Transition Metal (Fe, Co, Ni, and Mn) Oxides for Oxygen Reduction and Evolution

Bifunctional Catalysts in Alkaline Media

Hannah Osgood,^a Surya V. Devaguptapu,^a Hui Xu,^b Jaephil Cho,^{*,c} and

Gang Wu,^{*,a}

^a Department of Chemical and Biological Engineering, University at Buffalo, State University of New York, Buffalo, New York 14260, United States. E-mail: gangwu@bufflao.edu

^b Giner Inc., Newton, MA 02466, United States

^c School of Energy and Chemical Engineering, National Institute of Science and Technology (UNIST), Ulsan, 689-798, Korea. E-mail: jpcho@unist.ac.kr

Abstract:

In recent years, a large amount of focus has been given to the development of alternative energy sources that are clean and efficient; among these, electrochemical energy holds potential for its compatibility with solar and wind energy, as well as its applications in metal-metal and metal-air batteries. However, these technologies require the use of a catalyst to make this application feasible. Current catalysts consist of precious metals such as platinum, which are expensive and block common access to electrochemical energy. Transition metals, and their oxides, serve as a promising alternative to these precious metals. A wide range of these metals, including cobalt, manganese, nickel, and iron, have been researched as bifunctional catalysts, capable of driving both the storage and discharge of energy. Not only do they show innate electrochemical capabilities, but their structural diversity, as well as their ability to be mixed, doped, and combined with other materials such as graphene, make transition metal oxides a

highly attractive subject in electrochemical and materials research. This review serves to summarize the research currently available concerning transition metal oxides, and their applications as a bifunctional catalyst for the oxygen reduction and oxygen evolution reactions. Particularly, their structural properties are related to their electrochemical abilities, along with their behavior when introduced to other catalytic materials and dopants.

Keyword: *Transition metal oxides; electrocatalysis; energy conversion; oxygen reduction; oxygen evolution*

1. Introduction

Recently, there has been a push for technology that offers new and improved methods of energy storage and harnessing while being efficient, reliable, and low cost. Among these technologies, electrochemical energy offers promising capabilities. Its ability to both store and release energy makes it useful for applications such as fuel cells and batteries, and can also be used with renewable energy sources including wind and solar to convert them to storable chemical energy[1-4]. Applications discussed here focus largely on two reactions: the Oxygen Reduction Reaction (ORR) and the Oxygen Evolution Reaction (OER). Shown below are the mechanisms for both the ORR and the OER; as it can be seen, the ORR may be completed by either a 1-step 4-electron transfer reaction (A), or by a 2-step 2-electron transfer process (B), while the OER results in a release of electrons(C):

The ORR/OER couple is useful for energy applications as electrons from an applied current may be “stored” in OH^- through the ORR and released later through the OER. In addition, the abundance and ubiquity of oxygen throughout the world makes it a desirable resource for energy use. However, these reactions are slow on their own, and require catalysts to make them feasible for common application. In general, the most commonly used catalysts involve platinum-based catalysts for the ORR, and iridium or ruthenium oxide for the OER; some bifunctional catalysts also involve the use of metals such as silver or gold [5-10]. Chemically, this complicates the use of electrochemical cells for bifunctional applications, as two separate catalysts are required for

both reactions, and neither catalyst is effective for more than one reaction and may even hinder the opposite reaction [11]. Functionality aside, the use of these catalysts is very expensive and, as platinum and iridium are both precious metals, resources for making them are scarce, making them undesirable for commercial use. It is for these reasons that considerable research has recently been focused on finding a new bifunctional catalyst that can enhance both the ORR and OER, while being cost-effective and utilizing abundant materials. This is no simple task; though many materials may be found that display catalytic properties, the ability to catalyze more than one reaction is less common. In particular, the ORR and the OER require very different conditions, particularly the electric potentials present during the reaction. This narrows down the number of materials capable of catalyzing both reactions, and introduces more complicating factors that can inhibit catalytic activity. The most common way of measuring a good bifunctional catalyst for the ORR and the OER is by measuring its overpotential, or potential difference, which is the amount of added electrical potential required to transition between the two reactions. A smaller overpotential is a good indicator for a promising bifunctional catalyst.

Many new catalysts that are being researched involve the use of carbon supports, due to their high conductivity, which makes these materials perform comparably to precious metals as electrocatalysts, particularly for the ORR[12]. However, the wide range of applied potentials required to perform both the ORR and OER can lead to the eventual oxidation some carbon structure during the OER, hindering the catalyst conductivity during long term use [13-15]. Of these, nanostructured materials such as carbon nanotubes and nanowires display a higher resistance to corrosion than materials like graphene oxide[16]. Therefore, it is necessary to create a bifunctional catalyst that is stable enough to withstand both strongly reducing and strongly oxidizing environments encountered during the ORR and the OER, while still delivering

significant performance. Stability is also important when it comes to feasibility; there is no use in having a high-performing catalyst that only works a few times. If it is to be considered for commercial use, it must be able to withstand thousands of cycles before needing to be replaced. Ideally, the stability of the material should make its use outweigh its cost.

Currently, several different materials are being explored for use as bifunctional catalysts, including transition metal oxides [17]. Many materials involve either transition metals or organic materials like graphene, or even a mixture of both, as seen in metal-organic frameworks or carbides [18, 19]. Other electrocatalyst materials like transition metal nitrides are less common for bifunctional applications, as some have displayed degradation and corrosion at high anodic or cathodic potentials, which is undesirable for long-term ORR/OER cycling[20, 21]. The addition of dopants has been seen to improve nitride stability, but it could still benefit from improved bifunctional activity [22] Transition metal sulfides have displayed promising ORR and OER behavior, but can suffer from stability and conductivity problems; however, there have been instances of composite sulfide and transition metal oxide materials that have had improved stability [23].

Transition metal oxides have garnered attention as bifunctional catalysts for various reasons. Compared to the typical precious-metal catalysts, transition metal oxides are cheaper and easier to obtain, making them more realistic for commercial use. Furthermore, transition metal oxides show the ability to mix, introducing the possibility of combining good ORR and OER performance into one material in a synergistic effect [24]. Transition metals are unique in that they can form more than one cationic oxidation state; this is pertinent to their use as electrocatalysts, as the constant oxidation and reduction that occurs within an electrolytic cell would be better tolerated by a material that can easily shift between oxidation states, thus

improving stability. The structure of selected electrocatalysts also appears to have a large influence on catalytic activity; since the ORR and OER both involve oxygen, catalysts should have some amount of affinity for oxygen absorption, but not so strong that buildup occurs on the catalyst. This can be influenced to some degree by the introduction of vacancies in lattice structure. Catalyst structure should also have considerable surface area to volume ratio, as this is where catalytic active sites will be most accessible for reaction; as such, porosity is a favored feature, as well as structures that are created on the nanoscale[25]. Many transition metal oxides occur as various ordered structures, as well as amorphous structures, that may be tuned and manipulated to optimize the ORR and the OER. One of the most commonly occurring structures in this field is the spinel lattice structure. The spinel structure consists of 8 tetragonal subunits that form 1 cubic unit cell, and contains more than one type of cation; of interest, however, is the spinel structure's versatile ability to accommodate a large amount of disorder in the cation arrangement and the presence of vacancies, as well as the ability to switch the positions of the two present cations to form a reverse spinel structure. This may prove useful for the transfer of electrons that occurs during both the OER and the ORR [26]. Although transition metals display some degree of electrical conductivity, for the most part it is lower than the level desired for electrocatalysts, and must be augmented in some way. As mentioned before, the spinel structure of many transition metal oxides can accommodate vacancies and lattice defects, allowing the addition of dopants such as nitrogen into the structure, altering the conductivity of the material. Transition metals may also be combined with other materials such as carbon-based supports and organo-metallic frameworks, another possible route for enhancing the electrical properties of resulting catalysts.

The exact mechanism of transition metal oxides' role in the ORR and the OER is not completely understood, though observations and calculations through Density Functional Theory and Scanning Electron Microscopy have allowed for some suggestions to be made [27]. Generally in testing transition metal electrocatalysts, catalysts with a higher coverage of metal oxide complexes display higher levels of the ORR and/or the OER, suggesting direct involvement of transition metals in the electrocatalytic active site; furthermore, shifts in the oxidation state of transition metals are observed during the OER and the ORR, indicating a transfer of electrons to or from the metals during the oxygen reaction.

Herein, we review the different types of transition metal oxide catalysts currently being researched, and how their methods of preparation and performance are being improved in terms of their applications as bifunctional oxygen catalysts for reversible electrochemical energy technologies such as utilized fuel cells and metal-air batteries. **Table 1** summarizes selected catalysts discussed, along with details about their structure and performance as bifunctional catalysts. Information on precious metal catalysts platinum and iridium oxide are also given for comparison.

Table 1. Information on selected transition metal oxide catalysts for bifunctional activity, based on available data given in references stated above. Includes catalyst name, structural details, potential difference $\Delta E = E_{\text{ORR}} - E_{\text{OER}}$, and information regarding catalyst stability.

Potential				
Name	Structure Details	Difference (V)	Stability Details	Reference

$\text{Co}_3\text{O}_4/\text{NC}$	N-doped C nanotubes	0.87	Stable $\geq 40,000\text{s}$	[35]
$\text{Co}_3\text{O}_4/\text{N-GO}$	N-doped Graphene Oxide	~ 0.7	Stable $\geq 25,000\text{s}$	[36]
$\text{Co}_3\text{O}_4\text{C-NA}$	C nanowire on Cu foil	0.74	6.5% current loss, 100,000s	[31]
$\alpha\text{-MnO}_2\text{-SF}$	Tetragonal cryptomelane	0.49	0.02V ORR drop, 10,800s	[54]
$\text{CoMn}_2\text{O}_4/\text{G}$	Graphene support	~ 0.65	Complete current loss, 3 cycles	[72]
$\text{CoMn}_2\text{O}_4/\text{NG}$	Spinel on N-doped graphene	~ 0.75	54% round trip efficiency	[73]
$\text{MnCo}_2\text{O}_4\text{-NCNT}$	Spinel on C N- doped nanotubes	~ 0.65	Complete loss, 200,000s	[74]
NiCo_2O_4	Nanowires and nanotubes	0.84	0.14V ORR drop, 120,000s	[87]
$\text{MnO}_2\text{-LaCoO}$	Spinel perovskite	~ 0.5	0.24V OER drop, 3,600s	[125]
Pt/C	20% on carbon	~ 0.9	20-48% ORR decrease, 10,000s	[36]
IrO_2	-	1.32	-	[35]

2. Single Metal Oxides

2.1 Cobalt oxides

Cobalt Oxides have been a popular choice for bifunctional catalyst research due to their relatively good performance in both ORR and OER compared to other metal oxides, and their potential for improvement using different synthesis methods. Particularly, combination of Co oxides with carbon structures has been shown to alter the performance of the resulting catalysts[16, 28]. The high conductivity of materials such as graphene can boost the relatively low conductivity of Co oxides while providing increased catalytic surface area and a structure for Co to be embedded in to form active sites.

Although the exact mechanism of the catalyst active site is unknown, it has been demonstrated that increased ORR activity is associated with higher amounts of Co^{2+} oxidation states, and higher OER activity is associated with higher amounts of Co^{3+} oxidation states [29]. This may be explained by an increased absorption of OH^- anions by Co^{3+} active sites, which may act as reactants for the OER; conversely, more Co^{2+} active sites may aid in the adsorption of O_2 and subsequent electron transfer to create OH^- through the ORR. The increased availability and faster frequency of these reactants occurring at the active sites due to the respective Co oxidation states helps to increase the rates of reaction[30, 31]. The difficulty in using this information to one's advantage in making bifunctional catalysts is determining the optimal amounts of each Co oxidation state that would maximize the overall bifunctional activity between the ORR and the

OER, mainly by minimizing the potential difference between the two reactions. By tuning the ratio of Co^{2+} and Co^{3+} oxidized onto MIL-101(Cr), a highly stable metal-organic framework (MOF), He *et al.* showed that a high ratio of $\text{Co}^{3+}/\text{Co}^{2+}$ in the catalyst lead to the highest bifunctional activity [29]. The catalyst with the highest ratio, Co/MIL-101(Cr)-O, was created by using an oxidizing agent on basic Co/MIL-101(Cr), and had the lowest potential difference of 1.16 V, compared to 1.23 V for plain Co/MIL-101(Cr). This means that although other catalysts may have higher individual amounts of either Co^{3+} or Co^{2+} , thus making them have better OER or ORR performance, this does not equate to high bifunctional activity. It is the *ratio* between the two oxidation states that seems to be more important than the individual amounts when it comes to making a bifunctional catalysts. This research gives insight into the possible mechanisms of bifunctional catalytic active sites, which can prove useful for future research into bifunctional catalysts; mainly, that electrocatalytic activity involves more than just the presence of certain species, as the importance of ratios of these species between each other may indicate more complicated interactions occurring at the active site.

