Chapter

A Perspective on the Recent Amelioration of Co_3O_4 and MnO_2 Bifunctional Catalysts for Oxygen Electrode Reactions

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Abstract

Metal-air batteries with the aid of high theoretical energy density and affability are trusted as propitious energy storage systems in today's energy research. However, enforcement of the technology is still hindered by the sluggish kinetics of their electrode reactions, that is, oxygen evolution and oxygen reduction reaction (OER/ORR). Developing a catalyst with inherently greater bifunctional activity and durability is the finest solution to confront the aforementioned challenges. Transition metal oxides (TMOs) are the most appropriate choice of materials for that purpose since they are highly active, inexpensive, abundant and non-hazardous. Among the various transition metal oxides, MnO_2 and Co_3O_4 are gaining much attention due to their superior bifunctional performance and alkaline stability owing to their structural features and physicochemical properties. With the inspiration from promoted catalytic activity of MnO_2 and Co_3O_4, this chapter is fully devoted to these two catalysts. The activity structural relationship, recent developments and future directions of these materials for bifunctional catalysis have been discussed in more detail. Besides, the significant parameters judging the bifunctional activity, that is, phase, crystal facets, morphology, defects, strains and mixed metals oxide formations, have been illustrated with suitable evidence. In addition, the fundamentals of water oxidation and reduction reactions are explained with the mechanisms. Moreover, the physiochemical properties of MnO_2 and Co_3O_4 materials and their influence on the catalytic activity are related for a better understanding of bifunctional catalysis. This collective perception will be highly useful for the comprehension and designing of advanced metal oxide catalysts to further improve bifunctional catalysis.

Keywords: ORR, OER, water splitting, MnO_2, Co_3O_4, bifunctional catalyst

1. Introduction

As far the energy consumption is concerned in the current energy scenario, the role of fossil fuels is exceptional by delivering a rich source in comparison with other sources [1, 2]. The catastrophic changes to the earth's climate are unavoidable with these carbon-emitting energy supplies. As the depletion of fossil fuels alarms the scientific community to move forward for future fuels, the search is triggered with the application of renewable energy sources like solar, tidal and wind-assisted energy devices. Considering the electrochemical energy conversion devices such as batteries, alkaline fuel cells and solar water-splitting devices [3], these are the technological functions based on the electrochemical reactions such as oxygen evolution reaction (OER), oxygen reduction reaction (ORR) [4, 5], hydrogen evolution reaction (HER) [6] and hydrogen oxidation reaction (HOR) [7]. The chemistry behind the hydrogen-based oxidation and reduction is facile compared with the oxygen-based oxidation and reduction reactions. The OER and ORR reactions are uphill processes and thus drag more overpotentials, and hence, the voltage applied also increases [8]. In metal-air batteries (MABs), the activity of the device predominantly depends on OER and ORR taking place during the charge and discharge process, respectively. The most active catalysts are the expensive Pt (HER, ORR), IrO_2 and RuO_2 (OER), and the search for inexpensive catalysts is unavoidable for the commercial usage of MABs. Moreover, the use of two different catalysts for ORR and OER in MAB makes the device more complicated and expensive. Besides, the ORR being the most active catalyst, Pt is not a suitable candidate for OER owing to the formation of the oxide over the surface of the catalyst, which gives the catalytic ability of OER. Similarly, IrO_2 is a good candidate for OER, due to its high conductivity and stability, and is not preferable for ORR [9]. Therefore, the development of non-precious transition metal-based bifunctional catalysts, which can simultaneously catalyze both OER and ORR, becomes the utmost important parameter to enhance the efficiency of these electrode reactions. Even though there are catalysts with increased efficiency for the selective ORR-like carbon-derived metal catalysts and their oxides, the OER becomes a matter of concern as the conversion of carbon to their oxides occurs before the thermodynamic potential of OER. For OER, the chalcogenides and oxides of transition metals are found to be more active and stable catalysts in basic environment. Therefore, identifying electrocatalysts with significant activity in both OER and ORR is more important for applying them in the energy conversion MAB devices [10].

In addition to the bifunctional activity, the stability of the electrocatalyst in the electrolyte medium is also vital for commercializing the technology. The corrosive nature of acids during long-term usage restricts their commercial usage, and in such cases, alkaline electrolytes become preferable, which facilitates the sluggish oxygen electrode reactions (ORR/OER) with ease and thus provides relatively less corrosive to the transition metal-based materials. Additionally, transition metal-based catalysts have more advantages such as the ability to exist in multiple (two or more) and mixed oxidation states, different coordination environments, and flexibility to replace one transition metal by another that is highly desirable to further promote the bifunctional activity. Electrocatalysts derived from transition metals like transition metal oxides (TMOs), sulfides and hydroxides have been demonstrated as efficient electrocatalysts in oxygen electrode reactions [11]. Among all TMOs, particularly cobalt oxide (Co_3O_4, spinel oxide) and manganese oxides are found to be the superior bifunctional catalysts for oxygen electrode reactions [10].

Manganese oxides, with their highly affordable nature and handling, could also deliver enhanced ORR activity and moderate OER activity through the metal and lattice oxygen that act as active sites. The enhanced activity from manganese oxides is ascribed to the ease of conversion of Mn to higher oxidation states and its preferable four-electron transfer reduction pathway in ORR [12]. However, in spinel oxides like

Co_3O_4, Co^{2+} and Co^{3+}, ions assist the conversion of reversible adsorption-desorption of oxygen to facilitate the oxygen electrode reactions [9, 13]. Therefore, much effort has been dedicated based on these TMOs for the efficient conversion of both OER and ORR.

