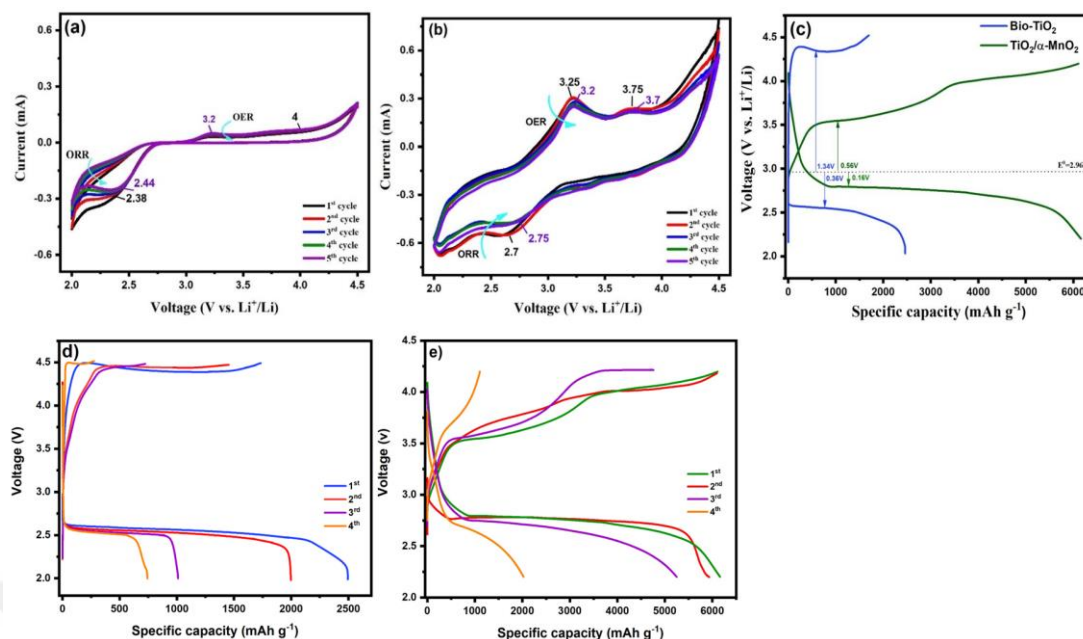


Figure 5.15. Cyclic voltammetry curves of a) Bio-TiO₂, b) TiO₂/α-MnO₂ electrodes between 2.0 and 4.5 V at 0.3 mV s⁻¹. c) A comparison of full discharge-charge profiles of Bio-TiO₂ and TiO₂/α-MnO₂ electrodes at a current density of 120 mA g⁻¹. Full discharge-charge curves of Bio-TiO₂ (d) and TiO₂/α-MnO₂ (e) electrodes for four cycles.

In addition, the capacity of Bio-TiO₂ and TiO₂/α-MnO₂ electrodes was limited to 370 and 600 mAh g⁻¹ to evaluate the cyclability of electrodes. Fig. 5.16(a,b) demonstrate the charge and discharge profiles of electrodes limited at a capacity of 600 mAh g⁻¹. TiO₂/α-MnO₂ electrode revealed good stability for 60 cycles and a relatively high coulombic efficiency of 58.5% after 60 cycles. The first discharge and charge potential plateaus of TiO₂/α-MnO₂ reached 2.8 V, and 3.9 V, and the charge potential was below 4.1 V after 60 cycles, which demonstrated good oxygen evolution reaction catalytic performance of TiO₂/α-MnO₂. By contrast, first discharge and charge potentials for Bio-TiO₂ reached 2.6 and 4.3 V at the end of the capacity limit, and coulombic efficiency was 46.6% after 35 cycles.

Moreover, Fig. 5.16c and 5.16d display stable cycling performance at a limited capacity of 370 mAh g⁻¹ for 130 (780 hrs) and 60 (360 hrs) cycles of TiO₂/α-MnO₂ and Bio-TiO₂, respectively. It is concluded that TiO₂/α-MnO₂ increased the life cycle of the battery due to its higher surface area and good ORR and OER kinetics. The active Bio-TiO₂ provides support for the sufficient growth of MnO₂ nanostructures, and the bifunctional electrocatalytic activity of TiO₂ and α-MnO₂ arises to the higher

number of active sites and good stability. The MnO_2 nanorods act as growth sites to accommodate Li_2O_2 and make it easy to sustain a large contact area between them. Hence, $\text{TiO}_2/\alpha\text{-MnO}_2$ demonstrated excellent OER activity with higher specific capacity and cyclability. The stability of core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ is substantially longer than the life cycles of some reported bifunctional catalysts cathodes, as noted in Table 5.2. From the table, we can observe that the morphology and structure can improve the life cycle of the batteries, and core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ exhibited superior cycling performance.

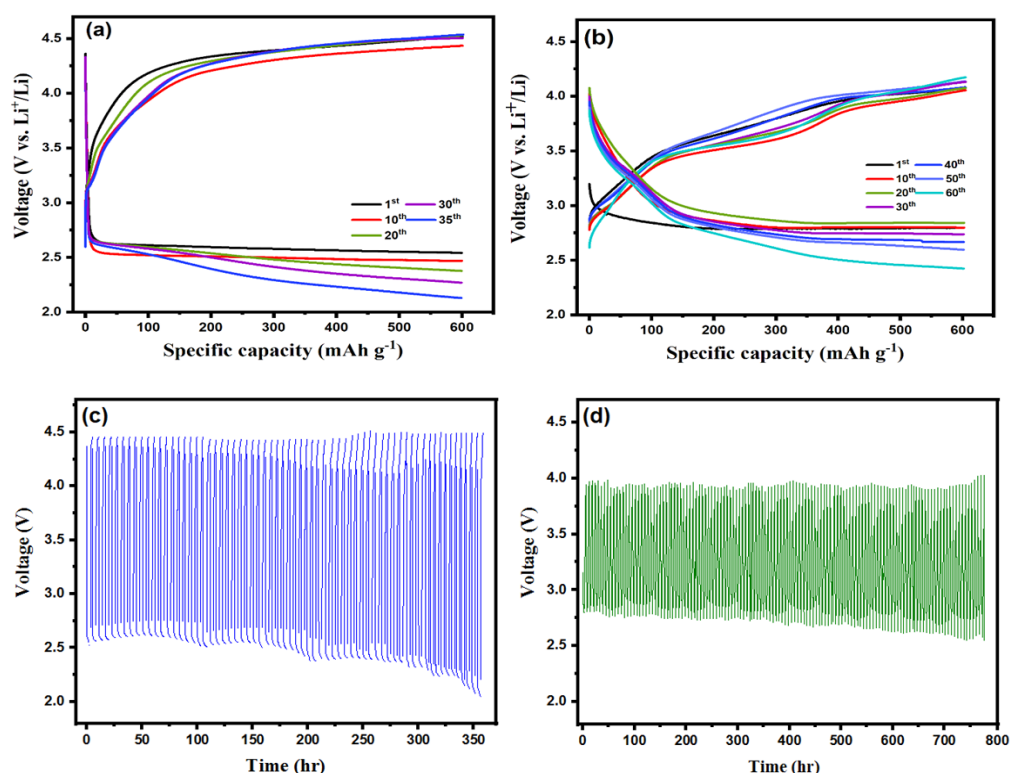


Figure 5.16. Discharge and charge profiles of the Bio-TiO₂ (a) and TiO₂/α-MnO₂ (b) cathodes at a limited capacity of 600 mAh g⁻¹, and cyclic performances of the Bio-TiO₂ (c) and TiO₂/α-MnO₂ (d) electrodes at a controlled capacity of 370 mAh g⁻¹.

Table 5.2. Cycling performance of some previous literature.

Cathode materials	Current density	Specific capacity	Cycles	Ref.
leaf-shaped Co- based metal	0.5 mA cm ⁻²	500 mAh g ⁻¹	7	[143]
RuO ₂ /α-MnO ₂ Nanotubes	0.1 mA cm ⁻²	500 mAh g ⁻¹	26	[144]
Hierarchical FeCo ₂ O ₄ /Ni	400 mA g ⁻¹	500 mAh g ⁻¹	30	[145]
Pd/Co ₃ O ₄ nanowires	0.1 mA cm ⁻²	300 mAh g ⁻¹	70	[146]
Pd/Co ₃ O ₄ nanosheets	100 mA g ⁻¹	300 mAh g ⁻¹	72	[147]
Core-shell TiO ₂ /MnO ₂	120 mA g ⁻¹	370/600 mAh g ⁻¹	130/60	This work

5.7. Post Characterization Of Bio-TiO₂ And TiO₂/α-MnO₂ Electrodes

To clarify the effect of core-shell TiO₂/α-MnO₂ catalyst, the morphologies of electrodes were visualized by FESEM after 35 charge-discharge cycles, and these electrodes indicated quite different morphologies. As shown in Fig. 5.17(a,b), the large toroid-like Li₂O₂ particles (200-900 nm) were deposited on the surface of the Bio-TiO₂ electrode, which caused low discharge capacity and poor electrical conductivity [148]. The toroid shape of discharge products has been reported in previous works [149,150]. In contrast, TiO₂/α-MnO₂ electrode was covered with granular products with a particle size of about 40 nm (Fig. 5.17c. and 5.17d.). The nanoparticulate morphology of discharge product (Li₂O₂) during ORR is reported in previous literature, which could reduce charge potential [151]. These granular particles led to better decomposition and a larger specific capacity. This morphology could be formed due to the urchin nanostructure of MnO₂ shell, which provided the smooth O₂ transport and nucleation sites for Li₂O₂ growth during ORR, and deposited Li₂O₂ would form into nanosized particles on TiO₂/α-MnO₂. Therefore, nanoparticulates Li₂O₂ can provide good electronic transport and inferior OER

potential. Furthermore, the large particles of Li_2O_2 in Bio- TiO_2 electrode caused inadequate decomposition of Li_2O_2 , which could block pores and passivation of the electrode, then cause poor reversibility of Li- O_2 cell.

It is found that during discharging, initially O_2 is reduced to LiO_2 , and later 2LiO_2 is gradually changed to Li_2O_2 and O_2 by a chemical reaction. Thereby, the main product is most likely Li_2O_2 . However, irreversible parasitic products such as Li_2O , Li_2CO_3 , and LiOH can be formed due to electrolyte/electrode decomposition. Furthermore, EDS spectra of electrodes before and after cycling performance indicated that the atomic % of oxygen increased from 48.46% to 76.05% for Bio- TiO_2 (Figures 5.18 a,b) and from 57% to 70.86 % (Figures 5.18c,d) for $\text{TiO}_2/\alpha\text{-MnO}_2$ electrodes. Increasing the atomic % of oxygen could imply the formation of discharge products. Further analysis of the nature structure of discharge products was detected by XRD and Raman spectroscopy.

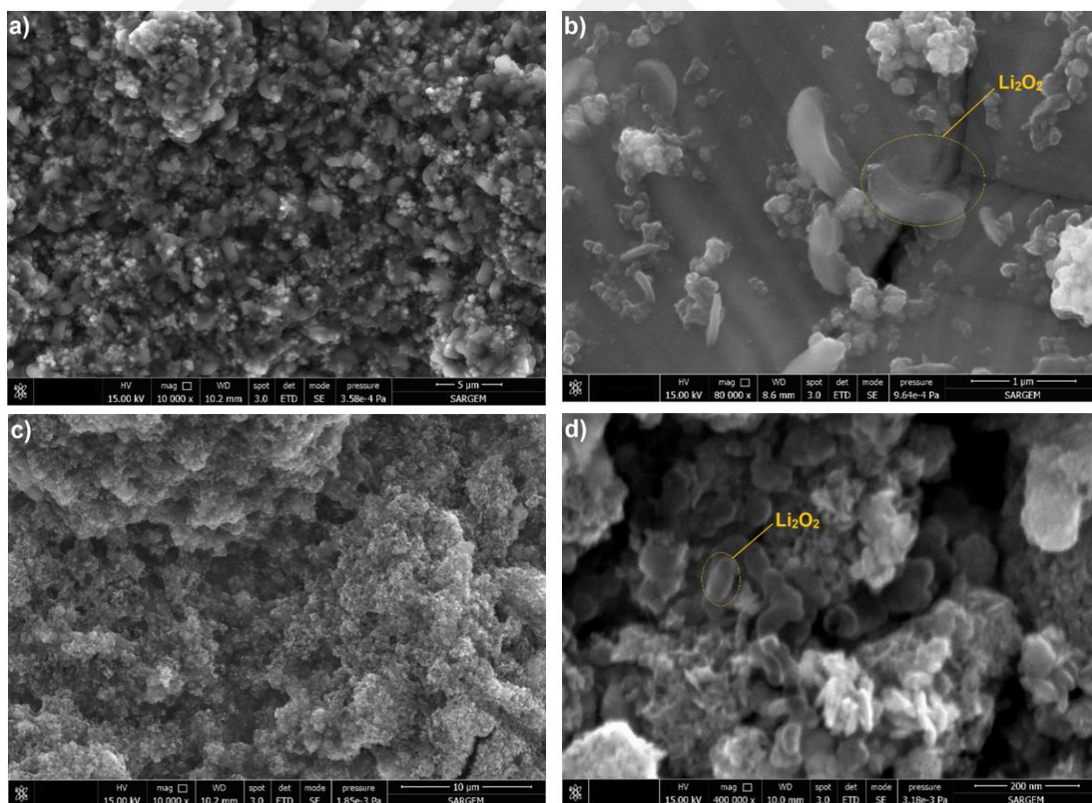


Figure 5.17. FESEM images of Bio- TiO_2 in (a) low and b) high magnification, and $\text{TiO}_2/\alpha\text{-MnO}_2$ at (c) low and (d) high magnification after 35 cyclic electrochemical tests, respectively.