Due to the gaps in understanding of the mechanism behind transition metals' involvement in electrocatalytic activity, many studies have also been conducted that study the variation of several synthesis techniques on the quality of resulting catalysts. For instance, as cobalt oxides can assume multiple molecular structures eg. Spinel, reverse spinel, amorphous, etc., it behooves researchers to understand how various synthesis procedures change catalyst structure, as well as determining which structures facilitate electrocatalytic activity the most. Many synthesis techniques for electrocatalysts involve a heat treatment or calcification, where the high temperatures ultimately lead to the formation of electrochemical active sites. Studied largely for its potential as a cathode material in Li-ion batteries, Maiyalagan *et al* studied the application of

lithium cobalt oxide (LiCoO_2) as a bifunctional electrocatalyst [32]. LiCoO_2 can be found in two structures, depending on the method of synthesis used; when formed at high temperatures of 800 °C and higher, LiCoO_2 has a rock-salt structure. At low temperatures, LiCoO_2 has a lithiated spinel structure. Structural analysis shows that LiCoO_2 treated at high temperatures has a uniform rock-salt structure up to the first few layers of the sample, indicating migration of Co ions into the Li ion layers. It was also demonstrated that the composition of low temperature-treated LiCoO_2 can be controlled by the heat treatment temperature and duration; long-term heating for several days resulted in a more consistent spinel structure. CV tests indicate that when exposed to high temperatures, LiCoO_2 not only undergoes oxidation of Co^{3+} to Co^{4+} , but also the extraction of Li^+ and insertion of H^+ ; this extraction/insertion activity is much less prominent in LiCoO_2 treated at lower temperatures, where Li diffusion is much slower due to the catalyst's lithiated structure and higher occurrence of defects (**Figure 1**). Furthermore, lower temperature treatment shows $\text{Co}^{3+}/\text{Co}^{4+}$ oxidation at lower potentials; this would mean that more Co^{4+} is present in low temperature-treated LiCoO_2 than high temperature-treated LiCoO_2 during OER potentials. High amounts of Co^{4+} have been shown to be present in good OER catalysts; accordingly, low heat-treated LiCoO_2 displayed the highest OER activity out of 4 catalysts studies, including Co_3O_4 and IrO_2 catalysts, while LiCoO_2 treated at high temperatures had the lowest activity [33]. However, it should be noted that IrO_2 displayed slightly lower overpotentials; despite this, the LiCoO_2 shows other promising behavior, including its stability and an increasing OER current density over 100 linear sweep voltammogram cycles, only showing a decrease in OER activity after 200 cycles. These results emphasize the important role that structure plays on electrocatalytic activity, even if it is not the only factor; for instance, Co_3O_4 also displays spinel structure like low temperature-treated LiCoO_2 , yet shows markedly

lower activity. This can be attributed to the altered distribution of Co ions within the structure due to the presence of Li ions, which enables more Co^{3+} to be oxidized to Co^{4+} in LiCoO_2 compared to Co_3O_4 , benefitting the OER.

Figure 1. HAADF-STEM images of A) Co_3O_4 , B) LT-LiCoO_2 and C) HT-LiCoO_2 . The unit cells for each composition with octahedral and tetrahedral arrangements are overlaid on higher magnification images that have been deconvoluted to reduce noise. D) Cyclic voltammograms of Co_3O_4 , LT-LiCoO_2

and HT-LiCoO₂ in 0.1 M KOH at scan rate of 5 mV s⁻¹. The purple, blue and green colours in the structures shown in the insets refer, respectively, to the polyhedra of Co³⁺, Co²⁺ and Li⁺ ions. Printed from [32] with permission from Nature Publishing Group.

Further testing of low heat-treated LiCoO₂ showed that increased heat treatment temperature leads to a rise in activity, peaking at 400°C for 7 days; any higher temperatures sharply decrease activity, associated with a shift to rock salt structure. The best LiCoO₂ catalyst shows a small coating of rock salt layer on the catalyst surface, with the bulk still remaining as a lithiated structure. The lattice mismatch between these layers could be what contributes to the increased OER, but this is still uncertain. Stability tests show that although rock salt LiCoO₂ degrades in both alkaline and neutral media, the mostly lithiated low temperature-treated LiCoO₂ maintains performance for 6 hours in both media. In contrast to low temperature-treated LiCoO₂'s outstanding OER performance, its ORR performance is worse than that of Co₃O₄. However, an increased amount of mixed Co³⁺/Co⁴⁺ valency caused by the introduction of an oxidizer and the subsequent reduction of Li in the catalyst resulted in an improved ORR performance, with Li_{0.5}CoO₂ having an increased ORR performance higher than that of Co₃O₄. This indicates a trend in higher amounts of delithiation associated with higher ORR performance. Increased ORR performance is accompanied by a slight decrease in stability in alkaline media, and a small decrease in the OER performance. However, despite this decrease in the OER, the best-performing Li_{0.5}CoO₂ still has an OER activity 1.5 times higher than that of Co₃O₄; since higher OER activity is associated with the oxidation of ions within the catalyst, the high OER activity of low heat-treated LiCoO₂ structures could be due to a decrease in crystal field stabilization energy, where the increased instability of some Co³⁺ ions makes them easier to oxidize (**Figure**

2). There may also be an increased conductivity in the catalyst arising from unfilled orbitals of Co^{4+} found on the edges of the spinel framework. In addition, the overlapping energies between $\text{Co}^{3+/4+}$ and O_2^- may facilitate the formation of O_2 for its subsequent release. This is supported by the decreased OER activity of high heat-treated LiCoO_2 , whose LiCo_3O_4 units do not show this energy overlap. The increased ORR performance due to delithiation of low heat-treated LiCoO_2 is due to the subsequent increase in mixed valence $\text{Co}^{3+/4+}$. This process is of interest because the performance of this LiCoO_2 was able to be improved without major alterations to the catalyst structure, as is often encountered with other common methods of improving catalyst activity such as heat treatment, where resulting enhancements reach a peak before leading to a general degradation of catalytic activity.

Figure 2. Mechanism of OER on Co_4O_4 cubane units in LT-LiCoO_2 . Printed from [32] with permission from Nature Publishing Group.

In general, one of the major flaws in using transition metal oxides as electrocatalysts is the lowered conductivity of these materials compared to other carbon-based materials. This has

significant detriments to catalytic activity due to the lowered levels of electron transfer between the catalyst surface and the electrolyte, lowering the rate of the ORR and OER. For instance, the preferred ORR reaction involves a 4-electron transfer process that produces water. However, a less efficient 2-electron transfer process can occur that produces hydrogen peroxide, which must then undergo another 2-electron transfer process to produce water. One way to increase the efficiency of the electron-transfer processes, by way of increasing conductivity, is through the addition of dopants to the catalyst structure. By inserting atoms into vacancies and distorting the lattice structure of the substrate material, the distribution of electrons can be altered on the material's surface, which can create areas where the conductivity is higher than if dopants were not added[34]. The conductivity of transition metal catalysts can be increased by combining it with other, more conductive materials such as graphene and nanostructured carbon materials. However, caution is advised, as some carbon materials can experience permanent oxidation that can degrade catalytic activity, as stated before. Despite this, resulting catalysts often still have a better durability than precious metal catalysts, and the improvements in conductivity are still valuable enough to be explored, especially as more durable carbon-based materials are developed.

Masa *et al* created MnO_x and CoO_x based catalysts supported on a N-doped Carbon matrix (NC) by heat treatment and calcification processes to compare its performance to catalysts made from non-doped metal oxide catalysts [35]. The cobalt catalyst has the structure of $\text{Co}_3\text{O}_4/\text{NC}$; it has better bifunctional activity than that of regular CoO catalysts, and shows an initial 80mV energy savings when compared to a Pt/C catalyst. Some Co-N₄ precursor is conserved through pyrolysis, indicating the presence of Co-N_x moieties within the catalysts, suggesting that N may also be involved in the actual oxidation and reduction processes rather than just affecting the

electron distribution of the catalyst. There was a mixture of unsaturated oxygen species, surface hydroxylated species and oxygen groups on the CN surface, as well as metallic Co. A $\text{Co}_3\text{O}_4/\text{NC}$ catalyst made using Co phthalocyanine as the precursor shows that Co-N species in the Co phthalocyanine are encapsulated within multiwalled carbon nanotubes, and a more complex Co environment is present within the $\text{Co}_3\text{O}_4/\text{NC}$ environment as opposed to typical CoO_x environments, with Co-O, Co-N and Co-Co species occurring as compared to just Co-O and Co-Co species in non-doped CoO_x catalysts. In total, it is believed that the presence of N-doping in the resulting catalysts improves activity by enhancing conductivity as well as playing a complementary role in the catalysis of the ORR, resulting a bifunctional activity higher than that of state-of-the-art catalysts RuO_2 , IrO_2 and Pt/C .

Combination of Co_3O_4 and graphene oxide, which individually show low catalytic activity, increases bifunctional abilities to compete with and in some aspects surpass the capabilities of traditional Pt catalysts [36]. The effects of the combined Co_3O_4 and graphene is further increased by doping the graphene with nitrogen, especially in ORR activity. The nitrogen also decreases the size of catalyst particles, and coordinates with the Co to assist in its oxidation. The resulting N-doped composite catalysts display almost complete 4-electron transfer, and a half-wave potential of 0.83 V for the ORR in alkaline media, compared to 0.86 V in Pt/C . OER activity shows a low overpotential of 0.31 V and performance surpassing that of other high-functioning bifunctional metal catalysts. Furthermore, the N-doped Co_3O_4 -graphene oxide catalyst display superior durability over a conventional Pt/C catalyst; where the Pt/C catalyst loses 20-48% of its activity, the composite transition metal catalyst displays little loss in activity after 25,000 seconds of operation. Despite the possible risk of corrosion posed by the use of graphene, the N-doped Co_3O_4 -graphene oxide catalyst is still more stable as a bifunctional

catalyst than precious metal catalysts. Another Co oxide catalyst synthesized by a solvothermal method uses Co_3O_4 nanocrystals grown on reduced graphene oxide and doped with Cu nanoparticles with the goal of implementing in a Li-air battery [37]; the solvothermal synthesis technique, which involves a reaction of precursors in an autoclave, is advantageous as it can be carried out at lower temperatures compared to hydrothermal methods and can yield higher amounts of product. The presence of small amounts of Cu can improve the current density for both the ORR and the OER [38, 39]. After Cu doping and subsequent calcification, Co_3O_4 forms into flowerlike porous microspheres composed of interweaving nanoplate petals, with crystallized Cu nanoparticles laying on top, as seen in **Figure 3A-B**. The addition of Cu onto the catalyst increases the performance of the catalyst as well as the cell cyclability in Li-air battery tests, with a slightly increased round-trip efficiency (75.7% compared to 72.1%). However, the efficiency of both catalysts still do not surpass that of a 50% Pt/carbon-black catalyst (83.0%)(**Figure 3C**). It is believed that the addition of Cu increases the inherently poor conductivity of the Co_3O_4 catalysts, but it should be further explored as to whether the addition of Cu can introduce other unseen problems. It is suggested that the synergistic effect on electrocatalytic activity between the Co and graphene oxide is related to the formation of bonds between the two species, and resulting changes in the chemical environment of the catalyst[40].

Figure 3. A) Overall morphology of the Co₃O₄ products, B) high-magnification SEM image of an individual Co₃O₄ microsphere revealing the constituent details of the microspheres, C) Comparison of the first charge and discharge curves of the prepared lithium–air batteries with various catalysts at a current density of 0.05 mA cm^{−2}. Reprinted from [37] with permission from Elsevier.

A bifunctional catalyst made from Co₃O₄ nanofibers supported on graphene nanoflakes was able to deliver a high discharge capacity of 10,500 mAh/g and a cycling stability of 80 cycles in a Li-O₂ battery[40]. Non-oxidized nanoflakes were utilized as opposed to nanoflakes made from the reduction of graphene oxide; they produce much thinner sheets, allowing better electron transport to the metal active sites while providing support for the Co₃O₄ nanofibers. Compared to catalysts made with reduced graphene nanoflakes, these catalysts show superior surface area and a higher purity in the graphene and cobalt crystalline structures. However, there was an accumulation Li₂O₂ products on the catalyst surface, inhibiting catalytic performance, which is related to the performing capacity being used by the battery. At a limited capacity, byproducts are removed from the surface of the catalyst during the charging cycle of the battery,

allowing the battery to operate through 80 charge-discharge cycles while maintaining stability, much longer than similar catalysts made using reduced graphene nanoflakes.

Figure 4. A) Scheme for the fabrication of hybrid Co_3O_4 -carbon porous nanowire arrays; EDS elemental mapping images of a Co_3O_4 -carbon nanowire array for B) Co and C) C. Reprinted with permission from [31]. Copyright © 2014 American Chemical Society.

Much research gives more focus to the ORR for bifunctional catalysts, as the ORR typically needs more improvement in transition metal catalysts than the OER. However, there is certainly still room to improve the OER, especially the current density and potentials that can be achieved. A catalyst developed by Ma *et al* by growing a Co_3O_4 -carbon nanowire array on a sheet of copper foil, as shown in **Figure 4A**, exhibits an OER onset potential of 1.47 V, comparable to traditional IrO_2 catalysts for the OER [31]; the catalyst has an ORR half-wave potential of 0.78 V, with a low overpotential of 0.74 V. In practical applications, the catalyst is able to deliver the typical current density for a solar fuel cell at a lower voltage than that of IrO_2 catalysts, and it shows high tolerance to methanol poisoning. Several factors have been proposed to account for the high performance of this catalyst: the catalyst itself is very porous, with a high effective area and evenly distributed Co_3O_4 active sites (**Figure 4B-C**). The direct growth of the nanowire array onto the carbon MOF is believed to aid in the stability and conductivity of the catalyst, and spaces between the nanowire structures may allow evolved O_2 to leave the catalyst, preventing performance reduction by accumulated products.

2.2. Nickel Oxides

Though not as commonly used for bifunctional electrocatalysts as other transition metals such as manganese or cobalt, nickel has certain properties that make it a candidate for electrocatalyst research. Nickel is more conductive than manganese, though it is still not as

conductive as platinum or carbon-based materials. Nickel has been found to be a capable OER catalyst, one of the more common applications for nickel-based electrocatalysts. The OER requires larger applied potentials in order to occur, and is often conducted in an alkaline solution; as such, many materials make poor catalysts for this reaction due to corrosion. However, nickel oxides are very resistant to corrosion, and although they too eventually show decreases in activity over time, nickel-based OER catalysts tend to have higher stability than other precious metal catalysts. In particular, the anhydrous brucite structure of nickel oxide, containing more Ni^{3+} than other structures, is considered the best to use for its good conductivity[41]. However, there is a tradeoff, as Ni^{2+} is considered much more stable. For instance, a catalyst was made for the OER by electrodepositing Ni^{2+} onto multiwalled carbon nanotubes (MWCNTs) with a potassium borate buffered solution, resulting in the catalyst $\text{H}_2\text{-NiO}_x\text{-MWCNTs}$ [42]. To improve conductivity even further, the catalyst was used in conjunction with a platinum spray. The catalyst displayed high stability, maintaining a current density after 36 hours of electrolysis. In the OER, the $\text{H}_2\text{-NiO}_x\text{-MWCNTs}$ display an onset potential of 0.91 V and multiple broad waves indicating more than one Ni oxidation step at 0.76 and 0.82V, resulting in an amorphous phase dubbed $\text{O}_2\text{-NiO}_x$. This suggests that the OER nickel mechanism contains multiple steps, with intermediate forms of Ni. When compared with Ni catalyst without MWCNTs, the presence of MWCNTs results in a higher stable current density, though both exhibited OER stability for 5 hours. pH dependence is also exhibited by this catalyst, with higher pH conditions in the electrolyte resulting in lower potentials for the OER. Overall, the catalyst has greater than 95% efficiency for the OER.