After evaluating the need for new and advanced energy conversion devices in brief, in this chapter, we have first introduced fundamental electrochemical parameters and requirements for the efficient ORR/OER electrocatalyst in basic electrolytes. The bifunctional behavior of the superior non-precious TMOs such as MnO_2 and Co_3O_4 is explained in more detail and its recent developments from the literature are reviewed in extreme depth [13]. The fundamental factors that can be used to enhance the bifunctional activity are summarized, which include morphology, phase, crystal facets, defects, mixed metal oxides and doping of metals on the metal oxide surface. From this chapter, one can easily find the fundamentals behind the formation of highly active, earth abundant transition metal-based catalysts for both OER and ORR processes with increased efficiency. In addition, the exact catalytic behavior of the bifunctional catalyst is not fully understood, which varies from material to material. To pinpoint the active sites and discover the mechanism of the particular catalyst, density field theory (DFT) calculation and in situ study by using specific analytical techniques such as Raman spectroscopy, Mossbauer spectroscopy, X-ray adsorption/diffraction and Fourier transform infrared spectroscopy are highly recommended. Theoretical studies combined with these in situ experiments are able to provide a deeper insight into structures and processes at the atomic level, which together with laboratory experiments could lead to a better understanding of the mechanistic steps involved in the reactions, and these can pave the way for the future directions of OER and ORR for commercial application. Finally, the existing challenges and much-needed effort for improving the catalytic activity of bifunctional catalysts are discussed as the future effort directions.

2. Fundamentals of oxygen electrode reactions (ORR/OER)

To provide good clarity of bifunctional electrocatalysis, first, the basics and fundamentals of oxygen electrode reactions and electrochemical parameters used in the evaluation of the performance of electrocatalysts are discussed in more detail. The intensive knowledge of the above-mentioned field is necessary to design a new non-precious transition metal-based material and to understand its behavior toward ORR/OER.

2.1 Mechanism of ORR

ORR is an electrochemically sluggish reaction with four-electron transfer in a multiple-step process, where the reaction begins with the diffusion of oxygen (O_2) toward the catalyst, adsorption of O_2 molecule on the active sites of the catalyst, transfer of electrons to the adsorbed O_2 molecules and passage through multiple steps. Finally, it is converted to products and desorbed from the active sites of the catalyst [14].

If we look at the ORR more deeply, there are two possible ways to adsorb O_2 molecules on the electrode surface such as associative (bidentate, side-on, two oxygens atoms of O_2 coordinates with the metal) O_2 adsorption and dissociative (monodentate, end-on, one oxygen atom of O_2 coordinates perpendicular to the metal) O_2 adsorption as shown in **Figure 1**.

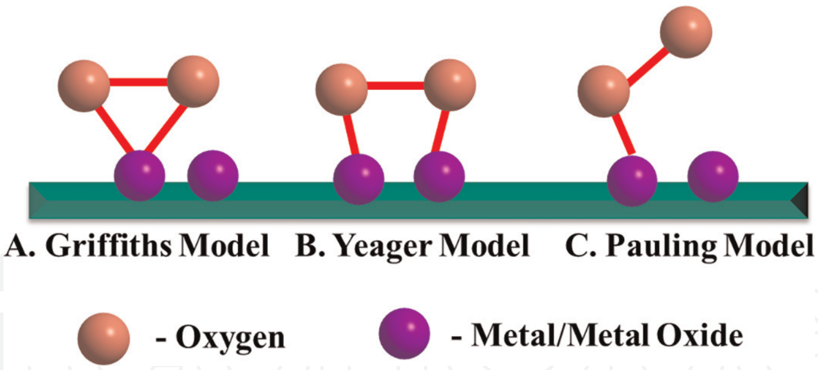


Figure 1.
The schematic representation of the adsorption of O_2 over the metal/oxide surface.

The adsorption mode of oxygen had the foremost influence and is crucially significant for the number of electrons transferred (n) during the ORR process. The associative adsorption mode of oxygen leads to the direct four-electron transfer reduction path and the dissociative adsorption mode of oxygen results in the two-electron transfer reduction path through the peroxide intermediate formation. Typically, noble metals predominantly follow four-electron transfer reduction, and carbon-based materials follow two-electron transfer reduction. On the other hand, non-precious metal oxides can follow either indirect two- or direct four-electron transfer path or both, influenced by the nature of metal oxide and overpotential region. The higher overpotential region offers highly desirable direct four-electron transfer reduction, whereas, in the lower overpotential region, two-electron transfer reduction with peroxide formation occurs predominantly. Therefore, the exact number of electron transfers and the mechanism of ORR on the metal oxide surface still remain unclear. However, the widely accepted mechanism of ORR is fairly complicated and involves oxygen-containing intermediates such as O*, OH* and OOH*. The mechanism of four-electron transfer pathway of ORR on a catalytic metal surface can be described as follows:

$$^{*} + O_2(g) \rightarrow O_2{}^{*} \tag{1}$$

$$1/2\, O_2{}^{*} \rightarrow O^{*} \tag{2}$$

$$O^{*} + H^{+}(aq) + e^{-} \rightarrow OH^{*} \tag{3}$$

$$OH^{*} + H^{+}(aq) + e^{-} \rightarrow H_2O^{*} \tag{4}$$

$$H_2O^{*} \rightarrow H_2O \tag{5}$$

Here, * represents the active sites of the catalyst under investigation [13, 15, 16]. The two-electron transfer mechanism of ORR is as follows:

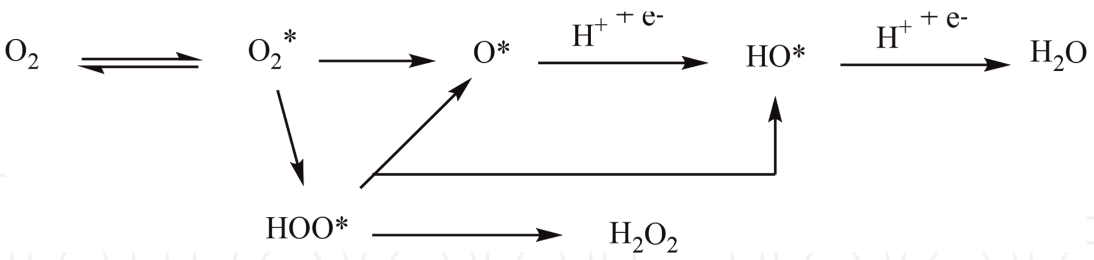
$$O_2{}^{*} + H^{+}(aq) + e^{-} \rightarrow HOO^{*} \tag{6}$$

$$HOO^{*} + H^{+} + e^{-} \rightarrow H_2O_2 \tag{7}$$

In some cases, OOH* dissociation may be involved on the same catalytic surface as follows:

$$HOO^{*} \rightarrow O^{*} + HO^{*} \tag{8}$$

All possible mechanisms of ORR are shortened here.