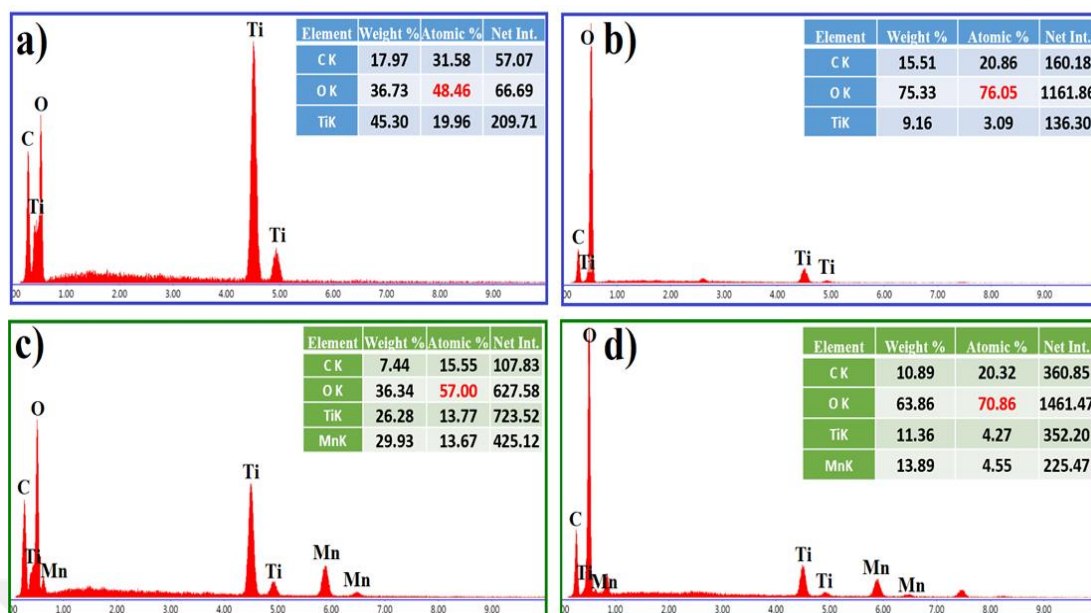


Figure 5.18. The EDS spectra of Bio-TiO₂ and TiO₂/α-MnO₂ cathodes before (a,c) and after cycling performance (b,d), respectively.

The XRD was performed to air cathodes after 35 galvanostatic charge-discharge cycles. The corresponding XRD spectrum of TiO₂/α-MnO₂ (Fig. 5.19a.) revealed peaks at 32.6°, and 40.6° were assigned to the formation of Li₂O₂ and matched well the reference XRD pattern of Li₂O₂ (JCPDS no. 09-0355). Also, a peak detected at 33.6° attributed to LiO₂ (JCPDS no. 77-2144), and no other parasite products were observed for TiO₂/α-MnO₂.

However, the XRD spectra of Bio-TiO₂ electrode demonstrated two peaks at 21° and 30.6° indexed to Li₂CO₃ (JCPDS no. 22-1141), which could be due to the high charge potential (>4.2 V) of Bio-TiO₂, which led to the decomposition of the electrolyte. It should be remarked that the irregular deposition of Li₂O₂ forms toroid-shaped particles and thick film, which cause pore blocking and poor cycling performance. Hence, it is obviously noted that the different growth modes of Li₂O₂ are influenced by electrocatalyst activity. Albeit XRD is poorly suited to detect discharge products, whereas Raman spectroscopy may determine superoxides sensitively from O-O vibrations. The Raman Spectrum of both electrodes after 35 cycles (Fig. 5.19b.) detect peaks at 790 cm⁻¹ attributed to the peroxide-type O-O

bonding of Li_2O_2 . LiO_2 (Li superoxide) for O-O features were noted at 1130 cm^{-1} . A peak at 1081 cm^{-1} was observed for Bio- TiO_2 electrode allocated to Li_2CO_3 .

The electrochemical impedance spectra (EIS) of the Bio- TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ electrodes before and after the electrochemical cycling test were measured to provide improved electrochemical properties. Figure 5.19 (c,d) display Nyquist plots of Bio- TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ before and after 35 electrochemical cycling tests. The EIS spectrums are well fitted on the equivalent circuit (inset Figure 5.19d). This equivalent circuit composed of electrolyte and ionic resistances (R_e), solid electrolyte interphase (SEI) film resistances (R_s) and capacitance (CPE_1), kinetics and charge transfer resistance (R_{ct}), and constant phase elements instead of double-layer capacitance (CPE_2), followed by the Warburg impedance (W_{dif}) corresponds to Li^+ diffusion. Before cycling, Nyquist plots of Bio- TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$ exhibited the R_{ct} value of $415\ \Omega$ and $207\ \Omega$, respectively. The charge transfer resistance decreased by the introduction of MnO_2 due to improving the electronic conductivity and boosted Li^+ migration. Thereby, the charge transfer resistance of $\text{TiO}_2/\alpha\text{-MnO}_2$ demonstrated a low charge transfer resistance. Whereas, after electrochemical cycling, the diameter of R_{ct} increased to $1153\ \Omega$ and $426\ \Omega$ for Bio- TiO_2 and $\text{TiO}_2/\alpha\text{-MnO}_2$, respectively, due to increased deposition of the insulating solid Li_2O_2 during the discharge and blocking pores, hence the impedance of the electrodes became larger, resulting in the poor electrical conductivity and higher polarization. The result demonstrated that the emerging of Bio- TiO_2 and MnO_2 might reduce the electrode interface polarization and enhance the performance of Li- O_2 cells due to the higher surface area and improving electrical conductivity of $\text{TiO}_2/\alpha\text{-MnO}_2$.

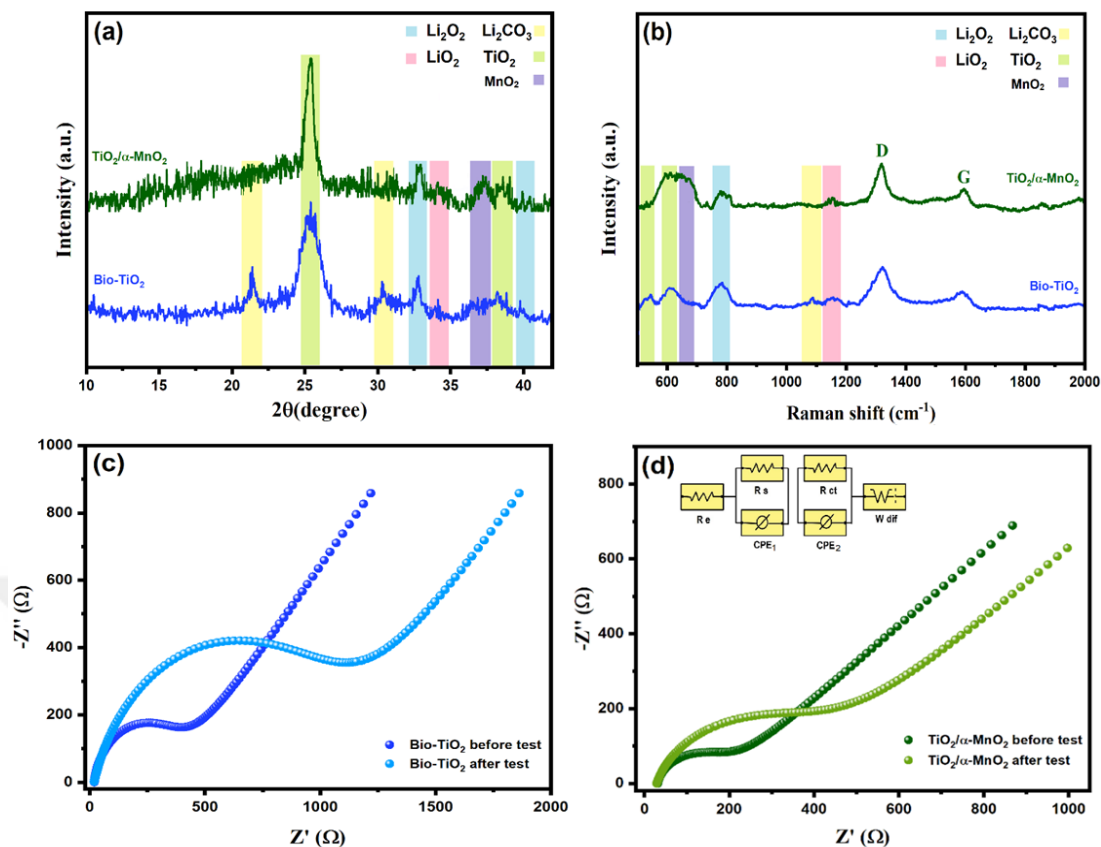


Figure 5.19. a) The XRD pattern and b) Raman spectra of the electrodes after 35 electrochemical cycling tests. Nyquist plots of Bio-TiO_2 (c) and $\text{TiO}_2/\alpha\text{-MnO}_2$ electrodes before and after 35 cycles.

5.8. Morphology And Chemical Composition Of Virus-Templated MnO_2 And Hybrid $\text{Ru}/\alpha\text{-MnO}_2$ Nanowires

Figure 5.20. illustrates a schematic view of the hybrid virus-templated $\text{Ru}/\alpha\text{-MnO}_2$ (marked as v- $\text{Ru}/\alpha\text{MO}$) nanowires via a bio-mineralization process in this study. The virus-templated $\text{Ru}/\alpha\text{MnO}_2$ nanowire was prepared by nucleation and growth of MnO_2 nanostructures (using MnSO_4 and KMnO_4 as precursors) on the surface of M13 phage through self-assembly and chemical bonding, and subsequent incorporation of Ru. M13 phage is known as a versatile bio-template based on a self-assembling protein coat of virus due to the overall negative charge surface of M13 phage.

The zeta potential curves of M13 phages were recorded in incubation at various pH values of 5, 7, 8, and 10 and indicated the negative charge of -5.4, -12, -21.2, and -27

mV, respectively (Figure 5.21a). Therefore, our experiment was controlled at the initial pH of 10 to enhance the affinity of the M13 phage for Mn^{2+} . The majority negative charge of M13 surface attributed to amino groups such as glutamate along of their chemical properties and external location [152]. After nucleation and growth of MnO_2 nanostructures on the surface of the M13 virus, the zeta potential of the obtained virus-templated MnO_2 (marked as v-MO) displayed a negative charge of -44.7 mV. Therefore, it is expected the Ru cations are incorporated on the surface of MnO_2 through electrostatic interaction. Furthermore, we found that by controlling the volume ratio of $\text{MnSO}_4:\text{KMnO}_4$, v-MO nanowires with various crystallographic phases could be obtained at 4 °C. The XRD analysis (Fig. 5.21b.) demonstrates three different crystalline structures of v-MO nanowires at volume ratios 2:8, 5:5, and 8:2.

It is apparent that the amount of K^+ ions play a critical parameter in determining the crystalline structure of MnO_2 products. When the $\text{MnSO}_4:\text{KMnO}_4$ volume ratio was 2:8, the XRD pattern demonstrates weak peaks at 2θ of 22.3°, 37.2°, 42.5°, 56.1°, and 65.3° consistent with $\gamma\text{-MnO}_2$ (JCPDS: 14-0644) phase. During the MnO_2 nucleation, the MnO_2 nuclei tend to the formation of the tunnel size of [1x2] because the small tunnel requires a lower amount of K^+ to be stabilized and may reduce the occupation of the [2x2] tunnel active site. By increasing the K^+ cations into a certain amount (ratio of 5:5), the diffraction peaks located at the 12.4°, 18.1°, 25.7°, 28.9°, 37.2°, 46.0°, 56.6°, and 65.1° positions are detected, which assigned to $\alpha\text{-MnO}_2$ (JCPDS: 44-0141) phase. When the volume ratio of $\text{MnSO}_4:\text{KMnO}_4$ increased to 5:5, there are enough K^+ ions in the solution, the [1x2] tunnel collapse into [2x2] and transit into a stable $\alpha\text{-MnO}_2$ nucleus. An excessive amount of K^+ is destructed the [2x2] structure, and MnO_2 nanocrystals with K^+ tend to form layered structures of $\delta\text{-MnO}_2$. The XRD pattern of MnO_2 with a ratio of 2:8 shows the diffraction peaks at 12.3°, 25.3°, 37.2°, 42.2°, and 65.9°, which is matched with $\delta\text{-MnO}_2$ (JCPDS: 80-1098) phase. As the spacing structure of $\delta\text{-MnO}_2$ is larger than $\alpha\text{-MnO}_2$, therefore, more K^+ cations are needed to stabilize the $\delta\text{-MnO}_2$ structure. Similar experiments are reported approving the influence of K^+ ions concentration on the formation of various crystal phases of MnO_2 [153,154]. The XRD pattern of v-Ru/ αMO hybrid nanowires sample still illustrates the $\alpha\text{-MnO}_2$ phase after incorporation of Ru nanoparticles and the

weak peaks at 2θ of 38° , 42° , and 44° corresponded to fine particles size and poor crystallinity of Ru.