Despite its capability as an OER catalyst, nickel has drawbacks which pose problems for use in bifunctional catalysts. Nickel ions have a tendency to migrate within crystal structures, caused by

the reduction of Ni^{3+} to Ni^{2+} and the creation of NiO impurities during high temperature heat treatment, which is common in catalyst synthesis[43]. This change in structure leads to a low reversibility, making catalysts suffer in their bifunctional properties. One way to minimize these stability problems is to incorporate iron into the nickel oxide structure, which will be discussed later. One nickel oxide-based catalyst was evaluated for both the ORR and the OER by Liu et al, which was synthesized via pyrolysis to form metal oxide nanoparticles on graphene oxide[44]. The coupling of the metal oxide directly onto graphene oxide served to increase conductivity for the ORR, as well as the even distribution of metal active sites on the graphene sheets. Ni^{2+} was identified as the primary contributor to the ORR and the OER, with the OER activity surpassing that of other cobalt and platinum-based catalysts. However, the ORR activity of the Ni-oxide catalyst was very poor, despite the increased conductivity given by the graphene oxide. Nickel's strong OER performance, yet weak ORR performance, suggests that although nickel alone may not be the best choice for a bifunctional catalyst, it could be a valuable component to a mixed-oxide catalyst.

2.3 Iron oxides

The use of iron oxides alone in bifunctional electrocatalysts is not very common; in most situations, catalysts made from iron oxides are focused on only the ORR or the OER, not both [45-47]. A review of applications of iron in ORR catalysts by Bezerra et al. outlines many of the advantages posed by iron, as well as the disadvantages that must still be overcome by scientists. For instance, iron typically has a high selectivity towards the ORR which, paired with its high abundance and low cost, makes it a desirable alternative to precious metal catalysts. In fact, it is considered to have one of the highest active centers towards the ORR, along with cobalt.

Furthermore, iron displays a high tolerance towards methanol poisoning that is not shared by other materials such as platinum. This is mostly due to the properties of platinum rather than iron, as platinum reduces the concentration of oxygen by catalyzing its reaction with methanol, while iron has no way of catalyzing such a reaction[48]. However, it still suffers from a lowered catalytic activity, and from stability issues when used in acidic media. These issues have been mitigated somewhat by strategies such as heat treatments, but still have a long way to go before they can match or surpass precious metal catalysts[45].

Compared to work with iron in ORR catalysts, there is very little work on its applications in OER catalysts. An analysis of the kinetics of the OER reaction with various metals by Scarr reports that the rate of the OER in iron-based catalysts is very similar to other metals such as platinum and nickel after normalization of the active surface area, suggesting that it is rather average as an OER catalyst[49]. Most other research on OER activity of iron oxides has been conducted by Lyons and Brandon using passivated iron electrodes. As iron oxidizes readily in many environments, iron electrodes tend to go through periods of transiency as a passive oxide layer is built up on the surface of the electrode; as such, it is difficult to reproduce OER data on fresh, non-oxidized iron electrodes. However, the charge capacity is observed to increase as the oxide layer forms, which Lyons and Brandon propose is due to the oxidation of Fe^{2+} to Fe^{3+} in the hydrous oxide phase coating the electrode, where the Fe^{3+} results from the reduction of higher iron oxidation states such as Fe^{6+} , which are proposed by Lyons and Brandon to be the OER active sites. In terms of reversibility, the formation of the oxide layer poses some issues, as the rates of the OER calculated through methods such as Tafel plots is not consistent between the forward and reverse OER, most likely due to changes in conductivity and thickness in the catalyst. This means stability and consistency is difficult to achieve in iron catalysts, even if it is

polished before and between uses. Stabilization of the electrode occurs after about 10 polarization cycles, whereupon the Tafel slope of the OER increases until it reaches a value of 44-47 mV/dec. The rate of the OER is also believed to be influenced by other factors, including the pH of the solution immersing the electrode, as this affects the chemistry and rate of formation of the oxide layer on the iron electrode, with higher concentrations of NaOH increasing the Tafel slope. However, when normalizing surface area and comparing between other transition metal catalysts such as nickel and cobalt, iron still performs the lowest, within orders or magnitude (**Table 2**). This appears to be in contrast to the observations made by Scarr, but it must be noted that Scarr's calculations were based on a normalized surface area; when taking real area into account, the trend observe agrees with Lyons and Brandon, suggesting that differences in activity between the metals may be due more to structural differences and available surface areas, rather than differences in chemical activity[46]. This is promising, as research into the structure of iron oxides and ways to manipulate it through synthesis could narrow the gap in performance observed between iron and other transition metal oxides. In addition, further research into iron oxide catalysts could do more to link the individual research done currently to gain more insight into iron's use as a bifunctional catalyst. **Table 2.** Comparison of parameters related to the OER catalytic activity of pre-reduced Ni, Co and Fe electrodes in 1.0 M NaOH at 25°C. Current densities are based off of the estimated active surface areas for the OER of each electrode. Printed from [46] with modifications for visibility.

Electrode	f_r	$b(\text{mV dec}^{-1})$	$i_0 (\text{A cm}^{-2})$	$i(0.302 \text{ V}) (\text{A cm}^{-2})$
Ni	6.3 $\pm$ 0.2	38.5	1.78 ($\pm$ 0.07) $\times 10^{-13}$	1.21 ($\pm$ 0.04) $\times 10^{-5}$
Co	12.9 $\pm$ 0.7	47.5	3.3 ($\pm$ 0.2) $\times 10^{-12}$	7.4 ($\pm$ 0.4) $\times 10^{-6}$

Fe	0.51 $\pm$ 0.02	39.5	2.9 ($\pm$ 0.2) $\times 10^{-14}$	1.3 ($\pm$ 0.1) $\times 10^{-6}$
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2.4. Manganese-Oxides

Manganese Oxides have attracted much attention as bifunctional catalysts for electrochemical reactions due to their existence in nature in the enzyme Photosystem II, found in the chloroplasts of plants and involved in water splitting during photosynthesis. The natural Photosystem II contains an organo-metallic complex consisting of manganese oxide and cadmium [50, 51]. Manganese oxide is a highly diverse compound with over 30 different crystal structures and 3 different oxidation states; this wide variety of structures is facilitated by manganese's octahedral structure, which allows for several different combinations and forms, most commonly layered or tunneled structures. Tunneled structures also offer the opportunity of storing water or other molecules within its pores[52]. Taking these factors into account, manganese offers a large variety of candidates for electrocatalytic study, and the possibility of creating a catalyst structure optimized for bifunctional activity. Added to this, manganese is the 10th most abundant element on Earth, making it a cheap and widely-available material, which is preferred for new bifunctional catalysts.

2.4.1. Structural Examination

As manganese is so diverse, it is important to recognize which forms are the most conducive to bifunctional electrocatalytic activity, and why. Several works of research compare the various structures of manganese oxide and determine why some forms work better as an electrocatalyst than others. In a work done by Gorlin and Jamarillo[53], inspiration was taken by the Oxygen Evolving complex found in nature to create a thin-film Mn₂O₃ catalyst that can outperform both Ir and Ru in the ORR, and comes within 130mV of the comparison Pt/C half-

wave potential. The oxidation state of the catalyst is Mn^{3+} , the most common form. In OER performance, the catalyst's performance rivals that of Ir and Ru catalysts, with a half-wave potential of 1.77 V compared to 1.61 V and 1.62 V, respectively. Its potential difference was measured to be 1.04 V; this outperforms the Pt catalyst and is within 0.12 V of the best performing Ir catalyst (**Figure 5**). The catalyst shows a highly nanostructured surface, which is believed to contribute to the catalyst's good performance.

Figure 5. Oxygen electrode activities of the nanostructured Mn oxide thin film, nanoparticles of Pt, Ir, and Ru, and the glassy carbon substrate. Reprinted (adapted) with permission from [53]. Copyright © 2010 American Chemical Society.

Further research by Meng *et al.* studies the behavior of different nanostructured Mn oxides and their possible involvement in bifunctional activity [54]. Four structures, α - MnO_2 made by a solvent-free method (SF), β - MnO_2 , δ - MnO_2 and amorphous oxide (AMO) catalysts, were studied. α and β oxides display tunneled structures of varying sizes, which are capable of hosting various ions and exhibit unique adsorptive properties that may prove beneficial for electrochemical reactions. The α structure consists of nanofibers and a tetragonal cryptomelane

structure much smaller than those of β , which match closely to the Mn oxide structure pyrolusite. The amorphous and δ oxides show sheet-like morphology, with δ showing highly structured crystals of birnessite forming into layers of spherical nano-flower shapes, and the AMO having more disordered layers (**Figure 6A-C**).

Figure 6. HRTEM images of manganese oxide nanostructures A) α -MnO₂-SF, B) AMO [the inset shows the SAED (selected area electron diffraction) pattern], C) β -MnO₂; D) OER electrocatalytic activity in 0.1 M KOH at 10 mA cm⁻² with manganese oxide structures displayed above. Reprinted (adapted) with permission from [54]. Copyright © 2014 American Chemical Society.

Although the AMO structure has the highest surface area, the α -MnO₂-SF catalyst has the highest pore volume. β -MnO₂ has the lowest surface area and pore volume, due to its small tunnel size. Since there has been some evidence that adsorption of K ions can play a role in electrocatalytic activity[55], as well as the amount of Mn⁴⁺ or Mn³⁺ oxidation states present, the

ratio of K to Mn and Mn^{4+} to Mn^{3+} was also studied. $\beta\text{-MnO}_2$ has no K^+ ions present, as they cannot fit within its tunnels; Mn^{4+} oxidation states dominate. AMO has a low presence of K^+ and a high amount of Mn^{4+} , and while $\delta\text{-MnO}_2$ also has a high amount of Mn^{4+} , it also has the highest K^+ content. $\alpha\text{-MnO}_2\text{-SF}$ has a considerable amount of K^+ present, as well as a high number of oxygen defects and an increased amount of Mn^{3+} . In terms of the ORR, the $\alpha\text{-MnO}_2\text{-SF}$ catalyst shows the best performance with (Figure 7B) and (Figure 7C).

Figure 7. A) CV curves of manganese oxides B) LSV curves of $\alpha\text{-MnO}_2\text{-SF}$, $\alpha\text{-MnO}_2\text{-HT}$, $\text{Ni}/\alpha\text{-MnO}_2\text{-SF}$, AMO, $\beta\text{-MnO}_2$, and $\delta\text{-MnO}_2$ C) Rotating disk electrode voltammogram (RDEV) of oxygen evolution reactions by using $\alpha\text{-MnO}_2\text{-SF}$, $\text{Ni}/\alpha\text{-MnO}_2\text{-SF}$, $\alpha\text{-MnO}_2\text{-HT}$, and 20 wt % Pt/C. Reprinted (adapted) with permission from [54]. Copyright © 2014 American Chemical Society.

A solvent-free method of preparation leads to the highest surface area, pore volume, and small crystal size, which would intuitively correlate to better catalytic activity. Stability increases when exposed to heat treatment, as well as the addition of a Ni^{2+} dopant. Comparing the electron transfer capabilities of all catalysts, only $\alpha\text{-MnO}_2\text{-SF}$ catalysts achieved a transfer number within 0.3 of the ideal transfer number of 4. This high performance overall seen in $\alpha\text{-MnO}_2\text{-SF}$ catalysts is attributed in part to structure, where large tunnels in $\alpha\text{-MnO}_2$ crystal structures can accommodate ions and allow for more active sites; more disordered structure also helps activity, with more deprotonation sites to oxidize water. Other factors can also be more chemical in nature; the presence of mixed valences can create more oxidation sites and facilitate charge transport between ORR and OER operations, and $\alpha\text{-MnO}_2\text{-SF}$ also shows a high affinity towards bonding with O_2 followed by AMO, further supporting the performance ranking of the catalysts examined in this work.

Figure 8. SEM images recorded for three different $\alpha\text{-MnO}_2$ nano shapes A) Nano-particles B) Nano-wires and C) Nano-tubes. Printed from [56] with permission from Elsevier.

Since catalysts made from α -manganese tend to perform better than other manganese structures, it would be beneficial to find more parameters that can optimize the performance of the catalysts. This was evaluated using 3 shapes of $\alpha\text{-MnO}_2$ catalysts in an alkaline medium[56].

Nanostructured materials can often lead to unique or improved behavior, and have a lower risk of corrosion over other carbon materials, so α - MnO_2 catalysts of nanotube, nanowire and nanoparticle structure were produced (**Figure 8**). Heat treatment results in a change in the Mn-oxide structure from MnO_2 to Mn_3O_4 . It takes longer for the heat treatment to remove all water from the nanotubes compared to the other structures, indicating a stronger interaction with water molecules compared to nanowires and nanoparticles. In OER tests at 0.8V, the nanowire catalyst had the lowest onset potential, and activity double that of the other 2 catalysts at 0.25 mA/cm^2 . It is believed that the OER reaction occurs preferentially on the nanowire surface. In the ORR, nanowires are shown to have a half-wave potential 70-90 mV lower than those of nanotubes and nanoparticles. Characterization tests of α - MnO_x nanowires indicate that within all catalytic structures, there is an equal presence of hydroxide and oxygen ions within the structure, and water is chemically bound, while magnetic structure readings indicate that oxygen defects and Mn^{4+} ions interact and coagulate into complex associates within the catalyst. By using Density Theory it was calculated that the (310) crystallographic plane displayed in the nanowire structure prefers the adsorption of water, which is connected to better ORR and OER performance.