The heterogeneous electrocatalysis (ORR/OER) occurs at the catalyst–electrolyte–reactant triple point, where the binding energy of the reactive species (intermediates/reactant) has been calculated to determine the catalytic performance of the electrocatalyst. The French chemist Paul Sabatier made a principle with respect to the binding energy of the reactive species and catalytic performance of the electrocatalyst in a heterogeneous system called the Sabatier principle (also called the volcano plot). It states that the interaction between the surface of the catalyst and the reactant should be optimum; That is, it should be neither too strong nor too weak [17]. Because too weak interactions result in the failure of making bonds between them, causing no further reaction, and too strong interactions lead to kinetically slow dissociation of the resultant intermediates, the catalytic surface is not accessible by the reactant for further reaction. In the case of ORR, three oxygen-containing species are involved as an intermediate such as O*, OH* and OOH*. The binding energy of these reactive intermediates is the leading factor that decides the activity of the catalyst [18].

2.2 Reaction mechanism of OER

Water oxidation reaction or OER is the reversible reaction of ORR, which occurs at a higher positive overpotential than ORR; to attain the reversibility of each step involved, the ORR should be reversed. Moreover, it is the core electrochemical reaction in fuel cells, MABs and water splitting with their complementary reaction such as ORR and/or HER. It is a multi-step electron transfer reaction; each step requires some energy to overcome the energy barrier, drag the overall kinetics of OER and necessitate a large overpotential [19].

The proposed mechanism of OER on the metal oxide surface is as follows:

$$^* + H_2O \rightarrow {}^*OH + H + +e- \tag{9}$$

$$^*OH \rightarrow {}^*O + H + +e\text{-or}\, 2{}^*OH \rightarrow {}^*O + * + H_2O \tag{10}$$

$$2{}^*O \rightarrow 2^* + O_2\,\text{or}\,{}^*O + H_2O \rightarrow {}^* + O_2 + 2H^+ + 2e^- \tag{11}$$

Although OER is relatively complex, it is considerably facile on the metal oxide surface rather than on the bare metal surface, since bare metals are more prone to oxidation at higher positive overpotentials. Moreover, the capability to exist in multiple oxidation states of metal oxides makes it a highly desirable candidate for OER, where the interaction between the metal and oxygen intermediates initiates the bond formation between them by change in the oxidation state of the metal. Therefore, metal oxides are the best choice of catalyst for OER. However, each metal oxide has a different OER mechanism on its surface; even oxides with identical element compositions due to the difference in the surface property of materials originated from the preparation method. The volcano plots relating the required overpotential to attain 1 mA current vs ΔG_O - ΔG_{OH} for OER have been constructed by the study of OER catalysis on a wide variety of metal oxide surfaces [20].

2.3 Bifunctional (ORR/OER) electrocatalysis

A single catalyst employment for the catalysis of two electrochemical reactions (both a reaction and its complementary reaction) is called bifunctional electrocatalysis. The catalyst used in the bifunctional electrocatalysis with the capability to catalyze two electrochemical reactions is termed as bifunctional electrocatalyst. The bifunctional electrocatalyst is primarily used to facilitate the electron transfer from the electrode to the reactant, which promotes oxygen electrode reactions (ORR/OER). A single catalyst employment to catalyze both OER/ORR, that is, a bifunctional catalyst is highly preferable particularly for energy storage and conversion devices, rather than employing two different catalysts separately. Either the catalyst itself or the catalyst decorated on the electrode surface is mostly used as a bifunctional electrocatalyst. The principal role of the electrocatalyst is to adsorb the reactant on its surface and develop the adsorbed reactant/intermediate, thereby promoting the kinetics of charge transfers from the electrode to the reactant. The equilibrium potential of the oxygen electrode reaction (ORR and OER) is 1.23 V versus reversible hydrogen electrode (RHE) [21]. However, the complicated mechanisms and sluggish kinetics of these reactions demand high overpotentials. In order to facilitate the oxygen electrode reaction, the bifunctional electrocatalyst must adhere to certain intrinsic structural features, that is, high inherent bifunctional catalytic activity; enlarged surface area; high electrical conductivity and favorable morphology with exposure of maximum active sites; a high electrochemical surface area; high chemical, electrochemical and mechanical stability; and good contact of electrochemical (electrode electrolyte) interfaces [22]. Although a material with aforementioned properties can perform as good bifunctional electrocatalyst, it has to be evaluated with certain electrochemical parameters for its comparison with other catalysts.

For a fair evaluation of the performance of electrocatalysts, all the electrochemical parameters must be taken into account such as the onset/overpotential, exchange current density, Tafel slope, turnover frequency (TOF), potential gap, number of electron transfers, amount of peroxide formation and electrochemical surface area [23]. Each and every parameter is very crucial and can provide much more insightful information about the catalyst material related to the mechanism of electrochemical reaction. For this reason, the detailed introduction of all the fundamental electrochemical parameters has been discussed elaborately in the following sections.

3. Efforts on the in-built possession of the catalyst materials to enhance the bifunctional activity

After the detailed discussion of the fundamental electrochemical parameters, it is now essential to highlight the significance of in-built possessions of the materials, which decide the properties of the catalyst materials. As stated earlier, a reputable candidate for electrochemical reaction must be recognized with certain properties such as intrinsic activity, density of active sites, conductivity, surface area, wettability (hydrophilicity) and stability. But all these properties are decided by their appropriate association with in-built possessions like phase, morphology, particle size, defects and strain. A slight change in these in-built possessions leads to the huge impact on the properties of catalyst materials. In addition, practically, there is no catalyst material with an adequate quantity of all these mentioned properties. To resolve this inadequateness, many efforts have been devoted on catalyst materials. A catalyst with optimum quantity of all the aforementioned properties can be attained only by a systematic fine-tuning of its in-built possessions such as phase, morphology, crystal facets, particle size, defects and strain. Therefore, to understand the linear thread connection between the in-built possessions, inherent properties and outperforming activity of the electrocatalyst, all these possessions have been discussed in more detail in this section.

