



Master's Thesis 석사 학위논문

Development of Efficient Electrocatalysts for Metal-Air Batteries

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The study was conducted in accordance with Code of Research Ethics¹⁾.

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Accepted in partial fulfillment of the requirements for the degree of Master of Science.

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Abstract

Metal-air batteries have a lot of merits whereas there are still facing various fundamental issues to reach commercial applications such as poor cycleability, low round-trip efficiency and poor rate capability. For instance, the round-trip efficiency of metal-air batteries with bare carbon electrode is below 70% in contrast with that of the conventional LIBs-in case LiCoO₂ is around 95%. These challenges are stem from instability of not only Li metal but also binder and electrolyte. Above all, the major challenge is the sluggish kinetics of oxygen reduction and evolution reactions at the oxygen electrode during battery discharge and charge. Therefore, the development of electrochemically active, stable and non-precious bifunctional catalyst is highly required for the commercialization of this technology for practical metal-air batteries.

We first focus on designing an inexpensive and highly active OER electrocatalyst, $Co_3V_2O_8$ with 1D morphology consisting of nanotubes and nanorods which can be used in Zn-air battery. In addition to looking for new cost-effective materials with stable structure and also tuning the morphology of the existing material to improve their catalytic activity which is directly related with battery performance has been considered to improve oxygen evolution reaction. From this point of view, one dimensional (1D) nanostructure materials possess better triple phase boundary to facilitate efficient transport pathways for electrons and ions. Moreover, high surface area of 1D nanostructure expected to provide high performance to suppress sluggish oxygen electrode kinetics. To understand the effect of $Co_3V_2O_8$ morphology on OER activity, we have synthesized 1D & 0D nanostructures and discussed their performance. The result demonstrates that the $1D-Co_3V_2O_8$ cathode exhibits superior OER activity and long term stability to those of $0D-Co_3V_2O_8$ and even for commercial precious metal catalysts. The excellent OER performance and long-term durability is attributed to the well-designed one dimensional nanorods and nanotubes like structure, the synergistic effect of different metal ions, and the presence of amorphous nitrogen-doped carbon.

In the second part of research, we developed Co-CoO/CNR catalysts as a bifunctional air cathode for the OER and ORR for application of Li-O₂ batteries. High power density could be achieved with this system since the Li-O₂ batteries possess higher open-circuit voltage of 2.96 V than that of Zn-air batteries (1.65 V). The Co-CoO/CNR cathode achieved a discharge capacity of 10569 mAh g_{catalyst}⁻¹ at a current density of 100 mA g⁻¹, which is higher than that of CNR electrode (7087 mAh g_{catalyst}⁻¹). This result demonstrates that Co-CoO/CNR cathode shows almost 6 times better cycling performance than CNR electrode with a cutoff capacity of 1000 mAh g_{catalyst}⁻¹. The poor cycleability of Li-O₂ batteries with CNR electrode should be caused by the accumulation of Li₂CO₃, which is the one of the major products in this oxygen electrode may due to the presence of uniform mesoporous nanostructure with high surface area so that it could diffuse Li⁺ easily and provide space to accommodate discharge solid products. Furthermore, Co-CoO nanoparticles on CNR electrode might help to minimize the oxidation of carbon structure and form nanosized Li products during the discharge process.

Keywords: Oxygen electrocatalyst, Metal-air battery, Lithium-oxygen (Li-O₂) battery, Cobalt vanadium oxide, Co-CoO/CNR

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|. Introduction

1.1 Forward

Growing energy demands provide opportunities for the development of new technologies and efficient materials for the electrochemical energy conversion and storage devices [1-2]. Particularly, Li-ion batteries (LIBs) are used to power new transportation that releases zero emissions for electric vehicles (EVs) as next generation energy storage systems. However, the practical energy densities of current LIBs based on an intercalation mechanism are much lower than the required target performance. To improve the energy density of LIBs, new battery systems such as Na-ion batteries, Mg-ion batteries and metal-air batteries have been investigated [3-4]. Most of all, metal-air batteries, which can deliver 2-4 times higher energy densities than those of the conventional LIBs are receiving intense interest at the present time [5]. Furthermore, metal-air batteries could use active material (O₂) from the atmosphere, so that it could give an additional benefit of cost reduction [6]. To demonstrate the superior properties of the metal-air batteries among energy storage and conversion devices, a comparison figure of battery systems for providing energy for a hybrid electric vehicle is illustrated in Figure 1.1 [7].



Figure 1.1 Practical specific energy for some rechargeable batteries, along with estimated driving distances and pack prices [7].

1.2 Objectives

The objectives of this study are to synthesize a highly active and stable noble metal-free OER electrocatalyst based on earth-abundant materials, $Co_3V_2O_8$ with one-dimensional morphology consisting of nanotubes and nanorods (denoted to 1D- $Co_3V_2O_8$). To understand the effect of $Co_3V_2O_8$ morphology on the OER activity, we will also synthesize $Co_3V_2O_8$ nanoparticles (0D- $Co_3V_2O_8$) and evaluate their performance. Further, the prepared porous 1D- $Co_3V_2O_8$ nanostructured materials as a cathode catalyst in aqueous Zn-air battery system and its performance based on the morphological effect will be evaluated.

In the second part of this study, we will develop one-dimensional mesoporous nanostructures of Co-CoO/CNR catalyst as an air cathode for Li-O₂ batteries. We have constructed an electrospinning method to *in-situ* prepare a Co-CoO/CNR catalyst. In order to improve the battery performance including discharge capacity and cyclability, we will optimize the porous nanostructured air cathodes and introduce the Co-CoO nanoparticles into the cathode and also on the surface.

II. Theoretical background

2.1 Metal-air battery

2.1.1 Metal-air battery fundamentals

Metal-air batteries have attracted much attention as a possible alternative, because their energy densities are extremely high compared to that of other energy storage and conversion devices [8]. In addition, metal-air batteries are compact and potentially less expensive batteries available. There are several kinds of metal-air batteries based on different metal anodes (Figure 2.1) [9]. Their reaction mechanisms are based on the types of cell components. Metal-air batteries are divided into two types according to the properties of electrolyte. One is a cell system using an aqueous electrolyte, which is not sensitive to moisture. The other is a water-sensitive system using an electrolyte with aprotic solvents [10]. Figure 2.2 presents the schematic diagrams of various types of metal-air batteries. The theoretical and practical energy densities of various types of rechargeable metal-air battery are illustrated in Table 2.1 based on the metal used as anode in the battery system [11].



Figure 2.1 The schematic illustration of a metal-air battery [9].



Figure 2.2 Types of metal-air batteries [9].

Table 2.1 The theoretical energy density (Wh/kg) and standard potential (E°) of various types of rechargeable metal-air battery [10].

Metal-air battery system	Li-air	Zn-air	Na-air	K-air
Theoretical energy density (Wh kg ⁻¹)	3,458 (Li ₂ O ₂)	2,288	1,605	935
E° (V)	2.96 (Li ₂ O ₂)	1.65	2.33	2.48

2.2 Aqueous metal-air battery system

2.2.1 Zn-air battery

Metal such as Zn, K, Al, Ca, and Fe are appropriate for the aqueous environment system. Among them, Zn-air batteries have powerful potential as alternative energy storage devices. Particularly, Znair batteries have the lowest cost of all existing systems (\$160/kWh), so they already used as the highest capacity primary battery in hearing aids. In case of other metals, for example AI metal can be more easily corroded than zinc metal in alkaline solution, although AI-air battery has much higher energy density than that of Zn-air battery. In addition, AI-air battery is facing several challenges such as high self-discharge rate, cell irreversibility, and low shelf life [12]. Zn-air batteries have high theoretical energy density (2,288Wh/kg) to meet the DOE target (2,100 Wh/kg) for electric vehicle application [13]. Moreover, zinc metal has various advantages such as abundance, low equilibrium potential, environmental-friendly, and a long shelf life. The important advantage of alkaline Zn-air battery is that non-noble metal based catalyst can be used for the oxygen reduction reaction [14].

Zn-air battery is composed of three parts; zinc metal as an anode, a separator, and an air electrode as the cathode, which is divided into a catalytic active layer and gas diffusion layer (GDL) as shown in Figure 2.3. Zn-air battery requires the air electrode to have proper catalyst for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), and also highly porous structure. The highly porous structure makes the diffusion path for oxygen and functions as a substrate for the catalysts to work with a triple phase interface. This three phase reaction occurs in the cathode side which is marked with red circle in Figure 2.4 [7].



Figure 2.3 Schematic illustration of Zn-air battery [9].

2.2.2 Working principles of Zn-air battery

Oxygen from the atmosphere diffuses into the porous carbon electrode, and then the catalyst facilitates the reduction of oxygen to hydroxyl ions in the alkaline electrolyte with electrons generated from the oxidation of zinc metal as the anode reaction. Generated hydroxyl ions migrate from the air cathode to the zinc anode to complete the cell reaction; these overall procedures during discharge of Zn-air cell are as follows [15].

Anode :
$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 (1)

$$Zn^{2+} + 4OH^{-} \rightarrow Zn(OH)_{4}^{2-} = E_0 = 1.25 V$$
 (2)

$$Zn(OH)_4^{2^-} \rightarrow ZnO + H_2O + 2OH^-$$
(3)

Cathode :
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^ E_0 = 0.4 V$$
 (4)

Overall reaction :
$$2Zn + O_2 \rightarrow 2ZnO$$
 $E_0 = 1.65 V$ (5)

It can also be described in Figure 2.4.



Figure 2.4 Working principles and each electrode reaction of Zn-air battery during discharge process [7].

2.2.3 Drawbacks of Zn-air battery

However, zinc corrosion in alkaline electrolyte can produce potentially explosive hydrogen gas according to the reaction: $Zn+2H_2O \rightarrow Zn(OH)_2 + H_2$ [16]. This hydrogen evolution reaction (HER) is not supposed to occur during discharge thus the suppression of hydrogen evolution is necessary for primary and secondary Zn-air batteries [17]. To overcome this problem, coating, alloying, and adding additives to the electrolyte have been applied in this research area. To make a secondary battery, the most important point is to understand the chemistry of the zincate ion in alkaline solutions. Also, controlling the zinc morphology which can affect the electrochemical behavior of Zn-air battery is important because zinc particles with high surface area can react efficiently with electrolytes.