2.4.2. Preparation Techniques

Since structure can play a significant role in the capabilities of bifunctional catalysts, it would make sense to hone synthesis techniques to maximize control of the catalyst's structure. As with cobalt-based catalysts, many synthesis procedures of manganese-based catalysts involve heat treatment and calcification, but the choice in precursor for the source of transition metal can make a difference in the structure of the resulting catalyst. In one Mn oxide catalyst, two types of precursors are used: porphyrins, and phthalocyanines, which are impregnated into nitrogen-doped carbon (NC) and subjected to heat treatment and calcination [35]. Spines of Mn_3O_4 as well

as Mn-N_x moieties form on the the NC matrix, corresponding to spinel and tetragonal hausmannite structures; while metal atoms are embedded in or surrounded by amorphous carbon, metal oxide complexes are surrounded by a shell of porous, nitrogen-rich carbon. The OER performance of the synthesized catalyst is slightly higher than that of other Mn-based structures, and for the ORR, the catalyst starts at a lower overpotential while generating a higher current. The catalyst was compared to a typical Pt/C catalyst, and is shown to have an overvoltage of 70mV. Although the precursor materials are degraded during pyrolysis, it is proposed that Mn-N ring structures are retained, and the following calcination step oxidizes some Mn-N groups into either lone Mn_xO_y , Mn with oxide layers, or surface Mn-oxide-N groups that are not present in other Mn-based structures (**Figure 9**).

Figure 9. Schematic illustration of the possible groups that are formed during pyrolysis of cobalt and manganese N₄-metallomacrocyclic complexes at 650 °C for 2 h under He, and subsequent calcination in oxygen at 200 °C for 30 min. Reprinted (adapted) from [35] with permission from John Wiley and Sons.

It has been shown through XAS measurements that more MnO_2 (associated with Mn^{4+}) is linked to better ORR performance. Various spectroscopy techniques can be used to characterize the behavior of Mn oxide based bifunctional catalysts[57]. A basic Mn oxide catalyst MnO_x was deposited onto a gold-coated silicon nitride window, and was compared to a Mn oxide catalyst on glassy carbon (MnO_x/GC). Although prepared similarly, the $\text{MnO}_x/\text{Au-Si}_3\text{N}_4$ has a disordered structure consisting of Mn(II)O and Mn(IV)O_2 , while the MnO_x/GC shows a clear crystal structure matching that of $\alpha\text{-Mn(III)}_2\text{O}_3$. After application of 0.7V ORR conditions, XPS reveals a change in the Mn(II)O to either Mn(III)O or $\text{Mn}_3(\text{II,III,III})\text{O}_4$, while no such change occurs in the MnO_x/GC catalyst. An OER-type potential shows a change in Mn(II)O to Mn(IV)O_2 to form Mn(II,IV) oxidation states. Again, this is not observed in MnO_x/GC . The catalyst shows a strong similarity to the Mn oxide structure known as birnessite, which is a layered structure with spaces to accommodate other ions, broken up by isolated regions of $\text{Mn}_3(\text{II,III,III})\text{O}_4$. A direct relationship between the OER activity of the catalyst and its thickness has been established, suggesting high porosity and active catalytic sites dispersed throughout the structure, including within pores. The structure of the catalyst also changes depending on the electrochemical environment, with ORR environments leading to disordered, spinel-like structures, and OER environments preferring the structure similar to birnessite (**Figure 10**).

Figure 10. A) Comparison of XANES data collected on as-prepared $\text{MnO}_x/\text{Au-Si}_3\text{N}_4$ film and on $\text{MnO}_x/\text{Au-Si}_3\text{N}_4$ film after in situ exposure to ORR and OER relevant conditions. Inset: corresponding lattice structures resulting from ORR and OER conditions. B) CV characterization of the ORR and the OER activities, illustrating that the OER activity scales with the thickness of MnO_x catalyst. Reprinted (adapted) with permission from [57]. Copyright © 2013 American Chemical Society.

2.4.3. Supported catalysts

Carbon supports

As with cobalt, many manganese oxides exhibit low conductivity, so it is necessary to find ways to increase the conductivity, and therefore the efficiency, of the catalyst. This can be done very similarly to cobalt catalysts, by using the transition metal with other more conductive materials[58]. For instance, a bifunctional catalyst made using $\alpha\text{-MnO}_2$ along with the MOF MIL-101(Cr) shows an electron transfer number of 3.74, suggesting a mix of 2 and 4 electron transfer pathways, with the 4-electron transfer dominating [59]. The catalyst was compared to pure $\alpha\text{-MnO}_2$ and Pt, and its performance after being soaked in deionized water for 40 hours to look for signs of degradation. For the ORR, the transition metal-MOF catalyst shows improved onset potentials and current densities compared to pure $\alpha\text{-MnO}_2$, but still lower than the performance of the Pt catalyst. $\alpha\text{-MnO}_2/\text{MIL-101(Cr)}$ shows the best OER activity, with an onset potential of 0.5V and a current density of 23.67 mA/cm^2 at 0.9V, compared to only 0.54 mA/cm^2 for Pt and performing 7 times better than pure $\alpha\text{-MnO}_2$. The performance of the catalyst for both ORR and OER decrease very little when soaked in deionized water for 40 hours, and maintains high stability, with 80.9% retention of performance after 20000 seconds. The increased

performance of the α -MnO₂ with the MOF can be attributed to strong interactions between the two components during heat treatment in synthesis; the α -MnO₂ nanoparticles are closely embedded into the MOF and the formation of a composite is evidenced (**Figure 11**). Nitrogen adsorption-desorption isotherms indicate a decrease in specific area and pore size, along with an increase in pore volume, compared to pure MOF. However, it is believed that the porosity of the MOF increases accessibility of active sites in the α -MnO₂, thus improving its performance despite the loss in specific area. The structure of the material shows very little change after soaking in water, further supporting the catalyst's high stability.

Figure 11. TEM images of the samples: A) MIL-101(Cr), B) α -MnO₂/MIL-101(Cr), C) α -MnO₂/MIL-101(Cr)-40; D) ORR activity of samples: (a) MIL-101(Cr), (b) α -MnO₂, (c) α -MnO₂/MIL-101(Cr), (d) α -MnO₂/MIL-101(Cr)-40, (e) 20 wt.% Pt/C. Reprinted from [59] with permission from Elsevier.

Many works using transition metal oxide catalysts in conjunction with conductive materials often use graphene-based materials or metal-organic frameworks, which can be difficult to make or obtain in commercially feasible amounts. To make use of common materials for bifunctional catalysts, Gao et al [60] tested a novel idea to use PVC plastic as a carbon source in conjunction with S-doped MnO. Furthermore, the synthesis of the catalyst directly integrates the active sites into the carbon in an even distribution, rather than requiring the combination of two separate carbon and transition metal sources (**Figure 12A**). Doping of elements such as S, N or P into graphene-like materials can improve both the OER and ORR activity, since it changes the electron density within the carbon structure [61, 62]. The prepared catalyst has a content of about 7%S and 4%Mn, and after heat treatment, the structure contains a mixture of Mn_3O_4 and MnO_2 structures. For the ORR, the S-doped Mn oxide catalyst has an onset potential of 0.94V compared to 1.01V for Pt, and a half-wave potential of 0.82, rivaling Pt's value of 0.88 (**Figure 12B**). OER performance shows an onset potential of 1.28V, much improved from Pt which shows very little OER activity. The catalyst's overall potential difference is 0.81V. Although the exact mechanism for the catalyst is not known, it is suspected that a series of 2 and 4 electron transfer reactions take place during performance, eventually leading to a total electron transfer of 4.

Figure 12. A) Procedure for synthesis of MnO_x/S-GC, where PVC is represented by yellow balls in the solution; B) LSV curve of the ORR at 2000 rpm of the MnO_x/S-GC hybrid, Pt/C and glassy carbon (GC). Reprinted from [60] with permission from Elsevier.

Alternatives to Carbon Supports

Attempts have been made to create Mn oxide catalysts in conjunction with carbon-free materials that can provide synergistic affects with the Mn, thus fulfilling the same role as one would using graphene or a metal-organic framework while avoiding the expense of graphene or possible corrosion. For instance, research by Ng, Tang, and Jamarillo involves the use of Mn oxide deposited on stainless steel [63]. While MnO performs well alone for the ORR, stainless steel shows some contribution to the OER. This is supported by structural analysis that shows porosity in the MnO which allows access to the stainless steel below, meaning it is accessible to reactants. Stainless steel is also a common and durable material that would be conducive to scaling-up. Calcification at 480°C during synthesis is linked to a transition in Mn oxidation states from Mn⁴⁺ to more ORR-active Mn³⁺. Tests against a Pt catalyst on stainless steel, as well as plain MnO on carbon, show improved performance to the carbon-based catalyst and ORR activity comparable to that of the Pt. Although the Pt performs better in the OER, the MnO on stainless steel is the only catalyst of the three not to display corrosion at the high potentials. Stability tests show that the MnO-stainless steel catalyst retains its performance after 100 cycles of ORR and OER, while the Pt catalyst shows a 90% drop in performance, most likely due to the oxidative environment during the OER. Calcination is believed to play a role in the catalyst's superior stability, as uncalcified catalysts show a higher drop in OER activity after cycling

(Figure 13). The catalyst was also tested in an anion exchange membrane unitized regenerative fuel cell (AEM-URFC) to test its performance in a realistic application. The cell reaches a peak power density of 27 mW/cm² in fuel cell mode, which is comparable to precious-metal catalyst performance. It also shows comparatively reliable stability, only dropping 1 mW/cm² over 4 cycles. In electrolyzer mode, the catalyst maintains a current of 60 mA/cm² at 1.75V over 10 cycles. The overall efficiency of the cell is measured to be 45%; however, extraneous inefficiencies in the exchange membrane may have contributed some to the lowered performance in the fuel cell.

Figure 13. A) Rotating electrode linear sweep voltammogram displaying oxygen reduction and evolution activities of MnO_x electrodeposited on stainless steel mesh (before and after calcination), commercial 20 wt% Pt/C deposited on stainless steel mesh, and MnO_x/C mixed with Ni/C deposited on carbon paper. B) Rotating electrode voltammograms displaying oxygen reduction and evolution activities of the MnO_x on

stainless steel mesh, Pt/C on stainless steel mesh, and MnO_x/C mixed with Ni/C after accelerated stress testing. Reproduced (adapted) from [63] with permissions from The Royal Society of Chemistry.

Another way to improve MnO_x catalysts without the use of carbon sources lies in the increase of vacancies within the crystal structure of the oxide, particularly oxygen deficiencies. Such deficiencies have previously been shown to improve the electrochemical performance of lithium batteries and oxide fuel cells, but little research has been done to demonstrate its effects on Mn systems [64, 65]. Cheng et al [66] made a catalyst out of rutile $\beta\text{-MnO}_2$ to measure the effects of induced oxygen deficiencies on electrocatalytic activity, particularly the ORR. Deficiencies were introduced through heat treatment for 2 hours, where there was a transition from MnO_2 to Mn_3O_4 . Both ORR and OER subsequently improved, with a 50 mV potential increase in the ORR compared to pristine $\beta\text{-MnO}_2$, supporting the idea that vacancies increase bifunctional activity by enhancing interactions between the catalyst and oxygen-containing species. There is one caveat, that too high a heat treatment leads to a permanent modification of the catalyst's structure, thus limiting the heat treatment and corresponding vacancies to 350-400°C. Density Functional Theory can approximately quantify the effects of oxygen vacancies; energy profiles for the ORR for pristine, one-vacancy and two-vacancy systems shows that a small amount of vacancies increases the adsorption of oxygen up to 5-fold (**Figure 14**). A small amount of vacancies is therefore beneficial, as too many vacancies can hinder ORR kinetics.

Figure 14. A) Constructed models of perfect and oxygen-vacant hydroxylated β -MnO₂ (110) surfaces. Configurations of B) O₂ and C) OOH adsorbed on different surfaces. D) Energy profiles and configurations of ORR on β -MnO₂ surfaces with one (Path I) and two (Path II) oxygen vacancies. Asterisks denote adsorbed species. TS=transition state. Reprinted from [66] with permission from John Wiley and Sons.

3. Mixed Transition Metal Oxides

A large bulk of bifunctional electrocatalyst research has focused on employing two or more different transition metals and mixing them to create a mixed-transition metal oxide [67]. This may occur as a uniform distribution of multiple oxides in a uniform lattice structure, embedding one oxide structure with another by doping. Currently, most mixed-transition metal oxide electrocatalysts are either binary, where two oxides are used together, and less commonly ternary, where three oxides are used. This is of great use, as many single-oxide electrocatalysts perform well in either the ORR or OER, but are lacking in the other. By mixing transition metal oxides with diverse benefits, a catalyst may be synthesized that contains the benefits of the

individual oxides, while making up for their individual setbacks. Most of these catalysts use either manganese, cobalt, or a combination of both, as they have attracted the most attention as individual transition metal oxide electrocatalysts.

3.1 Binary Transition Metal Oxide Electrocatalysts

3.1.1. Manganese-Containing Binary Oxide Electrocatalysts

Although cobalt and manganese are the most successful transition metals to use in bifunctional catalysts, there are also benefits to grouping them with different metals. For instance, both cobalt and manganese have relatively low electrical conductivity, so grouping them with another, more conductive metal could help improve the catalyst overall. Or, a different metal could be used that performs better in the OER. A comparison was made by Klápště, Vondrák and Velická with a MnO_x/C catalyst created on a stainless steel mesh by reducing birnessite KMnO_4 with carbon black [68]. Although the initial catalyst contains K^+ doping, the K^+ can be replaced by other ions including Ca, Mg, Ni, Bi and Cr to compare their bifunctional activity. Initial CV curves show that doped samples have steeper current peaks for both the ORR and OER, especially those doped with transition metals. This may be due to transition metals' various oxidation states, which may contribute towards ORR or OER depending on the valency. Of the transition metal dopants, Cr ions result in the highest half-wave ORR potential out of all dopants; Ni dopants follow close behind. However, performance is shown to decay, possibly due to dissolution of doped metals to form metal-oxide ions or hydroxyl-metal-oxide materials. Voltammograms for bifunctional activity show an overshoot peak in the reduction part of the reaction, which is more prevalent in non-transition metals. This may be linked to the inhibition of hydrogen insertion reactions or diffusion-control of oxygen in the solution.

