Rational Design of Spinel Oxide Nanocomposites with Tailored Electrochemical Oxygen Evolution and Reduction Reactions for Zinc-Air Batteries

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Abstract: The unique physical and chemical properties of spinels have made them highly suitable electrocatalysts in oxygen evolution reaction and oxygen reduction reaction (OER & ORR). Zinc-air batteries (ZABs), which are safer and more cost-effective power sources than commercial lithium-ion batteries, hinge on ORR and OER. The slow kinetics of the air electrode reduce its high theoretical energy density and specific capacity, which limits its practical applications. Thus, tuning the performance of the electrocatalyst and cathode architecture is vital for improving the performance of ZABs, which calls for exploring spinel, a material that delivers improved performance. However, the structure–activity relationship of spinel is still unclear because there is a lack of extensive information about it. This study was performed to address the promising potential of spinel as the bifunctional electrocatalyst in ZABs based on an in-depth understanding of spinel structure and active sites at the atomic level.

Keywords: spinel; oxygen reduction reaction; oxygen evolution reaction; zinc–air battery; bifunctional electrocatalysts

1. Introduction

The dominance of fossil fuels in energy production has become a massive problem in modern societies because of the resultant global warming and climate change. Because energy obtained from renewable sources faces challenges such as season, climate, and location dependency, the ability to store this energy for uninterrupted use is indispensable if demand is to be met. These circumstances introduce the role of electrochemical energy technology in converting and storing sustainable energy [1–5]. In the quest to store energy from renewable sources, metal–air batteries have been gaining attention because of their safety; they also use abundantly present oxygen as the cathode source, and they have 2–10 times the higher theoretical energy density than commercial lithium-ion batteries [6–9].

Compared with other metal-air batteries, zinc–air batteries (ZABs) demonstrate superiority owing to their higher safety, their minimal environmental impact, the abundance of zinc, their cost-effectiveness, and their theoretical specific capacity of 820 Ah kg$^{-1}$ and specific energy of 1084 Wh kg$^{-1}$ [10–13].

Generally, the oxygen evolution reaction and oxygen reduction reaction (OER and ORR) at ZAB cathodes are sluggish owing to complex electron transfer [14–17], and this results in higher
overpotential at the cathode than the anode. Because ORR is the surface reaction, O2 is reduced to OH− or H2O2 on the electrode surface after the electron is acquired. The ORR mechanism can happen in two ways: (1) In a two-electron transfer reaction, O2 reduces to OH− in two steps, and (2) in a four-electron transfer reaction, the oxygen reduction happens in one step. The former reaction is more feasible, and the latter is more effective because it avoids the byproduct of H2O2. Practically, the overpotential of OER is higher than that of ORR due to the formation of hydroxide, oxide, and oxy-hydroxide intermediates during the process, and overcoming the overpotential in ORR through four-electron transfer is quite difficult as well.

OER is the tailback of the electrochemical reactions because of the four proton-coupled electron transfers and the generation of an O=O bond. Thus, there is a need for a bifunctional electrocatalyst that catalyzes both the OER and ORR for large-scale applications of these reactions in energy devices [18,19]. Investigators have been using noble metal-based electrocatalysts such as Pt, RuO2, and IrO2 in zinc–air batteries to master the overpotential issues; however, the lower abundance, high cost, and reduced long-term durability of these materials hinder their usage [20]. With a focus on efficient performance, cost-effectiveness, and abundance as the criteria for a better electrocatalyst, transition-metal oxides are gaining more attention for their reactions in energy storage devices, particularly in metal–air batteries [21].

Spinel-structured transition-metal oxides with the formula AB2O4 (A, B = Fe, Co, Ni, Mn, Zn, Cu, and so on), as shown in Figure 1, can be in A3O4 type single-metal oxide, A4B3−xO4 type binary-metal oxide, and AxB3−yC3−x−yO4 type ternary-metal oxide forms. Spinel-based compounds consist of oxygen atoms (32) and one or two transition metals (eight in A site and 16 in B site) with a wide range of valence states. At the A site, one metal is surrounded by the four nearest neighboring oxygen atoms, and the B site has a metal that is surrounded by the six nearest neighboring oxygen atoms. In the spinel frame, A is the divalent cation, B is the trivalent cation, and O is an anion; generally, the spinel structure is classified into three types based on the occupancy of cations, whereas the anions are always accommodated by the polyhedral vertexes. The varieties of spinel are normal, inverse, and mixed spinel.

**Figure 1.** Normal spinel structure of Co2MnO4. Component structures, namely, tetrahedral and octahedral, are shown on the right-hand side [22]. Copyright 2010, AIP Publishing.

In normal spinel, A2+ has low crystal field stabilization energy (CFSE) and occupies tetrahedral sites. B3+ has high CFSE and occupies octahedral sites. It is represented as \((A^{2+})_{tet}(B^{3+})_{oct}O_4\). In inverse spinel, A2+ has high CFSE and occupies octahedral sites, and B3+ has low CFSE and occupies some
octahedral and some tetrahedral sites. It is represented as \((B^{3+})_{\text{tet}}(A^{2+}B^{3+})_{\text{oct}}O_4\). The complex spinel is the intermediate between the normal and inverse spinel structure in which both \(A^{2+}\) and \(B^{3+}\) cations partially occupy the two various sites [23,24]. Among the three types, normal spinel structures are generally cubic close-packed oxides with two tetrahedral and four octahedral sites per formula unit. \(B^{3+}\) ions occupy half the octahedral holes, and \(A^{2+}\) ions occupy one-eighth of the tetrahedral holes. The tetragonal phase presents the different sets of active lattice planes ready for the \(O_2\) adsorption and desorption process, which differs from the cubic phase.