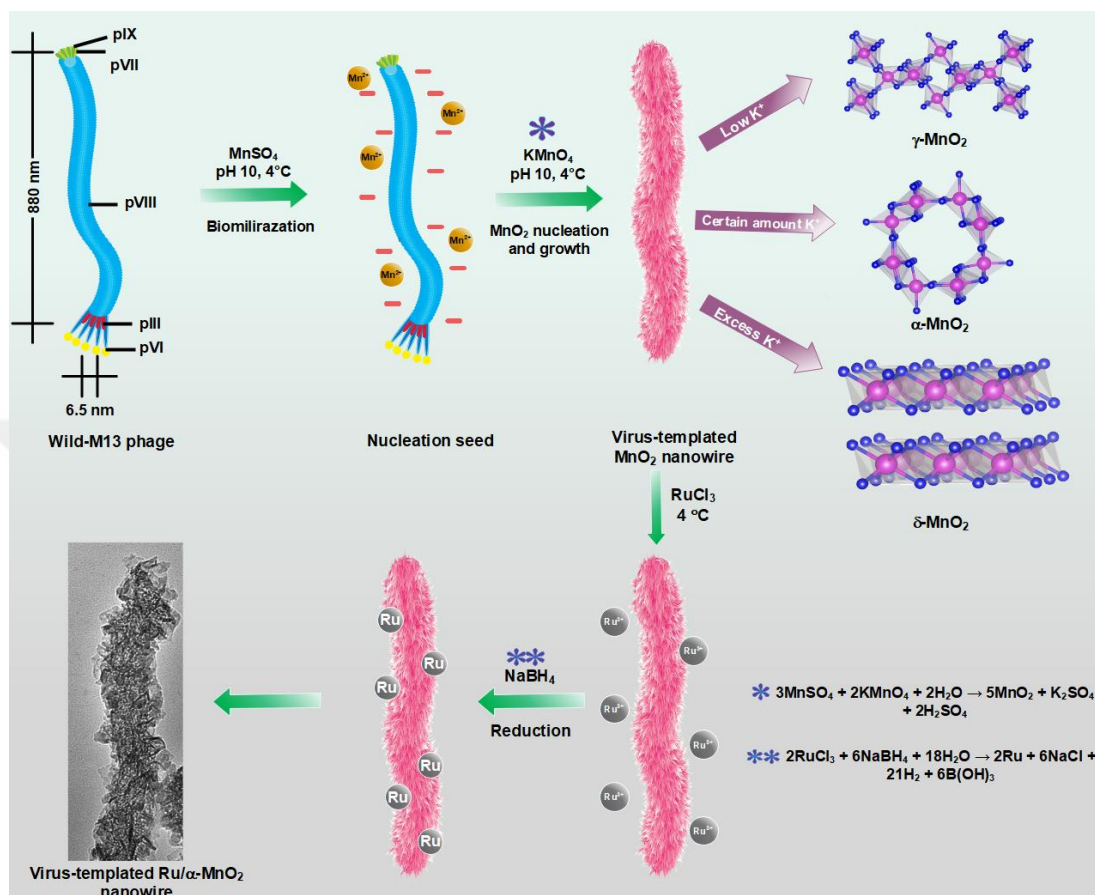


Figure 5.20. Schematic process of polymorphs virus-templated MnO₂ nanowires and hybrid Ru/αMnO₂ nanowires.

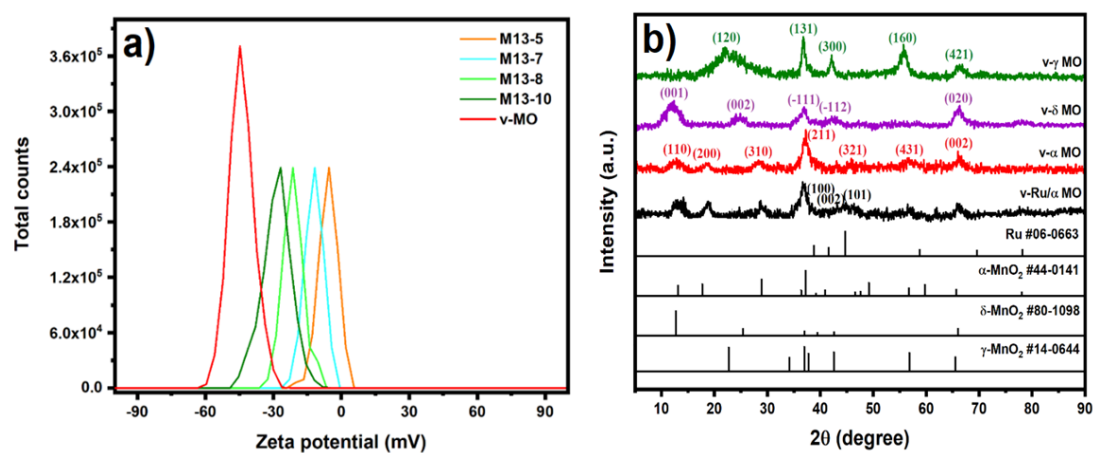


Figure 5.21. a) Zeta potential analysis of M13 phages at various pH values of 5, 7, 8, and 10 and virus templated MnO₂ nanowires. b) XRD spectra of polymorphs v-MO and v-Ru/αMO nanowires.

The study morphology of virus-templated MnO_2 with various crystal phases by FESEM revealed that the MnO_2 nanostructures are assembled by small and uniform urchin-like shape on the M13 phage surface and formed a uniform porous network of 1D MnO_2 nanowires and no distinguished difference between morphologies of α -, γ -, δ - MnO_2 nanowires was observed. However, the FESEM image of v - γ MO nanowires (Fig. 5.22a.) indicates a diameter of 30-70 nm, which is thinner than that of v - α MO (100-130 nm in diameter) (Fig. 5.23a.) and v - δ MO (a diameter of 140-160 nm) (Fig. 5.22b.). It is speculated a higher volume of KMnO_4 solution can cause a relatively high decomposition rate, resulting in growing the thicker nanowires. In TEM and HRTEM images of v - α MO (Fig. 5.23b and 5.23c.) clearly indicate that the MnO_2 nanowire is composed of an urchin-like structure. The HRTEM image of v - α MO nanowires illustrates the mixture of an amorphous and crystal phase of MnO_2 with lattice fringe d spacing of 0.47, 0.24, and 0.195 nm corresponding to planes of (200), (211), and (321), respectively.

In Fig. 5.23d can be seen that after the incorporation of Ru nanoparticles with v - α MO nanowires, the 1D nanostructures are preserved. Figure 5.23e shows the TEM image of v -Ru/ α MO nanowire with a rough structure and a diameter of 180 nm, which increasing the thickness of v - α MO could be due to anchoring Ru nanoparticles on the surface of MnO_2 . The HRTEM image in Figure 3f indicates the presence of spherical Ru nanoparticles in size between 5-15 nm with an interplanar distance of 0.23 nm, which is indexed to a crystal plane of (100) for metallic Ru. We believe that the network structure of virus-templated MnO_2 nanowires acts as a pathway to rapid transfer of oxygen, Li^+ , and reaction intermediate species, which may improve the electrochemical reactions of the battery. Besides, the small particle size of Ru is beneficial to obtain high catalytic activity, which can increase numerous active sites to accommodate more discharge products.

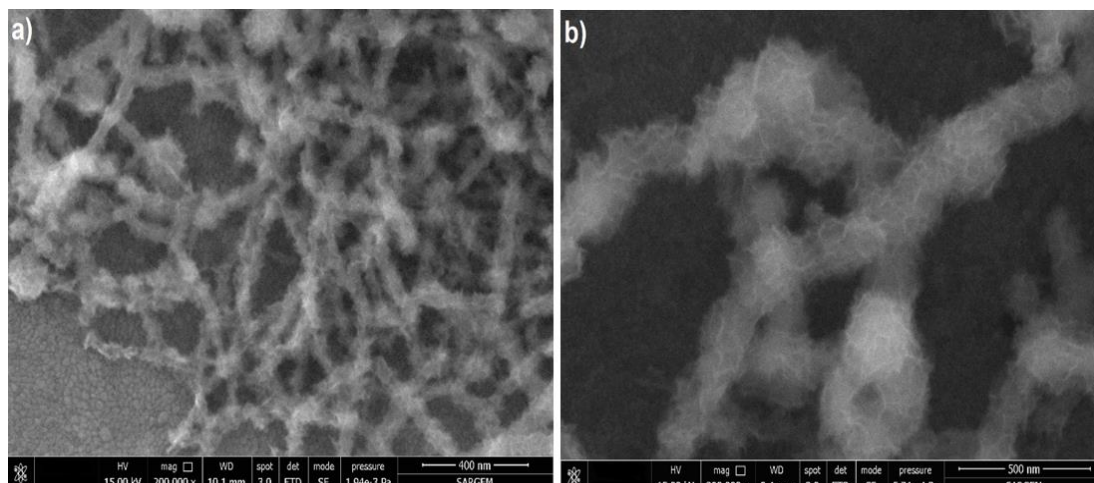


Figure 5.22. FESEM images of virus-templated γ -MnO₂ (a) and δ -MnO₂ nanowires.

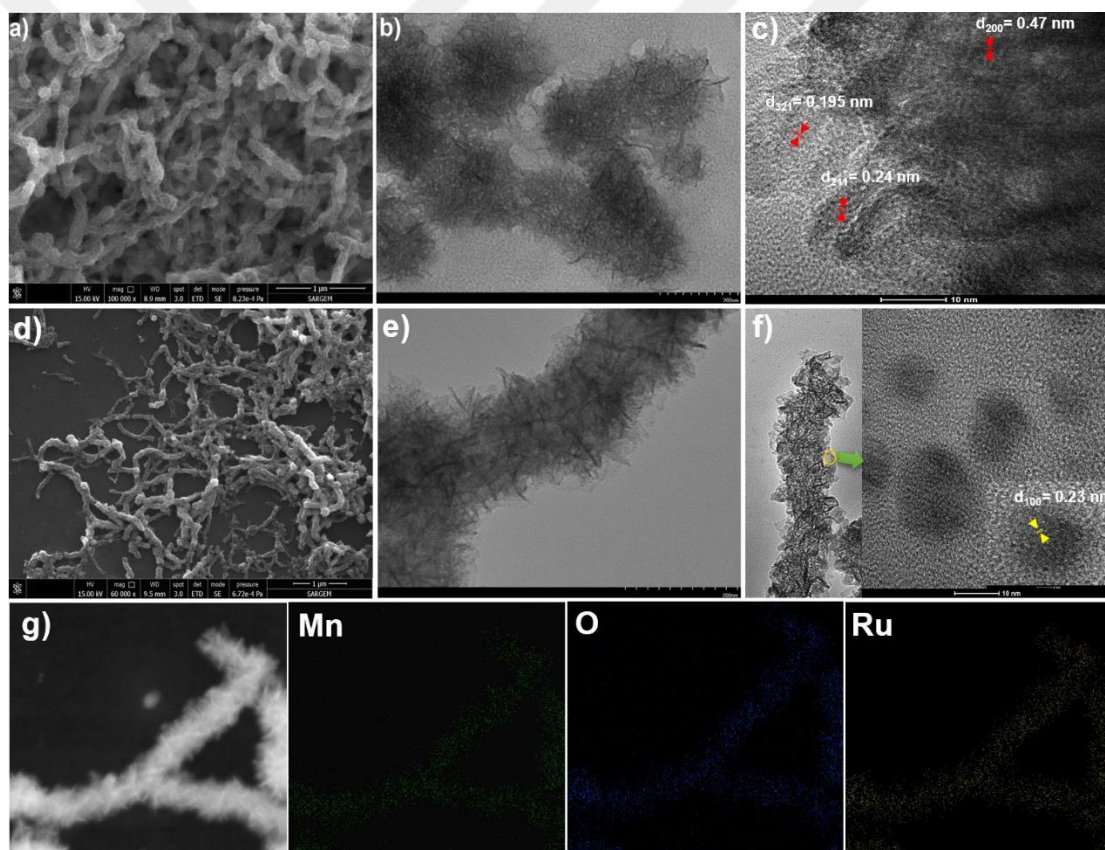


Figure 5.23. FESEM image represents network structure of 1D of virus-templated α -MnO₂ nanowires (a). TEM (b) and HRTEM (c) images of the virus-templated α -MnO₂ nanowire. FESEM image of virus-templated α -MnO₂ nanowires decorated by Ru nanoparticles (d). TEM (e) and HRTEM (f) images denote decoration of Ru on the surface of virus-templated α -MnO₂ nanowires, and (g) EDS mapping approves the distribution of Ru, Mn, and O elements in virus-templated Ru/ α -MnO₂ nanowire.

Furthermore, EDS spectra of the v- α MO and v-Ru/ α MO confirmed the presence of Mn, O, and Ru elements (Fig. 5.24a-b.). The v-Ru/ α MO sample is composed of

14.2% weight Ru in the hybrid structure. To further approve the elemental distribution within the hybrid structure, energy-dispersive X-ray spectroscopy mapping was performed. Fig. 5.23g. supports an even dispersion of Ru on the surface of v- α MO.

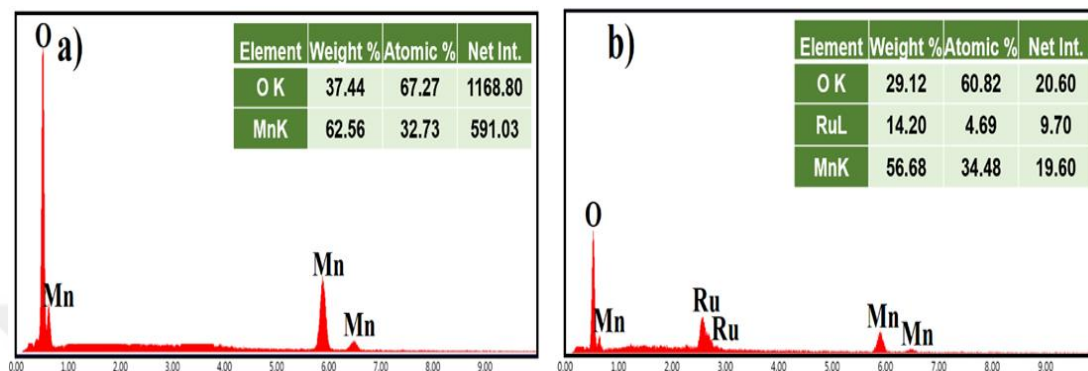


Figure 5.24. EDS spectra of v- α MO (a) and v-Ru/ α MO (b).

XPS spectroscopy was conducted to identify the chemical composition and valence state of each element for v-Ru/ α MO and various v-MO products. Fig 5.25. indicates the XPS spectra of different crystalline structures of v-MO products. The survey XPS spectra of all v-MO samples (Fig. 5.25a.) identified peaks at binding energies of 642, 530, 86, and 50 eV, which attributed to Mn 2p, O 1s, Mn 3s, and Mn 3p, respectively. The detected peaks of C and N are allocated to organic compositions of M13 phages. The high-resolution XPS spectra of Mn 2p and O 1s for all v-MO phases are presented in Figure 5.25b. and 5.25c., respectively. The high-resolution XPS spectra of Mn 2p for all the polymorphs v-MO samples are detected two main peaks at 642.4 and 654 eV. It has been reported in the literature that the binding energy of Mn⁴⁺ (MnO₂) is 642.3 $\pm$ 1 eV, while the corresponding Mn³⁺ (Mn₂O₃) with binding energy at 641.3 $\pm$ 1 eV [155,156]. All the v-MO samples indicate the formation of MnO₂. The O1s XPS spectra of all v-MO samples revealed the main peak at about 529.4 eV, which is assigned to lattice oxygen because of the metal oxides (marked as O _{α}). The peak at 531.0-532 eV is ascribed to chemisorbed oxygen caused by oxygen vacancies (marked as O _{β}). The XPS data of polymorphs v-MO are denoted in Table 5.3. Among the crystal forms of v-MO products, v- α MO possesses the highest intensity of O _{α} ,

which might perform higher catalytic activities due to its higher mobility than O_{β} [157].