Manganese-Cobalt Oxide Electrocatalysts

Individually, manganese and cobalt are the most common and successful of the transition metal oxide catalysts. Naturally, combining the two metals into one catalyst could create a promising hybrid [69, 70]. The synergistic nature of the combination can be observed with a mixed Mn-Co oxide catalyst, $\text{MnO}_2/\text{Co}_3\text{O}_4$, produced by using MnO_2 nanotubes embedded with Co_3O_4 nanoparticles [71]. The multistep hydrothermal synthesis process results in a tetragonal α - MnO_2 structure and cubic Co_3O_4 structure for the catalyst, and an overall composition of 72% MnO_2 and 28% Co_3O_4 , with the redox couple $\text{Co}^{3+}/\text{Co}^{2+}$ found in a ratio of 2:1. In ORR/OER tests, the hybrid catalyst has an onset potential of 1.05V, largely unchanged from the 0.9 and 1.1V for separate Co_3O_4 and MnO_2 . However, the hybrid catalyst displays an improved ORR current density in comparison to lone Co_3O_4 , at $3.4\text{mA}/\text{cm}^2$ versus $1.2\text{mA}/\text{cm}^2$. The hybrid catalyst has a higher activity than Co_3O_4 nanoparticles but slightly lower than that of lone MnO_2 nanotubes for the ORR. However, both single oxide catalysts are outperformed in the OER, with a higher onset potential and a smaller Tafel slope occurring in the hybrid. Though the hybrid catalyst's performance is just underneath that of commercial Pt/C, its OER activity competes. The hybrid catalyst's cycling stability is similar to that of MnO_2 nanotubes, and provides a maximum power density of $33\text{ mW}/\text{cm}^2$ in zinc-air battery applications; compared to lone MnO_2 nanotubes, the hybrid can match a current density with the nanotube catalyst while using a slightly lower potential, suggesting a higher activity in the hybrid $\text{MnO}_2/\text{Co}_3\text{O}_4$. In stability testing over 60 cycles, the $\text{MnO}_2/\text{Co}_3\text{O}_4$ catalyst has only a 5% potential change for both charge and discharge, compared to a 13% drop in lone MnO_2 . This further confirms that mixed oxide catalysts are, in general, superior to single oxides.

To improve conductivity, cobalt manganese oxide was synthesized in a Li-air battery on a graphene composite [72]. The semiconductor spinel metal structure is securely attached to the

conducting graphene composite, minimizing the risk of lowered conductivity by separation of the composite materials. The ORR performance of the catalyst came to within 90 mV of that of a 20 wt% Pt catalyst, and had a high OER performance of 83 A/g at 0.5V; high OER activity is helpful for Li-air batteries, as it improves energy efficiency by decreasing the charge/discharge voltage gap. This is further supported by a calculated electron transfer number of 3.9, close to the ideal value of 4. Cycling of the catalyst in a Li-air battery at a current density of 0.2 mA/cm₂ yields a high initial discharge capacity up to 3000 mA h/g; however it shows an almost complete loss in discharge capacity after 3 cycles, which is unacceptable for practical use. To mitigate the gap between charge and discharge and increase the efficiency and stability of the Li-air battery, the solvent in the battery was switched from organic to an aqueous electrode on the cathode side. Although a gap is still observed, it was decreased by over half, indicating that the poor stability of the battery may be due to other factors besides the catalyst, including the kinetic capabilities of the solvent.

N-doped carbon may also improve the stability and performance of transition-metal oxide catalysts, and can also be used in conjunction with other nanostructured carbon materials. This can be seen in a spinel CoMn₂O₄ catalyst made for a Zinc-air battery, using nitrogen-doped graphene[73]. N-doping is associated with an increased number of active sites, as it creates defects in the graphene which have a high reactivity to oxygen and an altered electrical distribution. It also contributes to reduced particle size and an improved dispersion throughout the catalyst; in contrast, metal-oxides in non-doped catalysts are not as well-dispersed, and form into aggregates instead. As a result, the N-doped catalyst has a higher surface area of 51.67 m²/g, as compared to 39.24 m²/g. As this would suggest, the N-doped CoMn₂O₄ catalyst has an ORR half-wave potential of 0.8V, 50mV more positive than non-doped catalyst. It also approaches the

state-of-the-art Pt catalyst value of 0.86V (**Figure 15A**). This may be attributed to direct interaction between metal-oxide nanoparticles and N, but may also be due to improved kinetic current densities resulting from the increased number of active sites. The OER performance of the N-doped catalyst also exceeds the non-doped catalyst, with a current density of 10 mA/cm² at 1.66V and a 10 mV smaller overpotential. In Zn-air battery testing, the N-doped catalyst shows a 0.86V voltage gap after 100 cycles, compared to a 1.01V gap in non-doped catalysts; this results in a round-trip efficiency of 54% for the N-doped catalyst and a 49% efficiency for the non-doped catalyst (**Figure 15B**). Although conventional Pt/C catalysts show better ORR performance, its poor charging and high overpotentials make it bifunctionally inferior compared to the CoMn₂O₄ N-doped catalyst. Mixed valences, higher oxygen adsorption sites, and stimulation of active sites due to N-doping may also contribute to the catalyst's performance, as well as the possibility of electron hopping within the catalyst, which could facilitate electron transfer during catalysis.

Figure 15. A) oxygen electrode activities of commercial Pt/C, rGO, N-rGO, CMO, CMO/rGO and CMO/N-rGO at 1600 rpm; B) cell voltage upon completion of each discharge and charge segment for CMO/rGO, CMO/N-rGO, and Pt/C catalysts. Reprinted from [73] with permission from Elsevier.

Although there is some risk of corrosion associated with the use of carbon in catalyst synthesis, not all carbon materials are created equal; depending on the structural configuration, carbon supports may vary in their cycling stability in OER potential ranges. As is common with many nano-structured materials, carbon nanotubes show promising structural stability; the addition of other materials such as nitrogen dopants may further increase this stability. N-doped carbon nanotubes encasing spinel Mn-Co oxides may be used to make a mixed-metal oxide catalyst with spinel metal structures either at the tip of the nanotube structure, strongly embedded inside the nanotube, or loosely agglomerated over the nanotube structure [74]. The formation of spinels inside the nanotubes ensures a strong connection between the metal and the carbon structure, maintaining the conductivity of the catalyst. As seen in **Figure 16**, heat treatment ruptures the tubes, exposing the metal oxide active sites embedded within. 4 such catalysts were synthesized by Zhao *et al.* using different heat treatment temperatures, from 300 to 600°C. Oxidation of the metal groups occurs at 300°C, occurring preferentially around mixed groups of Co and Mn. Although higher heat treatments and oxidation lead to a loss in weight, higher surface area and more defects, the ratio of Mn to Co is maintained at 1:2, indicating interaction between Mn and Co as a Mn-Co oxide spinel structure. There is a dramatic increase in the onset potential and reduction current of ruptured compared to non-ruptured nanotubes, indicating an overall improvement in the ORR as the active spinel structures within the NCNTs are exposed. Heat treatment itself increases bifunctional activity, boosting the electron transfer number from 3.4 to 3.8, and reducing occurrence of the 2-electron transfer reaction, as evidenced by a decrease in H₂O₂ production from 29% to 5%. The best catalyst is obtained at 500°C, with better ORR performance than IrO₂ and RuO₂ catalysts and an OER performance and stability similar to that

of RuO₂. This may be due to the relationship between the rupturing of the nanotubes in response to heat treatment, with higher temperatures ensuring a greater number of ruptures and therefore a greater number of exposed active sites.

Figure 16. Outline for synthesis of spinel Mn-Co oxide nanoparticles in NCNTs. A) NCNTs are grown using a Co-Mn-Al-Mg catalyst; B) poorly contacted nanoparticles are removed with a mild acid wash; C) spinel oxide active sites are formed by oxidative cutting at elevated temperatures. Reprinted (adapted) with permission from [74]. Copyright © 2014 American Chemical Society.

Nanotubes themselves provide benefit to catalyst performance and stability, even without N-doping, evidenced by NCNT/Co_xMn_{1-x}O, a catalyst made by the growth of metal salts on carbon nanotubes (NCNT) during hydrothermal treatment (**Figure 17**)[75]. The catalyst exhibits a low OER overpotential of 0.34 V at 10 mAcm⁻², compared to 0.39 V in commercial IrO₂, and a faster reaction rate. In addition, the catalyst's ORR performance is comparable to that of commercial 20% Pt/C catalysts. However, in terms of stability, the NCNT/Co_xMn_{1-x}O catalysts is superior to Pt/C; where the mixed-metal catalyst can maintain a current density at 0.85 V for 20,000 s with little change, Pt/C loses 20% of its activity.

Figure 17. A) Schematic for synthesis of NCNT/Co_xMn_{1-x}O; B) SEM image and C) TEM image of the synthesized NCNT/Co_xMn_{1-x}O catalyst. Reprinted from [75] with permission from Elsevier.

Similarly, another MnCo₂O₄ catalyst was synthesized with carbon nanotubes for applications in Zn-air batteries, using a hydrothermal method with Co and Mn nitrate precursors [76]. The resulting MnCo₂O₄ structure is dual-phase between cubic (77%) and tetragonal (23%) spinel phases, with crystal particles ranging between 30 and 60nm in length, slightly larger than other synthesis methods. The presence of cubic spinel phase uses Co³⁺ ions inside its octahedral sites, rendering them inaccessible as OER active sites; thus, the tetragonal phases in the synthesized catalysts helps retain activity, as it prevents the incorporation of all Co³⁺ ions into the cubic spinel lattice. Where Co ions are largely involved in the OER, it is believed that the Mn⁴⁺/Mn³⁺ redox couple plays a larger role in the ORR, suggesting good bifunctional activity for this mixed oxide catalyst. Carbon supports were also introduced with the hope that Mn-N-C interactions can reduce electron cloud density around Mn, thus facilitating the desired redox

couple. This was done by calcination on carbon nanotubes (CNT) and hydrothermal treatments to form N-doped reduced graphene oxide, N-rGO. A positive shift in binding energies for Mn leads to the preferential accumulation of Mn on the surface of the $\text{MnCo}_2\text{O}_4/\text{CNT}$ catalyst, improving the ORR activity. Prior to addition of N-rGO, the catalyst's ORR behavior is very similar to that of commercial Pt/C catalysts; the introduction of a carbon source, especially CNTs, results in further improvement, with ORR onset potentials of -0.11 and -0.09 V for CNTs and N-rGO mixed oxide catalysts, respectively, compared to Pt/C onset potential of -0.09V (**Figure 18A**). The hybrid catalysts also shows good OER performance, with onset potentials of 0.53 and 0.59 V for hybrid CNT and N-rGO catalysts, respectively (**Figure 18B**). Stability tests in a Zn-air battery show the $\text{MnCo}_2\text{O}_4/\text{CNT}$ hybrid catalyst to be fairly stable, able to sustain a current for 64 charge/discharge cycles, or 768 hours, with only a 0.08 and 0.13 mV/h degradation rate for the discharge and charge, respectively. This is in comparison to a Pt/C catalyst, which degrades after 9 cycles with rates as high as 3 mV/hour (**Figure 18C**).

Figure 18. A) RDE oxygen reduction polarization curves and B) RDE oxygen evolution polarization curves of *dp*-MnCo₂O₄, *dp*-MnCo₂O₄/CNT hybrid, *dp*-MnCo₂O₄/N-rGO hybrid, mechanically mixed *dp*-MnCo₂O₄ + CNT, CNT, N-rGO, and Pt/C in a 0.1 M KOH aqueous solution, with the rotating rate of 2000 rpm. C) Cycling performance of rechargeable zinc–air batteries with *dp*-MnCo₂O₄/CNT hybrid and Pt/C catalysts as the cathode. Reprinted (adapted) with permission from [76]. Copyright © 2014 American Chemical Society.

Synthesis Technique Development

For many bifunctional catalysts, synthesis requires a large amount of energy and little finesse, due to the high amount of heat needed to transform and activate the catalyst during pyrolysis. This usually imposes limitations to the catalyst, as too little heat leads to an incomplete reaction of precursors while too much heat degrades precursors into materials that are unusable or hinder activity through reduced conduction. Although alternative techniques such as sol-gel and organic co-precipitation exist, large particle sizes still limit surface area, especially in the Mn spinel structures that are good for catalysts. Cheng *et al.* developed a unique synthesis method for bifunctional catalysts that involves the reduction of amorphous MnO₂ precursors in an alkaline aqueous solution with metal cations M²⁺, such as Co²⁺, to form an electrocatalyst [77]. Amorphous MnO₂ forms linked MnO₆ octahedral structures, facilitating lattice formation; furthermore, any octahedral MnO₆ that is retained after reduction can still be used in the catalyst as an active moiety. By this method, two different Co_xMn_{3-x}O₄ spinels, CoMnO-P and CoMnO-B, have been made using different reductants. CoMnO-B has a tetragonal crystal structure, while

CoMnO-P forms a cubic spinel phase with some traces of birnessite, and a more shrunken lattice than CoMnO-B, indicating ionic vacancies. During spinel formation, CoMnO-P increases in particle size, while CoMnO-B retains its size and assumes a porous structure due to hydrogen bubbles forming as MnO_2 reacts with the reductant, BH_4^- . From these comparisons, it can be inferred that stronger reducing agents result in a tetragonal spinel structure, while weaker reducing agents create a cubic phase with some remaining birnessite. The surface areas of both CoMnO-B and CoMnO-P are higher than tetragonal and cubic spinels prepared by the traditional heat treatment method, and display higher numbers of defects. Koutecky-Levich plots also indicate a quasi-four-electron process with CoMnO-P showing the best number compared to traditionally prepared catalysts. The newly synthesized samples outperform their heat-treated counterparts in the ORR, with more positive onset potentials and larger current values, as well as the OER. CoMnO-B performs almost 2 times better than CoMnO-P, while CoMnO-P is the superior catalysts for the ORR. Of more importance, however, is their comparison to state-of-the-art precious-metal catalysts. In the ORR, performance is very close to that of Pt/C catalysts; with the addition of dopants, catalytic performance could be improved even more. The catalysts also shows good performance in neutral media, and CoMnO-P shows promise in applications with Zn-air batteries by making a stable discharge curve with considerable specific energy density. The improved performance in the ORR of CoMnO-P could be due to the stronger affinity for oxygen-binding in the cubic phase than the tetragonal phase. Co ions show strong binding with oxygen, but in cubic structures the bond is much stronger than that of tetragonal structures, forming an M-O_2 bond (**Figure 19**). Although the cubic and tetragonal structures have the same number of active sites, the cubic structure has a smaller unit cell area; this means that

for a given surface area there is a higher density of ORR active sites, giving the cubic structure better intrinsic ORR activity.