3.1 Phase engineering

The smallest repeating domain containing identical (in both distance and space) arrangement of atoms is called a crystal lattice. The extent of a single or a group of crystal lattice can be defined as a phase, a key factor in deciding the properties of the materials. Each phase has its own property and the variation in phases causes dramatic changes in the properties especially in the intrinsic activity, density of active sites, conductivity, wettability and stability, thus having more impact on the bifunctional activity. Controlling materials with desirable phases is an art associated with synthetic methodology. Hence, it is recommended to choose a suitable methodology to prepare the materials with desirable phase selectivity, so that the extent of the activity can be attained [24]. Therefore, it has been concluded that the phase of the material is the primary in-built possession deciding almost all inherent properties, and hence, by choosing the appropriate methodology, the selectively particular phase can be attained.

3.2 Morphology engineering

An inherent property, surface area is often morphology dependent since different morphologies have different surface areas even for identical phases [25]. The electrochemical reaction takes place only at the interface, where surface atoms are in contact with electrolytes rather than interior atoms. Although all surface atoms are in contact with the electrolyte, only their certain portions are capable of catalyzing bifunctional reactions called active sites. The morphology with the exposure of the maximum number of active sites is the most opted for better bifunctional catalysis.

3.3 Defect engineering

Defect engineering is another way to tune the properties of the catalyst material for enhancing the catalytic activity; due to this reason, it is intentionally introduced into the lattice of the materials although it drags the stability of the catalyst materials. The introduction of defects on the lattice can tailor the intrinsic property, especially the electronic configuration, conductivity, chemical reactivity and stability by adjusting electron distribution on the lattice. Defects also lead to the formation of unsaturated atoms on the surface of the catalyst, which are capable of intensively catalyzing the reaction and hence are highly desirable to promote the oxygen electrode reactions [26]. Defects can exist in many forms, namely, structure distortion, oxygen vacancy, cation vacancy, anion vacancy and lattice defects. All the forms of defects lead to the enhancement of the catalytic activity somehow, mainly impacting the conductivity and density of active sites of the catalyst materials [27]. Caution must be taken while improving the activity of the catalyst by defect engineering since a larger extent of defect density leads to a fall in stability due to the increase in the number of dangling bonds in the material. And it is recommended to adopt an effective and feasible way to create defects, rather than following tedious processes and harsh conditions so as to retain the other properties of the catalysts.

3.4 Mixed metal engineering

As stated in the earlier section, an esteemed electrocatalyst must be effectual in its inherent properties that are intrinsic activity, density of active sites, conductivity, surface area, wettability and stability. But practically, it is rare that a single material has all these mandatory properties for effective catalysis especially for bifunctional (ORR/OER) catalysis; hence doping the foreign metal into the lattice of the host material is a fruitful way to implant additional properties which were absent or inadequate in the host material. Among the various properties, electrical conductivity and catalytic activity are the most essential properties of the non-noble catalyst that are mainly considered inadequate and need to be improved as far as possible. These two properties could be significantly improved by two tactics: one is the doping of an appropriate metal into the host material and another is the formation of a core-shell-type hybrid structure, where the core part must be highly conductive and the shell part should be capable of catalyzing the oxygen electrode reactions [28, 29]. The enriched activity of the resultant hybrid catalyst is mainly due to the synergistic effect of both the guest and host materials. Hence, the hybrid catalyst has the advantage to utilize certain properties from one part and remaining properties from other parts of the catalyst to exhibit the improved performance of the oxygen electrode reaction. Therefore, it has been understood that mixed metal engineering is a profitable way for selective embedding of certain properties into the electrocatalyst for boosted oxygen electrocatalysis.

3.5 Catalyst/conductive substrate engineering

The notable drawbacks of non-noble metal/oxide-based electrocatalysts are their poor electrical conductivity and their agglomeration during the catalysis process, which limit their bifunctional catalytic performance in oxygen electrocatalysis. The succeeding forward step to resolve these issues is the decoration of catalyst materials over the highly conductive substrate, which simultaneously limits the agglomeration and improves the electrical conductivity. Carbon-based materials are promising candidates that serve as a substrate by providing a facile electron transfer path and flat facets to adhere catalytically active non-noble metals/oxides. Moreover, non-noble metal/oxide-based electrocatalysts are efficient candidates for OER and not for ORR, which is another remarkable drawback; meanwhile, carbon-based materials are demonstrated to be effective catalysts for ORR. When combined, these two materials can effectively catalyze both the oxygen electrode reactions without any interruption due to synergistic effect, where the ORR part is taken care of by carbon-based materials and the OER part by catalytically active non-noble metal/oxide. So, again hybrid material (catalyst/carbon substrate) engineering is the solution, which resolves the ORR activity issue along with electrical conductivity and agglomeration issues. But carbon materials are prone to oxidize in highly positive OER overpotential regions, causing thermodynamic instability as another issue. Hence, it is determined that the hybrid material (catalyst/carbon substrate) engineering is an effective strategy to proliferate electrical conductivity and ORR activity. However, proper selection of carbon-based substrates (stable at higher positive overpotentials) and feasible way of incorporation lead to better catalytic performance and durability.

Therefore, in this section, all the in-built possessions of the catalyst materials and their impact on their properties have been elaborately discussed and the possible ways of fine-tuning them for the improvement of bifunctional catalysis are also suggested. This collective knowledge ignites the interest of the research community to formulate efficient bifunctional catalysts and take them to the next level.

4. Detailed chemistry and electrochemistry of MnO_2 and Co_3O_4

The oxides of manganese and cobalt still remain prominent alternatives for precious materials and have been extensively investigated in many growing areas such as lithium-ion batteries, supercapacitors and electrochemical sensors, as well as in electrocatalysis, due to their appreciable unique properties, affordability and environmental friendliness. So, before moving to recent explorations of these materials, the detailed properties and their influence in electrocatalysis have been discussed here more elaborately one by one.