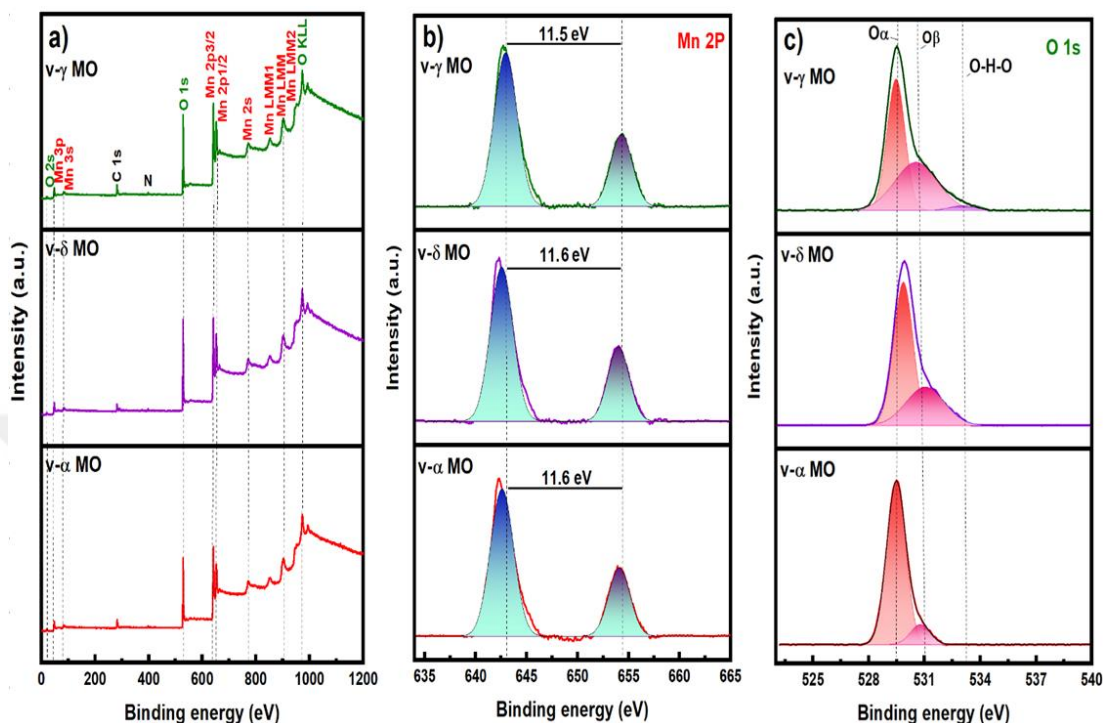


Figure 5.25. Survey XPS spectra (a), high-resolution spectra of Mn2p (b), O1s (c) of virus-templated MnO_2 with different crystal phases.

Table 5.3. The binding energy and atomic % of Mn and O of virus-templated MnO_2 polymorphs from XPS result.

Products	Mn 2p _{3/2}	Mn 2p _{1/2}	O 1s	Mn at. %	O at. %
v-γMO	642.8 eV	654.3 eV	529.4 eV	29.71	70.29
v-δMO	642.4 eV	654 eV	529.8 eV	30.28	69.72
v-αMO	642.4 eV	654 eV	529.4 eV	32.02	67.98

The XPS survey scan of v-Ru/αMO (Fig. 5.26a.) is verified the presence of Mn, O, and Ru elements. The high-resolution spectra of Mn 2p (Figure 5.26b.) demonstrated two peaks centered 642.3 and 653.9 eV and corresponded to Mn^{4+} (2p_{3/2}) and Mn^{4+} (2p_{1/2}) with a spin energy separation of 11.6 eV which is in well match with the previous literature for the MnO_2 phase [158,159]. Furthermore, the high-resolution spectra of O 1s (Fig. 5.26c.) are split into three peaks assigned to characteristic oxygen binds, which deconvoluted as Mn-O (529.7 eV), Mn-O-H (531.2 eV), and H-

O-H (533 eV). The high-resolution spectra of Ru 3p region (Fig. 5.26d.) revealed the peaks at 461.7 eV and 483 eV are contributed to Ru 3p_{3/2} and Ru 3p_{1/2} peaks, respectively, which implies the formation of metallic Ru [160].

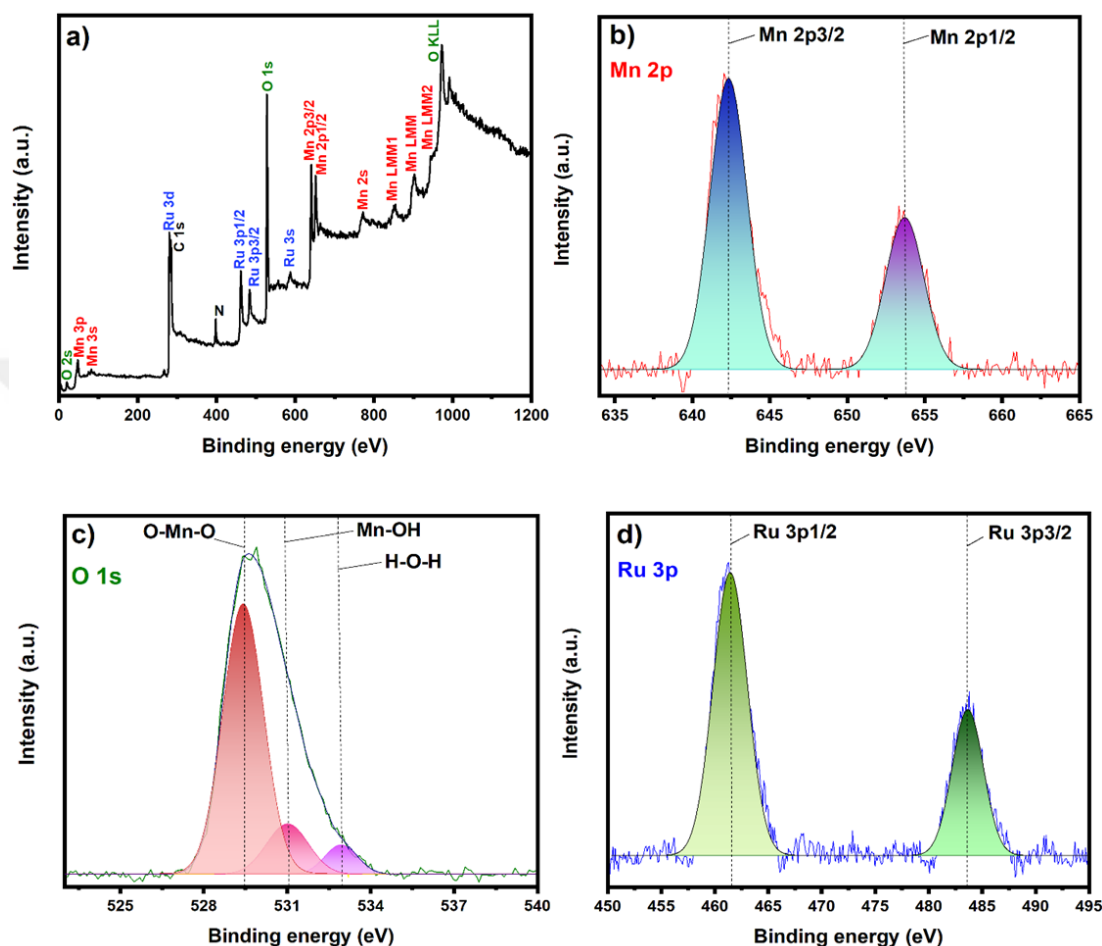


Figure 5.26. XPS spectra of a) survey, b) Mn 2p, c) O 1s, and d) Ru 3p for virus-templated Ru/α-MnO₂ nanowires.

The nitrogen adsorption-desorption isotherms of all samples illustrate the type IV hysteresis loop, displaying the mesoporous characterization of the prepared samples (Figure 5.27a.). Brunauer-Emmett-Teller (BET) specific surface area of v-γ/MO, v-δ/MO, v-α/MO and v-Ru/αMO is 84.3 m² g⁻¹, 137.1 m² g⁻¹, 169.9 m² g⁻¹, and 255.7 m² g⁻¹, respectively. The larger surface area of α-MnO₂ mostly derived from its one-dimensional [2 x 2] tunnels with a size of 4.6 Å^o x 4.6 Å^o. The pore volume is 0.292 cm³ g⁻¹, 0.325 cm³ g⁻¹, 0.386 cm³ g⁻¹, and 0.405 cm³ g⁻¹ for the corresponding samples. Fig. 5.27b. shows the narrow pore size distribution of the v-Ru/αMO, v-

α /MO, v - δ /MO, and v - γ /MO with an average pore size of 6.4 nm, 10.2 nm, 8.6 nm, and 13.8 nm, respectively, calculated by the Barret-Joyner-Halenda (BJH) method, suggesting that all the samples are mesoporous materials which are consistent with isotherm curves. It is clear that Ru nanoparticles incorporated with v - α MO enhanced the surface area, porosity, and pore volume of v - α MO, which could assign to the improved reversible capacity by providing higher active catalytic sites. In addition, the porous structure can efficiently enhance electrolyte permeability and mass transfer.

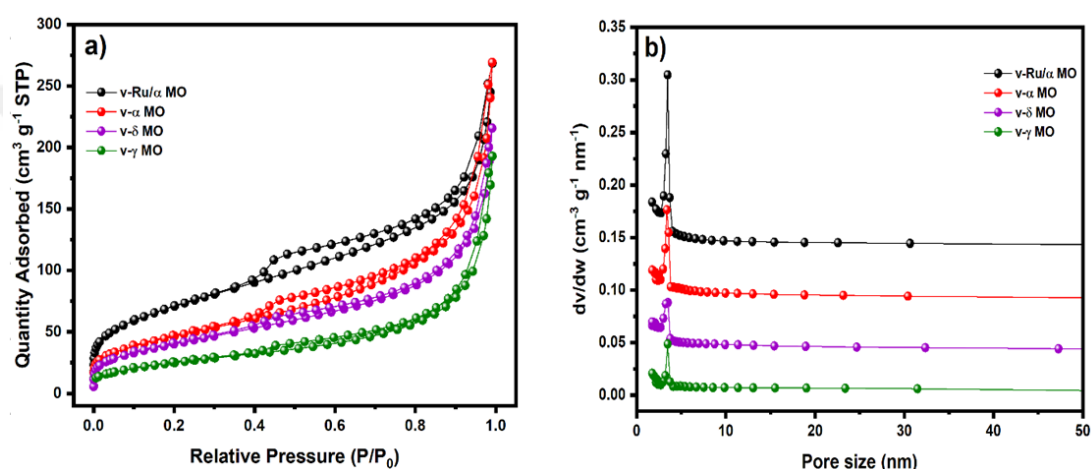


Figure 5.27. Nitrogen adsorption-desorption isotherm and b) pore size distribution of v -Ru/ α -MO and various crystalline structures of v -MO.

5.9. Electrochemical Performance Of Virus-Templated MnO₂ And Hybrid Ru/ α -MnO₂ Nanowires

The electrochemical performance of all samples was investigated as an electrocatalyst for lithium-O₂ cells by galvanostatic discharge-charge test. Figure 5.28a represents the first discharge and charge profiles of lithium-O₂ cells with v - γ /MO, v - δ /MO, v - α /MO and v -Ru/ α MO electrodes at the voltage window of 2.2-4.2 V with a current density of 200 mA g⁻¹. The v -Ru/ α MO electrode demonstrates the discharge voltage platform at 2.83-2.8 V, which is higher than that of v -MO electrodes by 50 mV, which could be due to the enhanced surface conductivity by Ru nanoparticles. Meanwhile, the overpotential of Li-O₂ cell with v -Ru/ α MO catalyst (0.97 V) is lower than those of v -MO electrodes (1.1-1.23 V). The discharge and

charge voltage plateaus of lithium-O₂ batteries could be remarkably enhanced with the utilization of bifunctional catalysts. The synergetic effect of Ru and α -MnO₂ catalysts significantly boosts the reversible reaction in lithium-O₂ systems by reducing polarization, which is essential toward the practical application of Li-O₂ batteries. Therefore, the results approve that the Ru catalyst improved ORR and OER catalytic activities to promote Li₂O₂ formation and decomposition.

Furthermore, the v-Ru/ α MO catalyst delivers a discharge capacity of 14,383 mA h g⁻¹, that is markedly higher than those of v- α MO nanowires (10,875 mA h g⁻¹), v- δ MO (9726 mA h g⁻¹), and v- γ MO (6575 mA h g⁻¹). The higher capacity of v- α MO could be due to the large tunnel spaces linked by the MnO₆ octahedrons in α -MnO₂, which promote the formation of Li_xO_y species. Moreover, the energy efficiencies of v-Ru/ α MO, v- α MO, v- δ MO, and v- γ MO are estimated to be 75%, 70.7%, 69% and 68.3% respectively. That means the synergetic effects of Ru and MnO₂ cause a lower overpotential. Some previous reports of carbon-free catalysts for Li-O₂ batteries in literature are cited in Table 5.4, and the virus-templated Ru/ α MnO₂ catalyst indicated the highest discharge capacity and surface area. The improved discharge capacity of α -MnO₂ catalyst is closely associated with the highly catalytic activity of Ru, which can provide a high number of active sites toward ORR/OER and a large storage void for Li₂O₂ products. Also, the network structure of v- α MO nanowires is an advantage to increase the porosity and rapid transportation of electrons and oxygen.