Spinel have gained more attention due to their easy synthesis methods, stability, structural flexibility, and a minimum of two orders of magnitude higher electrical conductivity than the equivalent single-metal oxide and helpful contributions from all A and B ions with multiple valence states (\(A^{3+}/A^{2+}\) and \(B^{3+}/B^{2+}\)) in the crystal structure [25]. Hence, spinel-based materials possess fair electrochemical activity. Particularly, in the key ZAB reactions such as ORR and OER kinetics (Figure 2), the adsorption and reduction of \(O_2\) vastly depend on the d-orbitals of cations placed in octahedral B sites relative to tetrahedral A sites. This phenomenon occurs due to the substantial overlap of the high lying \(e_g\)-3d orbital in the octahedrally coordinated metal cations with an orbital of \(O\) 2p and the weak overlap of the 3d orbital in the tetrahedrally coordinated metal cations with an oxygen atom [26].

Figure 2. Schematic representation of the role of spinels in a Zn–air battery (ZAB).

Based on the molecular orbital theory, the presence of octahedral site active cations in, \(e_g\)orbital accounts for spinel activity [27]. Thus, the structural flexibility and variable valence states of the spinel oxides demonstrate the potential to fine-tune their catalytic performance in zinc–air batteries. To date, several researchers have investigated spinel-based bifunctional oxygen electrocatalysts for ZABs. In this review, we summarize the role of spinel-based compounds as the bifunctional oxygen electrocatalysts for ZABs with a brief introduction and discussion of the batteries’ mechanism along with the mechanism in the air cathode.

1.1. Zinc–Air Battery

In 1878, Maiche proposed the primary Zn–air battery, which provided the highest available energy density in the group of primary battery systems. In the beginning, researchers used silver wire as the air
In 1878, Maiche proposed the primary Zn–air battery, which provided the highest available energy density compared to other primary batteries. These batteries are not commercially available due to poor battery efficiency. These reasons restrict the use of acidic electrolytes in ZABs. Neutral electrolytes are not commonly used because of their low conductivity and because they are less friendly toward oxygen electrocatalysis than alkaline electrolytes. In general, to carry out the ion transportation between the Zn anode and air cathode, alkaline electrolytes such as KOH or NaOH have been used widely in ZABs because of the better ionic conductivity and high Zn reaction kinetics. The acidic electrolyte reacts with the Zn anode and produces hydrogen; this leads to zinc corrosion, shape change, and production of heat, and results in poor battery efficiency. These reasons restrict the use of acidic electrolytes in ZABs. Neutral electrolytes are not commonly used because of their low conductivity and because they are less friendly toward oxygen electrocatalysis than alkaline electrolytes. In secondary ZABs, the negative anode, positive cathode, electrolyte, and membrane separator are electrochemically coupled, as shown in Figure 3a,b. The anode for alkaline secondary ZABs is a zinc electrode in the form of zinc metal foil, zinc powder, or zinc fiber, and the air electrode has two layers, the gas diffusion, and catalytic layers. There is a three-phase (solid-liquid-gas) reaction at the cathode. Here, the diffusion layer provides the physical support for the catalyst and runway for the passage of electrons to be collected as the current; the hydrophobic section of the gas diffusion layer has to permit the liquid electrolyte as well as protect the electrolyte from leaking out. Thus, an optimal gas–electrolyte–catalyst three-phase interface is required.

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As the battery discharges, in the anode, the zinc reacts with hydroxide and oxidizes to form zincate ion, and this process continues until the zincate ion is supersaturated; then, it decomposes to insoluble white zinc oxide powder and precipitates on the active zinc surface.
ZnO powder produced makes the active area less active. Simultaneously, in the cathode, the pressure gradient induces O\textsubscript{2} entry through the diffusion layer and reduction to hydroxyl ions at the catalytic layer by reacting with water and electrons. Hence, oxygen is reduced during battery discharging (ORR) and oxidized (OER) during charging. Along with O\textsubscript{2}, CO\textsubscript{2} enters the cathode and forms carbonates by reacting with KOH. This formation clogs the pore and restricts the entry of air to the cathode. These mechanisms are shown in Equations (1)–(6) [38].

Discharge condition

**Zinc electrode:**

\[
\text{Zn(s)} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2e^- \quad (1)
\]
\[
\text{Zn}^{2+}_{(\text{aq})} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-}_{(\text{aq})} \quad (2)
\]
\[
\text{Zn(OH)}_4^{2-}_{(\text{aq})} \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{OH}^- \quad (E^0 = -1.25 \text{ V vs. SHE}) \quad (3)
\]

**Air electrode:**

\[
\text{O}_2(\text{g}) + 2\text{H}_2\text{O}_{(\text{aq})} + 4e^- \rightarrow 4\text{OH}^-_{(\text{aq})} \quad (E^0 = 0.401 \text{ V vs. SHE}) \quad (4)
\]

**Overall reaction:**

\[
2\text{Zn}_{(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}_{(s)} \quad \text{(Cell potential: 1.65 V)} \quad (5)
\]