4.1 Chemistry and electrochemistry of MnO_2

Manganese oxide (MnO_2) is a two-dimensional (2D) layered semiconducting material. The outermost electronic configuration of Mn^{+2} is $3d^5$ $4s^0$, where the d orbital is in the half filled (unsaturated) state, which makes it more susceptible to loss or gain of electrons; this is the triggering property in the process of catalysis. So, it can behave as a good catalyst especially in the area of electrocatalysis. The major advantage with MnO_2 is the multivalent nature of manganese and its greater structural flexibility, due to which it can exist in more than 20 crystallographic forms like α-, β-, γ-, δ-, ε-, λ-types, amorphous MnO_2 (AMO) and others [30, 31]. All these crystallographic forms are formed by the basic unit MnO_6, where oxygen atoms are present at the top of eight surface body angles and manganese is located at the center. These crystal structures diverge from one another by way of linkage of their basic octahedral MnO_6 unit, which results in each crystal structure to have distinct properties. Along with many forms of crystal structures, MnO_2 is associated with many other advantages such as their capability to form many polymorphs, natural abundance, environmental compatibility, low cost and non-toxicity. There are many polymorphs of MnO_2: tunnel (1D), layered (2D) and spinel (3D) structures, prepared by dedication and great efforts. Nevertheless, most of the polymorphs of MnO_2 have an open tunnel structure, which can accommodate any of the small guest ions such as K^+, Ag^+, Na^+, Mg^{2+} etc. Moreover, in MnO_2, Mn centers are in mixed oxidation states (+3 and +4), where the charge neutrality is maintained by the assist of guest cations entrapped in the tunnels. The bifunctional activity of MnO_2 strongly depends on their crystal structure and morphology as well as their intrinsic properties. The bifunctional activity of MnO_2 with respect to the crystal structure follows the order α- > AMO > β- > δ-MnO_2 [32]. The superior OER activity of α-MnO_2 is attributed to the presence of mixed oxidation states of manganese (average oxidation state = 3.7), their capability to exist with enormous amounts of di-μ-oxo bridges as protonation sites and their suitable tunnel sizes (0.46×0.46 nm^2) affording high accessibility to electrolytes (reactant) as well as efficient charge transport. The excellent ORR activity (4 e^- transfer) of the same crystal structure is due to its expedient O_2 adsorption capability and enriched amount of higher oxidation state (+3, +4) of manganese on the surface, whereas other crystal structures follow 2 e^- transfer reduction pathways. Amorphous MnO_2 is the next better bifunctional catalyst because of the presence of excess oxygen defects and randomness. Besides, α-MnO_2 contains 2x2 tunnel structures along the c-axis made of double chain of the basic MnO_6 unit. The higher activity of the α-form is also supported by this tunnel and layered structures, having more number of edges and corner sharing of the MnO_6 unit. In addition, it is worth noting that the α-MnO_2 possesses higher activity per cost than Pt/C [33].

Although there is extensive information about MnO_2, the key factors influencing the OER and ORR activities are not well defined due to the lack of straightforward structure-related electrocatalytic activities. Many of the crystal structures of MnO_2 are still poorly understood. However, MnO_2 with various metal valences usually revealed different morphologies, which complicates the underlying relationship between metal valence and activity.

4.2 Chemistry and electrochemistry of Co_3O_4

The next superior electrocatalyst with competitive activity for bifunctional reaction is cobalt oxide (Co_3O_4) and is an extensive studied material especially for OER due to its excellent redox behavior, inexpensiveness, high abundance and great stability in alkaline medium. It is a spinel oxide, where oxygen atoms are arranged in a cubic close packed (CCP) matrix composed of two Co^{3+} and one Co^{2+} cations located in the octahedral (Oh) and tetrahedral (Td) lattice sites, respectively [34, 35]. The catalytic performance of spinel Co_3O_4 is deeply rooted in two factors such as exposed crystal facets and population of Td Co^{2+} and Oh Co^{3+} on it. The (110) facet of Co_3O_4 exhibits enhanced activity compared to other facets due to the existence of substantially higher density of the dangling bond and catalytically active Co^{3+} sites [36]. But the higher surface energy and existence of higher density of dangling bonds of this facet results in less possibility of the formation of this facet. The bifunctional activity of Co_3O_4 is oxidation state dependent; the higher occurrence of Co^{3+} in the octahedral environment is responsible for the superior performance of OER, whereas Co^{2+} in the tetrahedral environment is capable of releasing electrons under applied potential, which results in the formation of CoOOH, μ-OO peroxide intermediates over the surface of Co_3O_4, which is capable of acting as an active site in ORR. Although there are many efforts on Co_3O_4, the intrinsically poor electrical conductivity and relatively smaller surface area of the material still remain inadequate, which significantly drag the overall activity.

5. Recent exploration in Co_3O_4 and MnO_2

Transition metal oxides like manganese oxides α-MnO_2 [37, 38], β-MnO_2 [39], perovskite (i.e., $LaNiO_3$, $LaCoO_3$) [40] as well as spinel-based structures (Co_3O_4 and $NiCo_2O_4$) with multiple valences, serve as the most attractive non-precious metal catalysts for bifunctional OER/ORR electrocatalysis especially for the alkaline medium. This chapter particularly emphasizes the recent developments in metal oxides of manganese oxides and cobalt oxides, which are simple in composition yet very effective in promoting oxygen electrode reactions. The nature of active sites and their identification along with corresponding ORR/OER activities will be correlated with respect to their oxidation states, crystal structure, bulk structure and morphology with required experimental and computational analyses; all those concerns have been reviewed from the recent 10 years of literature. In addition to that, contrast results observed in those particular materials are discussed elaborately and possible strategies to further improve the activity of the catalyst have also been suggested at the end.

5.1 Recent exploration in MnO_2

Manganese oxides are one of the most widely investigated materials in bifunctional electrocatalysis and currently employed in commercial Zn air and alkaline batteries. The inspiration from the biological catalyst $CaMn_4O_x$ acts as an oxygen evolving centre in Photosystem II; Gorlin et al. developed a new catalyst α-Mn_2O_3 where Mn is in the +3 oxidation state, showing excellent bifunctional activity almost similar to the activities of precious catalysts like Pt, Ir and Ru [41]. To improve the activity of the catalyst, it is essential to understand the changes on the surface of the material during the process of OER and ORR. With this mind in their another study, a powerful in situ X-ray absorption spectroscopy technique was used to analyze the chemical nature of the surface during the process of OER and ORR [41]. Such an attempt reveals that the exposure of catalyst in ORR (0.7 V) and OER (1.8 V) potential causes the distortion of the $Mn_3^{II,III,III}$ O_4 phase and maximum (80%) oxidation of the catalytic surface to form a mixed $Mn^{III,IV}$ oxide. They also confirmed that the observed result is irrespective of the film thickness of the catalyst in both OER and ORR potential. At OER potential, $Mn^{III,IV}$ oxide is more dominant on the catalytic surface due to the electrochemical oxidation, indicating that it is the phase responsible for the observed OER activity rather than the $Mn_3^{II,III,III}$ O_4 phase [42]. Such an oxidation state changes upon the exposure to OER and ORR potential on α-Mn_2O_3, observed by the same group with the aid of ex situ X-ray photoelectron spectroscopy technique in their earlier studies [43, 44] and by Marcel Risch via in situ soft X-ray absorption spectroscopy study [45].