The practical working voltage of Zn-air battery is less than 1.65 V due to the internal loss of the cell, resulted from the activation, the ohmic, and concentration loss [18]. Most of all, the critical problem in Zn-air battery is still the sluggish reaction of oxygen chemistry originating from high overpotentials for

both ORR and OER (Figure 2.5). The architecture of air electrode is also an important factor affecting the overall performance of cathode electrode. In addition, rechargeable Zn-air battery suffers two critical issues which do not affect the primary battery: the stability of the air electrode during the battery charge and the formation of dendrites on the zinc electrode, leading to short circuits [19]. However, mechanically rechargeable Zn-air batteries have been developed by the Electric Fuel limited company for military application and fleet of electric vehicles [20]. In this concept, the discharged zinc anodes have to be mechanically replaced by fresh ones.

Finally, the migration of zinc(II) ions from anode to cathode can take place, which causes a decrease in the capacity of Zn-air batteries. Therefore, the pore size of the separator should be optimized to improve electrochemical performance. Carbonation in alkaline solution also has a negative effect on the lifetime of Zn-air cells. A CO_2 scrubber can be introduced to solve this problem.



Figure 2.5 Schematic polarization curves of Zn-air cell. The equilibrium potential of the Zn-air cell (black line) is 1.65 V, but the practical voltage (red line) in discharge is lower than 1.65 V due to the sluggish ORR. A large potential is needed to charge Zn-air battery, higher than the equilibrium potential (blue line) [18].

2.3 Non-aqueous metal-air battery system

For non-aqueous system, alkali metals such as Li, Na, Mg have been widely used because these metals are explosively reactive with moisture [9]. Since the lithium metal is the lightest highenergy metal with high open-circuit voltage (OCV) of 2.96 V, this battery has the highest theoretical energy density of 3,458 Wh kg⁻¹ (Li₂O₂ as discharge product) [10.11]. Therefore, Lithium–air battery system should be an appropriate choice among the non-aqueous based battery system [12].

2.3.1 Li-air battery

Lithium-air batteries have shown 5–10 times higher energy density than that of a standard Li-ion battery. Therefore, once we use Li-O_2 battery instead of Li-ion battery for EV, production cost can be 5 times saved (\$100) and energy efficiency will be 4 times improved (800km per single charge and energy output is 150kWh) as given in Table 2.2 [21].

The configuration of the non-aqueous electrolyte system is similar to that of conventional Li-ion batteries. Conventional Li-ion batteries use carbon or alloy materials as anode, Li metal oxides or phosphates as cathode, and Li salt dissolved in aprotic solvents as electrolytes [22, 23]. However, Li-air batteries use oxygen gases as a cathode material, so the catalyst composites with porous nanostructures must be added as the Li₂O₂ reservoir in the cathode. Also, Li metal must be used as the anode, because anode plays a role as the Li source in Li-air batteries. The critical difference between the two systems is that an open system is needed for Li-air batteries, because oxygen is obtained from the air (Figure 2.6). This open system requires additional components such as air-dehydration membranes.

	Li-ion battery	Li-air battery
Energy output	85 kWh	150 kWh
Production cost	\$650	\$100
Driving range	400 km	800 km
Development stages	Commercialized (smartphone, EV, etc)	Commercial production by 2020 (IBM target)
Unsolved issues	✓ High cost✓ Low energy efficiency	✓ Cyclability✓ Stability

Table 2.2 Comparison of Li-ion and Li-O₂ batteries for EV [21].



Figure 2.6 Schematic illustration of Li-O₂ battery [24].

There are four types of Li-air batteries based on electrolytes as shown in Figure 2.7: All of the Li-air battery systems use lithium metal as the anode and oxygen gas as the cathode material, but their electrochemistry differs according to the electrolyte types [8].



Figure 2.7 Types of lithium-air batteries: a) Aqueous electrolytic type, b) Non-aqueous (aprotic) electrolytic type, c) Mixed (aprotic-aqueous) type, and d) Solid-state type [8].

In non-aqueous/aprotic electrolytic type of Li-air battery, a liquid organic electrolyte is used. Lithium salt such as LiTFSI, LiPF₆, LiClO₄, LiN(SO₂CF₃)₂, and LiCF₃SO₃ are used and organic solvent such as organic carbonates (EC: ethylene carbonate, PC: propylene carbonate), ethers (DME: dimethoxyethane, TEGDME: Tetraethylene glycol dimethyl ether, THF: tetrahydrofuran), and sulfones (DMSO: dimethyl sulfoxide) are commonly used for electrolytes [25]. The properties of formulated electrolytes also play an important role in the performance of Li-air batteries. The effect is the result of the individual components of the electrolytes: Li salts, organic solvents, possible additives, and their

combination. An ideal electrolyte for non-aqueous Li-air battery should hold high chemical and electrochemical stability, low volatility or no volatility to guarantee long-term operation, high oxygen solubility, and especially, be inert to superoxide radicals [26].

Aqueous electrolytic type of battery has the same structure as an aprotic type Li-air battery except that electrolyte used is aqueous lithium salt. Lithium as an anode reacts excessively with water and corrodes. Therefore, it is necessary to have an artificial solid electrolytic interface (SEI) over the surface of the lithium anode. Usually lithium ion conducting ceramic or glass is used as the SEI layer. Several attempts have been made to introduce this effective Li⁺ conductive solid electrolyte interface. A protective glass ceramic layer of LiSICON, such as $Li_{2+2x}Zn_{(1-x)}GeO_4$ (-0.36 < x > 0.87), LiM(PO₄)₃ like LiTi₂(PO₄)₃ was introduced for the metal anode [27, 28].

In mixed (aprotic-aqueous) type of battery, both aprotic and aqueous type electrolytes are used to overcome the limitations of the aprotic type and aqueous type Li-air battery. A lithium ion conducting membrane is used to separate the two types of electrolytes. Typically, a lithium anode is in contact with an aprotic type electrolyte and a cathode of porous carbon is in contact with an aqueous type electrolyte. There is no cathode clogging and moisture problem in this type of Li-air battery and less production of spontaneous SEI layers due to aprotic electrolyte used [29, 30].

Usually polymer ceramic or glass with a Li⁺ conducting membrane separating the anode and cathode as the electrolyte is also used. This cell exhibited excellent thermal stability and rechargeability in the range of 30 to 105°C [31]. However, the main drawback of this type of battery is lower ionic conductivity of the glass-ceramic electrolytes such as NASICON structure.

2.3.2 Working principles of Li-air battery

Usually in aprotic electrolyte condition, cell reactions are as follows:

1. Non-aqueous(aprotic) electrolyte

Widely accepted mechanism of oxygen reduction reaction on discharge is [32]:

$$O_2 + e^- \to O_2^- \tag{1}$$

$$O_2^- + Li^+ \to LiO_2 \tag{2}$$

$$2\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2 \tag{3}$$

Several studies suggest also the direct reductions of oxygen [33, 34]:

$$\text{LiO}_2 + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{O}_2 \qquad (1)$$

$$Li_2O_2 + Li^+ + e^- \rightarrow 2Li_2O \qquad (2)$$

Common discharge product is Li_2O_2 , and the Li_2O can be formed during the deep discharge. This system is considered to be promising, and much attention has been attracted.

2. Aqueous electrolyte

$$2Li + 1/2O_2 + H_2O \leftrightarrow 2LiOH (E_0 = 3.45 V)$$

Schematic illustration of working principles of Li-O₂ batteries during discharge and charge process is also described in Figure 2.8.



Figure 2.8 Schematic of working principles of Li-O₂ batteries during discharge and charge process [8].

2.3.3 Drawbacks of Li-air battery

Although there has been promising progress, many aspects of Li-air battery are not fully understood, so it requires additional investigation. Here, some drawbacks and important points of Liair battery have been summarized.

For Li-air batteries:

i) The electrode porosity affects the electrochemical performance of the air cathode. As the porosity increases oxygen diffusion is efficiently facilitated, resulting in an improvement of the OER kinetics.

ii) The critical issues of the oxygen cathode that limit the practical use of $Li-O_2$ technology are including poor round-trip efficiency, rate capability, and cycle life, as shown in Fig. 2.9. For instance, the round-trip efficiency of $Li-O_2$ cells with uncatalyzed carbon electrode is below 70% [35, 36]. This is significantly lower than the round-trip efficiency of conventional Li-ion batteries such as $LiCoO_2$ (>95%) [37].

In addition, the current density of Li–O $_2$ cells is in the range of 0.1–1 mA cm $^{-2},$ which is - 15 -

~10 to ~100 times lower than that of Li-ion batteries (~30 mA cm⁻²) [38]. Moreover, the cycle life of Li–O₂ batteries shown to date is up to 100 cycles [39, 40], which is significantly lower than that of lithium-ion cells (up to 5000 cycles) [41]. These technological challenges are strongly related to various issues including the chemical instabilities (*e.g.*, O_2^- *vs.* carbonate solvents, Li₂O₂ *vs.* carbon electrode), the lack of fundamental understanding of the reaction kinetics (ORR and OER), and the transport kinetics (*e.g.*, ion transport and electron transport), as illustrated in Figure 2.9.

Various catalysts have been investigated for the air cathode, and polarization has been substantially decreased by these catalysts. Each oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) exhibits different catalytic reaction mechanisms, thus a bifunctional catalyst sholud favorable to decrease the resistances of both reactions.

As similar with Zn-air batteries, the most critical problem in Li-air batteries is still the sluggish reaction of oxygen chemistry originating from high overpotentials for both ORR and OER [36]. To date, precious electrocatalyst like Pt/C-RuO₂ and Pt/C-IrO₂ have been considered as universal choice of bifunctional catalyst, however these materials are suffered from scarcity and the high cost of production [42].

iii) The polarity, viscosity, and oxygen solubility of electrolytes are also important factors affecting the electrochemical performance. A major challenge is to find a stable electrolyte for the oxygen electrode. The initial results by Abraham and Jiang [43] reported discharging and charging of Li– O_2 cells with polyacrylonitrile mixed with ethylene carbonate (EC) and propylene carbonate (PC) as an electrolyte. However, the carbonate electrolytes, which are commonly used for lithium-ion batteries, have been shown [44, 45] to be unstable against the oxygen electrode. As reported at the first time by Aurbach et al., [46] the superoxide ion O_2^{-} , a reaction intermediate associated with the oxygen reduction reaction in non-aqueous electrolytes, reacts with carbonates to form carbonate-based species such as Li_2CO_3 and/or lithium alkyl carbonates [45]. Subsequently, the gas evolved on charge process was found to be CO_2 rather than O_2 [44]. Ethers are also

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attractive for highly stable with Li metal anode, stable to a high oxidation potential over 4.5 V versus Li/Li+, safe, inexpensive and low volatility. However, ether-based solvents are not completely stable upon charging and cycling [42, 43]. This remains as a major challenge in the development of rechargeable Li-air batteries.

iv) Developing a lithium metal electrode that can cycle safely is also a key issue. Stability of anode has been a challenge for 40 years due to the dendrites that form on repeated lithium dissolution and deposition. But it can be suppressed by the formation of a stable SEI film on the surface of Li metal. The additives in electrolytes are effective to forming a stable SEI film.