The morphology evolution of the v- α MO and v-Ru/ α MO electrodes after the full discharge-charge was evaluated using FESEM. The electrochemical test was performed in El-Cell Swagelok cells and the voltage of the cell was cut off at different stages during charging and discharging: During discharge, the cut-off voltage was applied (at 2.8 V for v-Ru/ α MO and 2.7 V for v- α MO) and 2.2 V, and in reverse, the cut off voltage was selected in the initial cut off at the initial charge stage (3.9 V), and end of the charge (4.2 V). The aim is to explain the chemical reactions of carbon-free and carbonaceous cathodes with ether-based electrolyte upon ORR/OER. When the v- α MO and v-Ru/ α MO electrodes were discharged to 2.7 V

and 2.8 V, respectively, the electrode surfaces were deposited by different morphologies of the generated discharged products.

Table 5.4. Previous report results of carbon-free catalysts as air electrodes for Li-O₂ battery.

Cathode material	Surface area (m ² g ⁻¹)	Electrolyte	Overpotentials (V)	Current density	Specific capacity (mAh g ⁻¹)	Ref.
IrNi Nanosheets	94.6	LiTFSI/DMSO	1.35	0.2 mA cm ⁻²	1120	[161]
FeCo ₂ O ₄ @Ni	68.6	LiTFSI/TEGDME	0.97	200 mA g ⁻¹	7733	[162]
Ru@Ni	58.3	LiClO ₄ /TEGDME	1	200 mA g ⁻¹	3720	[163]
NiCo ₂ O ₄	31	LiTFSI/TEGDME	1.4	0.05 mA cm ⁻¹	1535	[164]
La _{0.6} Ca _{0.4} Fe _{0.8} Ni _{0.2} O ₃ nanotubes	31.5	LiTFSI/DMSO	1.6	400 mA g ⁻¹	13019	[165]
MnO _{2-x} Nanosheets	117	LiTFSI/TEGDME	1.24	200 mA g ⁻¹	7300	[166]
Ni ₃ S ₂ /PrBa _{0.5} Sr _{0.5} Co ₂ O _{5+δ}	10.79	LiTFSI/TEGDME	0.68	100 mA g ⁻¹	12874	[167]
v-Ru/α-MnO ₂ nanowires	255.7	LiClO ₄ /TEGDME	0.97	200 mA g ⁻¹	14383	This work

In Figure 5.28b., the v-Ru/αMO electrode reveals the cathode surface is covered by film-like morphology after discharged to 2.8 V, whereas v-αMO electrode demonstrates a toroid shape with a size of about 1 μm (Fig. 5.28f.). And after a deeper discharge to 2.2 V, the v-Ru/αMO electrode surface is fully covered with film-like morphology, as shown in Fig. 2.10c. The v-αMO electrode also displays a significant amount of toroid discharge particles after discharged to 2.2 V (Fig. 5.28g.).

The different growth modes of discharge products could be attributed to two different reaction processes (solution-mediated pathway and surface-mediated pathway) due to the surface properties of the cathodes. The synergistic effects of Ru and α-MnO₂

could enhance the O₂ absorption through electrochemical reduction and drive toward surface growth of thin-film like [168]. In contrast, the weak O₂ absorption of the surface cathode in v- α MO containing carbon black formed the toroid shape through a solution mediated pathway, which is consistent with those of metal oxide mixed with carbon additives [169,170]. The larger discharge products in v- α MO electrode lead to lower capacity and higher charge potential compares to that of v-Ru/ α MO. The morphologies of v-Ru/ α MO hybrid and v- α MO electrodes at various charged states were also studied by FESEM and shown in Figure 5.28d-e and 5.28h-I, respectively. During the subsequent charge state, the deposited discharge products were reduced at the charge of 3.9 V in both electrodes.

However, when the v-Ru/ α MO electrode charged to 3.9 V, the capacity was about 10000 mAh g⁻¹ (70% of total capacity), and v- α MO capacity reached 4000 mAh g⁻¹ (36.7% of total capacity), suggesting substantial decomposition of thin-film like discharge products occurs under 3.9 V for v-Ru/ α MO, despite that toroid shape discharge products on v- α MO electrode surface require higher charge voltage to decompose. After charging to 4.2 V, discharge residue completely decomposed from the v-Ru/ α MO electrode (Figure 5.28d.), showing the high reversibility of the v-Ru/ α MO hybrid electrode. Nevertheless, when the v- α MO electrode charge to 4.2 V, the surface of the charged electrodes shows the presence of residual particles implying some inherent decomposition of electrolyte or other parasite reactions. From the above results, we can conclude that there is a correlation between Li₂O₂ growth modes and cathode materials, which affect the electrochemical performance of Li-O₂ cells. The carbon-free materials have a strong O₂ absorption compare to carbon-based materials, which leads to the formation of thin-film like discharge products resulting in lower charge potential. Thereby, minimizing the charge potential inhibits the electrolyte decomposition and surpasses the formation of by-products, which can maintain the stability of the cell.

To verify the composition of v- α MO and v-Ru/ α MO electrodes at different stages of discharge and recharge, XRD and FTIR were performed. The XRD pattern of the discharged electrodes of v-Ru/ α MO at discharge plateau 2.8 V (D 2.8V) shows peaks

at $2\theta = 32.5^\circ$, 35.2° , 40.6° , which are indexed to (100), (101), and (102) planes of Li_2O_2 (JCPDS no. 09-0355) and a peak at $2\theta = 33.5^\circ$ is associated with the presence of LiO_2 (JCPDS no. 77-2144) with crystal plane of (111) (Figure 5.29a.). The discharged v-Ru/ α MO cathode at 2.2 V (D 2.2 V) shows higher intensity peaks associated with Li_2O_2 indicating a higher amount of Li_2O_2 component is generated. For the discharged v- α MO electrode, the relative intensities of those peaks are much lower (both at 2.7 V and 2.2 V) (Fig. 5.29b.), which matches with the catalytic efficiency results from the battery test.

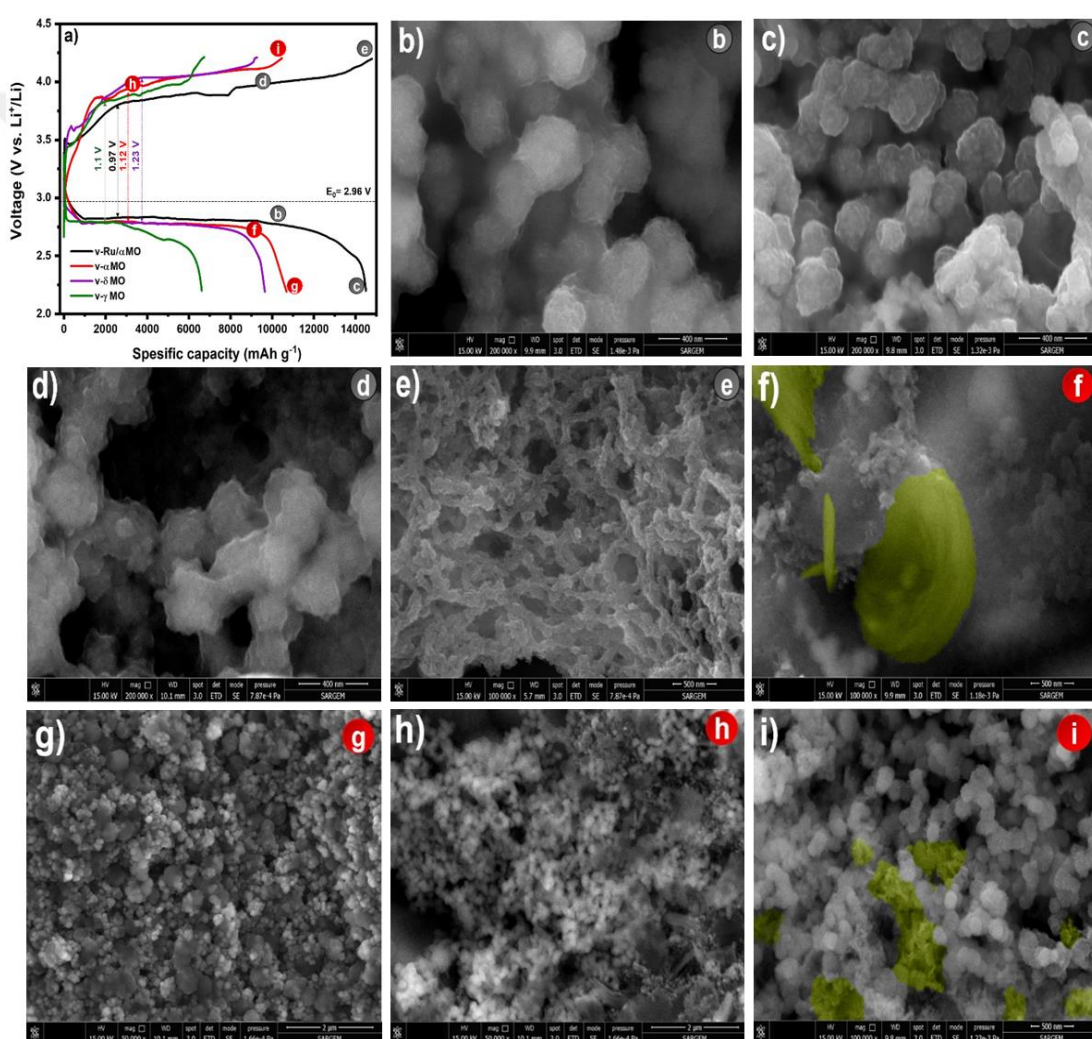


Figure 5.28. a) the discharge-charge profiles of v-Ru/ α MO and various v-MO electrodes along with morphological evolution FESEM images of discharge and charge states at different stages for v-Ru/ α MO (b-e) and v- α MO (f-i) cathodes. Each FESEM image is attributed to the marked points in the discharge-charge profiles. The yellow color represents discharge products.

Moreover, two peaks detected at 21.3° and 30.4° assigned to Li_2CO_3 (JCPDS no. 22-1141) for v- α MO due to the presence of carbon material, which interacted with Li_2O_2 . A small peak at 21.3° was detected for v-Ru/ α MO during discharge, indicating the reactivity of the electrolyte. The XRD results approve the synergetic effects of Ru and α - MnO_2 in reducing byproducts, which leads to lower charge potential. The peaks corresponding to Li_2O_2 and LiO_2 were reduced in the charged electrode of v-Ru/ α MO at 3.9 V (C 3.9 V) and completely decomposed at 4.2 V (C 4.2 V). At the end of the charge, the charged v- α MO electrode also has not exhibited peaks linked to Li_2O_2 . Nevertheless, XRD cannot sensitively detect the possible formation of other parasite products, such as HCOOLi and CH_3COOLi , which are derived from the interaction between the electrolyte and cathode, and further result in passivation of the cathode. Therefore, FTIR was employed at the range of $600\text{--}2000\text{ cm}^{-1}$. Figures 5.29c and 5.29d demonstrate FTIR spectra of v-Ru/ α MO and v- α MO electrodes after different stages of discharge and charge.

Upon discharge plateau, the typical peaks in the spectral range are attributed to the bonds such as $\text{O}=\text{C}-\text{O}$, $\text{C}-\text{O}$, $\text{C}-\text{H}$, and $\text{C}=\text{O}$ stretching modes. These peaks are likely assigned to organic deposits, which are derived from the decomposition of the TEGDME solvent on the electrode surfaces of v-Ru/ α MO and v- α MO during the kinetic reactions. In FTIR spectra of v- α MO, these organic deposits are Li_2CO_3 (at 865 cm^{-1}), HCO_2Li (at 1410 cm^{-1} and 1620 cm^{-1}), and $\text{CH}_3\text{CO}_2\text{Li}$ (at 1090 cm^{-1}), and after deeper discharge, to 2.2 V the intensity of these organic deposits increased. In the case of v-Ru/ α MO, smaller peaks corresponding to Li_2CO_3 (at 865 cm^{-1}), HCO_2Li (at 1620 cm^{-1}), and $\text{CH}_3\text{CO}_2\text{Li}$ (at 1090 cm^{-1}) were observed, indicating the presence of fewer amounts of organic deposits during discharging. These parasite products are driven by the reactivity and decomposition of electrolytes during electrochemical reactions. The results indicate higher reactivity of electrolyte at deeper discharge potential on the surface of both electrodes. The accumulation of carboxylate and carbonate side products on the cathode surface can gradually cause the loss of active sites and deteriorate durability. When compared to MnO_2 , ruthenium nanoparticles appear to minimize side reactions, most likely by arousing oxygen radicals into the formation of LiO_2 -like components. After the recharge at 3.9

V, a reduction in the intensity of the signals was observed, but upon charging at 4.2 V, the HCO_2Li and $\text{CH}_3\text{CO}_2\text{Li}$ peaks have increased, suggesting CO_2 release and the organic deposits could be electrochemically oxidized at potentials up of 4 V. The intensity of the peaks is, however, much lower than that of v-Ru/MO electrodes. We can suggest from the FTIR studies and previous reports that the side reactions were the TEGDME electrolyte decomposition, and Ru metals have an important role in reducing these side reactions [171, 172].

The electrochemical impedance spectroscopy (EIS) was also conducted to identify the electrochemical reactions by measuring series of EIS spectra at different charge-discharge stages. The recorded EIS from the discharge plateau of v-Ru/ α MO and v- α MO electrodes is exhibited in Fig. 5.29e. and 5.29f. On the equivalent circuit, the Nyquist plots are well configured (inset Figure of 5.29e.). This equivalent circuit is distinguished in three regions referred to as R_1 , R_2 , and R_3 . The high frequency of the semicircle (R_1) is contributed to the electrolyte, cathode, and contact resistances. Charge-transfer resistance (R_2) is represented by the semicircle in the medium-frequency zone at cathode/electrolyte and constant phase element (CPE). The linear rise in low-frequency is described as Warburg diffusion resistance (R_3) of Li^+ transportation at the cathode.