Moreover, the effect of surface manganese valence of MnO_2 on ORR activity is studied by Tang et al. [12]; from their observation, it has been understood that the oxidation state of the catalytic surface plays a crucial role in facilitating bi-functional catalysis. The main reason for the activity of manganese oxides is the presence of surface Mn^{+3} ion having Mn-O-Mn bonds, which are found to be more active for OER and are not found in the species having Mn^{+2}/Mn^{4+}. These labile Mn-O bonds allow the formation of surface Mn-OH_2 species and favor the cleavage of Mn-O_2 bonds, which increases the overall activity of the catalyst. Besides, in its electronic configuration, Mn(III) having one e_g^1 electron leads to the lattice distortion owing to the Jahn-Teller effect and contributing to the structural flexibility, promoting the catalytic activity of the material [46, 47].

The importance of surface facets on bifunctional activity has been discussed in another work [48], where different nanostructures of MnO such as nano-flowers, nanoparticles and nano-polypods are prepared with the exposure of different crystal facets. The detailed investigation of this study demonstrated that the maximum exposure of (100) facets of MnO nano-polypods largely promote the electrocatalytic activity in both OER and ORR compared to others facets. Therefore, it has been understood that (100) is the superior active facet of MnO_2 for both OER and ORR.

As mentioned earlier, MnO_2 can exist in large numbers of crystallographic forms, so it is essential to address the suitable crystal structure for encouraging electrolysis.

To resolve this issue, Meng et al. examined the influence of crystallographic structures of MnO_2 such as α-, β-, δ-MnO_2 and amorphous (AMO) MnO_2 on bifunctional activity. During the formation of various crystal structures of MnO_2, changes in morphologies such as nanoflakes, nanowires and nanoparticles were also obtained. The obtained results reveal that the bifunctional activity of MnO_2 is strongly dependent on the structures and follows the order $\alpha > \text{AMO} > \beta > \delta$-$MnO_2$ [32]. There is another study related to the crystal structure influence in water oxidation, which has been investigated under various conditions. In this study, the authors have prepared nine various MnO_x-based catalysts, that is, α_2-, β-, δ_2- and γ-MnO_2, Mn_3O_4, Mn_2O_3, L-MnO_2, γ-MnOOH, and R-MnO_2 and their water oxidation efficiency were analyzed and α-MnO_2 was found in alkali media as a superior one among all catalysts [49]. These studies confirm the influence of crystallographic orientation on catalytic activity, which is majorly controlled by the morphology of the catalyst. Moreover, Debart et al. explained the highest charge storage capacity, that is, 3000 mA g^{-1} of α-MnO_2, among other crystal structures such as β-MnO_2, γ-MnO_2, λ-MnO_2, Mn_2O_3 and Mn_3O_4 through the study of rechargeable lithium-air batteries [50]. They have also showed the surpassed catalytic activity of α- and β-MnO_2 nanowire compared to the bulk MnO_2, which is mainly due to the higher surface area and crystal structure. This further confirms the importance of the crystal structure and the nanoscale morphology of the electrocatalyst in bifunctional activity. Our group result also supports the above-stated information that α-MnO_2 nanowire turns out as the more preferable morphology and the crystal structure of MnO_2 for superior bifunctional activity over the other forms [37].

Another strategy to enhance ORR activity of MnO_2 is introduction of native oxygen defects without employment of any foreign additives, where the effort is devoted to identify the effect of oxygen nonstoichiometric on ORR activity in alkaline electrolytes. The study has introduced oxygen vacancy into the thermodynamically stable high purity rutile β-MnO_2 by a simple heat treatment method in argon atmosphere. And it is found that the oxygen defect bearing MnO_2 requires more positive overpotential, yields lower amount of peroxide in ORR and also facilitates the kinetics of OER [51].

In MnO_2, especially when we intended to tune metal centre valences (oxidation state), it lead to unavoidable changes in morphology along with changes in the oxidation state. Such circumstances usually add further complications to understanding of the actual relation between the metal valence and electrochemical activity. Although it is reported that MnOOH species is superiorly ORR active among manganese oxides [52], this study did not include the influence of morphology of the catalyst on activity. The influence of morphology on ORR activity is explained by two familiar examples, where nanoparticles and nanowires are the morphology. In MnO_2 nanoparticles, the activity increases in the order $\beta\text{-} < \lambda\text{-} < \gamma\text{-} < \alpha\text{-} \approx \delta$-$MnO_2$ [53], whereas in MnO_2 nanowires, the activity follows the order $\lambda\text{-} < \beta\text{-} < \alpha$-$MnO_2$ [54]. These results provide strong evidence for the influence of nanoscale morphology on ORR activity.

Although manganese oxide is a superior non-precious bifunctional catalyst, still it is unable to surpass the activity of precious metal catalysts due to its poor conductivity. The well-known approach to improve the conductivity of the material is decoration of metal oxides over carbon-based substrates. However, in the case of bifunctional electrocatalysis, the carbon substrate is not a preferable one due to the peroxide production and self-oxidation on OER condition. To resolve this issue, Ng et al. developed manganese oxide on a stainless-steel substrate (MnO_x-SS) through electrodeposition followed by calcination at 480°C. Calcination causes the phase conversion of MnO_x to Mn_2O_3 on stainless steel. Further, this MnO_x-SS material employed as an O_2 electrode in unitized regenerative fuel produces round-trip efficiencies of 42–45% at 20 mA cm^{-2} over 10 cycles that is excellent catalytic activity and durability in both OER and ORR even compared to the precious catalyst Pt/C-SS. The interaction between the stainless-steel substrate and catalyst significantly enhances the catalytic activity due to synergetic effect and prevents the agglomeration of catalysts by providing an appropriate platform [55].