**Parasitic carbonate formation:**

\[
2\text{KOH}_{(\text{aq})} + \text{CO}_2(\text{g})/\text{K}_2\text{CO}_3(s) + \text{H}_2\text{O}_{(\text{aq})} \quad (6)
\]

### 1.3. Cathode Mechanism

In S-ZABs, two types of electrode arrangements are available, a three-electrode system with a separate electrode for OER and ORR, or a two-electrode system that uses the same electrode for OER and ORR. The second system is more commonly used, in which the electrochemical reactions occur at the bifunctional air cathode [39,40]. The benefits are that using a single electrocatalyst for the two reactions reduces the cost and eliminates the side effects that come with using two catalysts. The redox reaction at the cathode corresponds to the charging and discharging of the battery. In the cathode, oxygen reduction and evolution take place, which involves a series of complex electrochemical reactions, either the Langmuir–Hinshelwood (LH) or the Eley–Rideal (ER) pathway; in the first one, intermediates react on the surface, and in the second, the electrolyte reacts with the surface intermediate. Due to the lower reaction energy barrier, many researchers have theoretically studied OER and ORR based on the ER mechanism, which takes one of two reaction paths, with either two or four electrons depending on the electron transferred during the reduction of O\textsubscript{2} on the catalyst [41–43]. The four-electron transfer is the direct dissociation of an O–O bond without any byproduct, which requires more energy to dissociate O\textsubscript{2}.

Two-electron transfer dissociates O\textsubscript{2} by generating intermediate species of HO\textsubscript{2}\textsuperscript{−} or H\textsubscript{2}O\textsubscript{2}. Among these two, four-electron transfer is more capable because it does not spend its energy in byproduct formation.

In an alkaline electrolyte,

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad \text{(Four-electron transfer)} \quad (7)
\]
\[
\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^- \quad \text{(Two-electron transfer)} \quad (8)
\]
\[
\text{H}_2\text{O} + \text{HO}_2^- + 2e^- \rightarrow 3\text{OH}^- \quad (9)
\]
During charging, OER occurs in which the formed hydroxyl ions give away electrons and $O_2$ forms. As in ORR, intermediates also form, such as hydroxide, oxide, and oxy-hydride. The four elementary steps of the OER mechanism are described as follows:

$$\text{OH}^- + M \rightarrow \text{MOH}_{\text{ads}} + e^- \quad (10)$$

$$\text{MOH}_{\text{ads}} + \text{OH}^- \rightarrow \text{MO}_{\text{ads}} + \text{H}_2\text{O}(l) + e^- \quad (11)$$

$$\text{MO}_{\text{ads}} + \text{OH}^- \rightarrow \text{MOOH}_{\text{ads}} + e^- \quad (12)$$

$$\text{MOOH}_{\text{ads}} + \text{OH}^- \rightarrow M + O_2(g) + \text{H}_2\text{O}(l) + e^- \quad (13)$$

Figure 4a,b depicts a schematic illustration of the gas diffusion layer, the part of the air cathode at which the oxygen electrocatalysis takes place, and the OER and ORR reaction pathways of NiCo/Pyri-NG in multiple steps. The round-trip efficiency of rechargeable ZAB decreases because of the overpotential at the cathode, and the cell potential decreases as well. These complex intermediate reactions must be accelerated to achieve ZABs with commercial value.

![Figure 4](image)

**Figure 4.** (a) Schematic illustration of fabricating a self-supported Co$_3$O$_4$/Ni/Gas Diffusion Layer [44]. Copyright 2019, Elsevier. (b) Oxygen reduction reaction (ORR, clockwise), and oxygen evolution reaction (OER, anticlockwise) mechanisms for NiCo/Pyri-NG, where pyridinic N bonds with surface three-fold coordinated Co [45]. Copyright 2018, John Wiley and Sons.

### 2. Spinels as an Electrocatalyst

Spinel-based materials exhibit better catalysis because of their controllable composition, structure, valence, and morphology. In particular, transition metal oxides with a spinel structure have received attention as catalysts for ORR and OER because these structures enable good electrical conductivity due to the ready electron hopping between metals at different valence states. The spinel structure also provides surface redox centers for oxygen adsorption and stimulation. The existence of the different transition metals in the interlaced structure of the spinel-based transition-metal oxides is the reason for the high electrocatalytic activity because it is well established that the catalytically energetic element always governs the surface [46]. In addition to spinel, other structural forms can be used as substitute electrocatalysts. However, their usage has been limited because of the high synthesis temperature of perovskite oxides (ABO$_3$) [47], the properties of metal–organic frameworks such as electrical insulating and bad stability in electrolytes [48], the difficulty in raising the concentration of active sites in graphene [49], and the poor OER activity of metal–N-decorated nanocarbon materials [17]. Even the noble metals rarely possess bifunctional electrocatalytic activity for both ORR and OER [50,51].

Therefore, spinel-based compounds with their diverse compositions, bifunctional catalytic activity, and low cost are suitable oxygen electrocatalysts. Synergism between the elements in the structure, spinel frame, compositing, and the supporting material escalates the electrocatalytic activity. Above
and beyond, the incorporated cations can form redox couples for the favored catalytic actions. To date, materials with cobalt, manganese, nickel, copper, and iron in spinel structure are widely used as oxygen electrocatalysts in ZABs. Since 1980 Co$_3$O$_4$ has been widely investigated as an electrocatalyst owing to its chemical and physical properties. The efficiency of electron transport between the Co$^{2+}$ and Co$^{3+}$ ions promotes catalytic activity in an alkaline medium. The spinel structures with Cobalt in the octahedral sites are more resourceful for the OER and ORR [52,53]. Co$_3$O$_4$, with the advantages of high activity and stability, has been identified as a catalytically active material for air batteries [54–56].