Notably, the pristine v-Ru/ α MO electrode demonstrates the semicircle in the middle-frequency zone has a smaller diameter than the v-MO electrode, which distinctly manifests that v-Ru/ α MO electrode has a lower charge transfer resistance (R_2). The superconductivity of Ru nanoparticles, which also facilitated electron transport and intimate contact between the catalyst and Li_2O_2 , can be allocated to a lower charge transfer resistance of the v-Ru/MO electrode. After discharge plateau, the diameter of R_2 semicircle increased in both electrodes. The increase of R_2 can be assigned to the formation of Li_2O_2 on the surface of cathode, which prevents the charge transfer and diffusion of oxygen through cathode pores. Increasing the R_3 indicates the blocking of the cathode pores, which means that Li^+ ion migration is hindered. At the end of the discharge, polarization resistance increased, which corresponded to Li_2O_2 layer thickness. The R_1 was shifted toward the right. It could be due to changes in the

resistance due to electrolyte decomposition and Li_2CO_3 formation. During the initial charge, R_1 diameter was reduced, implying the electrical resistivity decreases due to the Li_2O_2 decomposition. At the termination of the charge, the R_1 semicircle was close to the pristine electrode for v-Ru/ α MO showing the high reversibility of the bifunctional catalyst.

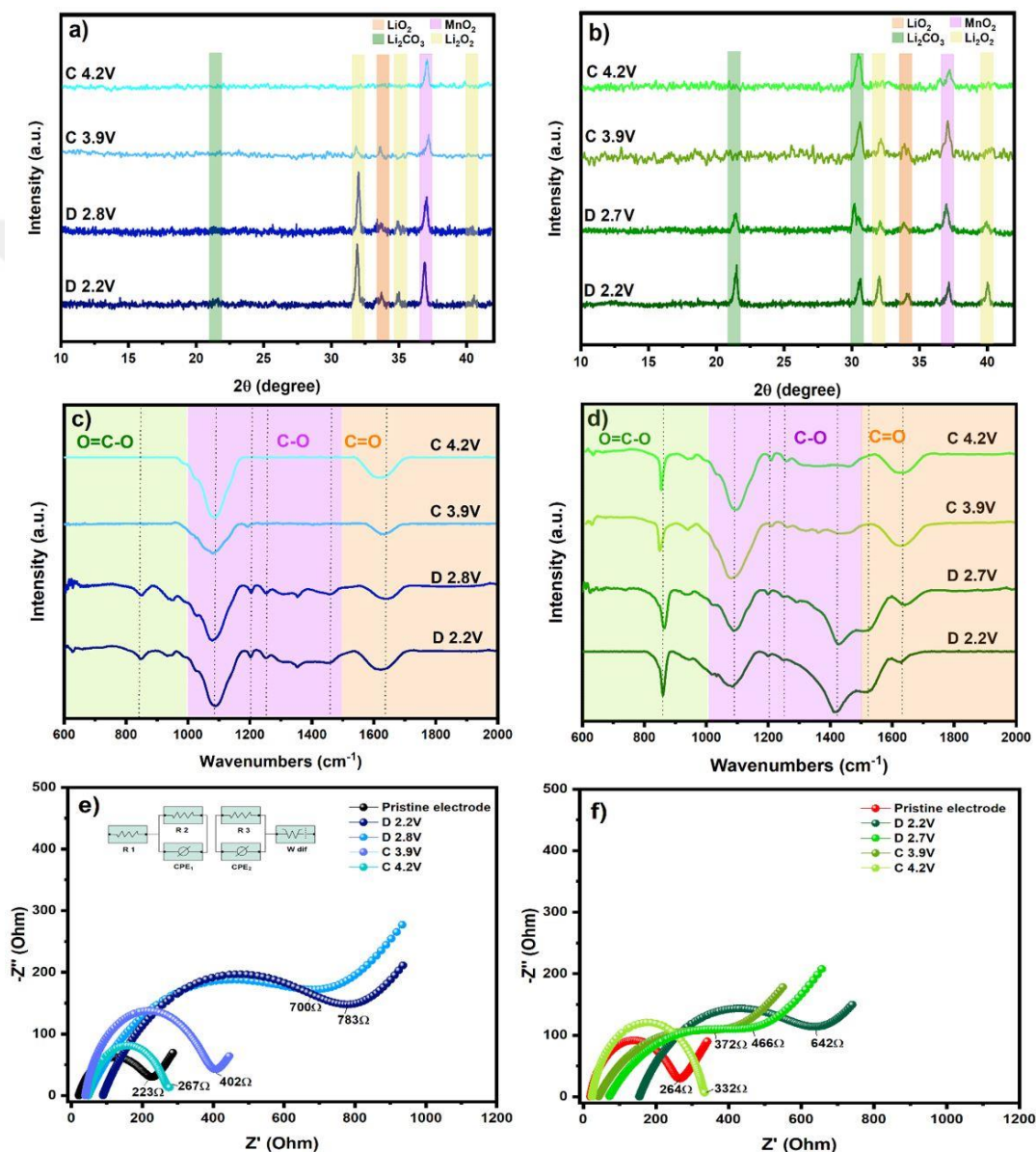


Figure 5.29. The XRD and FTIR spectra of v-Ru/ α MO (a,c), and v- α MO (b,d) after discharge and charge at different stages, respectively. The EIS spectra of v-Ru/ α MO (e) and v- α MO (f) electrodes at different charge and discharge stages.

The further catalytic activity of v- α MO and v-Ru/ α MO was examined by cyclic voltammetry (CV) and a capacity-controlled regime of 1000 mAh g⁻¹. Cyclic voltammetry (CV) scans of v-Ru/ α MO and v- α MO electrodes were recorded at the voltage window of 2-4.5 V with a scan rate of 0.3 mV S⁻¹, as presented in Figures 5.30a and 5.30b, respectively. During the anodic reaction, a broad oxidation peak can be seen at 3.2-3.9 V for both electrodes, showing most discharge products are decomposed in this voltage range, which is consistent with XRD and FESEM results. However, in both cathodic and anodic scans, v-Ru/ α MO demonstrates a higher current density compared with v- α MO electrodes, implying increased reaction kinetics during discharge product formation and decomposition. The excellent electrochemical performance of the v-Ru/ α MO electrocatalyst could be accredited to the intrinsic high catalytic efficiency of Ru coupled with urchin-like α -MnO₂ nanowires, which enriched the porosity and O₂ diffusion.

Figures 5.30c and 5.30d show the cycling performance of v- α MO and v-Ru/ α MO for 32 and 48 stable cycles at a controlled capacity of 1000 mAh g⁻¹. Over the following cycles, the v-Ru/MO hybrid electrodes revealed stable voltage behaviour with a slight drop. (Fig. 5.31a). In contrast, the charge and discharge voltage profiles of v- α MO dropped after 25th cycle. The discharge voltages of the v-Ru/MO hybrid were moderately decreased from 2.8 V at the first cycle to 2.7 V at the thirties cycle, although this discharge potential in the v-MO was gradually decreased to 2.4 V as the cell cycled to the 30th cycle, assuming that internal resistance increased due to parasite reactions.

Moreover, the terminal charge potential of v-Ru/ α MO electrode after 30th cycle reached 3.8 V, while for v- α MO electrode increased to 4.25 V. Notably, the low charge potential could prevent decomposition of electrolyte, thereby maintain the cycling performance of the cell. When the cell with the v- α MO cathode cycled longer than 30 cycles, the capacity rapidly failed after 32nd cycle while the v-Ru/ α MO cathode could be cycled for more than 48 cycles in a stable manner. After 50 cycles, the capacity of the cell with v-Ru/ α MO electrode declined to 750 mAh g⁻¹, which corresponds to 75% capacity retention (Figure 5.31b.). On the contrary, v-MO

electrode demonstrated a specific capacity of 216 mAh g⁻¹ after 50 cycles, that corresponded to 21.6% capacity retention (Figure 5.31d.). Meanwhile, the round-trip efficiency of the v-Ru/ α MO at 48th cycle is still high as 62.5%. However, after disassembling the Li-O₂ cell after 48 cycles for v-Ru/ α MO electrode, we have observed the lithium foil were completely corroded (Fig. 5.32.) due to reactivity with O₂ and electrolyte. Thereby, further study on the development of a solid-state electrolyte and lithium anode coating is required to achieve a longer cycle life.

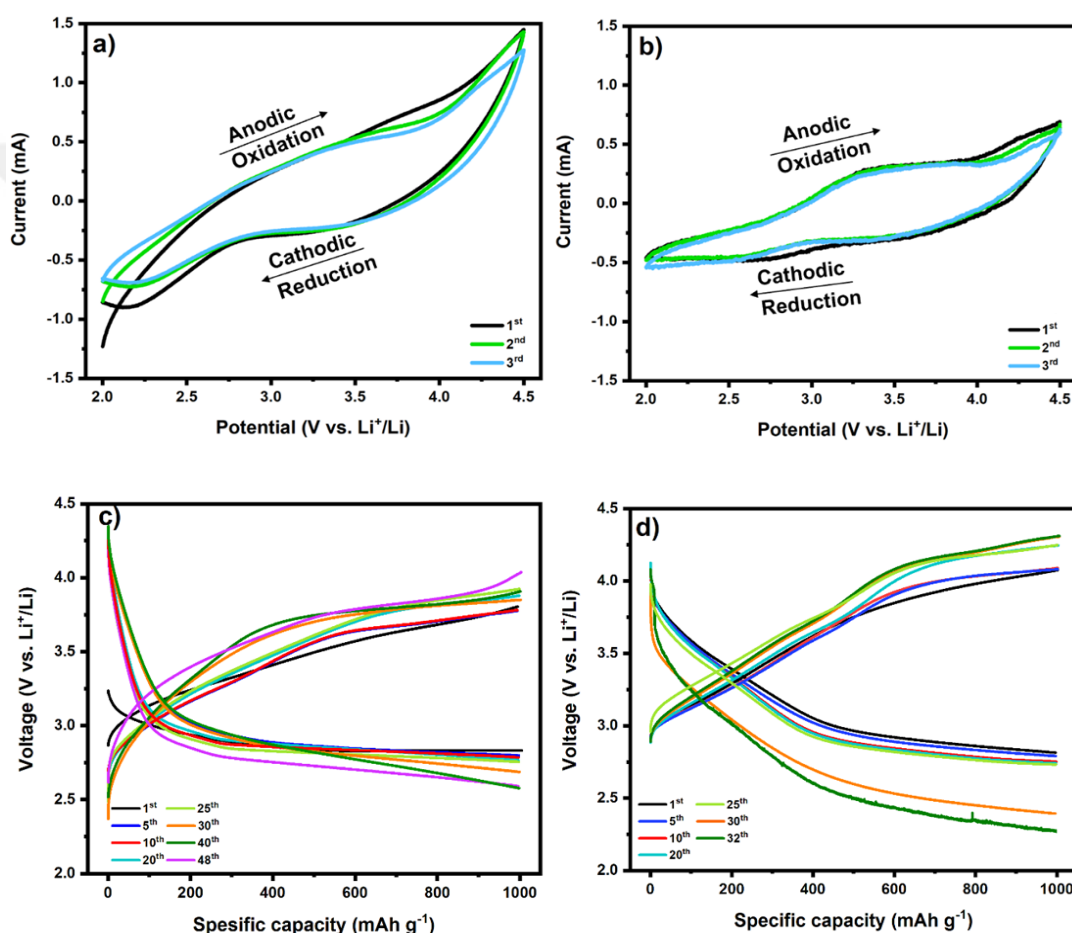


Figure 5.30. Cyclic voltammetry scans of v-Ru/ α MO (a) and v- α MO (b) electrodes. The selected discharge-charge scans of v-Ru/ α MO (c) and v- α MO electrodes (d) at a fixed capacity of 1000 mAh g⁻¹.

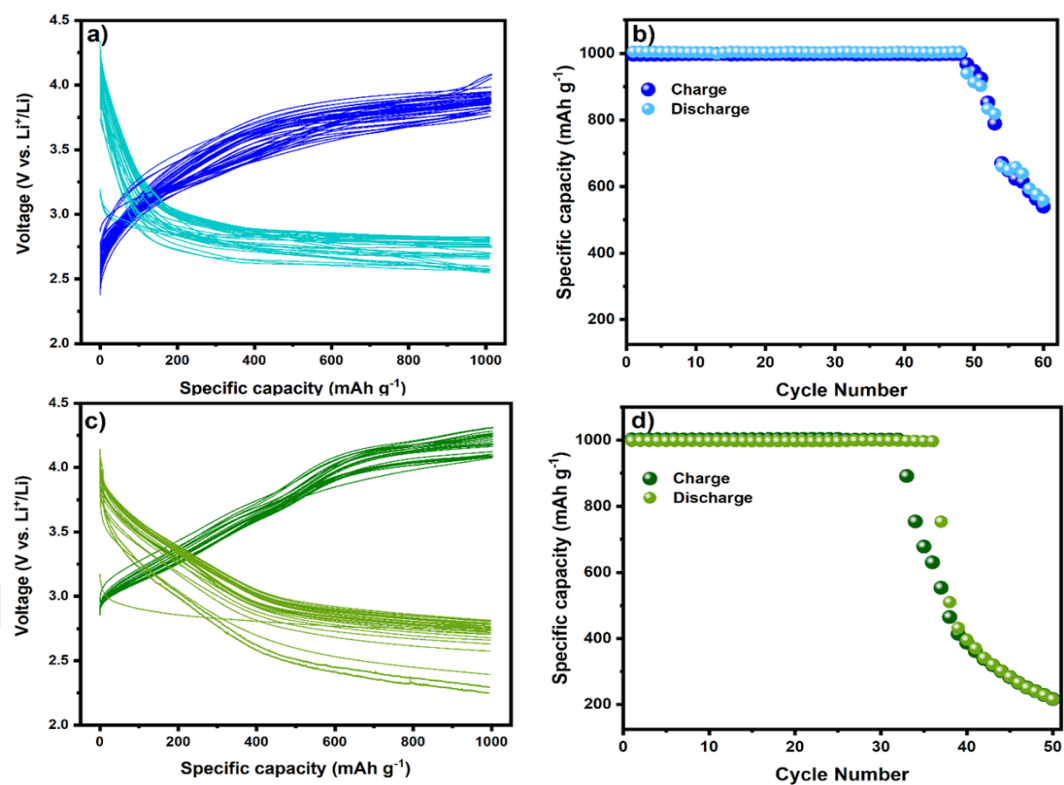


Figure 5.31. Cycling performance of the virus-templated $\text{Ru}/\alpha\text{-MnO}_2$ for 48 cycles (a,b) and virus-templated $\alpha\text{-MnO}_2$ (c,d) electrodes for 32 cycles at a fixed capacity of 1000 mAh g^{-1} .