Figure 2.9 Challenges in making practical Li-air batteries [47].

2.4 Literature survey on bifunctional (OER & ORR) catalyst

In order to accelerate the reaction rate and lower the cathode overpotential, an efficient bifunctional catalyst is essential. So far, the noble metal catalysts such as RuO₂, IrO₂, and Pt/C have shown to be promising candidates as bifunctional catalysts. Despite their good catalytic activity, high cost and scarcity limit their commercial applications. Thus, a material with high-performance, inexpensive and eco-friendly design is required.

Recently, first-row transition metal oxides such as cobalt, nickel, and perovskites have been reported as highly active and robust catalysts for OER in alkaline medium. Among them, cobalt-based oxides exhibit an outstanding OER performance [48–51].

Yang et al. reported bi-(FeNi) and tri-metal (Fe, Ni and Co) based layered double hydroxide (LDH) ultrathin nanosheets with controlled Co incorporation. They reported the OER catalytic kinetics of catalysts enhanced with the increase of Co incorporation, which were arise from the increased specific surface area that provided more catalytic active sites as well as improved electronic conductivity [52]. *Zhao et al.* also reported Fe and Ni doped mesoporous Co₃O₄ (mCo₃O₄) catalysts for enhancing oxygen evolution reaction [53].

In addition to looking for new cost-effective materials with stable structure, and also tuning the morphology of the existing material to improve their catalytic activity has been practicing and taken into consideration. From this point of view, one dimensional (1D) nanostructured materials possess structurally appropriate electrode/electrolyte interface to facilitate efficient transport pathways for electrons and ions [54]. *Eychmüller et al.* reported the nickel cobalt oxide hollow nanosponges (HNSs) as efficient OER electrocatalysts due to their porous and hollow nanostructures with large surface area and tunable compositions [55]. Also, the modification of surface with an electrically conductive material such as carbon is proven to be an effective way for enhancing the electrocatalytic activity, transport properties and durability of materials [56]. *Yang et al.* reported that the electrocatalytic activity enhanced after surface coating with a thin layer of carbon using sucrose as a carbon source [57].

However, most of these electrocatalysts reported in many papers still suffer from limited catalytic performances due to their low specific surface area and electrical conductivity. To overcome these

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issues and enhance the bifunctional catalytic activity, transition metal or metal oxides were introduced onto the conducting carbon substrate. This hybrid electrocatalyst could show superior bifunctional performance due to the synergistic effect between metal/metal oxide and carbon material [58-60].

To explain in detail, in accordance with the carbon–metal spacing and the Fermi level difference between carbon and the metal, a charge transfer happens across the carbon–metal interface. Such a charge transfer may be the main reason why some nanoparticles supported on a carbon surface show enhanced catalytic activities [61]. Furthermore, coupling metal with semiconductor metal oxides is supposed to enhance the electrochemical performance, as the formation of the Schottky barrier between metal and metal oxide is beneficial for charge separation [62].

Hence, carbon is becoming one of the most important air cathodes for $Li-O_2$ battery application. [63–67] Unfortunately, they suffer from passivation due to the formation of Li_2CO_3 by the side reaction mainly at the carbon/ Li_2O_2 interfaces [68, 69]. Carbon is relatively stable below 3.5 V (vs Li/Li⁺) on discharge or charge step, but it is not stable on charging step above 3.5 V which can oxidatively decomposing to form Li_2CO_3 thereby also produces Co_2 with the presence of Li_2O_2 (Figure 2.10) [70].



Figure 2.10 The carbon electrode in non-aqueous Li–O₂ cells [70].

Thus, it is essential to develop a protected carbon-based cathode to achieve the high energy density of Li-O₂ batteries as well as reduce the side reaction. So as to protecting the carbon and reducing the side reaction, the high adsorption energy material which can induce the growth of Li_2O_2 on its surface rather than carbon surface should be utilized. [71–72] Recently, *Cui et al.*, reported that CoO had high LiO₂ adsorption energy (from -2.7 to 13.4 eV based on the different crystal faces) thereby showing enhanced cycling performance than the super P as pure carbon electrode [73].

Also, the optimization the porosity of the oxygen electrode to provide large space for insoluble discharge products, and facilitate oxygen diffusion and electrolyte impregnation throughout the electrode, is needed. *Xiao et al.* first compared the electrochemical performance of Li–O₂ batteries with different commercial carbon powders [74]. The results indicated that the uniformity of the pore size plays an important role in determining the electrochemical performances of Li–O₂ batteries. *Mitchell et al.* developed the carbon nanofiber electrodes for Li–O₂ batteries and achieved high gravimetric energies up to 2500 W h kg_{discharged}⁻¹, which was about four times higher than LIBs with LiCoO₂ as cathode materials (≈600 W h kg_{electrode}⁻¹) [36]. Graphene with different porous architectures was also studied as cathode materials by several groups and achieved significantly improved specific discharge capacity [75-77]. 3D-ordered mesoporous/macroporous carbon sphere arrays (MMCSAs) were synthesized and applied as the air cathode in Li–O₂ batteries by *Guo et al* [78]. The ordered mesoporous channels and hierarchical mesoporous/macroporous structure of the MMCSAs provide enough places for discharge products, which improving the electrochemical performance of Li–O₂ batteries. Hence, the development of porous nanostructures is also promising strategy to improve the electrochemical performance of Li–O₂ batteries.

III. Experimental

3.1 Preparation of electrocatalysts

3.1.1 Chemicals

PAN (Polyacrylonitrile, $Mw = 150,000 \text{ g mol}^{-1}$), Dimethylformamide (DMF), cobalt acetylacetonate ($C_{10}H_{14}CoO_4$) and vanadyl acetylacetonate ($VO(C_5H_7O_2)_2$) were obtained from Sigma Aldrich and used as received. For the second part of this study, PAN, Dimethylformamide, and cobalt acetylacetonate were used.

3.1.2 Synthetic approach

Synthesis of 1D and 0D Co₃V₂O₈ catalysts:

One dimensional (1D) and zero dimensional (0D) nanostructures of $Co_3V_2O_8$ materials were synthesized by the electrospinning method. One gram of PAN was used as a carbon precursor and cobalt acetylacetonate, vanadyl acetylacetonate were used as metal precursors. The weight of metal precursor in the precursor solution was varied to 0.5 and 0.25 g, resulted in 1D- and 0D-Co₃V₂O₈ nanostructures, respectively. By tuning the weight ratio of PAN to the metal precursor, the viscosity of electrospinning solution was different, leading to the products with different morphologies [79]. During the electrospinning process, a voltage of 12 kV was applied between the needle tip and an aluminium foil collector with a distance of 10 cm and a flow rate of 1 mL h⁻¹. As-spun fiber mat was stabilized in air at 250 °C for 1 h, followed by crystallization process at 500 °C for 3 h under air atmosphere with a heating rate of 3 °C min⁻¹. The preparation of 1D- and 0D-Co₃V₂O₈ catalysts was schematically shown in Figure 3.1.



Figure 3.1 Schematic representation of preparation of 1D- and $0D-Co_3V_2O_8$ catalysts.

Synthesis of $Co_3V_2O_8$, Co_3O_4 and V_2O_5 :

For comparison, the preparation of $Co_3V_2O_8$ (without any carbon), Co_3O_4 and V_2O_5 catalysts was also carried out via the electrospinning method. To get a carbon-free metal oxide $0D-Co_3V_2O_8$ nanofibers, as-spun fibers were preheated in air at 250 °C for 1 h and followed by crystallization process at 600 °C for 2 h. PAN (1g) was used for both catalysts and 0.5 g of cobalt acetylacetonate, and vanadyl acetylacetonate were used as metal precursors for Co_3O_4 and V_2O_5 nanofibers, respectively and also Co_3O_4 nanotubes were obtained by calcination of as-spun fiber 1 h and then at 500 °C for 2 h. In order to get a V_2O_5 with nanorods morphology, the mat was annealed in air at 250 °C for 1 h and 600 °C for 2 h.

Synthesis of Co-CoO/CNR catalyst

Co-CoO/CNR was prepared via cost-effective and single step *in-situ* synthesis method. PAN (1g) was used for the carbon source and 0.5 g of cobalt acetylacetonate, was used as metal precursor. To obtain Co-CoO/CNR catalyst, as-spun fibers were preheated in air at 275 °C for 4 h with a heating rate of 3°C min⁻¹. Subsequently, the preheated sample was carbonized at 800 °C for 30 min in an Ar atmosphere with a heating rate of 5°C min⁻¹.

Synthesis of Co/CNR catalyst

For comparative studies, the preparation of Co/CNR was also carried out via the electrospinning method. The composition and the ratio of the precursors is the same. As-spun mat was annealed in air at 250 °C for 2.5 h, followed by the carbonization step at 800 °C for 2 h.

Synthesis of CNR catalyst

CNR catalyst was also prepared, with PAN alone for comparative studies. As-spun PAN fiber mat was annealed in air at 275 °C for 2 h and 800 °C for 2 h in an Ar atmosphere.
3.2 Characterization

3.2.1 Material characterization

Crystal structure of the materials has been confirmed by X-ray diffractometer (Rigaku, Miniflex 600). The morphology of the samples was analyzed by the field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800II, 3 kV) and a field emission transmission electron microscope (FE-TEM, Hitachi, HF-3300). For SEM microscopy analysis, samples were coated with osmium. The microstructure and lattice fringe of catalysts were determined by field-emission transmission electron microgen and carbon in these samples were confirmed by elemental analyzer (CHNS analysis). The graphitization nature of carbon present in the samples and existence of Co-O bond were examined with a Raman microscope (NICOLET LMECAXR) using a laser source wavelength of 514 nm. In order to study the oxidation state and understand the bonding nature of the material, the samples were characterized by X-ray photoelectron spectroscopy(XPS) using a JEOL JPS-900 in an ultra-high vacuum X-ray photoelectron spectrometer with an Al monochromatized cathode source at 25 W. The binding energy values were calibrated based on the graphite C 1s peak at 284.6 eV. Furthermore, to understand the specific surface area and pore size distribution of the material, Bruner-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models were used.