Aside from producing highly promising catalysts, the synthesis method used here is fairly efficient, forming product within 5 minutes where others can take hours or days. Furthermore, the resulting spinel product is high in purity due to the lowered energy barrier of amorphous MnO_2 precursor. By selecting different reducing agents and modifying precursor shape, there is some degree of control over catalyst; for instance, wire-like Co-Mn-O nanostructures can be produced by using MnO_2 nanowire precursors. Cheng further proposes a mechanism to this new synthesis process; the reduction of MnO_2 into Mn_3O_4 in the absence of other metal ions shows a negative free Gibb's energy, indicating thermodynamic feasibility. A comparison can be drawn between this reaction and the reduction of MnO_2 in the presence of other metal ions, where some MnO_2 is reduced to either Mn^{3+} or Mn^{2+} , while the rest of the amorphous MnO_2 forms a spinel structure, where the metal ion diffuses and replaces Mn ions spontaneously. This technique can also be used to form other mixed-metal catalysts using Zn and Mg as the metal ions.

Figure 19. Schematic representation of A) tetragonal and B) cubic spinels; C-D) Corresponding density of states of bare and O₂-adsorbed spinels. Reprinted by permission from Macmillan Publishers Ltd: [77].

Manganese-Nickel Oxides

Since nickel-based catalysts have not been found to perform very well in the ORR, it has been applied with other transition metal catalysts to compensate. In addition, nickel's capability as an OER catalyst could make up for manganese's lower OER capabilities. This approach was taken with α -MnO_x catalyst to be applied in Li-air batteries[78]. Surprisingly, doping Ni ions into MnO_x structures can enhance the reduction of oxygen, despite nickel normally being weak in the ORR; such behaviors were further studied with α -Mn oxide catalysts of varying structures. α -Mn oxide catalysts are believed to be effective for ORR due to the high number of defects and hydroxide present. α - MnO₂ nanorods, nanowires and dendrites prepared by solvent-free and reflux methods and treated under high and low temperatures were compared, as well as their performance with and without Ni doping (**Figure 20**). All preparations have tetragonal cryptomelane structure, a tunnel structure formed by negatively charged Mn oxide ions (**Figure 20A**). However, solvent-free nanorods have the smallest particles, while dendrites have the largest. The solvent-free nanorods also have the largest pore volumes and surface area, and smallest pore size; in addition, they have the lowest oxidation states present in higher numbers

than expected; this may be due to a higher amount of oxygen defects present. However, the inherent mixed valency of α - MnO_2 suggests that Mn oxidation states of (III), (IV) and possibly (II) are also present in the oxide framework. ORR activity was measured and shows that low heat-treated nanorod and dendrite catalysts have lower limiting current densities than solvent-free nanorods (**Figure 20E**). When Ni^{2+} was doped into the solvent-free nanorod, there was a decrease in pore size and volume and an increase the exchange current density (**Figure 20F, G**). Ni^{2+} lowers the amount of $\text{Mn}^{3+}/\text{Mn}^{4+}$ couples, which is detrimental to the catalyst; however, this is most likely overshadowed by an increase in conductivity due to the Ni^{2+} that leads to the increased exchange current density and limiting current density, which is a net benefit for Li-air batteries. Doping with Ni also increases the rate of hydrogen peroxide decomposition, which is formed from the 2-electron transfer pathway for the ORR; while pure MnO_2 nanorod catalysts decompose hydrogen peroxide at a rate of about $0.53 \text{ s}^{-1}\text{g}^{-1}$, the addition of Ni drastically raises that rate up to about $2.7 \text{ s}^{-1}\text{g}^{-1}$, highly desirable for a bifunctional catalyst.

Figure 20. SEM images depicting morphology of α -MnO₂ catalysts: A) reflux, inset: Structure of α -MnO₂ (cryptomelane), B) nanowire, C) dendrite, and D) solvent-free. Background corrected oxygen reduction RDV scans of E) pure cryptomelane catalysts F) nanorodSF (solid line) and Ni-nanorodSF (dashed line) in 1 M KOH vs SCE ($\nu = 5 \text{ mV s}^{-1}$) and G) the corresponding Tafel plots. Reprinted (adapted) with permission from [78]. Copyright © 2011 American Chemical Society.

3.1.2. Cobalt-Containing Binary Oxide Electrocatalysts

Similarly to manganese, cobalt could also benefit from being paired with other metals to create a bifunctional catalysts that has the best traits from both metals; in particular, while cobalt contributes good OER performance and stability, its ORR performance and conductivity could be improved. Not only are there different types of metals to compare when improving catalytic behavior, but again there is the factor of synthesis methods and materials to take into account. Various designs and preparation techniques for mixed oxide electrocatalysts are compared by Nikolova et al, wherein 4 different catalysts are prepared by either thermal decomposition, vacuum co-evaporation or electrochemical deposition[79]. $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ is prepared as a powder, Co-Te-O and Co-Ni-Te-O are prepared as vacuum evaporated thin films, and $\text{Co}_x\text{O}_y/\text{ZrO}_2$ is prepared as an electrodeposited thin film. It is found that depending on the precursor used, the crystal sizes and surface areas of the prepared catalysts can be varied, as in $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$, for instance: although all Cu-containing catalysts have spinel structure, use of carbonate precursors results in a catalyst with smaller crystal sizes and higher surface area, as compared to using nitrate as a precursor. In Ni-containing catalysts, by varying the ratio of Co and Ni to Te, as well as the ratio of Co to Ni, the resulting catalysts can either be amorphous or nanocrystalline in

structure, with mixed-valence Te/Te^{4+} present, or cubic CoO embedded in an amorphous matrix with no Te^{4+} present. In $\text{Co}_x\text{O}_y/\text{ZrO}_2$, it is found that Co^{2+} exists as two types, CoZrO_3 and Co_3O_4 ; the amount of each oxidation state can be varied by heat treatment temperature, with the occurrence of Co^{3+} increasing with higher heat. CV tests show that several different conversion reactions take place within the catalysts, depending on their structure; Cu-containing catalysts have one conversion reaction taking place, $\text{CoO}_2/\text{CoOOH}$, whereas CoTeO catalysts has several conversion reactions including CoO/CoOOH , CoO/CoO_2 and $\text{Co}(\text{OH})_2/\text{CoO}_2$. CoO/ZrO_2 films deposited on stainless steel show no contributions made to the reaction by ZrO_2 , making the catalyst based only on transitions of CoO to various Co oxidation states including Co^{2+} , Co^{3+} and Co^{4+} . Thin film catalysts have broad CV curves indicating a highly porous or rough surface which is absent in chemically synthesized catalysts, further showing the difference in catalyst surfaces depending on preparation method. When comparing potential differences between the catalysts, the nitrate-precursor $\text{Cu}_{0.2}\text{Co}_{2.8}\text{O}_4$ catalyst has the lowest potential difference, with Cu-containing powder catalysts having the highest performance in both the ORR and the OER; Co-Te-O catalysts has the lowest performance, and is not optimal for operations in air. However, it should be noted that powder catalysts are typically present in much higher amounts on the electrode, as the catalyst loading is considerably higher than thin-film deposited catalysts. The high-performing $\text{Cu}_{0.2}\text{Co}_{2.8}\text{O}_4$ was further tested in a metal-hydride battery at $20 \text{ mA}/\text{cm}^2$ for 200 cycles; the catalyst shows almost no loss in performance for the anode side over 200 cycles, while the cathode side shows degradation by over 100 mV over 200 cycles.

Cobalt-Nickel Oxides

As with manganese-nickel oxide catalysts, cobalt-nickel oxide catalysts have also been made in attempts to improve the conductivity and overall performance of Co-based catalysts [80-

85]. A $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ catalyst was synthesized on Ni foil to study the influence of the amount of Ni-doping on bifunctional activity, and to find the optimal amount of nickel to use in binary oxide catalysts [86]. By varying the ratio of Ni to Co precursors, it is shown that not all of the Ni is incorporated into the catalyst's spinel structure along with Co, with some Ni being retained as ions. The addition of Ni to the catalyst improves the ORR half-wave potentials and terminal current densities from basic Co_3O_4 by 0.76V and $0.16\text{mA}/\text{cm}^2$, respectively. In comparison to a 20% Pt/C film catalyst, although the Pt/C catalyst has a 0.072V more positive onset potential, the half-wave potential and current density of the Ni-doped catalyst is much improved. It was also tested as to whether the Ni foil support influenced the behavior of the catalysts; although powdered $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$ catalysts show a high electron transfer number of 3.9, its ORR performance is not as good as the catalyst on Ni foil, suggesting improved conductivity by the Ni foil. In the OER, the $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$ catalyst outperforms both 20% Pt/C and 20% Ir/C catalysts, making this sample very successful as a bifunctional catalyst. The main OER catalyst in this case is the Ni foil, but the spinel oxide film also contributes to OER activity, improving the onset potential from 1.6V to 1.57V. For realistic applications the catalyst was tested for methanol tolerance, as many state-of-the-art catalysts are prone to methanol poisoning; this is evidenced by the 46% decrease in Pt/C current density after exposure to methanol, compared to a mere 6% decrease in current density in the $\text{Ni}_{0.6}\text{Co}_{2.4}\text{O}_4$. Optimization of the amount of Ni precursor used in synthesis reveals that both the ORR and the OER perform best in catalysts that contain the least amount of Ni, despite the presence of Ni showing improved activity over plain Co_3O_4 catalysts. The catalyst with the best bifunctional activity, having a potential difference of 0.96V, is $\text{Ni}_{0.4}\text{Co}_{2.6}\text{O}_4$; this competes with Ir/C's potential difference of 0.92V. The increased presence of Ni increases the relative electrochemical surface area and BET surface area, and may also lead

to a decrease in crystal size and a subsequently greater loss in O_2 during heat treatment. Why then does the catalyst with the lowest Ni content have the best performance? There may be a trade-off in the decreased particle size, as smaller crystallite sizes could decrease conductivity, thus hindering electron transfer. This is further supported by the apparent loss in conductivity in catalysts with a Ni content between 0.5 and 0.6. This loss in conductivity may be due to the metal oxide transitioning from semi-conductor to semi-metallic behavior, or perhaps the presence of NiO particulates within the spinel structure of higher Ni-content catalysts, but the exact reason for this is as of yet unknown.

Ni-Co mixed metal catalysts are popular for their high abundance, good conductivity, and high stability. Further work on synthesis techniques could improve catalysts by altering the distribution of metal cations and controlling oxidation states. For instance, Prabu, Ketpang and Shanmugam refined the synthesis of 1-dimensional $NiCo_2O_4$ nanostructures using an electrospinning method, varying precursors and weight ratios[87]. All catalysts have cubic spinel structure; however, using metal nitrate precursors during synthesis results in interconnected agglomerated clusters of particles while metal acetylacetonate precursors results in hierarchical nanostructures such as nanorods and nanotubes. Higher concentrations of metal precursors and the carbon precursor polyacrylonitrile (PAN) increase the viscosity such that the resulting product is a thick gel with dispersed nodes. Ni, Co and O_2 are evenly distributed throughout the catalyst, especially those with nanostructured morphology. Mixed valences are present in all catalysts, but interestingly, the ratio of Ni^{2+} to Ni^{3+} can be altered depending on the amounts of precursors used in synthesis; although there is more Ni^{3+} than Ni^{2+} in all catalysts, catalysts made with metal nitrate precursors, denoted NCO-N, have the most Ni^{2+} while catalysts made with metal acetylacetonate precursors, denoted NCO-A, have the least Ni^{2+} . In ORR tests, NCO-A

type catalysts display a more positive onset potential than NCO-N type catalysts, by 20 to 40 mV, but is still behind commercial Pt/C catalysts. Promisingly, Koutecky-Levich plots suggest that the nanostructured catalysts undergo the ORR by the more efficient 4-electron transfer route. The best performer is NCO-A, with a half-wave potential of 0.78 V and good mass activity. It also shows high OER activity, its current density of 10 mA/cm² at 1.62 V being comparable to commercial Ir/C and Ru/C OER catalysts. This performance is also reportedly higher than previously made NiCo₂O₄ catalysts with graphene[88]. This is most likely due to the nanotube structures, which increase porosity and inter-particle connectivity. Acetylacetonate precursor catalysts also have resistivities up to 3 times lower than that of nitrate precursor catalysts. As this would suggest, the acetylacetonate precursor catalyst NCO-A has the best bifunctional activity, with the lowest potential difference between the ORR and OER at 0.84 V. Tests of NCO-A in Zn-air batteries show good rechargability, with an initial charge/discharge voltage gap of 0.7 V and a final voltage gap of 0.84 V after 50 cycles. Its discharge capacity is also comparable to other CoO/N-CNT catalysts used in Zn-air batteries at a value of 580 mA h/g.