Figure 5.32. Digital image of corroded lithium anode after 48 cycles of the v-Ru/ αMO electrode.

Further investigation of the v- αMO and v-Ru/ αMO electrodes after cycling was performed by FESEM. Figure 5.33 demonstrated the morphologies of v- αMO and v-Ru/ αMO after 32 cycles. From Figures 5.33a and 5.33b, can clearly observe the

surface cathode of v- α MO is deposited by toroid discharge products and α -MnO₂ nanowires are decomposed. The EDS result (inset Fig. 5.33b.) shows the highly atomic % of oxygen (92.77%), approving deposition of discharge products. While the v-Ru/ α MO electrode (Figure 5.33c. and 5.33d.) still maintained the network structure of α -MnO₂ nanowires structures, which provides adequate space to store the discharge residue and prevents the full coverage of the active sites to avoid the passivation of the catalyst and sustain the lifespan. In addition, the v-Ru/MnO₂ nanowires were covered with a layer of discharge products, assuming the role of Ru catalyst in inducing thin film-like morphology after cycling. Despite toroidal products will clog the channel and passivate the electrode surface, resulting in high charge overpotential and poor cycling performance.

EDS mapping of v-Ru/ α MO electrode (Fig. 5.33e.) displays the Ru nanoparticles are still homogeneously present on the surface of α -MnO₂ nanowires. This feature imparts further evidence that Ru did not passivate the catalytic activity during cycling performance. The XRD analysis approves the formation of Li₂O₂ as the main discharge product after 32 cycles in both electrodes (Fig. 5.34.). However, the XRD spectra of v- α MO identified the presence of Li₂CO₃, which fading the cell cycling function, could be due to the accumulation of irreversible Li₂CO₃. In comparison to the v-MO with carbon, we assume Ru nanoparticles suppress side reactions and thus provides a good capability to thoroughly form and decompose Li₂O₂. Some previous works have been explored the cyclability performance of the MnO₂-based electrodes in lithium-oxygen batteries. For instance, Hang et al. have constructed α -MnO₂ nanorod electrodes containing 60% xc-72 carbon, which stabled for 24 cycles with a limited capacity of 1000 mAh g⁻¹ [173]. To improve the performance of the cell, α -MnO₂ nanorods were grown on graphitic carbon nitride, and the cell was survived up to 40 cycles, implying the effect of bifunctional catalytic activity in the performance of the lithium-O₂ cell.

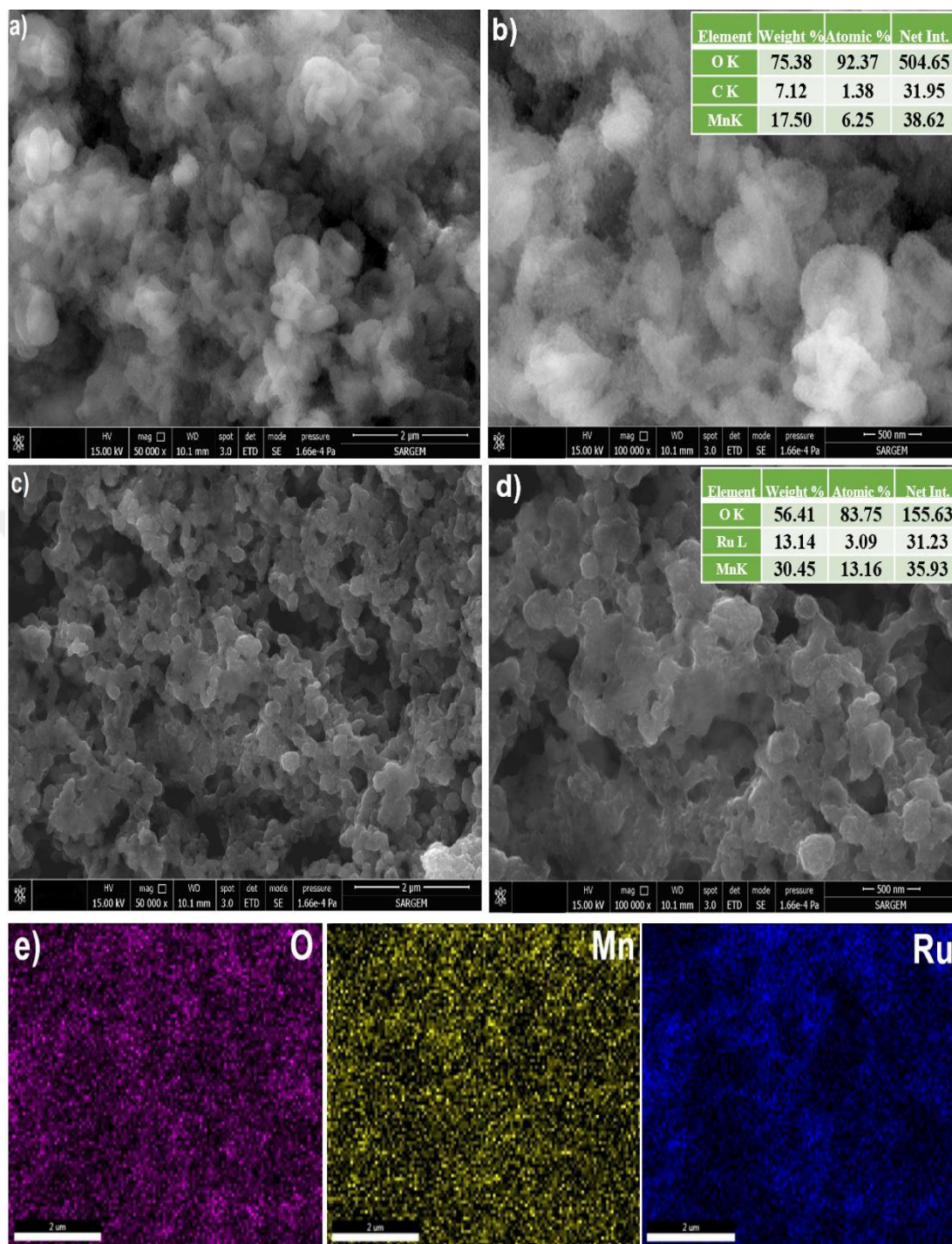


Figure 5.33. FESEM images in low and high magnification of v- α MO (a,b) and v-Ru/ α MO (c,d) cathodes after 32 cycles. e) EDS mapping of v-Ru/ α MO electrodes represents the presence of Mn, O, and Ru after 32 cycles.

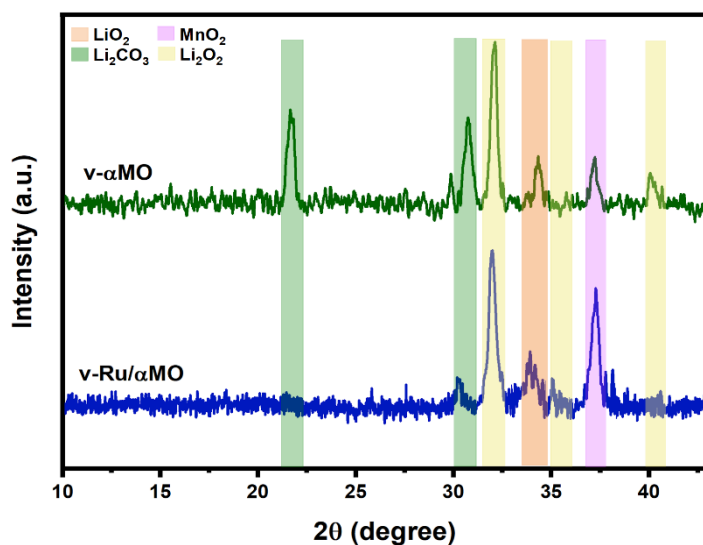


Figure 5.34. The XRD analysis of v-αMO and v-Ru/αMO after 32 cycles.

In detail, Fig. 5.35 indicates the performance of lithium-O₂ cell and various reaction mechanisms for the efficient formation and decomposition of lithium peroxide on carbon-free and carbonaceous electrodes during discharging and recharging. For the carbon-free Ru/α-MnO₂ electrode, the thin film-like Li₂O₂ was deposited on the cathode's surface through the surface absorption model due to its strong adsorption for oxygen. The generated surface absorbed oxygen (O₂^{*}) was initially reduced to LiO₂ (O₂^{*} + e⁻ + Li⁺ → LiO₂). The absorbed LiO₂ undergoes a disproportionation or electrochemical reduction reaction on the surface to generate the thin film-like Li₂O₂ on the v-Ru/αMO surface (LiO₂ + e⁻ + Li⁺ → Li₂O₂ or 2LiO₂ → Li₂O₂ + O₂). In contrast, there is a weak oxygen absorption for carbon-based electrodes as reported. Therefore, the weak adsorption of oxygen on the surface electrode of v-αMO with carbon additives drives the Li₂O₂ growth through a solution-mediated pathway. The absorbed oxygen dissolved in the electrolyte (noted as O₂ (sol)) and LiO₂ are formed due to interaction with Li⁺ to form and nucleated in the electrolyte (shown as LiO₂ (sol)). This solution pathway disproportionated to induce toroid shape Li₂O₂ (LiO₂ (sol) + LiO₂ (sol) → Li₂O₂ + O₂). According to the previous works, the formation of toroid morphology displays the solution-mediated Li₂O₂ growth on the electrode surface.

In summary, the emergence of Ru and 1D α -MnO₂ nanowires alleviated the overpotentials and promoting the round-trip efficiency of Li-O₂ cells. In addition, the distribution of Ru nanoparticles on the surface of virus-templated urchin-like α -MnO₂ nanowires exposed higher active sites to boost the ORR and OER kinetics and induced different Li₂O₂ growth on the surface. Besides, the network structure of v-MO nanowires can provide adequate storage space for Li₂O₂, rapid transporting, and diffusion of Li⁺ and O₂. The unique design merged with the intrinsic high catalytic efficiency of ruthenium nanoparticles remarkably improves the electrochemical performance, including the discharge specific capacity, round-trip efficiency, and cycling constancy of lithium-O₂ cells.

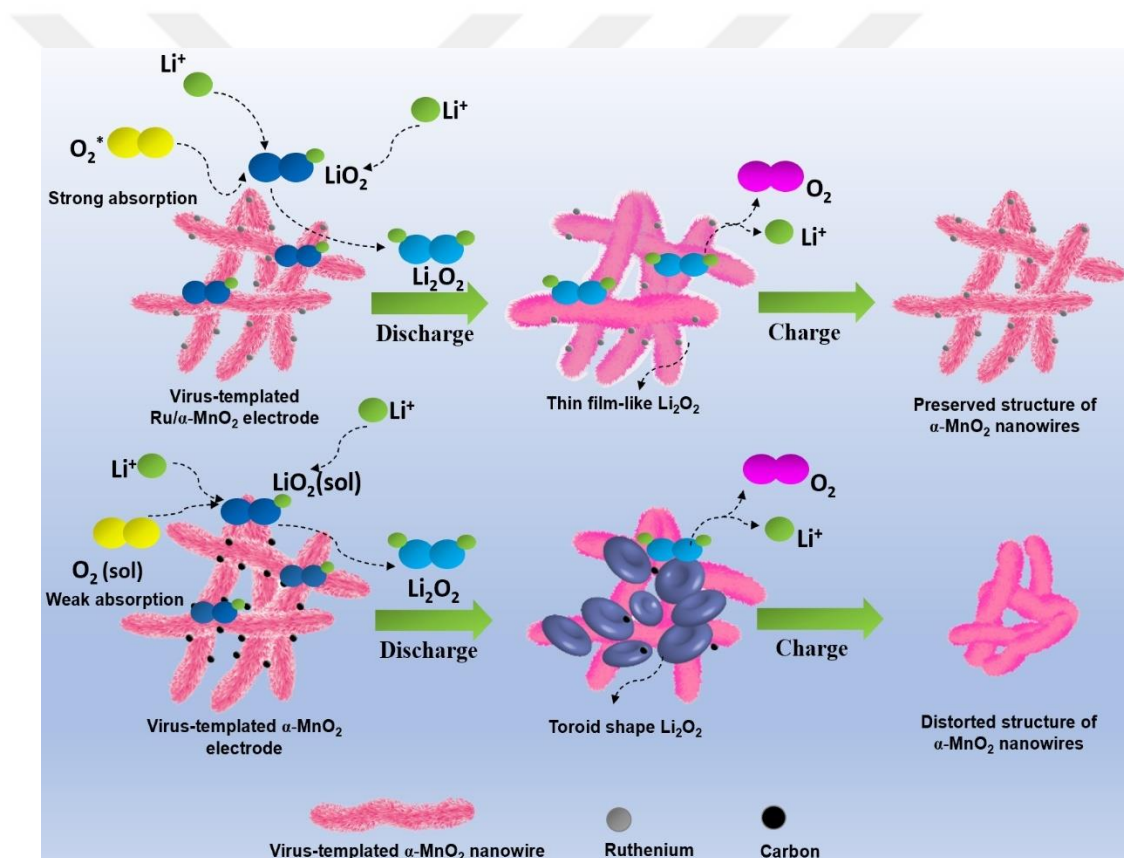


Figure 5.35. Schematic illustration of the performance of Li-oxygen cell and the reaction mechanism for v-Ru/ α MO and v- α MO electrodes.

CHAPTER 6. GENERAL CONCLUSIONS AND PERSPECTIVES

Today, the rapidly developing technology and the increasing daily usage of electronic devices and vehicles cause high demand for energy systems. It has become necessary to produce higher performance but low cost and environmentally friendly energy systems without allowing the depletion of natural resources in the long term and avoid environmental effects to fight against climate change. Therefore, energy systems come as the priority research topic worldwide and in Turkey.