To further improve the catalytic performance, the active sites in the single metal oxide should be increased by adding other metals while synthesizing the spinel structure. For example, MnCo$_2$O$_4$, NiCo$_2$O$_4$, CuCo$_2$O$_4$, and MnFe$_2$O$_4$ have been reported as active catalysts for air batteries [57–61]. The above-mentioned spinel structures as the electrocatalyst for Zinc–air batteries are discussed in the following sections.

### 2.1. MnCo$_2$O$_4$ Spinels

To date, many cationic distributions of MnCo$_2$O$_4$, such as Co$^{2+}$[Co$^{2+}$Mn$^{4+}$]O$_4$ and Co$^{3+}$[Mn$^{2+}$Co$^{3+}$]O$_4$, have been proposed. Through different synthetic methods, these cations can be tuned to enhance the physical, physicochemical, and interfacial properties. Besides the porosity and surface area, they offer a fast pathway for electrolyte/electron diffusion and more electroactive sites [62]. Tatsumi Ishihara et al. studied mesoporous MnCo$_2$O$_4$ spinel oxide because it consisted of two transition metals in a lattice; thus, they expected high ORR/OER activity because the catalytically active element always dominantes on the surface. The authors prepared mesoporous MnCo$_2$O$_4$ by a hard template method with mesoporous silica as an inorganic template. This process formed material with more surface area, an average pore size of 2 nm, and lower overpotential in ORR/OER. Ishihara et al. then evaluated the material’s catalyzing property in a ZAB with 4 M KOH aqueous electrolyte and Hg/HgO as a standard electrode, and it showed a capacity of about 700 mAh/g-Zn, discharge potential of 1.05 V, and could withstand more than 200 charge–discharge cycles [46].

Cui Shenghai et al. coated carbon on MnCo$_2$O$_4$ nanowire by self-templating from a NiCo$_2$O$_4$-nitrogen triacetic acid (MnCo$_2$-NTA) nanowire precursor. The resulting material, MnCo$_2$O$_4$@C, showed better ORR than MnCo$_2$O$_4$. The authors proposed that the improved ORR was attributable to the conductivity of MnCo$_2$O$_4$@C nanowire, where the carbon layer helped in the electron movement of MnCo$_2$O$_4$ nanoparticles, thereby decreasing the charge transfer resistance. Additionally, the porous texture and large surface promoted the diffusion of mass transfer and enlarged the triple-phase contact area, and the rigid carbon shell provided mechanical strength to gain progressed stability. The evaluated bifunctionality $\Delta E$, which is a small difference, is the reason for excellent reversibility in oxygen electrocatalysis. The authors obtained galvanostatic charge–discharge plots at 10 mA cm$^{-2}$ and power density status that revealed admirable stability of 70 h in a homemade ZAB (Figure 5) [54].

A combination of spinel compounds and N-doped carbon enriches the electrocatalytic activity of ORR and OER. Duan et al. adopted this strategy and achieved good OER activity of MnCo$_2$O$_4$ because OER and ORR are the core components of ZABs. Therefore, the authors decorated MnCo$_2$O$_4$ on the N-doped macroporous carbon nanofiber arrays (MnCo$_2$O$_4$/NMCNA). The researchers synthesized the macroporous carbon nanofiber array (MCNA) using the surfactant-templating self-assembly of organic resol and a natural crab shell comprising a well-aligned porous macrostructure as a hard template; they attained an interpenetrating ordered array. The pores were larger in the pristine form than in the MnCo$_2$O$_4$/NMCNA; the authors analyzed the porosity by N$_2$ adsorption-desorption and confirmed microporous structure formation.

Chao Wei et al. stated that the $e_g$ occupancy of the active cation in the octahedral site is the activity descriptor for the ORR/OER of spinels, consolidating the role of electron orbital filling in metal oxide catalysis. The spinel structure affords multiple sites for transition-metal cations and an extensive range of valence states to give rise to a large number of oxides. In this work, the researchers varied
the temperature to tune the electronic structure of MnCo$_2$O$_4$ cubic spinels, which they prepared by solid-state chemistry. Activity on spinel as a function of the Mn valence state of the active element at the octahedral site resulted in a volcano shape, as displayed in Figure 6a,b. Hence, it was demonstrated that $e_g$ theory applies to not only the perovskite family but also to the spinel family [63].