The next approach to improve the activity is expanding the surface area and active sites by introducing porosity. The activity of the catalyst is directly proportional to the surface area due to the rise in the density of active sites. But there are many ways to introduce porosity, like the template-assisted method, surfactant-assisted micelle/inverse micelle sol-gel method, etc. However, each method is associated with its own merits and demerits. In the case of template-assisted process, although uniformity in the pore size and stability was achieved, the template had to be etched post synthesis, which added complexity to the method and was time consuming. However, although the surfactant-assisted method is a simple and cost-effective approach, there is no assurance for uniformity in the pore size.

In this view, Kuo et al. developed a highly effective mesoporous MnO_x material with a crystal structure of Mn_2O_3 via a simple inverse micelle template approach. This adopted methodology has the advantage of being a single-step synthesis, does not require any post-synthesis treatment, can be scalable and most importantly controls the formation of Mn_2O_3 with enriched Mn^{3+}. Then, the prepared mesoporous Mn_2O_3 material demonstrated superior catalyst property in both electrochemical water oxidation and photochemical processes with the highest TOF value [56].

Some other attempts have also been made to tune the Mn oxidation state, that is, the introduction of foreign elements into manganese oxide. It was found that the incorporation of foreign elements like gold nanoparticles [57, 58], Ca^{2+} [59] and cesium [60] into manganese oxide promotes the formation of Mn^{+3} ions, which significantly enhances the ORR activity.

Recently, Kang et al. have reported the influence of the interlayer distance of MnO_2 on OER activity by systematically varying the interlayer distance with the aid of intercalation of dissimilar-sized alkaline cations such as Li^+, Na^+, K^+, Rb^+ and Cs^+ between the layers and the observed interlayer distance values are 0.5, 0.6, 0.9, 1.05 and 1.5 nm, respectively. At the end, they concluded that the Cs^+ ion intercalated MnO_2 possesses a larger interlayer distance along with the accommodation of larger quantities of water molecules as a result of superiority toward OER activity, whereas Li^+ ion intercalated MnO_2 is inactive for OER due to their smaller interlayer distance and dehydrated structure [61]. In contrast to the aforementioned report, Kosasang et al. reported that the Li^+ intercalated MnO_2 is a superior candidate for both OER and ORR, where they intercalate the alkali cations such as Li, Na, K, Rb and Cs between the layers of MnO_2 and their bifunctional activity was examined. They have further ensured the observed result by the DFT calculations [62].

From the above revealed mechanistic insights, it is understood that developing an efficient method to facilitate both ORR and OER on a single active site is not an easy task due to the drastic difference in their overpotential as well as the rate-determining step (RDS). In fact, an efficient ORR active site naturally renders a poor OER activity and vice versa, making it challenging to maintain a proper balance for reversible OER/ORR catalysis on a single electrode surface. Due to this reason, typically employed bifunctional catalysts are a combination of precious metals and their oxides like Pt, Ru/RuO_2 and Ir/IrO_2, where ORR and OER reactions are taken care of by pure metal and metal oxides, respectively.

Therefore, a probable way to simultaneously catalyze both OER and ORR is to design bifunctional catalysts inherited with different active sites for ORR and OER separately. That can be achieved by the deliberate engineering of transition metal oxides, particularly their oxidation state, crystal structure, exposure of crystal plane and morphology are the efficient routes to develop an efficient inexpensive bifunctional electrocatalyst for oxygen electrode reactions.

5.2 Recent exploration in Co_3O_4 to enhance bifunctional catalysis

Another simple and most investigated metal oxide for bifunctional catalysis is Co_3O_4 due to its superior activity and durability. As mentioned earlier, Co_3O_4 is a spinel-type metal oxide, where Co^{2+} and Co^{3+} occupy the Td and Oh sites, respectively. The Co^{2+} tetrahedral sites are the active sites for ORR, and the Co^{3+} octahedral sites are the active sites for OER. The optimal amount of both ions would lead to overall bifunctional activity and will minimize the potential difference between the two reactions.

5.3 Effects of particle size and surface area

Esswein et al. elucidated the size dependence activity of Co_3O_4 crystallites on electrocatalytic OER in an alkaline medium [63]. They prepared cubic Co_3O_4 nanoparticle materials with the average size of 5.9, 21.1 and 46.9 nm. Then, the prepared materials were loaded onto a Ni foam support to evaluate the OER performance with a constant loading amount of 1 mg cm^{-2}. They attained 10 mA cm^{-2} current density at 328, 363 and 382 mV for small (5.9 nm), medium (21.1 nm) and large (46.9 nm) sized Co_3O_4 particles, respectively. The activities were correlated with the surface area of the isolated Co_3O_4 particles.

Menezes et al. established a method to produce nanochains of cobalt oxide (Co_3O_4) via low-temperature degradation of cobalt oxalate dehydrate [64]. In fact, they were able to display exceptional OER performance at low overpotentials in both basic and neutral media with the as-prepared Co_3O_4 nanochains. They also additionally prepared nanostructured Co_3O_4 materials by the solvothermal method and compared the activity of commercial Co_3O_4 of various morphologies. Remarkably, the ORR performance of carbon-supported Co_3O_4 nanochains displays remarkable activity compared to that of Pt. Surprisingly, they found that even though the nanochain Co_3O_4 prepared by the reverse micelle route possesses a lower BET surface area (12 $m^2\ g^{-1}$) than solvothermal Co_3O_4 (18 $m^2\ g^{-1}$) and commercial Co_3O_4 (49.4 $m^2\ g^{-1}$), it displays a low overpotential toward OER in both alkaline and neutral media.

5.4 Effect of mesoporosity and morphology

Sa et al. reported ordered mesoporous Co_3O_4 spinels with a gyroid mesostructure, obtained by the assistance of a KIT-6 mesoporous silica template through the nanocasting method, which emerged as one of the best methods to obtain ordered mesoporous structured materials. Particularly, silica supports such as KIT-6, which possess a double gyroid mesostructure, can deliver large active sites than that of analogous materials with a 2D hexagonal structure [65]. Furthermore, the ordered mesoporous Co_3O_4 spinels template from KIT-6, with a highly interconnected network structure, is expected to show enhanced stability under harsh catalytic or electrocatalytic reaction conditions.