The most common technology to power mobile devices and electric vehicles is lithium ion battery as a type of rechargeable battery. However, the low power and energy density of Li-ion cells cannot provide the energy required for electric vehicles and devices. The Lithium-O₂ system, with its high energy density, can improve the energy density of fully packaged batteries by three times that of current Li-ion cells. However, the current Li-O₂ cells suffer from poor life span, large charge potential, low round trip efficiency, and electrolytes' instability after cycling.

The work in this thesis has focused on overcoming issues in the developing of lithium-O₂ batteries:

- Enhancing the capacity
- Lower overpotential
- Longer cycle life
- Eliminating side reactions
- Improving round trip efficiency

To achieve this goal designing unique catalysts with high porosity and surface area as cathode materials were developed.

The main research objectives of this thesis are:

- To prepare cathode material based on metal and metal oxides.
- To establish facile and cost-effective techniques to synthesize metal/metal oxides.
- To synthesize metal oxides such as TiO_2 through a green method by using plant extract.
- To control the particle size by manipulating the initial pH solution.
- To evaluate the electrochemical performance of bifunctional catalysts by preparing the core-shell structure of $\text{TiO}_2/\alpha\text{-MnO}_2$ and the hybrid structure of virus-templated $\text{Ru}/\alpha\text{-MnO}_2$.
- To optimize the synthesis of M13 phage-based electrode materials at low temperature.
- To develop new methods to synthesize the hybrid structure while preserving the surface morphology of the M13 phage template.
- To investigate how parameters such as concentration, temperature, and pH alter the crystal form of the products.
- To examine the growth modes of Li_2O_2 in the presence of different electrocatalysts.

Metal Oxides such as MnO_2 and TiO_2 have been utilized in energy systems due to their excellent catalytic activity, less expensive, eco-friendly, and chemical stability. Therefore, the electrodes produced in this thesis are included:

- TiO_2 was prepared via sol-gel and green method combined with 5% carbon black.
- Core-shell urchin-like $\text{TiO}_2/\alpha\text{-MnO}_2$ mixed with 10% carbon black.
- Virus-templated α -, γ -, δ - MnO_2 nanowires in combination with 10% carbon black.
- Carbon-free hybrid virus-templated $\text{Ru}/\alpha\text{-MnO}_2$ nanowires.

The preparation of TiO_2 nanoparticles were performed by the sol-gel method and green method (using plant extract), named as C- TiO_2 and Bio- TiO_2 nanoparticles, respectively. The morphology and surface area study shows:

- Less agglomeration in Bio- TiO_2 due to presence of biomolecules in plant extract that act as capping agents.
- Finer particle size in Bio- TiO_2 particles was observed compare to C- TiO_2 particles.
- A higher surface area for Bio- TiO_2 particles was obtained.
- At full discharge, the Bio- TiO_2 cathode had a specific of 2000 mAh g^{-1} and was maintained relatively stable for 30 cycles at a fixed capacity of 500 mAh g^{-1} .

The electrochemical performance of C- TiO_2 and Bio- TiO_2 indicated a higher and stable capacity for Bio- TiO_2 electrodes due to their properties mentioned above. The electrochemical result showed the importance of particle size and surface area on the performance of the battery.

However, the electrochemical test of TiO_2 electrodes revealed a high overpotential, which derived from the low conductivity of TiO_2 and different growth mode of

Li_2O_2 . Therefore, in chapter four, improving the performance of TiO_2 is discussed. To lower the charge potential and enhance the cyclability, the urchin-like MnO_2 was grown on the surface of Bio- TiO_2 nanoparticles to design a core-shell structure. The core-shell structure improved the specific capacity and durability of TiO_2 due to the following reasons:

- Rough structure MnO_2 shell provides a higher number of the active site for Li_2O_2 storage.
- The emergence of MnO_2 and TiO_2 changed the growth mode of Li_2O_2 from toroid to nanoparticulates morphology.
- The nanoparticulates Li_2O_2 are caused a better decomposition and reduced charge potential.
- The discharge capacity of core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanostructures increased to 6100 mAh g^{-1} .
- In comparison to Bio- TiO_2 nanoparticles with a discharge capacity of 2500 mAh g^{-1} and 60 stable cycles, core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanoparticles indicated a longer life cycle (130 cycles) at a fixed capacity of 370 mAh g^{-1} .

M13 phage was used as a bio-template to assemble MnO_2 nanocrystals to obtain MnO_2 nanowires with a high aspect ratio and enriched porosity (Figure 6.1). M13 phage is a filamentous virus that infects E. Coli bacteria and is harmless to humans. Due to the negative charge of the M13 surface, the cation metals could interact with the M13 surface through ion exchange. The crystal forms of MnO_2 could alter by controlling the volume ratio of precursors (e.g., MnSO_4 and KMnO_4) and approved by X-ray diffraction.

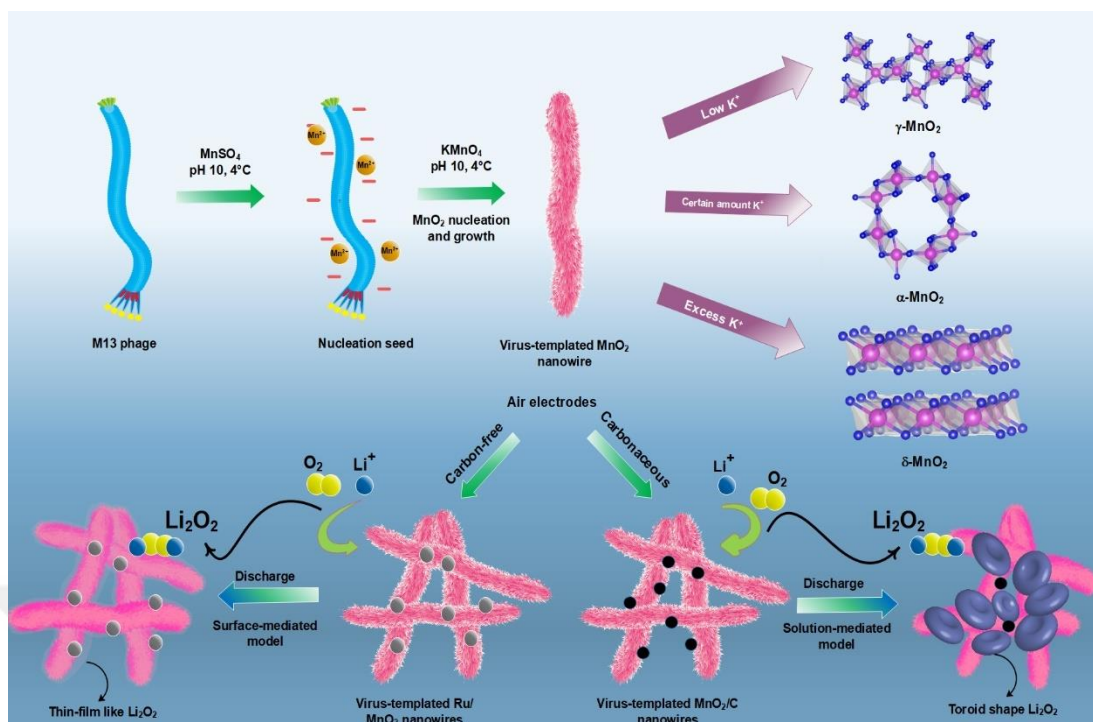


Figure 6.1. The overview preparation of virus-templated MnO₂ and Ru/MnO₂ nanowires and their electrochemical behavior.

The electrodes electrochemical properties were estimated as follows:

- The virus-templated α -MnO₂ nanowires demonstrated the highest specific capacity compare to δ - and γ -MnO₂ nanowires due to their high surface area by providing a larger tunnel size in their structure.
- The carbon-free hybrid virus-templated Ru/ α -MnO₂ nanowire delivered a higher specific capacity than only α -MnO₂ due to its higher surface, which enhanced the number of active sites for discharge product accommodation.
- The carbon-free hybrid virus-templated Ru/ α -MnO₂ nanowire and virus-templated α -MnO₂ electrodes indicated two different Li₂O₂ growth modes.
- The synergetic effect of Ru and α -MnO₂ enhanced oxygen absorption and led to the Li₂O₂ formation through the surface-mediated pathway, which induced the formation of thin-film like Li₂O₂. This morphology resulted in lower charge potential, which reduced the side reaction and electrolyte decomposition.

- On the contrary, the virus-templated α -MnO₂ electrode revealed the toroid shape Li₂O₂, which formed via a solution-mediated model. The toroid morphology of Li₂O₂ required higher charge potential; therefore, the formation of parasite products increased and shortened the cycle life of the cell.

Overall, in this thesis, highly efficient catalysts were prepared as air electrodes for lithium-O₂ cells. The products were obtained through biocompatible and eco-friendly processes by using natural materials. We hope our research sheds light on encouraging engineers to utilize biomaterials.

I would like to mention that the main issue in this research was the decomposition of electrolytes during the cycling test, which limited the life cycle of the cell. Therefore, further study requires finding a stable electrolyte or investigation using different solvents such as DME and DMSO. On the other hand, the non-aqueous electrolyte and the presence of oxygen caused the corrosion of the lithium anode, which terminated the performance of the cell. As a consequence, it is critical to approach a strategy to protect the lithium chips from corrosion.

The other challenge that still remains is high overpotentials due to the formation of by-products, which could result from the reactivity between discharge products and binders. Therefore further controlled studies with binder-free electrodes will be essential to probe the stability of electrolytes and catalysts in the presence of discharge intermediates. For this purpose, the cathode material can directly grow on a current collector (e.g., Nickel foam) or preparation of aerogel materials to develop free-standing electrodes.

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RESUME

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EDUCATION

Degree	School	Graduation Year
Ph.D.	Sakarya University / Natural Science Institute / Nanoscience and Nanoengineering	2021
Master	Osmania University / Science Institute / Genetics	2013
Bachelor	Kharazmi University / Science Institute / Biology	2010
High School	14 ma'esum	2006

JOB EXPERIENCE

Year	Place	Position
2017-Still	SARGEM Laboratories	Project assistant
2016-2017	Ostrava technical university	Researcher
2014-2015	Dr. Kariminejad Lab.	Genetics expert
2012-2013	Bioaxis Institute	Trainee
2013	Genetics institute and hospital for genetic disease	Trainee
2013	DNA Lab of India	Trainee

FOREIGN LANGUAGE

English
Turkish
Arabic
Persian

PRODUCTS (article, paper, project, etc.)

1. Sara Pakseresht, Tugrul Cetinkaya, Ahmed Waleed Majeed Al-Ogaili, Hatem Akbulut, Urchin-like core-shell $\text{TiO}_2/\alpha\text{-MnO}_2$ nanostructures as an active catalyst for rechargeable lithium-oxygen battery, *Advanced powder technology*, 32(3), 2021, 895-907.
2. Sara Pakseresht, Tugrul Cetinkaya, Ahmed Waleed Majeed Al-Ogaili, Mihrac Halebi, Hatem Akbulut, Biologically synthesized TiO_2 nanoparticles and their application as lithium-air battery cathodes. *Ceramics International*. 47 (3), 3994-4005, 2021.
3. Ahmed Waleed Majeed Al-Ogaili, Tugrul Cetinkaya, Sara Pakseresht, Hatem Akbulut, Graphene-based nanocomposite cathodes architecture with palladium and $\alpha\text{-MnO}_2$ for high cycle life lithium-oxygen batteries. *Journal of Alloys and Compounds*, 854, 157293, 2021.
4. S. Pakseresht, A.W.M Alogaili, H. Akbulut, D. Placha, E. Pazdziora, D. Klushina, G.S. Martynková, Silver/Chitosan Antimicrobial Nanocomposites Coating for Medical Devices: Comparison of Nanofiller Effect Prepared via Chemical Reduction and Biosynthesis. *Journal of Nanoscience and Nanotechnology*. 19 (2018) 2938–2942.
5. S. Pakseresht, S. Ghaderi-Sohi, J. Michel, G. Lesca, M.H. Kariminejad, P. Edery, A. Kariminejad, Microcephalic osteodysplastic primordial dwarfism type I in two siblings aged 2.5 years and 18 gestational weeks. *Genetics in the Third Millennium*. 13, (2015) 3970–3975.
6. Ahmed Waleed Majeed and Sara Pakseresht, Transformation of penicillin resistance plasmid from penicillin resistant soil bacteria to *E.coli* DH5 α , *Helix Journal*, 1 (2014) 491- 493.
7. Sara Pakseresht and Ahmed Waleed Majeed, Production and Qualitative Analysis of Secondary Metabolites of *Staphylococcus* Bacteria having Antibiotic Activity, *Helix Journal*, 2 (2014) 527- 530.
8. Projects: a) Novel carbon-free cathode materials for metal-air rechargeable batteries. Supported by TÜBİTAK under contract number 217M979. (2018-2021)

b) A new approach to electrochemical energy storage: development of multi-cell lithium-air flow batteries. Supported by TÜBİTAK under contract number 315M461 (2017-2019).

9. S.pakseresht, oral presentation titled: Biosynthesized MnO_2 Nanowires for Carbon-Free Air Breathing Cathode to enhance Cyclability of Li- O_2 Battery, International symposium on Nanoparticles/Nanomaterials and Applications, Caparica, Portugal, 2020.

10. S. Pakseresht, oral presentation titled: Facile synthesis of a Core/shell nanostructured $\text{TiO}_2@\text{MnO}_2$ for free-carbon air breathing cathode to enhance cyclability of Li- O_2 battery, Electrochemistry Conference (ISI), Istanbul, Turkey, 2019.

11. S. pakseresht, oral presentation titled: Synthesis of Silver/Chitosan nanocomposites by green method using linden extract for antibacterial coating, NanoOstrava, Ostrava technical university, Czech Republic, 2017.

12. A. Al-ogaili, S.pakseresht, Grazyna Simha, Poster titled: Fabrication of Sulfur/Carbon/Clay mineral cathode material and its electrical performance, NanoOstrava, Ostrava technical university, Czech Republic, 2017

HOBBIES

Reading, Movies, Sport