2.2. CuCo$_2$O$_4$ Spinels

The spinel structures with cobalt in the octahedral sites are more resourceful for the OER and ORR, and copper-based materials have exhibited excellent ORR and OER catalytic activity due to the intense interfacial contact of Cu and its surroundings [64,65]. In Cheng et al.’s work, nitrogen-doped carbon nanotubes were ornamented by spinel CuCo$_2$O$_4$ quantum dots (CuCo$_2$O$_4$/N-CNTs) with successful Co$_3$O$_4$ doping without changing its crystalline structure. Carbon nanotubes (CNTs) are used to confer high electrical conductivity, large surface area, and intrinsic flexibility. The CNTs are doped to solve the problem of weak catalytic performance. CuCo$_2$O$_4$/N-CNTs was tested in liquid alkaline and a solid-state electrolyte because of its ORR (onset potential of $-0.04$ V, the large diffusion-limited current density of $-5.53$ mA·cm$^{-2}$, and low Tafel slope of 76.53 mV·dec$^{-1}$) and OER ($-0.61$ V with a potential of 0.69 V to get 10 mA·cm$^{-2}$ and low Tafel slope of 118.80 mV·dec$^{-1}$ compared with Co$_3$O$_4$/N-CNTs, CuO/N-CNTs, and CuCo$_2$O$_4$). The capability of Cu and Co as ORR and OER catalysts gives a $\Delta E$
value of 0.90 V. It is evident from the analysis of the other materials that CuO/N-CNTs outperform the Co3O4/N-CNTs in ORR, and the reverse was true for OER.

Figure 6. (a) ORR and (b) OER activity on various spinels as a function of e_g occupancy of the active element at the octahedral site. The black circle represents cubic MnCo2O4 spinels with Mn as the active element. The red circle represents the Mn of tetragonal spinels (Mn2CoO4, Mn2.5Co0.5O4, and Mn3O4). The orange circle represents the Mn of ferrite. The green “up” triangle represents the Mn of cubic Li1.4Mn0.2O2 spinels. The blue diamond represents the Co of cubic spinels (Co3O4, ZnCo2O4, and CoFe2O4). The pink square represents the Ni of cubic spinels (NiCo2O4 and NiFe2O4) [63]. Copyright 2017, John Wiley and Sons.

To learn the role of the N-CNTs, researchers performed electrochemical impedance spectrum (EIS), electrochemical double-layer capacitance (Cdl), and XPS analysis. In the findings, with lower resistance (EIS) and greater capacitance (electrochemically active surface area) along with BET measurement (11.18 m² g⁻¹), N-CNT provided a large surface area and restricted the aggregation and bonding between N and Cu; additionally, Co offered pyridine nitrogen for good ORR by generating more catalytic sites in CuCo2O4. The catalytic process of CuCo2O4/N-CNT is illustrated in Figure 7. Further, the authors measured the chronoamperometry and chronopotentiometry to identify the stability and used a rotational ring disk electrode to identify the number of electrons transferred.

Methanol tolerance results are demonstrated as a control measure to examine the analyzed material as a stable catalyst for the ORR and ve high durability towards the poisoning of any oxidized products [39,41,66-68]; CuCo2O4/N-CNTs was found to be a promising oxygen electrocatalyst comparable with Pt/C (ORR) and IrO2 (OER) with a power density of 83.83 mW cm⁻² and energy density of 653.9 Wh kg⁻¹. Investigators tested the ZAB stability at 20 mA cm⁻², and after 24 h, both the Pt/IrO2 electrode and CuCo2O4/N-CNTs showed some slipping. CuCo2O4/N-CNTs, with their lower overpotential than that of noble metal electrodes, showed very stable charging and discharging potential even after 48 h [39].

To rectify the drawback of less surface area between the active material and the electrolyte in the carbon matrix, Xiaojun Wang et al. electrospun the CuCo2O4@C nanotubes via coaxial electrospinning. The researchers studied the morphology and nanostructure of the obtained cubic spinel-type CuCo2O4 by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images showed that CuCo2O4@C nanotubes formed with an ample number of pores with a rough texture and unremitting length; this could be the reason for the increased diffusion kinetics of hydroxide and the adsorption–desorption of oxygen. The TEM image showed the outer and inner diameters of the nanotube (130 nm and ~80 nm), wall thickness (25 nm), and double the active surface area, which enhanced the contact between hydroxyl, oxygen, and catalyst. The small CuCo2O4 nanoparticles increased the utilization rate. Figure 8 shows the uniform distribution of Cu, Co, O, C, and N with a hollow carbon substrate confirmed by TEM elemental mapping. The carbonization temperature varied from 700 to 900 °C. Compared with H-CuCo2O4 and L-CuCo2O4@C (higher and lower oxidation
temperature), CuCo$_2$O$_4$@C exhibited improved OER (low overpotential of 327 mV at 10 mA cm$^{-2}$), ORR (positive half-wave potential of 0.850 V), and electrochemically active surface area; CuCo$_2$O$_4$@C (313.8 cm$^2$), L-CuCo$_2$O$_4$@C (80.0 cm$^2$), and H-CuCo$_2$O$_4$ (61.3 cm$^2$) showed better interaction of reactants with the active surface area, as shown in Figure 9. The results showed the excellent catalytic activity of CuCo$_2$O$_4$@C. In the full cell test, the discharge–charge voltage gap of 0.79 V at 10 mA cm$^{-2}$ cycled up to 160 numbers for 80 h. The methanol tolerance of the material is higher than that of Pt. Additionally, N-doping and interconnected 1D open-ended nanotubes might play roles in oxygen catalysis and conductivity [66].

Figure 7. The catalytic process of CuCo$_2$O$_4$/N-CNTs [39]. Copyright 2017, John Wiley and Sons.