3.2.2 Electrochemical characterization

The OER and ORR activities of catalysts were assessed using a RDE system with three electrode system in which a glassy carbon electrode, saturated calomel electrode (SCE) and Pt wire as the working, reference and counter electrodes, respectively. All potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation E (RHE) = E(SCE) + 0.991 V. The potentials reported in this work were iR corrected and the electrolyte ohmic resistance (iR) was ~65 Ω in 0.1 M KOH measured with high-frequency AC impedance. In order to make a catalyst ink, 1.5 mg of catalyst was dispersed in 30 µL DI water and 160 µL IPA (Isopropyl alcohol) and then 10 µL of Nafion (5 wt%) was added into the mixture. By sonication for 30 minutes, a homogenous ink was formed. After that, 2 µL of the catalyst ink was drop casted onto the surface of polished glassy carbon electrode with an

area of 0.071 cm⁻² resulted with a catalyst loading of 0.21 mg cm⁻². Then OER polarization curves were recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV s⁻¹ at 1600 rpm in 0.1 M KOH electrolyte. Chronoamperometric stability tests were carried out for the 1D and 0D-Co₃V₂O₈ catalysts at overpotential of 1.59 V vs. RHE.

3.2.3 Metal-air battery test

Discharge and charge cycles of Zn-air cell were done in constant current mode using a battery analyzer (BST8-3). While charging-discharging cycles, 1 atm oxygen was continuously fed in the cathode compartment. All experiments were carried out at room temperature.

The Li-O₂ cell was also galvano-statically cycled by a MTI Korea battery analyzer at room temperature between 2.0-4.5 V vs. Li⁺/Li at a current density of 100 mA g⁻¹. During the battery tests, pure oxygen (1 atm) gas was continuously circulated at the air cathode.

3.2.4 Air cathode preparation and Zn-air cell assembly

Zn-air battery cell was assembled using a coin cell (CR2032-CASE-304-MESH-MTI Korea) configuration with openings allowing air to enter the cathode part (Figure 3.2). Coin cell is consisting of bottom case with Ø12mm x 1.0mm thick mesh disc (Ø1 mm holes on it) and top case with PP (Polypropylene) sealing O-ring.

Zinc metal foil (Alfa aesor) with the thickness of 0.1 mm and an area of 1.54 cm² was used as the anode and Whatman-GF/A was used as the separator. The separator was saturated with the 6M aqueous KOH electrolyte. The disks of oxygen electrode had an area of 2.54 cm². The cathode was prepared by 7 mg of catalyst and 3 mg of activated carbon. Subsequently, it was ultrasonically dispersing with 1 mL of IPA (Isopropyl alcohol) and 64 μ I of 5 wt% nafion ionomer for 30 minutes. Then prepared catalyst ink has been coated on GDL (Gas diffusion layer-carbon paper) by using brush coating and then dried in a vacuum oven for overnight at 80 °C.

3.2.5 Air cathode preparation and Li-O₂ cell assembly

The air cathode was prepared as a thin film over the GDL current collector. We used carbon paper as GDL. N-methyl-2-pyrrolidone (NMP) slurry of synthesized catalyst (3.5 mg) was mixed with 1 mg of super P carbon black (Daejung, Korea) as electronic conductor and 0.5 mg of poly-(vinylidenefluoride) (PVdF, Solvay Solef-6020) as binder in the weight ratio of 70:20:10, respectively.

After that, this mixture was coated over the GDL using the doctor blade technique. This film was dried at 110 $^{\circ}$ C for overnight to get a composite cathode with an electrode loading of about 1 mg cm⁻². A dual oxygen cathode was prepared which was composed of two interconnected porosity systems: a catalyzed and a non-catalyzed side (backside). The non-catalyzed system (GDL with a micro-porous layer) has fibrous morphology and it facilitate the transport of oxygen into the electrode even when the catalyzed system becomes finally blocked by reaction precipitates which is shown in Figure 3.3.

The Li-oxygen cell was assembled in an Ar-filled dry glove box using a coin cell (CR2032-CASE-304-MESH-MTI Korea) configuration (Figure 3.4). A lithium chip with the diameter of 15.6 mm and the thickness of 0.25 mm (EQ-Lib-LiC25-MTI Korea) was used as the anode and Whatman-GF/A was used as a separator. The separator was saturated with various electrolytes; 1) 1 M LiTFSI (Bis(trifluoromethane)sulfonimide lithium salt) DMSO (Dimethyl sulfoxide, Sigma Aldrich), 2) 4 M LiNO₃ (Lithium nitrate, Sigma Aldrich) salts with DMSO solution, 3) 1 M LiTFSI in TEGDME (Tetraethylene glycol dimethyl ether, Sigma Aldrich), and 4) 1 M LiPF₆ in EC/DMC (1:1) (Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate, Sigma Aldrich)).



Figure 3.2 Li-oxygen cell assemby.



Figure 3.3 The FE-SEM images of bare GDL (a) front side and (b) backside.



Figure 3.4 Lab-made Li-oxygen battery system setup using the open coin cell configuration.

IV. Results and discussion

4.1 Development of cost-effective and efficient Co₃V₂O₈ catalyst for aqueous Zn-air battery

4.1.1 Structural analysis

(i) Phase analysis by X-Ray diffraction pattern

X-ray diffraction (XRD) patterns of 1D and 0D-Co₃V₂O₈ nanostructures are shown in Figure 4.1(a). The XRD patterns of both Co₃V₂O₈ samples match well with the standard patterns of Co₃V₂O₈ (ICSD PDF no. 98-000-2645). This data is based on an orthorhombic crystal structure with Cmca space group which has the lattice parameters of a= 6.0300 Å, b= 11.4860 Å, c= 8.3120 Å. The BET surface area of 1D-Co₃V₂O₈ is 21.9 m² g⁻¹, whereas 0D-Co₃V₂O₈ is 10.3 m² g⁻¹ with mesoporous nature. The higher BET surface area can provide more active surface sites available for the electrochemical reaction, improving electron transfer by shortening the diffusion path and increasing the conductivity. The XRD patterns of single metal oxide, such as Co₃O₄ and V₂O₅ were presented in Figure 4.1(b).



Figure 4.1 XRD patterns of (a) 1D, $0D-Co_3V_2O_8$ and (b) Co_3O_4 , V_2O_5 nanostructures.

(ii) Elemental analysis (CHNS analysis)

The amount of nitrogen and carbon in 1D and 0D $Co_3V_2O_8$ samples were confirmed by elemental analyzer. The surface of 1D and 0D- $Co_3V_2O_8$ nanostructures are coated by a nanometer-thick amorphous carbon layer. Since PAN contains nitrogen, it produces a nitrogen-doped carbon during the pyrolysis process without requiring any additional nitrogen doping technique. The carbon and nitrogen elemental analysis of $Co_3V_2O_8$ nanostructures are listed in Table 4.1. The carbon and nitrogen contents determined from the elemental analysis were found to be 1.25, 1.27, and 1.32, 1.19 wt% for 1D- $Co_3V_2O_8$ and 0D- $Co_3V_2O_8$ catalysts, respectively.

Table 4.1 Elemental analysis of the $Co_3V_2O_8$ catalyst with respect to their morphologies using CHNS analysis.

Catalyst	C (wt%)	N (wt%)
1D-Co ₃ V ₂ O ₈	1.25	1.27
0D-Co ₃ V ₂ O ₈	1.32	1.19

(iii) Raman analysis

The further proof of the successful synthesis of $Co_3V_2O_8$ and the presence of turbostatic carbon were also revealed by Raman spectra, presented in Figure 4.2. Raman spectra exhibited peaks at 1352 and 1586 cm⁻¹, which corresponding to a turbostratic nature of carbon materials derived from polyacrylonitrile (PAN) [80, 81]. Turbostratic carbon means less structurally ordered graphite. The graphene layers are stacked irregular or haphazardly folded, tilted or split in turbostratic structure [82].



Figure 4.2 Raman spectra of 1D and 0D-Co₃V₂O₈ catalyst.

4.1.2 Morphology analysis

The morphology and microstructure of the materials were characterized using a field-emission transmission electron microscope (FE-TEM) and a field emission scanning electron microscope (FE-SEM).

FE-SEM images, as shown in Figure 4.3(a) and (d), clearly show the formation of 1D and 0D- $Co_3V_2O_8$ with porous nanostructures due to the partial removal of the PAN with carbon residue samples which enhancing the ionic transportation and the charge transfer on the catalyst surface [83]. The average particle size of 0D- $Co_3V_2O_8$ material is about ~200 nm while 1D- $Co_3V_2O_8$ is comprised of nanotubes and nanorods shaped morphology with an average diameter of approximately 135 nm (Figure 4.3b and e). 1D- $Co_3V_2O_8$ catalyst is composed of well interconnected nanoparticles which enhance the mobility of electrons and ions with a large number of active sites on the surface, leading to superior OER activity (Figure 4.4a and b). However, 0D- $Co_3V_2O_8$ catalyst shows that the particles were agglomerated (Figure 4.4c and d). For comparison, we also synthesized oxides of individual metal oxides such as Co_3O_4 and V_2O_5 with 1D morphology, and carbon-free $Co_3V_2O_8$ catalyst (Figure 4.5a, b and c).

TEM images in Figure 4.3c and f clearly show the surface of 1D and $0D-Co_3V_2O_8$ nanostructures are coated by an amorphous carbon layer. In addition, the TEM elemental mapping analysis clearly shows that carbon, cobalt, vanadium, oxygen and also nitrogen are uniformly distributed in $Co_3V_2O_8$ nanostructures as shown in Figure 4.6. The dotted lines in Figure 4.3(c, f) indicate the thickness of the carbon layer was found to be 6.73 and 17.0 nm for 1D and 0D nanostructures, respectively.

In Figure 4.3(c, f), the lattice fringes with d spacing of 0.25 nm and 0.20 nm matched well with the (221) and (240) plane of $Co_3V_2O_8$ (ICSD PDF no. 98-000-2645) respectively, which are in good accordance with the results of XRD analysis. Additionally, the selected area electron diffraction (SAED) pattern confirms the polycrystalline nature and the diffraction rings can be indexed to the (221) plane of the $Co_3V_2O_8$ phase (Figure 4.4e).



Figure 4.3 (a) FE-SEM and (b, c) FE-TEM images of $1D-Co_3V_2O_8$, (d) FE-SEM and (e, f) FE-TEM images of $0D-Co_3V_2O_8$. Carbon coating in (c, f) is outlined with dotted lines.





Figure 4.4 Additional FE-SEM images of $Co_3V_2O_8$ catalyst with (a) 1D and (c) 0D morphologies, TEM images of (b) 1D and (d) 0D morphologies, and (e) Selected area electron diffraction (SAED) pattern of $1D-Co_3V_2O_8$.