5.5 Effect of the nature of hydrous oxide

Zhan et al. demonstrated the bifunctional activity of hydrothermally prepared $Co(OH)_2$ hexagonal nanoplates and cobalt oxides (CoO and Co_3O_4) in basic medium, where the hydroxide of cobalt ($Co(OH)_2$) displayed a superior activity than the oxides of cobalt (CoO and Co_3O_4) [66]. The bifunctional catalysis ability mostly shown by the OER/ORR potential difference (ΔE) could be achieved as lower as 0.87 V (RHE), comparable to that of metal-based catalysts, when the $Co(OH)_2$ nanoplates were anchored on N-doped reduced graphene oxide. In addition, both Co_3O_4 and CoO possess a lower n value of 2.6–2.7 for ORR, which testified that pristine cobalt oxide catalysts predominantly follow a two-electron pathway of ORR. $Co(OH)_2$ was therefore highly ORR active than other cobalt catalysts. Similarly, in the case of ORR, $Co(OH)_2$ was most OER active than Co_3O_4 and CoO even though it has a lower number of cobalt site and surface area. Therefore, it is understood that the hydroxide of cobalt is a better bifunctional catalyst than the oxides of cobalt.

5.6 Existing challenges and future directions

After the detailed review of each stairway of non-precious metal oxide (i.e., MnO_2, Co_3O_4), it is absolutely necessary to address the existing challenges and future working directions that could be highly supportive for the research community for finding more insightful information on the catalysts and their further development to enhance the bifunctional activity.

The exact mechanisms and underlying fundamental process of the oxygen electrode reactions are still unclear; they vary from material to material. There was a drastic difference at the electrode electrolyte interface of each electrocatalyst, and it possessed different binding energies with the reactant species. So it is highly recommended to adopt sophisticated in situ spectroscopic techniques to study the interface during the electrochemical reaction so that its exact mechanism could be identified. Along with this, the theoretic prediction (DFT calculation) of interface especially for the possible way of reactant species adsorption and desorption has to be developed. There is another study called post-experimental analysis that is the analysis of the catalyst after the employment of electrochemical reaction for a certain period. The deeper analysis and its comparison with its fresh nature provides more insightful information about the moiety, which is the exact reason for the catalytic activity. And finally, the collective analysis and interpretation of all these, that is, in situ spectroscopic study and theoretical prediction of the interface and post-experimental analysis, will lead to a loophole for the identification of the exact mechanism of the oxygen electrode reactions for the particular catalyst. The understanding of underlying mechanisms is the heart of knowledge, which is the key to trigger the researcher for the establishment of marvelous candidates for the oxygen electrode reactions.

Now the question is why the pinpoint mechanism of oxygen electrode reactions is not yet strongly declared even after knowing the route to identify it. The reason is that the existing issues in the aforementioned sequence of the route are (1) insufficient knowledge in theoretical prediction and (2) lack of the appropriate in situ spectroscopic technique and its integration into the electrochemical setup. Hence, it has been suggested that more efforts have to be devoted in the field of experimental characterization, and theoretical study leads to better fundamental understanding of electrochemical reactions. In addition, the integration of various characterization techniques into the electrochemical setup is also recommended to track the reaction.

If we look at the Co_3O_4 catalyst, it has a multi-oxidation state (Co^{2+} and Co^{3+}) compound, where there is still no clear-cut idea about the optimum level of Co^{2+}/Co^{3+} ratio for better performance of bifunctional activity. Moreover, there are some reports of Co_3O_4 highlighting that Co^{2+} and Co^{3+} are responsible for ORR and ORR, respectively. In recent years, some researchers have reported the exact opposite trend of responsibility in bifunctional reaction (ORR/ORR) with strong evidence, which creates more puzzles. In addition, Co_3O_4 is a good catalyst for OER but not for ORR; the intentional tuning on it for the improvement of ORR activity affects the OER performance. Therefore, it is recommended that a more in-depth study of this material has to be explored well rather than its advanced study.

In the case of MnO_2, it is a good candidate for ORR (can follow the four-electron transfer mechanism), but it is not so for OER. As stated earlier, the intentional tuning of one side of the reaction drastically affects the other side of the reaction. Hence, such a way of fine tuning the material for the catalytic enhancement of OER activity without affecting its ORR performance is highly desirable. Therefore, the existing challenges strongly direct the researcher to explore things in the area of understanding the mechanism of ORR/OER, tuning the composition of the existing atom of the catalyst to obtain optimum composition and development of novel synthetic approaches for selectively attaining certain properties of the catalyst.

6. Conclusions

A rechargeable metal-air battery with the aid of high theoretical energy output will be of prime competence for the carbon-based energy sources that we rely on hugely as of now. Metal-air batteries lack in commercial scale due to the limited kinetics behind OER and HER. The search for bi-functional catalysts that are earth abundant and kinetically facile is important to meet energy crisis. Previously, many breakthrough works have been done with superior activities, and among them, MnO_2 and Co_3O_4 have attracted researchers with their kinetic activities and structure-activity relationships. In this chapter, the important parameters judging the activities of both Co_3O_4 and MnO_2 such as phase and morphology engineering, defects and crystal facets engineering, strains and mixed metals oxide formations have been portrayed with proper investigations along with the fundamentals of water oxidation and reduction reactions. Moreover, the electrochemistry behind MnO_2 and Co_3O_4 has been investigated for the better understanding of catalyst reactions and mechanisms. This will be highly useful for developing and designing mixed oxides for the increased kinetics of rechargeable metal-air batteries with commercial production. This chapter urges the importance of MnO_2 and Co_3O_4 as better bi-functional catalysts with the introduction of fundamental electrochemistry, structure-activity relationship and finally the future directions in the field of metal-air batteries.

Acknowledgements

The authors thank the funding support from CSIR through the 12th FYP project MULTIFUN (CSC0101). S.V. and V.D. thank the UGC, New Delhi, for financial support through the SRF (21/06/2015(i)EU-V, Roll no 123184) and Rajiv Gandhi National Fellowship (RGNF, Grant No: F1-17.1/2016-17/RGNF-2015-17-SCTAM-21830), respectively. K.S. thanks, the financial support through the CSIR-HRDG, New Delhi, India, for SRF (Grant no: 31/20(159)2 k17).

Conflict of interest

The authors declare that there is no conflict of interest.

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