Figure 8. (a,b) Scanning electron microscopy (SEM) and (c,d) transmission electron microscopy (TEM) images of CuCo$_2$O$_4$@C. (e) TEM elemental mapping images of CuCo$_2$O$_4$@C [66]. Copyright 2017, American Chemical Society.
Figure 9. (a) ORR polarization curves of L-CuCo2O4@C, CuCo2O4@C, H-CuCo2O4, and Pt/C samples. (b) ORR polarization curves of the CuCo2O4@C nanotubes at different rotation speeds and the corresponding K–L plots at different potentials (inset). (c) ORR polarization curves of CuCo2O4@C and Pt/C samples before and after 3000 potential cycles. (d) OER polarization curves of L-CuCo2O4@C, CuCo2O4@C, H-CuCo2O4, IrO2, and the overpotential schematic at 10 mA cm⁻² (inset). (e) Tafel plots derived from (d). (f) OER polarization curves of CuCo2O4@C and IrO2 during the cycling durability test [66]. Copyright 2017, American Chemical Society.

2.3. NiCo2O4 Spinels

In the group of transition metals, nickel has emerged as one of the most hopeful electrocatalysts due to its exciting electronic properties and anticipated synergistic effect to alter surface properties of materials to dramatically favor electrocatalysis. The poor conductivity of electrons and noteworthy self-aggregation of Ni particles in the Nickel-based spinels control their application as electrocatalysts [69]. Bohong Chen et al. synthesized NiₓCo₃₋ₓO₄ (x = 1.25) on aminated carbon nanotubes (NH₂-CNTs) in a composition-controlled technique to rectify the above issues. NH₂-CNTs make the catalyst more active by providing conductivity and more surface area for fast charge transfer, and the easy diffusion of the catalyst. This took place through a hydrothermal reaction in the presence of nickel ions from Co₃O₄/NH₂-CNTs, in which the cation exchanged. Nickel ions amend the metal oxide nucleation and growth due to the hydrolysis difference between cobalt and nickel ions. This exchange does not change the size, crystal structure, and weight of the metal oxide. Nitrogen in NH₂-CNTs fastens the nanoparticles and, in so doing, improved the electronic coupling along with amine. As usual, the researchers verified ORR in N₂/O₂-saturated 0.1 M KOH electrolyte, and the O₂-saturated material performed better. Though its onset and half-wave potential were close to those of Pt/C, its limiting current density was more than in Pt/C. The researchers also confirmed the electron transfer number that resulted from the KL plot slope and rotating ring disk electrode technique. After ORR, investigators verified OER in O₂-saturated 0.1 M KOH solution and found that it has a small overpotential and Tafel slope. They analyzed the bifunctionality of NiₓCo₃₋ₓO₄/NH₂-CNTs from the ΔE, the difference in the potentials between ORR and OER (OER (the potential of the current density at 10 mA cm⁻² - E₁/₀) and ORR current density at 3 mA cm⁻²). ΔE of this material was lower than the best bifunctional electrocatalysts reported. There was a nil effect in the methanol tolerance test, as shown in Figure 10. NiₓCo₃₋ₓO₄/NH₂-CNTs was applied in a ZAB and exhibited a power density of 168 mW·cm⁻² and 100 charge–discharge cycles without a change in voltage [67].
At low temperature, NCO annealed at 250 °C changed to be Co(Tetrahedral)²⁺ as Ni ions were doped in the structure. Thus, the Co³⁺/Co²⁺ ratio was higher in the oxide samples synthesized at higher annealing temperatures. At low temperature, NCO annealed at 250 °C with high Ni³⁺/Ni²⁺ sites and low Co³⁺/Co²⁺ sites, and porous 2D nanosheets, which increased the surface area and exhibited superior OER and ORR (ΔE = 0.8 V of reduced value). The power density of the battery reached 166 mW cm⁻² [70].

2.4. Fe-Based Spinels

Mn–Fe-based spinels are highly electrocatalytically active for the cathode and anode redox reactions on oxygen electrodes. The increment of active sites ensures the further boosted catalytic efficacy [71]. Xiuju Wu et al. prepared spinel MnFe₂O₄/Fe hybrid nanoparticles in nitrogen-doped mesoporous hollow carbon nanospheres (Fe/Mn-N-C) by pyrolysis to increase the active centers with the addition of Fe. Though the spinel-built oxides showed good catalytic efficacy, the conductivity was inefficient. Here, the porous nature of the catalyst augments the OER and ORR activity of a transition metal spinel oxide.
was nearly the same as Pt for OER and better than Pt in terms of methanol tolerance, ORR, and ZAB (MNCO-01, FNCO-01, CNCO-01, and ZNCO-01), respectively. Due to the cation substitution in Ni and Co, the lattice expanded and contracted. The oxidation state of these doped metal ions (i.e., M0.1Ni0.9Co2O4 with M: Mn, Fe, Cu, and Zn) by hydrothermal and annealing processes. The authors synthesized ternary-spinel oxides (i.e., M0.1Ni0.9Co2O4 NPs, NiCo/NG, NiCo/NLG-270, and Pt/C, in 0.1 M KOH solution (rotation rate: 1600 rpm). (b) ORR half-wave potential of the hybrid catalysts with different contents of pyridinic and pyrrolic N bonded with Co ions, and Pt/C. (c) Comparison of the kinetic currents and the electron transfer number for the ORR process of the control samples, along with the corresponding contents of pyridinic and pyrrolic N bonded with Co. (d) ORR LSVs of NG, NLG-270, NiCo2O4 NPs, NiCo/NG, NiCo/NLG-270, and Pt/C, in 1 M KOH solution. (e) OER Tafel plots of the hybrid catalysts with different contents of pyridinic and pyrrolic N bonded with Co ions, and RuO2. (f) Comparison of the kinetic currents for the OER process of the control samples, along with the corresponding contents of pyridinic and pyrrolic N bonded with Co [45]. Copyright 2018, John Wiley and Sons.