Figure 4.5 SEM images of (a) Co_3O_4 , (b) V_2O_5 and (c) carbon-coating free $Co_3V_2O_8$.



Figure 4.6 (a) STEM image of one-dimensional $Co_3V_2O_8$ catalyst (b) mixing of all elements, and the corresponding elemental mappings of (c) C-K edge, (d) Co-K edge, (e) V-K edge, (f) O-K edge, and (g) N-K edge.

4.1.3 Studies on the electrochemical activities of catalyst

(i) OER activity of the catalyst

To evaluate the morphological influences of $Co_3V_2O_8$ nanostructures on the OER electrocatalytic activity, we examined by rotating disc electrode linear sweep voltammetry (LSV) at 1600 rpm and with a 0.21 mg cm⁻² using a three electrode system in 0.1 M aqueous KOH electrolyte.

1D-Co₃V₂O₈ catalyst exhibits the higher electrocatalytic activity towards OER, since the overpotential at 10 mA cm⁻² is only 350 mV vs. RHE, whereas, 0D-Co₃V₂O₈ catalyst showed 397 mV, benefited from the morphological characteristics of 1D nanostructure to facilitate efficient transport channels for electrons and ions. Additionally, both 1D and 0D like Co₃V₂O₈ nanostructures exhibited much lower OER onset potential values than that of single metal oxides such as Co₃O₄ nanotubes and V₂O₅ nanorods (Figure 4.7), which were attributed to the change the energy levels of valence band due to the presence of V⁵⁺. Nevertheless, the noble metal catalyst RuO₂ had slightly lower onset potential than that of 0D-Co₃V₂O₈, OER current density of 0D- Co₃V₂O₈ catalyst rose sharply from 1.60 V vs. RHE. Similarly, we observed the same phenomenon in 1 M KOH as shown in Figure 4.9, 1D Co₃V₂O₈ nanostructure exhibits an outstanding OER current density of 179.4 mA cm⁻² at 1.8 V vs. RHE. Interestingly, even the same morphology, Co₃V₂O₈ nanoparticles as synthesized in this work show better catalytic OER activity with an overpotential lower by 17 mV and 39 mV to result in a current density of 10 mA cm⁻² in 1 M KOH aqueous solution compared with that of the previously reported Fe-doped Co₃V₂O₈ (V-Co-Fe-343) and Co₃V₂O₈ (Table 4.2), respectively [84-86].

The observed results stem from the presence of nanometer-thick nitrogen-doped carbon layers, which can promote the transportation for electrons by improving the conductivity and the beneficial effect of unique 1D nanostructure which results in a better OER catalytic properties.



Figure 4.7 Comparison of OER polarization curves measured in 0.1 M KOH aqueous solution at a scan rate of 5 mV s⁻¹.

To better understand the OER electrochemical kinetics, we measured the Tafel slope. As shown in Figure 4.8(a), the Tafel slope for 1D-Co₃V₂O₈ catalyst is 46 mV dec⁻¹, which is almost a half of that of 0D-Co₃V₂O₈ (89 mV dec⁻¹), indicating the faster OER electrochemical kinetics provided by the 1D-Co₃V₂O₈ catalyst. This can be further supported by the OER mass activity measured at 1.58 V vs. RHE for 1D-Co₃V₂O₈ and 0D-Co₃V₂O₈, and they are found to be 50.1 and 20.7 mA mg⁻¹, respectively (Figure 4.8b). The OER mass activity of 1D-Co₃V₂O₈ catalyst.

We also evaluated the OER activity using 1 M KOH solution, and it was found to be 49.6 and 9.35 mA mg⁻¹ for $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ catalyst, respectively. Mass activity (mA mg⁻¹) which is one of the ways to demonstrate the OER electrocatalytic activity has a significant importance to develop the practical applications such as metal-air batteries and regenerative fuel cells due to the price of

catalyst depends on the amount of catalyst loading [87]. Therefore, these results clearly demonstrate the importance of catalyst morphology effect on the OER performance.

Modification of the morphology affects the electronic conductivity, which plays a significant role in OER catalytic activity. Figure 4.8(c) illustrates the EIS curves of the $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ catalysts measured at 1.60 V vs. RHE. We also made carbon- free $Co_3V_2O_8$ nanoparticles (denoted carbon-free- $Co_3V_2O_8$), which exhibits much higher R_{ct} and possesses higher onset potential. The electrochemically active surface area (ECSA) for 1D and $0D-Co_3V_2O_8$ catalysts were calculated using a specific capacitance of 60 μ F cm⁻² based on the literature [88]. The ECSA of 1D and $0D-Co_3V_2O_8$ catalysts showed 6.6 and 3.4 cm², respectively, estimated from the electrochemical double-layer capacitance (C_{dl}).

The lower charge transfer resistance (R_{ct}) observed for 1D-Co₃V₂O₈ catalyst when compared to 0D-Co₃V₂O₈ catalyst, indicating an outstanding efficient electron transport for accelerating the rate of oxygen evolution reaction. This low R_{ct} value was attributed to the cooperative effect from its unique rod-like and tube-like porous architecture to diffuse ions and electrons efficiently at the interface between electrolyte and the electrode surface. We also evaluated the electrical conductivity of our catalysts using a four-probe technique. The electrical conductivity of 1D-Co₃V₂O₈ and 0D-Co₃V₂O₈ are formed to be 0.39 and 0.33 S m⁻¹, respectively. The conductivity results are in good agreement with the R_{ct} values obtained from EIS studies. Furthermore, as observed from the HR-TEM analysis, the existence of a thin layer of amorphous carbon coating on the surface of Co₃V₂O₈ will be beneficial to improve the electrical conductivity [89]. Thus, the lower R_{ct} value and higher conductivity of 1D-Co₃V₂O₈ catalyst ensure easy electron pathway, therefore showing better OER catalytic performance.

As listed in Table 4.2, our $Co_3V_2O_8$ catalyst exhibited a lowest OER overpotential compared to those reported for some cobalt-based nonprecious catalysts. Based on the above experiments, the superior OER performance of $Co_3V_2O_8$ with one-dimensional (1D) nanostructures is attributed to:

- (i) its novel structures with strongly interconnected particles that can diffuse electrons and through the channels rapidly,
- (ii) presence of carbon to enhances the conductivity and helps to sustain the catalyst structure,
- (iii) porous nanostructures with larger surface area which can produce more active sites for OER, and (iv) the favorable composition with binary metal oxide, expected to provide high OER performance.



Figure 4.8 (a) OER Tafel plots for $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$, (b) OER mass activity histograms at 1.58 V, (c) electrochemical impedance spectra of $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ at 1.58 V vs. RHE.



Figure 4.9 OER studies were investigated in a 1 M KOH electrolyte. (a) OER polarization curves for $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ catalyst. (b) OER Tafel plots for $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$. (c) OER mass activity histograms of $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ at 1.52 V vs. RHE. (d) Electrochemical impedance spectra of $Co_3V_2O_8$ with different morphologies at 1.59 V vs. RHE.

 Table 4.2 Comparison of experimental conditions and OER performance of different

 electrocatalysts in 1 M KOH.

Catalysts	Morphology	Catalyst loading (mg cm ⁻²)	Tafel slope (mV dec ⁻¹)	Over potential @10 mA cm ⁻² (mV)	Ref.	
Co ₃ V ₂ O ₈	Nanorods and nanotubes (1D)	0.21	24	290	This work	
	Nanoparticles (0D)	0.21	80	320		
Co ₃ V ₂ O ₈	Nanoparticles	0.21	65	359	84	
Co ₃ V ₂ O ₈ /MWCNT	Nanoplates	-	64.7	390	86	
	Nanospheres	-	68.6	380		
V-Co-Fe oxide	Nanoparticles	0.28	36	307	85	
Co ₃ O ₄	Nanoparticles	1.0	47 <u>+</u> 7	328	51	
CoOx@N-doped C	Nanoparticles	1.0	115	260	48	
Co ₃ O ₄ /N-rmGO	Nanoparticles	1.0	42	~310	49	
CuCo ₂ O ₄ /N-rGO	Nanoparticles	0.14	64	360	50	

(ii) OER stability of the catalyst

The OER stability test was carried out between 1.2 and 1.7 V vs. RHE for 6000 CV cycles at a scan rate of 200 mV s⁻¹ (Figure 4.10). The value of overpotential at 10 mA cm⁻² and current density were almost same as compared with the initial values after 1500^{th} cycles. Interestingly, after 100 cycles, it showed better OER activity than the 1st cycle. By contrast, the stability of 0D-Co₃V₂O₈ was less stable than that of 1D-Co₃V₂O₈ catalyst, in which 22 mV shifts was necessary to achieve a current density of 10 mA cm⁻² (Figure 4.11).



Fig. 4.10 OER polarization curves of $1D-Co_3V_2O_8$ catalyst upon cycling between 1.2 and 1.7 V vs. RHE with a scan rate of 200 mV s⁻¹.



Figure 4.11 OER polarization curves obtained using (a) $0D-Co_3V_2O_8$ and (b) Co_3O_4 as catalysts before and after 6000 cycles between 1.2 and 1.7 V vs. RHE at a scan rate of 200 mV s⁻¹.

In addition, chronoamperometric durability tests for 11 h with $Co_3V_2O_8$ at 1.59 V vs. RHE (Figure 4.11(b)) showed no loss of catalytic activity, indicating the good stability of the material in electrocatalysis. Due to a larger production of oxygen bubbles, chronoamperometric stability curves for $1D-Co_3V_2O_8$ catalyst has been fluctuated over the time. As we expected, the ECSA of $1D-Co_3V_2O_8$ had almost twice that of $0D-Co_3V_2O_8$, which informs that $1D-Co_3V_2O_8$ has more exposed accessible active sites to the electrolyte. So the current density of $1D-Co_3V_2O_8$ first increased due to the electrolyte penetration into the porous nanostructure and more active sites accessible for oxygen evolution reaction and then stabilized. A similar phenomenon was also observed by other researchers for OER durability studies [90]. The higher stability of $1D-Co_3V_2O_8$ catalyst was believed by:

(1) Enhancement of interconnectivity between nanoparticles that composes the special one dimensional porous nanostructure and,

(2) The presence of nitrogen-doped carbon, which helps to sustain its original structure.