The amounts and ratios of each metal used in mixed-oxide electrocatalysts can influence the behavior of the catalyst, so it is helpful to learn more about how to manipulate them with synthesis methods and precursor amounts. A NiCo₂O₄ mixed oxide catalyst spinel made using a KIT-6 silica template impregnated with Ni and Co nitrate precursors demonstrates how catalyst loading influences performance[80]. The test of performance comes in charge-discharge curves in Li-O₂ batteries using the catalyst in varying amounts at a current density of 0.1 mA/cm². Specific capacity of the battery increases as catalyst amount versus Ketjen Black increases until it reaches a peak, before decreasing again; although the NiCo₂O₄ catalyst may have a higher electrocatalytic activity than Ketjen Black, there is a tradeoff between the improved activity and

smaller surface area, which eventually negates any benefits. 20% NiCo_2O_4 loading obtained the best specific capacity at 4357 mAh/g, much higher than other NiCo_2O_4 catalysts using nanoflakes or nanowire arrays. 45% catalyst loading has the highest cycling performance, with an efficiency of 65.3%; although it does not have a specific capacity as high as the 20% catalyst test, it is the second highest, at 4120 mAh/g. This is an improvement to simple Ketjen Black-based batteries, which lose capacity retention after 12 cycles (Figure 21). XRD examination of the catalyst during charge and discharge indicates the formation of deposits on the catalyst during discharge, which are then reduced and almost absent after recharge. However, the disappearance of the deposits is not complete, and there is an incomplete recovery in morphology for the catalyst; this may either be due to the inability of the catalyst to decompose reversible Li_2O_2 discharge products, of the formation of irreversible electrolyte decomposition products on the surface (Figure 21 D-E). The complete composition of the deposits is not fully clear as of yet.

Figure 21. A) The first discharge-charge curves and B) cycling performance for 5 cycles of Li-O₂ batteries with different contents of OM NiCo₂O₄/KB and KB electrodes with a voltage restriction of 2.0-4.3 V at a current density of 0.1 mA cm⁻². SEM images of C) as-prepared ordered 3D mesoporous NiCo₂O₄, D) OM NiCo₂O₄/KB electrode before discharge, and D) after first recharge. Reprinted from [80] with permission from Elsevier.

These catalysts may also benefit from having more unique structures, which can be manipulated to make the best of the metals' base properties. This can be seen in the use of metal-organic frameworks and other carbon-based supports, which can increase catalyst surface area and electron transfer[89, 90]. For instance, structures have been made using zeolitic imidazolate frameworks (ZIF) to create double-shelled nanocages (DSNC), which can have varying compositions between each shell layer [91]. ZIF templates containing cobalt may be mixed in solution with nickel precursors to create a DSNC with nickel oxides found on the outer shell, and cobalt oxides dispersed throughout. This structure has proven beneficial, as these catalysts display superior stability and lower overpotentials compared to single-shelled nanocages. The inclusion of nickel oxides improves catalytic capabilities even more, due to the increase in active sites as Ni²⁺ is incorporated into the cobalt spinel structure; over 12,000 cycles, nickel-containing DSNCs lose only 7.5% capacity, whereas nickel-containing single-shelled nanocages lose 16.6% and nickel-free DSNCs lose 24.2% capacity. The benefit of DSNCs is believed to lie in its structural stability and ability to house electrolyte between its shells to aid in electron transfer.

Cobalt-Iron Oxides

In nature, water splitting is carried out through a light-driven process, as seen in photosynthesis. These photochemical properties are present in many transition metals due to their ability to change oxidation states so readily, and can be used to supplement potential-driven electrochemical processes[92]. Two such catalysts that contain mixed oxides of Co and Fe compare whether crystalline (CIO-1) or amorphous (CIO-2) structures display better photocatalytic abilities (**Figure 22**)[93]. CIO-1 follows the inverse spinel cubic CoFe_2O_4 , while CIO-2 is truly amorphous with an approximate formula of $\text{CoFe}_2\text{O}_{3.66}$ and a much higher surface area. CIO-2 contains more Co^{3+} than CIO-1, suggesting better ORR performance. Fe is present in many forms, Fe^{2+} and Fe^{3+} , as well as $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . The catalysts were first tested for photochemical water oxidation properties (OER) with the use of photosensitizer $[\text{Ru}(\text{bpy})_3](\text{II})$ and electron acceptor $\text{Na}_2\text{S}_2\text{O}_8$. CIO-2 produces the most O_2 by far, with 60mmol/mole of catalyst being produced after 200s as compared to 16 in CIO-1. However, both catalysts display superior photochemical oxidative activity as compared to commercial single metal Fe and Co oxides, and display a higher efficiency, with mass activity 3 times better in CIO-1 and 11 times better in CIO-2. The strong behavior of CIO-2 is not only due to high surface area, but also due to the higher levels of Co^{3+} , which play a role in water oxidation. Although the photochemical properties of these catalysts is beneficial, they are not sufficient alone, as necessary electron acceptors and photosensitizers are much less stable than the catalysts themselves. However, CIO-2 also shows superior abilities in electrochemically driven OER, attaining a current density of 400mA/mg where CIO-1 only reaches 370mA/mg. The ORR performance of the CIO was rather low; therefore, the CIO catalysts were deposited as 20% on Vulcan X-72 carbon. Surprisingly, the amorphous CIO-2 shows a high ORR efficiency, which is uncommon for amorphous mixed

metal oxides [94]. This activity is also shown to be relatively stable, with a 92% efficiency in CIO-1 and a 94% efficiency in CIO-2 after 100 minutes.

Figure 22. Scheme for preparation and accompanying TEM images of A) CIO-2 and B) CIO-1, with inset diffraction patterns. Reprinted (adapted) with permission from [93]. Copyright © 2014 American Chemical Society.

Co-Fe mixed oxide catalysts have also been considered as good bifunctional catalysts when used in conjunction with other supports such as a MOF [95]; a MOF(Co/Fe) electrocatalysts prepared by a hydrothermal process is capable of producing an ORR current density of 1.19 mA cm^{-2} with a given potential of 0.3V; it also displays some OER activity, with a current density of 0.38 mA cm^{-2} given a potential of 0.75V. Compared to carbon black, this is almost 79 times greater for the OER, and 17 times greater for the ORR. The ORR activity is

linked to the reduction of Fe^{3+} to Fe^{2+} ; however, the mechanism of the ORR is uncertain, with several possible pathways depending on the potential. At more negative potentials, a 4-electron transfer pathway is more likely to occur. Despite the uncertainty in its mechanism, this catalyst is stable and shows a high surface area; further insight into its mechanism, as well as the kinetics of the ORR and the OER in the catalyst could possibly help to improve its performance further.

3.1.3. Nickel-Iron Binary Oxide Electrocatalysts

When discussing nickel oxide electrocatalysts, it was seen that nickel had poor ORR activity, and low stability due to the change in nickel's valency and structure. However, these flaws can be reduced by incorporating iron into nickel catalysts [96]. For instance, nickel catalysts made with the addition of iron have led to a greater stability and OER activity than commercial Ir-based catalysts [97-99]. The interaction between iron and nickel suppresses nickel's transition between $\text{Ni}^{2+}/\text{Ni}^{3+}$, stabilizing active sites. The oxidation state of nickel can be controlled, as the addition of more iron generally leads to the presence of more Ni^{2+} [43, 100]. Nickel-iron catalysts are very prone to degradation at high temperatures, making it difficult to create active nickel-iron catalysts with high surface area through traditional heat-treatment methods. Therefore, a synthesis method has been developed by mixing Ni and Fe precursors with the surfactant Tween 85 [99]. The presence of the surfactant helps to maintain a more porous catalyst structure during heat treatment, thus increasing the effective surface area. Testing of the OER for synthesized catalysts determine the optimum ratio of nickel to iron content to be 85:15; at higher iron contents, the OER performance deteriorates until it is all but absent at ratios over 70:30.

3.1.4. Mixed Oxide Electrocatalysts Using Transition and Non-Transition Metals

Transition metal oxides are not the only materials being considered as alternatives to precious metal electrocatalysts; other materials like organics and perovskites have also made considerable progress. The combination of transition metal oxides with carbon-based supports has already been shown to have beneficial effects on the strength and conductivity of catalysts; similarly, combination of transition metal oxides with other metal oxides may also have positive results. Although not a transition metal, zinc is commonly used in battery applications, due to its oxidative properties; it has also been used in metal-organic framework electrocatalysts [80, 101]. A catalyst using mixed Zn and Co oxides as a cathode material for Li-air batteries was made with the goal of reducing the buildup of unwanted solid discharge products, which is a common issue in Li batteries[102]. The resulting ZnCo_2O_4 catalyst had a ternary cubic spinel structure; this structure displays highly mesoporous features, which can accommodate Li_2O_2 discharge materials. In ORR performance, the ZnCo_2O_4 catalyst cannot compete with commercial 20% Pt/C catalysts, in both onset potential and limiting current density; however, the catalyst does have a better OER performance close to similar Ni-containing catalysts [88]. In Li- O_2 coin-battery tests, the ZnCo_2O_4 lends a round-trip efficiency of 65%, and reversible cycling for 30 cycles. Furthermore, the Li- O_2 battery has an energy density 103% higher than commercial Li-ion batteries; despite imperfect performance, the Li- O_2 battery still has the ability to outperform today's standard Li-ion batteries in certain areas. Further improvements to this design could lead to catalyst with even higher energy densities, as well as improved ORR onset potentials and current densities.

3.2 Ternary Transition Metal Oxide Catalysts

Though there has been more research on binary mixed metal oxides, there has still been some work using more complicated mixed metal structures as bifunctional catalysts. If binary mixed-

metal oxides can provide more benefit than the individual metal oxides, it is possible that the introduction of more metal oxides could continue this trend, either through the combination of separate precursors, or by metal doping. A majority of work done on ternary oxide catalysts for the ORR and the OER has included the use of precious metals such as platinum, palladium and iridium, as well as the mixture of other non-transition metals; few of it has yet to be applied to bifunctional catalysts, mostly focusing on either the ORR or the OER [103]. However, what information there is can still prove useful as work continues on creating catalysts without the use of precious metals. The introduction of a third species of metal to electrocatalysts can increase activity in the ORR and/or the OER, mostly due to the alteration of the electronic structure of the active sites, increasing the release of products and making active sites available more quickly. It can also decrease costs of production by substituting a portion of more expensive material with a cheaper one [103-107].

Research on tertiary transition metal oxide electrocatalysts was done by Koninck, Manseau and Marsan using CuCo_2O_4 on Nb-doped TiO_2 nanoparticles as conductive supports for use in Zn-air batteries [108]. The TiO_2 supports replace the role of carbon supports in increasing conductivity, while also playing a direct role in the electrocatalytic activity of the catalyst. Ti-based materials have high conductive abilities and good stability, and the presence of Nb with Ti can further enhance the electrochemical stability of precious metal catalysts [109, 110]. Several different catalysts are made by pairing them with Nb-doped TiO_2 nanoparticles with varying degrees of Nb-doping and annealing temperatures. Higher annealing temperatures are associated with more rutile phase crystal structures in un-doped TiO_2 , accompanied by enhanced particle crystallinity, while Nb-doped TiO_2 display more rutile transitions at lower temperatures. Interestingly, higher levels of Nb-doping result in smaller particle sizes, which may be helpful in

creating high surface area electrocatalysts. While normal TiO_2 is typically dominated by Ti^{4+} , more Nb-doping is reported to introduce Ti^{3+} oxidation states, as well as traces of Ti^{2+} and Ti^0 . The support is desired to have low H_2 evolution (HER) activity and preferably good OER activity. In anatase-phase samples, an affinity is seen for the HER; however increased Nb-doping shows a decrease in this activity. The reduction of Nb^{5+} to Nb^{4+} , which is more prevalent in higher Nb-doped supports, helps to suppress Nb- TiO_2 contributions towards the HER. Nb-doped rutile phase structures show the largest range of electrochemical stability, but Nb-doped anatase phases prepared at lower temperatures are also considered, as they too have a large stability range. Testing for individual ORR and OER activity of the Nb- TiO_2 show that some ORR activity is present as a 2-electron transfer mechanism. The rutile phase sample produces more HO_2^- during this process than the anatase phase, but higher competition with the HER is detrimental towards bifunctional activity. Anatase and rutile $\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$ used with a CuCo_2O_4 electrocatalyst compared to individual CuCo_2O_4 and Ebonex Ti show that where individual TiO_2 -based samples show next to no OER performance, the combination of CuCo_2O_4 with either $\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$ or Ebonex show the highest activity, due to the activity of Co cation active sites. The carbon-supported catalyst appear to perform well, but after normalizing for surface area it performs the lowest. In the ORR, however, the carbon-supported catalyst has a more positive peak potential due to cooperative reduction mechanisms by both the Vulcan and the CuCo_2O_4 , whereas the Ebonex and $\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$ contribute less to the ORR; however this shift is small, between 5 to 30 mV, and when looking at long term applications the carbon supported catalyst is characterized by a much more rapid decrease in activity compared to the others. Between the two synthesized $\text{Nb}_{0.05}\text{Ti}_{0.95}\text{O}_2$ supports, the low temperature anatase phase has a greater ORR activity, suggesting a small contribution by the support towards the ORR. The use of Ti based

supports is also associated with the ability to maintain intrinsic current density at high potentials, at a higher amount than the carbon-supported catalyst.

Perovskites are unique oxides that have garnered much attention in electrocatalytic applications, and several reviews have already been written summarizing their progress as electrocatalysts [111, 112]. They have shown to be proficient bifunctional electrocatalysts on their own, and are consistently being improved, with some of the best perovskite-based electrocatalysts rivaling precious metal catalysts [113-123]. A mixed-metal catalyst containing MnO_2 and the perovskite LaCoO_3 has been made, which was compared with a fluorite-related catalysts using MnO_2 and Nd_3IrO_7 [124]. Both are also used to study the role of K^+ intercalation in metal oxide catalysts' bifunctional activity. Although the Nd_3IrO_7 catalyst contains precious metal Ir, what is of interest in this work is the behavior of MnO_2 - LaCoO_3 . The goal of mixing MnO_2 with more unique mixed oxide structures such as perovskites is to couple the good ORR of MnO_2 and OER of perovskites, while negating their respective poor OER and ORR abilities. Comparing their individual components, the fluorite and MnO_2 catalysts have similar onset potentials of 750mV and peaks of 300 and 500mV for the ORR, respectively, while the perovskite shows next to no ORR activity due to sluggish electron transport kinetics.