The ORR and OER evaluation results showed that the material with a 2:1 ratio of Fe3+ to Mn2+ was nearly the same as Pt for OER and better than Pt in terms of methanol tolerance, ORR, and ZAB full cell tests. In ORR, Fe/Mn-N-C exhibited slightly more positive onset potential and half-wave potential and, surprisingly, much lower current density than Pt/C. TEM images suggested that the ordered graphitic carbon was responsible for good conductivity and high corrosion resistance and that the disordered carbon accommodated the number of M-Nx active centers. Although metal agglomeration somewhat increased the current density, the onset value was the same with and without its presence, demonstrating efficient methanol tolerance, durability, and cyclability. The power density of Fe/Mn-N-C (37 mW cm−2) and Pt/C (28 mW cm−2) exhibits its capacity as an excellent oxygen electrocatalyst [41]. Yu-Ju Chien et al. engineered a ternary-spinel oxide based on the octahedral site preference energy (OSPE) model; the OSPE is the difference between crystal field stabilization energies at octahedral and tetrahedral sites (CFSEoct and CFSEtet). The authors synthesized ternary-spinel oxides (i.e., M0.1Ni0.9Co2O4 with M: Mn, Fe, Cu, and Zn) by hydrothermal and annealing processes. The inverse spinel structure of NiCo2O4, in which Ni atoms were in the octahedral sites and Co atoms occupied both octahedral and tetrahedral sites, was confirmed by XRD. Further, the same spinel structures were found in Mn0.1Ni0.9Co2O4, Fe0.1Ni0.9Co2O4, Cu0.1Ni0.9Co2O4, and Zn0.1Ni0.9Co2O4 (MNCO-01, FNCO-01, CNCO-01, and ZNCO-01), respectively. Due to the cation substitution in Ni and Co, the lattice expanded and contracted. The oxidation state of these doped metal ions can alter the mean oxidation states of Ni and Co; therefore, the site preferences of all metallic ions can vary. The activity of the catalyst is based on the metal atoms’ occupancy sites in the spinel structure. The authors

Figure 11. (a) ORR linear sweep voltammetry (LSV) curves of NG, NLG-270, NiCo2O4 NPs, NiCo/NG, NiCo/NLG-270, and Pt/C, in 0.1 M KOH solution (rotation rate: 1600 rpm). (b) ORR half-wave potential of the hybrid catalysts with different contents of pyridinic and pyrrolic N bonded with Co ions, and Pt/C. (c) Comparison of the kinetic currents and the electron transfer number for the ORR process of the control samples, along with the corresponding contents of pyridinic and pyrrolic N bonded with Co. (d) ORR LSVs of NG, NLG-270, NiCo2O4 NPs, NiCo/NG, NiCo/NLG-270, and Pt/C, in 0.1 M KOH solution. (e) OER Tafel plots of the hybrid catalysts with different contents of pyridinic and pyrrolic N bonded with Co ions, and RuO2. (f) Comparison of the kinetic currents for the OER process of the control samples, along with the corresponding contents of pyridinic and pyrrolic N bonded with Co [45]. Copyright 2018, John Wiley and Sons.
calculated the OSPE following the crystal field theory, and there were more cations at the octahedral sites than at the tetrahedral sites at higher OSPE. The inverse spinel structure had Co\(^{2+}\) and Co\(^{3+}\) at the tetrahedral sites and Co\(^{3+}\), Ni\(^{2+}\), and Ni\(^{3+}\) at the octahedral sites. The abovementioned metals were doped by substituting for Co\(^{2+}\), Co\(^{3+}\), Ni\(^{2+}\), or Ni\(^{3+}\) based on their OSPE. The OSPE of the doped metals is given in Figure 12a [11].

![Figure 12](image)

**Figure 12.** (a) The Octahedral site preference energy (OSPE) diagram of Mn, Fe, Cu, and Zn ions at various oxidation states. (b) The discharge–charge profiles under galvanodynamic (1 mA cm\(^{-2}\)) mode and the corresponding power density profile for the ZAB using the FNCO-01-coated air electrode under ambient air and (c) the steady-state discharge–charge profile under galvanostatic (10 mA cm\(^{-2}\), 40 min per cycle) mode for a ZAB using the FNCO-01-coated air electrode in 6 M KOH and 0.2 M Zn(CH\(_2\)COO\(_2\))\(_2\) in ambient air [40]. Copyright 2013, Royal Society of Chemistry.

Surprisingly, Fe\(^{3+}\) in FNCO-01, with a small OSPE, substituted smoothly for Co\(^{3+}\), with an increased Co\(^{2+}/Co^{3+}\) ratio and decreased Ni\(^{2+}/Ni^{3+}\) (Fe\(^{3+}\) is replaced by Ni\(^{2+}\) because of large OSPE) FNCO-01 with better oxygen-evolving and oxygen-reducing activity because of its high voltammetric charge, onset potential of 1.503 V (vs. RHE), a relatively high order of ORR onset potential, and electron transfer number of 3.65. In the ZAB test, a rare phenomenon occurs because of the redox transitions of Ni and Co species prior to the OER (Figure 12b). In the current density vs. potential vs. power density graph, the cell voltage increases suddenly due to the high overpotential, and a much higher power density of 150 mW cm\(^{-2}\) occurs at a current density of 250 mA cm\(^{-2}\). The wettability of FNCO-01 with an anhydrous surface reduced the discharge cell voltages in the initial five cycles, and after 5–10 charge–discharge cycles, OER improved the wettability of catalysts at nearly 100 cycles without any change (Figure 12c) [40].