In contrast, $0D-Co_3V_2O_8$, which was formed with separated nanoparticles, was sensitive to the agglomeration under the highly oxidizing conditions of the durability test which was presented in Figure 4.13, corresponding to the previous report [91]. Hence, the current density of the $0D-Co_3V_2O_8$ maintained for 5 h and then quickly falled down as shown in Figure 4.12.



Figure 4.12 Chronoamperometric curves for $Co_3V_2O_8$ nanostructures at 1.59 V vs. RHE.



Figure 4.13 FE-SEM images of $Co_3V_2O_8$ catalyst after 6000 CV cycles of stability test with (a) 1D and (c) 0D morphologies.

4.1.4 Zn-air battery test

(i) Primary Zn-air battery studies

The primary Zn-air battery studies have been evaluated using $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ catalysts loaded on the gas diffusion layer as the air cathode and paired along with a polished zinc metal foil in a glass fiber membrane soaked on 6M KOH electrolyte. The results shown in Figure 4.14 indicated the open-circuit voltage of 1.16 V, which was 70.3% of theoretical voltage (1.65 V). All specific capacity and energy density values were normalized by the mass consumed by zinc anode. The specific capacity of $1D-Co_3V_2O_8$ electrode was 609 mAh g⁻¹_{zinc} which shows ~ 73.4% utilization of the theoretical capacity of Zn-air battery (~820 mAh g⁻¹_{zinc} × 1.16 V), which shows only ~31% utilization of the theoretical energy density of Zn-air battery (~2288 Wh kg⁻¹_{zn}) due to a huge voltage loss.



Figure 4.14 Zn-air battery discharge capacity with different catalysts at a current density of 5mA cm⁻².

(ii) Secondary Zn-air battery studies

To understand the morphology effect in rechargeable Zn-air battery system, we cut down the capacity of 400 mAh g⁻¹ based on the mass loading of catalyst in the cathode compartment at the current density of 5 mA cm⁻². The results shown in Figure 4.15 represents the $1D-Co_3V_2O_8$ electrode showed very low overpotential of 0.66 V at first cycle and the overpotential increases on cycling the electrode, which mainly stem from the discharge profile related with oxygen reduction reaction. On the other hand, a charge profile remained stable until 29th cycles with an overpotential of 0.81 V. 0D-Co₃V₂O₈ based electrode observed similar trend, having an overpotential of 0.94 V and 1.41 V, respectively.



Figure 4.15 Discharge and recharge polarization curves of 1D and $0D-Co_3V_2O_8$ with respect to the cycle number.

4.1.5 Summary

In summary, one- (1D) and zero- (0D) dimensional porous $Co_3V_2O_8$ nanostructures with nitrogendoped carbon have been successfully synthesized *via* a single step of pyrolysis using a simple electrospinning technique to understand the morphology-property relationships in OER activity. Simply, by varying a weight ratio of polymer to the metal precursor permits the morphologycontrolled fabrication of $Co_3V_2O_8$. The result demonstrates the 1D- $Co_3V_2O_8$ catalyst exhibits superior OER activity and long-term stability in alkaline medium compared with those of 0D- $Co_3V_2O_8$, even for commercial precious metal catalysts without any additional treatment (e.g., via elemental doping). The excellent OER performance and stability is attributed to the well-designed one dimensional nanorods and nanotubes like structure, the synergistic effect of different metal ions and the presence of amorphous nature of nitrogen-doped carbon.

We also investigated the air cathode performance of our $1D-Co_3V_2O_8$ and $0D-Co_3V_2O_8$ catalysts. The activity of $1D-Co_3V_2O_8$ catalyst shows as a promising material for air cathodes in both primary and secondary Zn-air battery systems. Therefore, this study shows the importance of controlling the catalyst morphology could be a guide for developing an inexpensive, robust, and efficient catalyst for metal-air batteries.

4.2 Rational design of bifunctional air cathode for Lithium-oxygen battery

4.2.1 Structural analysis

(i) Phase analysis by X-Ray diffraction pattern

The XRD patterns of Co-CoO/CNR, Co/CNR, and CNR were shown in Figure 4.16. The observed broad peak in the range of 26° was attributed to the graphitic carbon (002) diffraction (ICSD 98-005-3781). The diffraction peaks achieved around at 36, 42, 61, 73 and 78° can be indexed to the (111), (002), (022), (113) and (222) planes of CoO (ICSD 98-024-5320), respectively, and the peaks at 44, 52 and 77° reflect the (111), (002), and (022) planes of the Co (ICSD 98-062-2437). These results indicate that metallic cobalt and cobalt oxide were coexisted in the Co-CoO/CNR catalyst.



Figure 4.16 XRD patterns of Co-CoO/CNR, Co/CNR, and CNR.

(ii) Raman analysis

Raman spectra revealed typical the characteristic peaks of G-band (vibration for all sp² bonded carbon atoms) and D-band (the vibrations of carbon atoms with dangling bonds with sp³ defect sites) of carbon at around 1340 and 1580 cm⁻¹, respectively for all samples (Figure 4.17). Additional peaks appear at 470 and 677 cm⁻¹ which can be attributed to the F_{29} mode and A_{19} mode of CoO, respectively, further proving the presence of CoO in the Co-CoO/CNR catalyst [92]. Commonly, the G band of carbon materials is associated with the graphitic structure, while D band arises from partial disorders or structural defects of the graphitic domains. Hence, the intensity ratio between D and G band (I_D/I_G) is widely used to evaluate the amount of defects or graphitization degree of carbon materials. The near zero value of I_D/I_G means high crystallinity, and a value near one indicates a large portion of structural defects in the carbon framework [93, 94]. The I_D/I_G values for Co-CoO/CNR, Co/CNR, and CNR were 1.10, 0.93, and 1.03, respectively. The high peak intensity ratio indicates the presence of several structural defect sites on the carbon nanorods. The defect sites in Co-CoO/CNR can contribute to provide more reaction sites for the oxygen adsorption and subsequent reactions. In addition, the Raman results were in good agreement with XRD observation and suggest the existence of the turbostatic nature of carbon nanorods in the samples.



Figure 4.17 Raman spectra of Co-CoO/CNR, Co/CNR, and CNR.

(iii) Elemental analysis (CHN analysis)

The CHN elemental analysis (EA) was carried out to measure the detailed elemental composition of all nanostructured samples. The obtained carbon and nitrogen compositions were observed to be similar for Co-CoO/CNR and Co/CNR samples (Table 4.3). Particularly, the carbon content was found to be 43.5 and 43.4 (wt%) for each sample, nearly equal to one another. However, the carbon and nitrogen contents of CNR were observed to be 76.0 and 9.47 wt%, respectively.

Catalyst	C (wt%)	N (wt%)
Co-CoO/CNR	43.5	1.11
Co/CNR	43.3	1.18
CNR	76.0	9.47

Table 4.3 Elemental analysis (CHN) of Co-CoO/CNR, Co/CNR and CNR.

(iv) X-ray Photoelectron spectroscopy (XPS) analysis

The chemical composition of the Co-CoO/CNR catalyst was determined by XPS measurement. The XPS survey spectrum shows that a set of peaks corresponding to C 1s (284.1 eV), N 1s (400.5 eV), O 1s (532.8 eV) and Co 2p (779.1 eV) were observed (Figure 4.18).

The existence of Co and CoO with nitrogen-doped carbon was further confirmed. The Co $2p_{3/2}$ and $2p_{1/2}$ high-resolution spectra were fitted with two components corresponding to Co⁰, Co²⁺ peaks (Figure 4.19). The peak centered at 780.5 eV was matched with Co $2p_{3/2}$ with a satellite at 785.9 eV and the peak centered at 796.7 eV was assigned to Co $2p_{1/2}$ with a satellite at 802.1 eV, which both belong to Co²⁺. In addition, Co in a zerovalent state was identified by the peaks at 778.2 and 793.7 eV

[95-97].

The C 1s deconvolution spectrum shows four types of C species: C=C (graphitic carbon), C=N & C-O, C-O-C & C-N, and -O-C=O with the binding energy values of 284.7, 286.0, 287.6 and 289.0 eV, respectively (Figure 4.20) [95, 97].

The high-resolution XPS spectrum of the N 1s peak reveals pyridinic, graphitic and pyrrolic-N species in Co-CoO/CNR, and the graphitic-N dominates the majority (Figure 4.21) [92, 98]. It has been reported that graphitic-N could greatly increase the limiting current density, and pyridinic-N could improve the onset potential, while other N species such as pyrrolic-N or oxidized-N had little effect on the electrochemical performance of N-doped carbon materials [99]. And these results indicate the existence of carbon atoms connected to N and O heteroatoms.

Moreover, the high-resolution O 1s spectrum could be fitted into three peaks at 533.3, 532.1 and 530.4 eV, which corresponds to hydroxyls, carboxyls and the oxygen related to the cobalt (II) oxides, respectively (Figure 4.22) [100].



Figure 4.18 XPS survey spectrum of Co-CoO/CNR, Co/CNR, and CNR.



Figure 4.19 The XPS high-resolution spectrum of Co 2p.



Figure 4.20 The XPS high-resolution spectrum of C 1s.



Figure 4.21 The XPS high-resolution spectrum of N 1s.



Figure 4.22 The XPS high-resolution spectrum of O 1s. - 53 -

(v) BET analysis

The specific surface area and the pore structure of materials were determined by BET N_2 absorption-desorption isothermal analysis and all the parameters extracted from the N_2 absorption-desorption plots were listed in Table 4.4.

Figure 4.23 represents the isotherm plots of all samples. Both Co-CoO/CNR and Co/CNR exhibit type IV isotherm with hysteresis loops which is often shown in large mesopore structures. In the contrary, CNR shows a type I isotherm. The differences in isotherm plots were attributed to the different morphology of all the samples and the N₂ adsorption ability. Co-CoO/CNR and Co/CNR show similar specific surface area of 370 and 373 m² g⁻¹, whereas CNR exhibits 29.5 m² g⁻¹. In addition, the BJH pore volume of Co-CoO/CNR (0.22) and Co/CNR (0.21) were much higher than that of CNR (0.033 cm³ g⁻¹), suggesting limited availability of active pores (Table 4.4). The BJH pore size distribution of all samples display mesopore structure (Figure 4.24). As a result, the Co-CoO/CNR and Co/CNR and Co/CNR samples with wide pore size (~4 nm) and high BET surface area (370 and 373 m² g⁻¹) are favorable for rapid diffusion of oxygen and electrolyte ions without blocking in the pores and provide sufficient spaces to gather discharge products.

Table 4.4	Specific	surface	area a	and E	BJH þ	oore	size	structure	parameters	measure
from BET	and BJH	l method	ls.							