However, both fluorite- and perovskite- MnO_2 catalysts show ORR peak potentials near 480mV, due to the reduction of Mn^{4+} to Mn^{3+} . The reduction current densities are also higher than each individual component. In the OER, MnO_2 - LaCoO_3 shows a decrease in overpotentials and Tafel slopes when compared with individual oxides, and a lower overpotential than the mixed-precious metal oxide catalysts MnO_2 - Nd_3IrO_7 at 440mV compared to 510mV. In terms of stability, fresh MnO_2 - LaCoO_3 has a higher stability than the fluorite-based catalyst, with only a 19mV increase in potential after 2 hours compared to a 141mV increase in the same time frame.

The insertion of K^+ into catalyst structures may recover lost bifunctional activity due to high cycling [125]; knowledge of this phenomenon is expanded by studying whether it is specific to K^+ , whether it can improve initial bifunctional activity, and whether different methods of K^+ intercalation vary in effect. MnO_2 - $LaCoO_3$ shows improved initial ORR performance, with a current density 3 times higher as compared to intercalation with other hydroxides; both K^+ and Cs^+ shows the ability to improve the OER potential of MnO_2 - $LaCoO_3$ by an order of magnitude. This could be due to an increased hydrophilicity of the catalyst, facilitating interaction with O_2 and the OER. The apparently higher efficacy of K^+ compared to other ions may be due to vacancies; intercalation may occur in vacancies created during electrode potential cycling and the reduction of Mn^{4+} to Mn^{3+} . Since K^+ is much larger than Mn^{4+} , intercalation may induce lattice distortion which may in turn effect the binding energies or provide adsorption sites for ORR and OER intermediate species. Potential-driven intercalation (PDI) is one method of inserting K^+ into catalysts, and is faster than conventional methods. The PDI process can still improve the performance of the catalysts, with ORR peak potentials shifting from 465 to 635mV in MnO_2 - $LaCoO_3$ after 6 cycles, and improving OER current densities. Furthermore, this shift is much more dramatic in MnO_2 - $LaCoO_3$ as compared to MnO_2 - Nd_3IrO_7 , and there is a higher OER shift seen in PDI as compared to conventional K^+ intercalation methods, resulting in a current density of $14\text{mA}/\text{cm}^2$ as compared to $9.5\text{mA}/\text{cm}^2$. Intercalation is also improves the performance of individual oxide catalysts, making it a promising method of bifunctional activity recovery in other electrocatalysts. PDI activation is beneficial to efficiency, reducing OER potentials between 110 and 152 mV in both catalysts. Furthermore, the stability of MnO_2 - Nd_3IrO_7 is increased after PDI activation, with an average potential loss being lowered from 70.5mV/h to 10mV/h. Compared to other bifunctional catalysts reported in other works, these

two catalysts show very good activity, with $\text{MnO}_2\text{-LaCoO}_3$ OER activity superior to that of conventional precious-metal catalysts, despite still showing comparatively lower ORR activity.

One of the biggest hurdles that limits progress for more complex mixed-oxide catalysts is structural; as more species are added into the composition of the catalysts, it becomes more difficult to control their distribution. Since structure plays a large role in the behavior of catalysts, this is a challenge. In addition, many existing methods for making amorphous materials are not overly compatible with multiple-oxide mixtures. A new method developed by Smith et al. involves making amorphous mixed-metal oxide structures using photochemical metal-organic deposition techniques, PMOD, demonstrated on a Fe-Co-Ni oxide catalyst [126]. First, $\text{Fe(III)2-ethylhexanoate}$ precursors were used to make a $\alpha\text{-Fe}_2\text{O}_3$ thin film, which was then irradiated with 185 and 254-nm light and annealed at 100°C . The intensity of the annealing temperature lends some degree of control over the thickness and amount of defects present in the $\alpha\text{-Fe}_2\text{O}_3$ film, as well as the level of porosity. PMOD was then carried out to make several mixed metal oxides including $\alpha\text{-Fe}_{50}\text{Co}_{50}\text{O}_x$, $\alpha\text{-Fe}_{50}\text{Ni}_{50}\text{O}_x$, and $\alpha\text{-Fe}_{33}\text{Co}_{33}\text{Ni}_{33}\text{O}_x$. These structures have an even distribution of metal oxides throughout the catalyst, in contrast to conventional thermal and coprecipitation techniques, which often lead to phase separations. The mixed oxide catalysts display improved kinetics for the OER compared to single oxide catalysts, and lower Tafel slopes in Fe-containing catalysts evidences increased catalytic efficiencies at higher potentials. Despite results in this research being limited to the OER, Smith et al. introduces a new room-temperature synthesis technique for amorphous mixed-metal oxides that may make it easier for further research to be done in the field of ternary and higher mixed metal oxide bifunctional electrocatalysts.

Another synthesis method that would benefit ternary oxide catalysts is a coprecipitation method demonstrated with TeO_2 , Co and Ni at room temperature [127]. All precursors are evaporated in crucibles and deposited onto C-Ni based gas diffusion membranes that provide conductivity support, then heated. Two different catalyst compositions were studied, labeled GDE1 and GDE2 (for gas-diffusion electrode), both having amorphous structure. In particular, GDE1 contains much more Co than Ni and more Co and Ni combined than Te compared to GDE2. While some Co is present as Co^{2+} , CoO dominates the composition of the structure. Interestingly, Ni is not detectable on the surface of the catalyst, but is found within the catalyst as Ni^{2+} ; likewise, while only Te^{4+} is detected on the surface, Te^0 can be found within the catalyst. This confirms the reaction of TeO_2 with elemental Co and Ni to form new Co and Ni oxides in the catalyst, resulting in a catalyst of mixed Ni, Co and Te oxides. ORR behavior of GDE1 and GDE2 results in an average Tafel slope of 66 and 59 mV/decade, as well as 128 and 50 mV/decade for the OER. GDE1 has higher Tafel slopes for both the OER and the ORR, and a greater difference between the OER and ORR than GDE2. This may be due to a difference in the mechanism of the anodic reaction between the two catalysts; however, the exact mechanism is as of yet unknown. Comparing OER and ORR behavior, a pattern appears where the GDE catalyst with better OER has lower ORR, and vice versa. The higher OER activity corresponds to a Ni-rich catalyst compared to Co, while the opposite is seen for a high ORR performer. Although Te it does not display capabilities of being a catalyst on its own, Te and TeO do show some minor electrocatalytic activity for both the ORR and the OER. Comparing the GDE with NiCo_2O_4 made by sol-gel methods and $\text{NiO}\cdot\text{CoO}$ by low temperature synthesis, GDM does not have the highest apparent current density for a given potential, but it has by far the superior mass activity, with 328 mA mg/cm^2 compared to the next highest value of 115 in the sol-gel synthesized

catalyst. The significant superiority in mass activity for mixed metal oxide catalysts is a hopeful sign that further improvements on their design and synthesis could improve other aspects of their performance.

4. Summary and perspective

Research into creating catalysts for electrochemical reactions, particularly for the reduction and oxidation of oxygen, has been maintained as a promising field for the commercialization of alternative forms of energy. Current technologies in fuel cells and metal-air batteries are a luxury, widely unavailable to the majority of people due to the high expense and rarity of their materials, as well as the relatively low performance and stability of these materials in comparison to current common forms of energy. To reduce cost and increase the capabilities of metal-air batteries and fuel cells for commercial use, much work has been focused on using transition metal oxides in bifunctional catalysts; their unique electrical properties and abundance of oxidation states and structures gives a wide amount of diversity in catalyst synthesis that is helpful in discovering how these catalysts work, and what factors influence their performance. Despite this, transition metal oxide catalysts often suffer from poor conductivity, and subsequently display inferior onset potentials and limiting current densities than current precious metal catalysts; however, the higher levels of stability and smaller potential differences in some currently synthesized transition metal catalysts show promise, and a better understanding of how these catalysts work could eventually lead them to surpass precious metal catalysts. Indeed, research has already led to methods that can help bridge these gaps. So far, promising breakthroughs have been made in increasing the conductivity and efficiency of these catalysts, allowing them to run longer at higher levels of current output; by combining transition metal active catalytic sites with other more conductive materials such as carbon, metal-organic

frameworks, stainless steel or titanium, the mass activity of these catalysts has been improved. In some cases, the onset potentials and current densities of transition metal catalysts combined with organic supports surpass those of precious metal catalysts. In addition, the introduction of vacancies and the insertion of dopants such as nitrogen have also been used to alter the electronic structure of transition metal catalysts, improving their stability and half-wave potentials for the ORR and the OER.

The structure of electrocatalysts has been a common theme throughout this review; many aspects of catalyst structure have been observed to accompany changes in performance, from surface area and porosity, to lattice structure, to chemical composition of the catalyst. As follows from this observation, synthesis techniques also have a direct relationship to catalyst performance, as the synthesis technique affects the structure of the resulting catalyst. In general, higher catalyst performance has been associated with higher surface areas and greater porosity; this is a natural conclusion, as a greater surface area would indicate a higher level of accessible active sites. Porosity also increases access to active sites, as well as providing a space to accommodate for the accumulation of deposits when used in scenarios such as Li-air batteries. The accessible area of synthesized catalysts is related to heat treatment temperatures, where higher temperatures increase performance up to a point, until the heat is so great that it degrades the sample. The use of various precursors and solvents also affect particle sizes of catalysts when using solvothermal synthesis techniques. When observing the organization and structure of catalysts, structures that facilitate the transfer of electrons and ions have performed well as catalysts, including amorphous structures; in addition, tunneled structures such as can be seen in manganese oxides are beneficial to catalyst performance, as they can accommodate and release species such as oxygen and water.

The mechanism of the ORR and the OER at the transition metal active sites is not fully understood yet, but the use of methods such as density functional theory have allowed us to gain greater understanding. In cobalt oxide catalysts, for instance, it has been observed that the amount of oxidation states present in the catalyst is related to the performance of the catalyst in the ORR and the OER; higher levels of Co^{3+} indicate higher OER activity while higher Co^{2+} indicates higher ORR activity, and high ratios of $\text{Co}^{3+}/\text{Co}^{2+}$ correspond to higher bifunctional activity; similarly, other metal oxide redox couples have been tentatively linked to either ORR or OER activity, with the exception of nickel, which seems to undergo more than one redox reaction through the course of the OER.

Much research has been focused on manganese and cobalt oxides in bifunctional catalysts, either alone or in conjunction with other metals, due to their high abundance and intrinsically superior bifunctionality. Many mixed-oxide catalysts are also based on the combination of manganese and cobalt; as mixed-oxide catalysts seem to combine the traits of the mixed species, taking the two most active individual bifunctional catalysts and combining them makes sense. However, other mixed-oxide catalysts exist, including those using nickel and iron, as well as some that use sulfur, copper or titanium [81, 128, 129]. Very little research exists that explores ternary or more mixed-oxide catalysts, as they are difficult to synthesize and control, but some groundwork has been laid by discovering new synthesis techniques that will facilitate the production of more complex mixed-oxide catalysts including solvothermal, electrospinning, and deposition techniques performed at low temperatures.

Up to this moment, many catalysts have been made that exceed the performance of current materials in at least one category, but the difficulty is producing a catalyst that has the best of all worlds, with superior ORR and OER activity while also being stable and low cost. Though this

can be improved through the use of conduction enhancers and doping, work still needs to be made to find a compromise between high conductivity, bifunctionality, and stability. There has been some work done in this respect already, with the avoidance of carbon structures, which could corrode, in favor of other materials like stainless steel, though these are far fewer. The use of dopants has been a very promising avenue for improving the electronic properties of transition metal catalysts, as seen with the use of nitrogen, as well as other dopants including potassium and niobium ions that have been used in a handful of research projects; this may become the standard, as dopants can be used along with several other methods of conductivity and stability improvement.

Focus has also been made on understanding the mechanisms behind the catalytic activity of these metal oxides, as well as the influence of geometry on catalytic performance. As such, a certain amount of intricacy is required in catalyst synthesis which may not be possible with many current techniques used, such as calcification and heat treatment techniques. Therefore, a fair portion of research into this topic has been focused on honing and developing different methods of synthesis. As ternary metal catalysts using precious metals have already been demonstrated to improve stability and catalytic activity, it would most likely be beneficial to apply this research to transition metals, and may be the key to surpassing precious metal catalysts. However, this would first require improved synthesis techniques. Synthesis methods that do not require heat treatment may be a more viable route for further research; although heat treatment methods are common and show the ability to improve results, there is very little finesse or control over particle size or lattice structure with this brute-force method. Furthermore, based on current research on ternary and more complex mixed-metal catalysts, the heat treatment technique is not

conducive to structures with more than two metals, with solvent-based and deposition methods appearing more viable.

Although there appears to be a bright future for electrocatalysts, we are not currently to a point where cheap and abundant catalysts can be used in commercial application. Until then, precious metals like platinum and iridium will continue to be used; however, we may be able to bridge the gap between our current catalysts and precious metal-free catalysts for the time being by combining precious metals with metal oxides. This can cut the cost of the catalyst by lowering the required amount of precious metals, and may also provide the added stability of the transition metal oxides. With its ability to be paired with other materials in this way, transition metal oxides can be introduced into regular use incrementally until precious metals are no longer needed. This will most likely be achieved by a combination of techniques, including the use of composite carbon –transition metal materials and the addition of dopants to increase conductivity; the synthesis of complex catalysts using multiple transition metal oxides; and a greater understanding of active site structure to optimize the rate of catalysis through the synthesis of desirable crystal structures.

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Graphitic Table