In the above reports, researchers designed various spinel structured cathode materials with different morphologies and compositions that greatly improved their OER and ORR performance. Table 1 summarizes the recent research on the bifunctional electrocatalytic activity of the spinel-structured compounds in ZABs, and Figure 13 presents the ZAB power densities for the varied spinels as the electrocatalysts. In summary, spinel-based compounds that consist of Ni, Mn, Cu, and Fe at the A site and Co, Mn, Fe, Ni at the B site with oxygen at the X site have been widely used in ZABs as electrocatalysts. Other halogens can replace the X site, for instance, selenide, sulfide, and nitride. With the better bifunctional activity of spinels, strategies such as improving porosity and surface area, nanostructuring, carbon coating, doping with nitrogen, phase change, etc., could greatly improve the catalytic activity.
Table 1. Summary of OER/ORR performance of recently reported bifunctional spinel electrocatalysts.

| Spinel Feature | ORR | OER | ZAB |
|----------------|-----|-----|-----|
| Electrolyte (OER & ORR) | *E assat [V vs. RHE] | *E half [V vs. RHE] | *J [mA cm⁻²] | *νOER [mV] | *νOER Tafel [mV dec⁻¹] | Electrolyte (Battery) | ΔE (V) | Power Density [mW cm⁻²] | Cycles | Ref no |
| NiCo₂O₄ | 0.1 M KOH | 0.96 | 0.82 | 5.55 | 3.96 | 1570 | 88 | 6 M KOH with 0.2 M ZnCl₂ | 0.75 | 30 | 100 | [45] |
| MnFe₂O₄ | 0.1 M KOH | - | - | 6.0 | 3.9 | 360 | 60 | 6 M KOH and 0.2 M ZnOAc₂ | - | - | - | [41] |
| NiCo₂O₄ | 0.1 M KOH | 0.87 | 0.76 | 3.5 | 3.5 | 344 | 46.7 | 6 M KOH + 0.2 M ZnOAc₂ | 0.87 | - | - | [89] |
| NiCo₂O₄ | 0.1 M KOH | 0.95 | 0.75 | 3.5 | 3.5 | 320 | 48 | 6 M KOH with 0.2 M ZnOAc₂ | 0.8 | 166 | - | [70] |
| Mn-Co oxide | 0.1 M KOH | 1.02 | - | 3.34 | - | 43.7 | - | 6 M KOH with 2% ZnO | - | - | - | [35] |
| Co-Mn ternary oxide | 0.1 M KOH | 0.975 | 0.749 | 6.1 | 3.9 | 410 | 120 | 6 M KOH + 0.2 M ZnOAc₂ | 0.88 | 154 | 100 | [96] |
| CuCo₂O₄ | 0.1 M KOH | - | - | 6.0 | 3.9 | 450 | - | 6 M KOH | - | - | - | [30] |
| Ni-Co-Mn oxide | 0.1 M KOH | 0.95 | 0.94 | 3.8 | - | 61.5 | - | 6 M KOH | 0.7 | 313 | - | [98] |
| Ni-Co-Mn oxide | 0.1 M KOH | - | - | 6.0 | 3.9 | 350 | - | 6 M KOH | - | - | - | [35] |
| CoFe₂O₄ | 0.1 M KOH | 0.82 | 0.8 | 4 | 4.5 | 63 | - | 6 M KOH | - | - | - | [30] |
| Ni-Co-Mn oxide | 0.1 M KOH | - | - | 6.0 | 3.9 | 350 | - | 6 M KOH | - | - | - | [35] |
| Mn-Co oxide | 0.1 M KOH | 0.85 | 0.85 | 4.8 | - | 6 M KOH | - | 6 M KOH | - | - | - | [35] |
| FeO₂ | 0.1 M KOH | 0.74 | 0.58 | 3 | 3.07 | 500 | 67 | 6 M KOH | 1.56 | 89 | - | [92] |

* Values were approximately converted from their own reference electrode to RHE.
Overall, several research efforts have been devoted to investigating ZABs as well as designing bifunctional ZAB electrocatalysts. On considering the practical usage of ZABs, excellent performance and long-term stability are the key properties that promote their adoption. Consequently, the catalyst needs to be designed with the maximum exposure of active sites. Critical anode behavior, cathode architecture, three-phase interfacial reactions at the gas diffusion layer, ZAB fabrication procedure, and electrolyte effects in ZABs should also be considered during catalyst design. With the development of theory, techniques of characterization, innovative synthesis methods, catalyst design, and in...
operando analysis, the mechanistic features of spinel-based electrocatalysts in ZABs can be unleashed, and practical applications of ZABs will become a reality. In short, the challenge remains to design well-performing spinel-based electrocatalysts along with the commercialization of sustainable clean energy techniques, such as metal–air and metal–ion batteries, water splitting, supercapacitors, and CO\textsubscript{2}, CO, and NO\textsubscript{x} reduction.

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