Catalysts	BET Surface Area	BJH pore size	BJH pore volume	
	(m ² g ⁻¹)	(nm)	(cm³ g⁻¹)	
Co-CoO/CNR	370	3.76	0.22	
Co/CNR	373	3.59	0.21	
CNR	29.5	3.75	0.033	



Figure 4.23 Nitrogen adsorption/desorption isotherms of all the samples.



Figure 4.24 The BJH pore size distribution of all the samples.

4.2.2 Morphology analysis

The morphology of all samples was analyzed by FE-SEM and FE-TEM. The Co-CoO/CNR and Co/CNR sample exhibit similar nanorod architecture with an average diameter of 200 nm (Figure 4.25a,c). Figure 4.25b,d show the mesoporous nanostructure appeared on the nanorods surface. To understand the role of Co and CoO materials, the nanostructure of CNR was also investigated as a comparison sample. As shown in Figure 4.25e, f, CNR displays rod shaped morphology with the same average fiber diameter of 200 nm with smooth surfaces. From FE-SEM images of Co-CoO/CNR and Co/CNR, the presences of Co or CoO nanoparticles along the carbon nanorod surface were not clearly observed.

However, FE-TEM images show that those Co or CoO nanoparticles were obviously embedded inside the carbon nanorod and also placed on the surface (Figure 4.26). Furthermore, FE-TEM images also demonstrated the existence of disordered carbon frameworks and a low degree of graphitization. The TEM elemental mapping analysis clearly reveals that carbon, cobalt, oxygen and nitrogen were uniformly distributed in Co-CoO/CNR catalyst as shown in Figure 4.27.



Figure 4.25 FE-SEM images of (a, b) Co-CoO/CNR, (c, d) Co/CNR and (e, f) CNR.



Figure 4.26 FE-TEM images of Co-CoO/CNR.



Figure 4.27 (a) STEM image of Co-CoO/CNR, (b) mixing of all elements, and the corresponding elemental mappings of (c) C-K edge, (d) Co-K edge, (e) N-K edge, and (f) O-K edge.
4.2.3 Electrochemical characterization

To evaluate the OER catalytic activity of Co-CoO/CNR catalyst, LSV measurements were conducted by using a rotating disk electrode in an aqueous 0.1 M KOH with a scan rate of 10 mV s⁻¹ at 1600 rpm and all the results were plotted after iR-correction (~65 Ω of ohmic resistance in 0.1 M KOH electrolyte). For comparison, similar measurements for the Co/CNR and CNR catalysts were also performed.

Co-CoO/CNR shows a much lower onset potential for OER and greater current density than that of Co/CNR and CNR catalysts. Especially, once we introduce the Co or CoO nanoparticles, the current density was much improved, implying that an excellent catalytic OER activity arises from those nanoparticles in the catalysts. Normally, OER catalytic activity is evaluated by the potential needed to oxidize water at a current density of 10 mA cm⁻², which is commonly used in the OER literature, and a metric relevant to solar fuel synthesis [101]. Co-CoO/CNR catalyst shows considerable OER performance at such current density with an overpotential of 400 mV (Figure 4.28), which is much lower than that of Co/CNR (440 mV) and CNR catalyst. Moreover, it is comparable with the performance of the best reported carbon-supported OER catalysts: Co/N-C-800 (371 mV) [95], Co₃O₄-mMWCNTs (390 mV) [102], and N-doped graphene/carbon nanotube hybrids (400 mV) [103].

In order to study the ORR catalytic activity of all samples, ORR polarization curves were obtained with the same catalysts. As shown in Figure 4.29, the Co-CoO/CNR displays an onset potential of 0.90 V and the half wave potential of 0.83 V, and the values were similar with respect to those of Co/CNR (0.89 V and 0.82 V) and much better than CNR samples (0.85 V and 0.74 V).

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Figure 4.28 OER polarization curves of Co-CoO/CNR, Co/CNR, and CNR.



Figure 4.29 ORR polarization curves of Co-CoO/CNR, Co/CNR, and CNR.

In addition, LSVs at various rotating speeds from 400 to 2000 rpm were conducted (Figure 4.30a), and they show a typical increasing current density with higher rotation rates by shortened diffusion distance at high speeds, which are in related with other studies [104].

The electrochemical reduction of O_2 is a multi-electron reaction that has two possible pathways: one is the transfer of two electrons to produce H_2O_2 and the other is a direct four-electron pathway to produce H_2O . To achieve a maximum energy capacity, reducing the oxygen through the four-electron pathway is highly required [105]. The number of electrons (n) can be calculated based on the Koutecky-Levich (K-L) equation which indicates the kinetic aspects of oxygen reduction. K-L equation is as follows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

 $\label{eq:J_L} J_L: \mbox{ density } J_L: \mbox{ density } J_L: \mbox{ density } I_L: \mbox{ density } B = 0.62 \mbox{ nFA}(\mbox{CO}_2) \ \mbox{ D}_0^{-2/3} \mbox{ v}^{-1/6}$

where n is the electron transfer number, F is the Faraday constant (96,485 C mol⁻¹), A is the geometric surface area of the rotating disk electrode, CO_2 is the bulk concentration of O_2 (1.2 x 10⁻⁶ mol cm⁻³), D_0 is the diffusion coefficient of O_2 in the 0.1 M KOH solution (1.9 x 10⁻⁵ cm² s⁻¹), v is the kinematic viscosity (0.01 cm² s⁻¹), and ω is the rotating speed of the disk electrode (rpm) [106].

The corresponding Koutecky-Levich plot (Figure 4.30b) of Co-CoO/CNR presents a good linearity and parallel line indicating that the ORR catalytic activity follows first-order kinetics over a wide potential range. Also, it could be noticed that the ORR of Co-CoO/CNR catalyst was followed a four-electron transfer reaction (n=3.83).



Figure 4.30 (a) Rotating disk voltammograms of Co-CoO/CNR in 0.1 M KOH with the sweep rate of 10 mV s⁻¹ at the different rotation rates and (b) the corresponding K-L plot.

4.2.4 Li-oxygen battery test

(i) Effect of electrolyte on the catalytic activity performance

To examine the effect of solvent on the discharge performance of Li-oxygen battery, we used different kinds of electrolyte by using the Co-CoO/CNR as an air cathode at a current density of 100 mA g⁻¹ with cutoff voltage of 2.0 V (Figure 4.31). All electrochemical results were normalized based on the mass loading of catalyst (\approx 1 mg cm⁻²).

The Li-oxygen cell using 4 M LiTFSI in DMSO as an electrolyte achieved the highest discharge capacity of 11,831 mAh g^{-1} showing that the oxygen reduction reaction is much facile in the 4 M LiTFSI in DMSO electrolyte. Moreover, the discharge voltage of 4 M LiTFSI in DMSO electrolyte based battery shows a plateau voltage of 2.78 V which was much higher than that of other cells. In addition, once we increased the concentration of Li salt in the same DMSO solvent (-4 M), the discharge capacity was 2.5 times improved. We also tested the Li-oxygen cell using 1 M LiPF₆ in EC:DMC (1:1) electrolyte that commonly used in Li-ion battery. The cell achieved discharge capacity of only 790 mAh g^{-1} , which was much lower than that of the electrode with TEGDME and DMSO based electrolytes. These results indicated that the electrolyte could give a huge effect on the performance of Li-O₂ battery. Even though DMSO electrolyte with high concentration of Li salt shows the best discharge performance, the electrolyte of 1 M LiTFSI in TEGDME was used which has a good stability toward lithium metal anode and formed a stable solid-electrolyte interphase between the lithium anode and electrolyte.



Figure 4.31 Discharge capacity profile of Co-CoO/CNR electrode using various electrolytes at a current density of 150 mAh g⁻¹.

(ii) Primary Li-oxygen battery studies

In this study, the full discharge study of lithium-oxygen battery has been evaluated using all catalysts as the air cathodes at different current densities. First, the discharge performance was examined at 50 mA g⁻¹ as shown in Figure 4.32. It shows the discharge capacity of 13,159, 11,285, and 8,958 mAh g⁻¹ for each electrode, respectively. The increase in the capacity of Co-CoO/CNR was mainly due to their unique mesoporous nanostructures with large voids between some nanorods, which could facilitate the electrolyte impregnation and oxygen diffusion.



Figure 4.32 Discharge capacity profiles of Co-CoO/CNR, Co/CNR, and CNR electrodes at a current density of 50 mAh g⁻¹.

When the current density increased up to 500 mA g^{-1} , the Co-CoO/CNR electrode still could deliver high discharge capacity of 7,490 mAh g^{-1} (Figure 4.33). Meanwhile, as presented in Figures 4.34 and 4.35, Co/CNR and CNR electrodes exhibited discharge capacity of 2,274 and 1,890 mAh g^{-1} at high current density of 500 mA g^{-1} , respectively. Also, the rate capability of Co-CoO/CNR electrode was 57.1% when the discharge current density increased from 50 to 500 mA g^{-1} , which was almost 3 times higher than that of Co/CNR (20.3%) and CNR electrode (21.2%), respectively as shown in Figure 4.36. The improved high current rate performance of Co-CoO/CNR electrode could be related to the optimized highly porous nanostructured air cathodes. On the contrary, in case of CNR electrode, the capacity fading was caused by the rapid accumulation of byproducts in the oxygen electrode so that it couldn't transport electrolytes and oxygen properly.



Figure 4.33 Rate capability of the Co-CoO/CNR electrode at different current densities.



Figure 4.34 Rate capability of the Co /CNR electrode at different current densities.



Figure 4.35 Rate capability of the CNR electrode at different current densities.



Figure 4.36 The comparison of capacity retention of Co-CoO/CNR, Co/CNR, and CNR electrodes.



Figure 4.37 The comparison of discharge voltage of Co-CoO/CNR, Co/CNR, and CNR electrodes.

(iii) Rechargeable Li-oxygen battery studies

In this study, we examined the catalytic activity of the Co-CoO/CNR, Co/CNR, and CNR electrodes by reducing the cutoff capacity of 1000 mAh g^{-1} and evaluated the lithium-oxygen battery cyclability performance under voltage limitation between 2.0 V to 4.5 V at a current density of 150 mA g^{-1} .

The Co-CoO/CNR electrode shows an overpotential of 1.02 V at the 1st cycle and 1.19 V at 86th cycles with 170 mV losses (Figure 4.38). As many researchers have been reported, the OER activity of carbon materials is not sufficient for the high-performance of lithium-oxygen battery. So we introduced Co and CoO nanoparticles as an oxygen evolution reaction promoter into the CNR electrode and also on the surface to decrease the overpotential which lead to the improvement of the round-trip efficiency. Therefore, the round-trip efficiency in 1st cycle of Co-CoO/CNR electrode was further improved with 75.7%, which was higher than that of CNR electrode (66.4%). Furthermore, there was no significant change of the charge, discharge voltage profiles and the loss of specific capacity up to 86 cycles, indicating the excellent reversibility of the Co-CoO/CNR electrode (Figure

4.41).

For the comparison, Co/CNR and bare CNR electrode, the discharge voltage plateau began to decrease and the discharge capacity dramatically decreased after 10 and 21 cycles, respectively (Figures 4.39, 4.40).

The above results show that lithium-oxygen cell with Co-CoO/CNR electrode can operate reversibly with high energy efficiency and good cycling stability under the cutoff capacity. The significantly improved electrochemical performance could be attributed to the unique architecture of mesoporous nanorod morphology combined with the highly active Co-CoO nanoparticles. This electrode can provide large spaces to accommodate the discharge products, thus effectively reducing the volume change during the discharge and charge and also facilitate the electrolyte impregnation and oxygen diffusion. Furthermore, Co-CoO material shows more favorable adsorption of LiO₂ on Co-CoO surface [113] so that it can reduce the direct contact of LiO₂ to carbon materials, which can prevent the degradation of carbon and some side reactions.



Figure 4.38 Charge and discharge profiles at different cycles of lithium-oxygen batteries with Co-CoO/CNR electrode.



Figure 4.39 Charge and discharge profiles at different cycles of lithium-oxygen batteries with Co/CNR electrode.



Figure 4.40 Charge and discharge profiles at different cycles of lithium-oxygen batteries with CNR electrode.



Figure 4.41 The discharge capacity versus cycle number with Co-CoO/CNR, Co/CNR, and CNR electrodes in Figure 4.37, Figure 4.38, and Figure 4.39.

4.2.5 Air cathode post-mortem analysis

To identify the discharged products of Li-O₂ batteries with Co-CoO/CNR, Co/CNR and CNR cycled electrodes, we characterized using XRD and FE-SEM.

XRD patterns of the Co-CoO/CNR electrode at different state for the 1st cycle and the recharge state for the 88th cycle at current density of 100 mA g⁻¹ were shown in Figure 4.42. As compared with the XRD pattern of the fresh electrode, new diffraction peaks were observed for the discharge electrode which is assigned as the Li_2O_2 , LiO_2 and Li_2O (marked in Figure 4.42). These peaks indicated that Li_2O_2 is the major discharge product. After recharging the battery, these peaks were almost invisible, demonstrating that the reversible discharge and charge capacities were mainly attributed to the formation and decomposition of Li_2O_2 discharge product.

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By contrast, for discharged Co/CNR electrode, new diffraction peaks of CoO, Li₂O, Li₂CO₃, and Li₄CO₄ were presented (Figure 4.43). Li₂CO₃, and Li₄CO₄ were the main products and the presence of CoO was due to the oxidization of Co metal nanoparticles during the process. For the CNR electrode, Li₂CO₃, Li₂O₂ and Li₄CO₄ peaks were presented in the XRD pattern. Among them, Li₂CO₃ was strongly formed on the electrode surface as shown by XRD pattern and FE-SEM images (Figure 4.44). While in the recharge process, the Li₂CO₃ discharge product was not decomposed because of the strong bond formation of lithium ion with the carbonate at the carbon and electrolyte interfaces.



Figure 4.42 XRD patterns of discharged and recharged Co-CoO/CNR electrodes.



Figure 4.43 XRD patterns of discharged and recharged Co/CNR electrodes.



Figure 4.44 XRD patterns of discharged and recharged CNR electrodes.

The surface morphological changes of Co-CoO/CNR electrode during the electrochemical reaction were observed by FE-SEM in Figure 4.45.

In Figure 4.45a, it shows that some nanoparticles that consisted of super P as an electric conductor and PVDF as binder were co-existed with the Co-CoO/CNR catalyst. From the Figure 4.45b-d, Li₂O₂ formed on the Co-CoO/CNR electrode after discharge and then decomposed in the recharge process, in accordance with XRD results. Additionally, even after 88 cycles with discharge and recharge process, the structure of Co-CoO/CNR electrode was maintained well (Figure 4.45e,f). As we mentioned above, CoO in the Co/CoO particles has been proved to have a high LiO₂ adsorption energy, which usually induce a surface-nucleation process. Thus, Li₂O₂ first grows around the surfaces of Co-CoO nanoparticles favorably. These results demonstrate that Co-CoO/CNR electrode could operate reversibly with high energy efficiency and good cycling stability at a cutoff capacity of 1000 mAh g⁻¹. The superior electrochemical performance could be due to the unique architecture that carbon nanorod combined with the highly efficient Co-CoO nanoparticles. Additionally, well optimized mesopore Co-CoO/CNR nanostructures with large voids between each nanorods could provide sufficient spaces to accommodate the discharge products. Furthermore, CoO nanoparticles play an important role in reducing the overpotential during the charge process.

By contrast, on the Co/CNR and CNR electrode, Li_2O_2 grows through the carbon surface and the solution due to the superoxide which is dissolved in the electrolyte thus it can be trapped on the defect sites of CNR and formed as Li_2CO_3 and Li_4CO_4 (Figure 4.46, 47). For both Co/CNR and CNR electrodes, several toroidal and film-like Li_2Co_3 and Li_4CO_4 with irregular morphologies formed on the electrodes after 21th and 10th cycles, respectively, which produce more byproducts and lead to a limited cycle life.



Figure 4.45 FE-SEM images of Co-CoO/CNR (a) pristine, (b) 1st discharged, (c, d) 1st recharged, and (e, f) 88th recharged electrode.



Figure 4.46 FE-SEM images of Co/CNR (a) pristine, (b) 1^{st} discharged, (c, d) 1^{st} recharged, and (e, f) 10^{th} recharged electrode.



Figure 4.47 FE-SEM images of CNR (a) pristine, (b) 1^{st} discharged, (c, d) 1^{st} recharged, and (e, f) 21^{th} recharged electrode.

4.2.6 Summary

Co-CoO/CNR was successfully synthesized as bifunctional catalyst by a simple electrospinning method which was cost-effective and single-step *in-situ* synthesis method. The high full discharge capacity of 13,181 mAh g⁻¹ was achieved at a current density of 50 mAh g⁻¹ for Li-O₂ battery demonstrating a good ORR activity. In case of rechargeable battery, it lasts for over 86 cycles with a cutoff capacity of 1000 mAh g⁻¹ at the current density of 100 mAh g⁻¹. Furthermore, compared with the Co/CNR and CNR electrode, Co-CoO/CNR air cathode exhibited reduced overpotential and improved cycling stability.

To understand the mechanism behind the catalytic performance, we examined the post-mortem analysis by using XRD and FE-SEM and confirmed the formation and decomposition of discharge product during discharge and recharge, respectively.

V. Conclusions

Alternative energy storage devices such as Zn-air and Li-air batteries have been studied. For this upcoming technology, highly active and durable electrocatalysts on the cathode side are highly required to catalyze oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during the recharge for the rechargeable batteries. Therefore, we developed the electrochemically active, stable and non-precious bifunctional catalyst for Zn-air and Li-air batteries.

First, we focus on designing an inexpensive and highly active OER electrocatalyst, $Co_3V_2O_8$ with 1D morphology consisting of nanotubes and nanorods which was used in Zn-air battery and tried to understand the morphology effect on the oxygen evolution reaction. The activity of 1D- $Co_3V_2O_8$ based electrode shows as a promising material for air cathodes in both primary and secondary Zn-air battery systems.

In the second part of research, we developed Co-CoO/CNR catalysts as a bifunctional air cathode for Li-O₂ batteries. The high full discharge capacity of 13,181 mAh g^{-1} was achieved at a current density of 50 mAh g^{-1} for Li-O₂ battery demonstrating a good ORR activity, and it exhibits reduced overpotential and improved cycling stability. To understand the working mechanism behind the catalytic performance, we also examined the post analysis of cathode material in Li-oxygen batteries.

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국문요약문

금속 공기전지용 고효율 양극촉매 개발

본 논문은 현재 상용화된 이차전지 중 에너지 밀도가 가장 높은 리튬이온전지보다 이론 에너 지 밀도가 훨씬 높아 전기 자동차 등의 차세대 에너지원으로서 활발하게 연구되고 있는 금속 공 기전지의 양극 촉매 개발 연구에 대해 다룬다. 대기 중의 산소를 양극 활물질로 사용하는 금속 공 기전지의 상용화를 위해서는 무엇보다도 전지의 충·방전시 공기극에서의 느린 산소발생 및 환원 반응을 촉진하는 고효율의 이원기능 촉매 개발이 필요하다. 이를 위해 Pt/C, IrO₂, RuO₂ 등 귀금속 기반의 촉매가 현재 사용되고 있으나, 제조단가가 높으며 낮은 선택성 및 내구성에 관한 문제점이 제기되고 있다. 따라서, 비귀금속계의 내구성을 지닌 고효율의 이원기능 촉매의 개발이 요구된다.

본 논문의 첫 번째 파트에서는 간단하고 저렴하며 대량생산이 가능한 전기방사법을 통해 아 연 공기전지 (Zn-air battery)에 적용할 수 있는 나노로드 및 나노튜브 구조로 이루어진 일차원의 Co₃V₂O₈ 나노촉매를 개발하였다. 또한 촉매의 형태 및 구조가 촉매의 활성에 미치는 영향을 종합 적으로 확인하기 위해 나노파티클 구조의 Co₃V₂O₈ 촉매를 합성한 후 그 성능을 비교하였다.

본 논문의 두 번째 파트에서는 이원기능의 Co-CoO/CNR 촉매를 합성하였고, 이를 리튬 공기전 지에 적용하였을 시 100 mAh g⁻¹의 전류밀도에서 10,569 mAh g⁻¹의 높은 방전용량을 얻었다. 이 는 같은 전류 밀도에서의 CNR 촉매보다 1.5배 증가한 용량이며, 또한 1000 mAh g⁻¹의 제한용량에 서 86 사이클 이상의 안정적인 특성을 확인하였다. 이러한 기존의 낮은 안정성과 값비싼 귀금속 촉매를 대체할 수 있는 새로운 양극촉매 개발에 관한 연구는 금속 공기전지의 상업화를 앞당기는 데 기여할 수 있을 것이다.

핵심어: 공기 촉매, 금속 공기전지, 리튬 공기전지, 코발트 바나듐 옥사이드, Co-CoO/CNR

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